

Practical sanitary science : a handbook for the public health laboratory / by David Sommerville.

Contributors

Sommerville, David.
Royal College of Physicians of Edinburgh

Publication/Creation

London : Bailliere, Tindall and Cox, 1906.

Persistent URL

<https://wellcomecollection.org/works/ep9pyhcw>

Provider

Royal College of Physicians Edinburgh

License and attribution

This material has been provided by This material has been provided by the Royal College of Physicians of Edinburgh. The original may be consulted at the Royal College of Physicians of Edinburgh. where the originals may be consulted.

Conditions of use: it is possible this item is protected by copyright and/or related rights. You are free to use this item in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you need to obtain permission from the rights-holder(s).



Wellcome Collection
183 Euston Road
London NW1 2BE UK
T +44 (0)20 7611 8722
E library@wellcomecollection.org
<https://wellcomecollection.org>



PRACTICAL
SANITARY SCIENCE

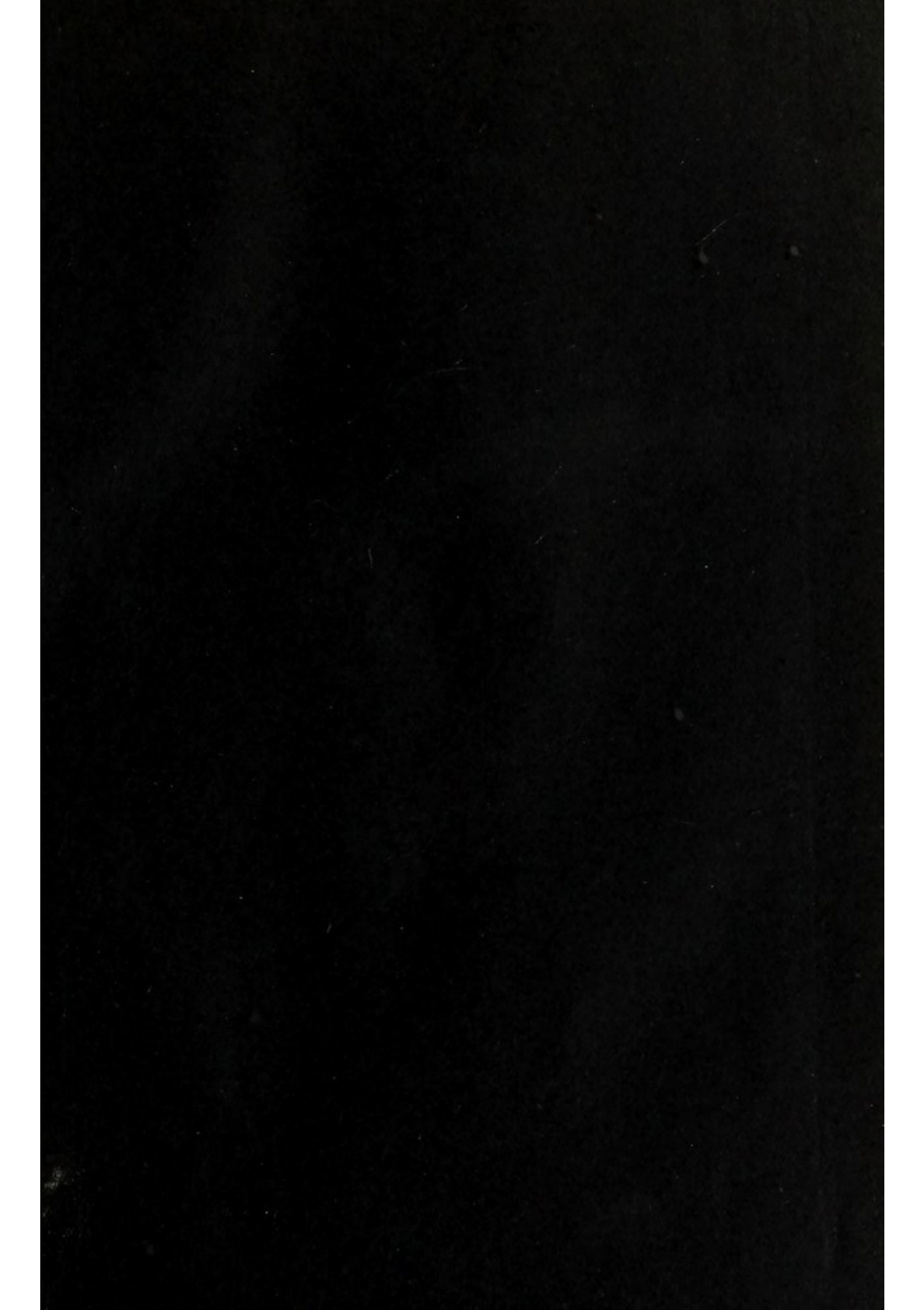


D. SOMMERVILLE



R.C.P. EDINBURGH LIBRARY





10/6mt

T. 7~~8~~. 29.

PRACTICAL SANITARY SCIENCE



PRACTICAL SANITARY SCIENCE

A Handbook for the Public Health Laboratory

BY

DAVID SOMMERVILLE, B.A., M.D.

D.P.H. (CAMB.), M.R.C.P. (LOND.)

LECTURER IN PUBLIC HEALTH, KING'S COLLEGE, LONDON;

LATE DEMONSTRATOR OF PHYSIOLOGY IN THE MEDICAL SCHOOL OF ST. THOMAS'S HOSPITAL.



LONDON
BAILLIÈRE, TINDALL AND COX
8, HENRIETTA STREET, COVENT GARDEN

1906

[All rights reserved]



Digitized by the Internet Archive
in 2016

<https://archive.org/details/b21963496>

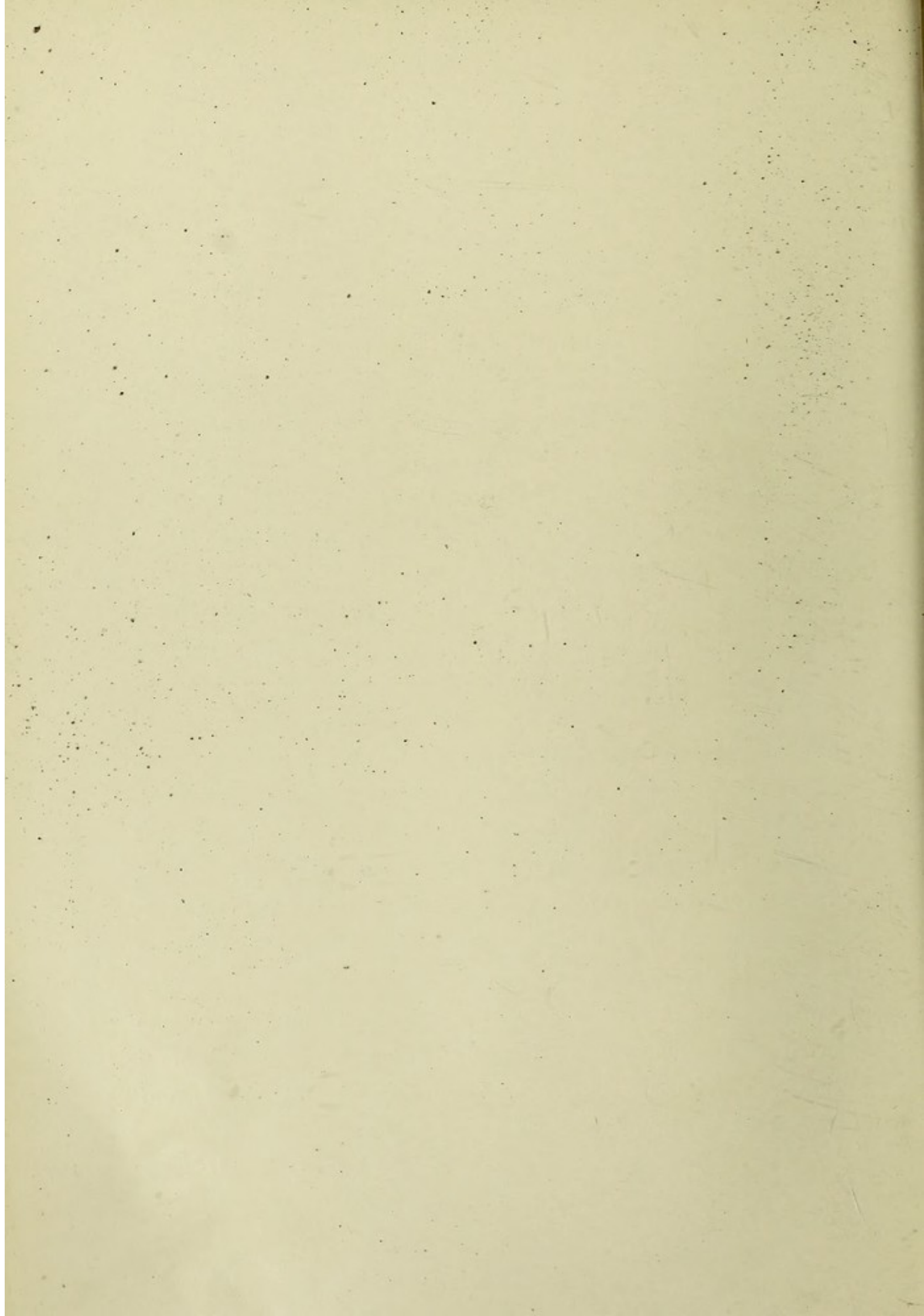
P R E F A C E

THIS little book is a brief summary of the course of practical lecture-demonstrations given to the D.P.H. class at King's College, London. Its intention is to put in the hands of students working in laboratories of Public Health a short outline of the more important matters—chemical, physical, etc.—discussed at practical examinations in Sanitary Science.

The methods described are few, but it is hoped they will be found reliable. It is felt that where a large field must be cultivated in a limited time, it is better to use a few tools which have been well tried. Whilst going through the work, the student will do well to constantly refer to elementary up-to-date text-books in the subjects of experimental physics, systematic organic and inorganic chemistry, analytical chemistry, geology, and bacteriology. Further, it will be necessary for him at the outset to bear in mind that no amount of theoretical reading can be made a substitute for the laborious and constant use of the test-tube, microscope, etc., which must take place at the benches.

A short account of the preparation of the standard solutions referred to in the work, and a few brief notes on the general chemical reactions of the more commonly occurring metals and acids, are set out in an appendix.

D. S.



CONTENTS

CHAPTER	PAGE
I. GENERAL OBSERVATIONS UPON POTABLE WATERS IN RELATION TO THEIR SOURCE, AND METHODS OF EXAMINATION ADOPTED FOR SAFEGUARDING THEIR PURITY -	1
II. THE PHYSICAL EXAMINATION - - - - -	7
III. MODE OF PERFORMING THE PHYSICAL EXAMINATION -	11
IV. THE CHEMICAL EXAMINATION - - - - -	14
V. HARDNESS - - - - -	24
VI. SOLID RESIDUE - - - - -	29
VII. POISONOUS METALS - - - - -	33
VIII. ORGANIC MATTER IN WATER - - - - -	38
IX. OXIDIZABLE ORGANIC MATTER IN WATER - - - - -	48
X. OXIDIZED NITROGEN—NITRITES AND NITRATES -	51
XI. GASES IN WATER - - - - -	59
XII. WATER SEDIMENT - - - - -	65
XIII. BACTERIOLOGICAL EXAMINATION OF A WATER SAMPLE -	76
XIV. INTERPRETATION OF RESULTS OF CHEMICAL ANALYSIS -	79
XV. SEWAGE EFFLUENTS - - - - -	91
XVI. ANALYSIS OF SOILS - - - - -	94
XVII. AIR ANALYSIS - - - - -	97
XVIII. MILK - - - - -	125
XIX. BUTTER - - - - -	152
XX. MEAT - - - - -	164
XXI. CHEESE - - - - -	172
XXII. DISINFECTANTS - - - - -	175
XXIII. CEREALS - - - - -	191
XXIV. ALCOHOL - - - - -	213
XXV. PRESERVED FOODS - - - - -	248
APPENDIX - - - - -	251



LIST OF ILLUSTRATIONS

FIG.	PAGE
1. Geological fault, etc. -	4
2. Ground-water level, and curve - - - -	5
3. Two-foot tube, etc. -	8
4. Hot-air oven, etc. -	12
5. Chemical balance, etc. -	15
6. Measuring-flasks, etc. -	19
7. Diagrammatic scheme of organic pollution undergoing purification - - - -	40
8. Retort and condenser -	42
9. Apparatus for estimating oxygen dissolved in water by Thresh's method - - - -	61
10-17. Objects found in water sediments - 69, 71, 73, 75	
18. Barometer and vernier scales - - - -	100
19. Hempel's gas burette -	107
20. Air-jars - - - -	110
21. Stokes tubes, Soxhlet apparatus, Westphal balance, etc. - -	135
22. Specific gravity bottle, stoppered 100 c.c. cylinder, etc. -	137
23. Valenta tube, beakers, platinum basin, etc. -	153
24 and 25. Apparatus for Reichert-Wollny process - - - -	160, 161
26. Head of cysticercus -	166
27. <i>Tænia solium</i> - - -	166

FIG.	PAGE
28. <i>Trichina spiralis</i> - -	168
29. Head of <i>Distoma hepaticum</i> - - - -	168
30. <i>Ascarus lumbricoides</i> -	170
31. <i>Oxyuris vermicularis</i> -	170
32. Wheat starch - -	195
33. Barley starch - -	196
34. Rye starch - - -	196
35. Rice starch - - -	197
36. Oat starch - - -	197
37. Maize starch - - -	198
38. Sago starch - - -	198
39. Tapioca starch - -	199
40. Pea starch - - -	199
41. Bean starch - - -	200
42. Arrowroot starch - -	200
43. Potato starch - -	201
44. <i>Vibrio tritici</i> - - -	202
45. <i>Bruchus pisi</i> - - -	202
46. <i>Acarus farinae</i> - - -	202
47. <i>Penicillium glaucum</i> -	203
48. <i>Aspergillus glaucus</i> -	203
49. <i>Mucor mucedo</i> - - -	203
50. <i>Peronospora</i> - - -	203
51. <i>Ustilago segetum</i> - -	204
52. <i>Tilletia caries</i> - -	205
53. Wheat-stem infected with puccinia - - - -	206
54. Wheat-stem infected with puccinia, more highly magnified - - -	207
55. Teleutospores - - -	207
56. <i>Æcidium berberidis</i> -	207
57. Gonidiospores, etc. -	207
58. Ergot in rye - - -	208

FIG.	PAGE	FIG.	PAGE
59. Sclerotium-bearing stromata - - -	208	74. Ground coffee, etc. - -	233
60. Stroma containing ascocarps - - -	208	75. Lacteal vessels of chicory	234
61. Ascocarp containing asci -	209	76. Dotted vessels of chicory	234
62. Ascus containing ascospores - - -	209	77. Ova of Bilharzia hæmatobia - - -	240
63. Apparatus for estimation of alcohol - - -	214	78. Sarcoptes scabiei, etc. -	240
64. Cells of cuticle of mustard	224	79. Pulex irritans - -	241
65. Black pepper - - -	225	80. Pediculus vestimenti -	241
66. Cuticle of tea-leaf - -	227	81. Pediculus capitis - -	242
67. Idioblasts in section of tea-leaf - - -	228	82. Pediculus pubis - -	242
68. Tea-leaf - - -	228	83. Beggiatoa alba - -	243
69. Elder-leaf - - -	230	84. Daphnia pulex - -	243
70. Willow-leaf - - -	230	85. Vorticella - - -	244
71. Sloe-leaf - - -	230	86. Amœba coli - - -	244
72. Cuticle of tobacco-leaf -	230	87. Leicestershire wool -	245
73. Coffee-berry - - -	233	88. Chinese silk - - -	245
		89. Jute fibres - - -	246
		90. Cotton fibres - - -	246
		91. Flax fibres - - -	247
		92. Hemp fibres - - -	247

ERRATA

Page 67, line 6, *for* 'Baggiatoa' *read* 'Beggiatoa.'

Page 171, line 4, *for* 'Tricocephalus' *read* 'Trichocephalus.'

WATERS

CHAPTER I

GENERAL OBSERVATIONS UPON POTABLE WATERS IN RELATION TO THEIR SOURCE, AND METHODS OF EXAMINATION ADOPTED FOR SAFEGUARDING THEIR PURITY

WATER is often the vehicle of infectious diseases, poisonous metallic salts, and a large number of undesirable materials—animal, vegetable, and mineral. When we consider how drinking waters are obtained, and how liable they are to contamination at all points from source to final distribution, it will be readily admitted that every potable water should be the object of the most careful, intelligent, and constant concern. The primary object of a water analysis for public health purposes is to ascertain whether or not it contains sewage, as in the organic matter contributed by sewage are found the organisms of infectious disease, such as *Bacillus typhosus*, *Vibrio cholerae asiaticæ*, etc. All other information is of very secondary import compared with this. The detection of organic filth, whether of animal or vegetable origin, and of harmful inorganic matters, when in small quantities, is often a work of no little difficulty. In certain cases where a small amount of sewage containing pathogenic micro-organisms finds its way into a water-supply, no chemical analysis, however delicate, can furnish evidence of the pollution. So also in other cases the most exact bacteriological examination may wholly fail to discover a dangerous water. The well-informed analyst will not pin his faith to one method of examination to the partial or total exclusion of others, but will

welcome all reliable scientific methods that can assist in throwing light on his search.

At present four methods of examination are utilized—viz., Physical, Chemical, Biological, Bacteriological—each of which has its place and its limits.

The physical examination may detect pollution so gross that further inquiry is quite unnecessary.

The chemical analysis can render no information concerning liability to contamination, and is useless in detecting small quantities of sewage. A systematic chemical analysis is of value in demonstrating variations in character, produced, for example, by the lowering of the level of well waters, by changes in rainfall, action on lead, iron, and zinc, in pipes, mains, cisterns, boilers, etc. Where the estimation of saline constituents must be determined for health purposes, manufacturing and engineering purposes, etc., the chemical method alone is of value. Here it may be stated as a general principle that waters most suitable for domestic purposes are also most suitable for manufacturing and engineering purposes. Acid waters corrode boilers, so do waters containing marked quantities of $MgCl_2$ and $CaCl_2$, as these chlorides at high temperatures decompose, forming HCl , which at once attacks the iron. $CaSO_4$, being insoluble, is deposited as a crust. $CaCO_3$ and $MgCO_3$, together with salts of Fe , render water unsuitable for tanning, dyeing, paper-making, and other industries, owing to their great insolubility, whereby particles are left in the fabrics.

Neutral and alkaline (Na_2CO_3) waters are best suited for boilers.

Special chemical analyses are required in dealing with medicinal waters.

By careful and systematic study of the lower forms of animal and vegetable life much information may be acquired as to the source, place, and mode of entry of surface waters into water-supplies. Such biological examination has not had in this country the attention it deserves.

Where the question of infective micro-organisms in water arises, which to the sanitarian is of all questions the most important, the bacteriological examination only can afford positive evidence.

The examination of the source of a water-supply is of the first import, and should never be omitted. Personal inspection of the

catchment area, all streams arising therefrom, and all feeders of such streams, should be made *in situ*, and the relations of these to possible sources of pollution carefully noted. When the gathering ground has been thoroughly investigated, attention should be turned to the storage reservoirs, and finally the efficiency of filtration should be bacteriologically tested. Such examination presupposes an intimate knowledge of the entire area set apart for collection, which should be protected from all possibility of contamination from manured soil, house drainage, and storm waters. A good working knowledge of the geology of the district is essential, and every student of water analysis should intimately cultivate the solid and drift maps of the Ordnance Survey.

The following brief table gives an outline of the more important strata in this country, detailed descriptions of which will be found in any textbook of geology.

Post-tertiary deposits :

Alluvium, sands, gravels, boulder clay.

Tertiary deposits :

Sands of the Eastern English counties.

Bagshot sands (upper, middle, and lower).

London clay.

Secondary deposits :

Chalk.

Greensands—upper and lower—with gault lying between.

Weald clay.

Purbeck marble.

Kimmeridge clay.

Oolite.

Lias.

New red sandstones.

Primary deposits :

Coal, ironstones.

Limestone.

Old red sandstones.

Shales and slates.

Crystalline rocks.

Shallow wells sunk in the post-tertiary sands and gravels are very liable to pollution.

The Bagshot sands yield a fairly soft water.

The London clay is an impervious stratum, and the waters resting immediately on it are generally hard.

The chalk formations of England, which are extensive, yield both hard and soft waters. The hardness is mostly temporary. Fissures make it possible for pollution to readily get access to these waters.

The greensands, especially the lower, bear waters rich in calcium and iron salts.

Oolites produce waters almost identical with those of the chalk.

The magnesium limestones (dolomite) and new red sandstones give origin to much hardness, of which a large portion is permanent.

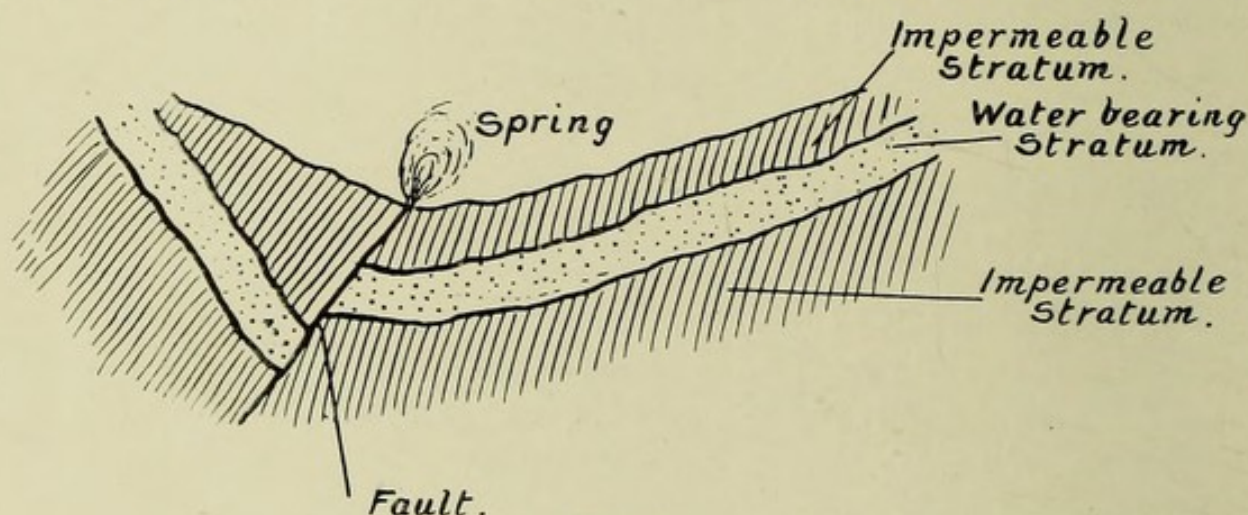


FIG. I.

Slates and igneous rocks, being practically insoluble, yield waters destitute of saline matters, and are consequently very soft.

The drainage area of a well depends upon the depth of the well, the porosity of the soil and subsoil, direction of flow of ground water, and the daily depression produced by pumping. It may be considered as the base of a cone whose apex is the water-level in the well.

Even with a good knowledge of the geology of the catchment area and districts through which the water passes, the analyst is subject to pitfalls at all points. Strata may contain caverns and fissures which lodge pollution in the most unlikely positions. Geological faults account for unexpected positions of springs. Where a water-bearing, permeable stratum intervenes between two impermeable strata, and a fault occurs, the imprisoned fluid may

become subject to such pressure that it escapes at the surface with tremendous force.

It is to be noted that the curve of the ground water near the well is steep, but rapidly shades off into the horizontal. It is obvious that with different types of soil the form of this curve changes as the surface water in the well is lowered. The drainage area increases in direct proportion to the porosity.

This area should be protected from all forms of organic pollution, including cultivated soils, and it has been laid down as a minimum requirement that it should have a radius of twenty times the maximum depression of the water through pumping—*e.g.*, if the depression in the well be 5 feet the area should have a radius of 100 feet, etc. Outside this cone it is considered that filtration

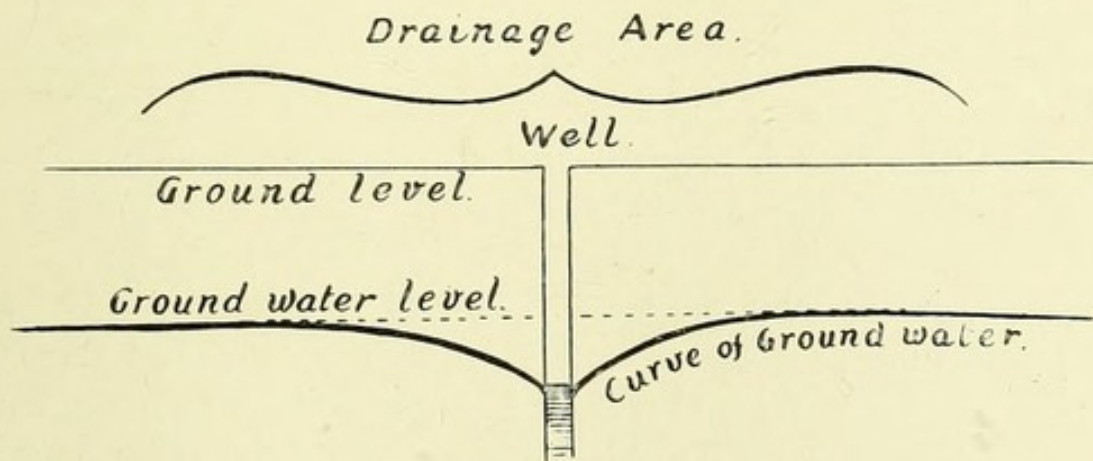


FIG. 2.

is so slow that purification is complete. A wide margin, however, should be allowed in the drainage area to meet the effects of increased rainfall, possible faults in the brickwork of the well, and other factors, so that wells supplying drinking waters should be removed widely from all sources of drainage, farmyard manure, etc. A slight acquaintance with the situations of many rural wells in this country must call forth unqualified condemnation. There is no doubt that many epidemics of typhoid fever have their origin in the waters of these wells. It is a matter of little difficulty to determine whether or not leakage from the immediate surroundings takes place into a well, and a solution of fluorescein, Prussian blue, an emulsion of the *Bacillus prodigiosus*, or a concentrated solution of NaCl, poured around its mouth and thoroughly washed into the soil, will afford the necessary evidence within a limited time.

Peat which lies for the most part on igneous rocks imparts to water certain organic acids capable of dissolving lead. Wherever possible such waters should be cut out of a supply. If this cannot be done the acids should be neutralized before the waters pass to the consumer.

Rivers and streams from which water-supplies are procured should be scrupulously preserved from the entrance of pollution, with a special view to the exclusion of infective bacteria. All river water should be filtered before use, and the efficiency of filtration should be constantly tested by bacteriological examination.

All forms of animal and vegetable life should be excluded from service reservoirs, cisterns, mains, etc. It is well known that certain low vegetable forms, especially when dead, give origin to offensive odours.

Water is constantly performing a cycle. Evaporation produces clouds, which return to the earth as rain. This rain, according to the nature of the soil, subsoil, and rocks, pursues various paths. If it fall on impervious granite it runs off in large quantity; a part may be evaporated, and this will occur to the greatest degree during dry, hot, and windy weather. If it fall on sandy soil a large proportion percolates, and the more porous and deep the sand, the more rapidly and deeply the water sinks into the earth. When it meets with an impermeable stratum its further course is directed by the slope and contour of this stratum. Should the latter take the form of a basin the water will accumulate until it overflows the lip of the basin, forming a spring at a point where the stratum outcrops. Again, if the stratum form an inclined plane, as on the sides of a river valley, the water will flow along the plane to its outlet at the lowest point. Such pure waters may be intercepted before reaching polluted rivers by sinking wells at the bases of the hills forming the sides of the river valleys. The upper surface of this mass of moving ground water is indicated by the level of the water in superficial wells. This surface is not necessarily horizontal. It is in constant motion, travelling towards the outflow, and the rate of movement is governed by the porosity of the soil, slope, nature of outlet, etc. An intimate knowledge of the entire history of a water will often be necessary to an intelligent comprehension of certain analytical data.

CHAPTER II

THE PHYSICAL EXAMINATION

THE physical examination comprises a determination of the turbidity, colour, odour, and taste.

Turbidity.—Pure waters are always free from visible particles in suspension, and the slightest degree of opacity should render a water suspicious. On the other hand, the most transparent and brilliant waters may contain the most pronounced pollution. Turbidity may be produced by access of the contents of cesspools, drains, manure heaps, and surface refuse of all types, especially after rains, when it forms often the worst kind of pollution. It may be produced by particles of clay, iron, chalk, etc., when a chemical and microscopical examination may be necessary to disclose the nature of the matter in suspension. Waters containing iron very often deepen in opacity during the first day or two after collection, owing to the formation of persalts of that metal, which are highly insoluble. Such opacity immediately disappears on the addition of a small quantity of dilute HCl. The degree of turbidity in a report is generally expressed by such phrases as clear, slightly turbid, turbid, very turbid.

Colour.—Uncontaminated rain water presents a pale-blue tint in the 'two-foot' tube. Yellow tints point to organic matter, brownish-red suggest a peaty origin, and reddish-yellow indicate iron. Any appreciable shade of yellow or brown will excite suspicion, and lead to a careful search for the cause. Colour tables have been formulated for the use of water analysts, but do not seriously assist a trained eye.

Odour.—Drinking water should be free from all odour. Dissolved gases may be liberated by slightly warming the water, say to a temperature of 100° F. In the case of peaty waters it has been

found at times that even after the most careful filtration a slight odour still attaches to the water. For many reasons peaty waters do not furnish good supplies, and where other sources are available,

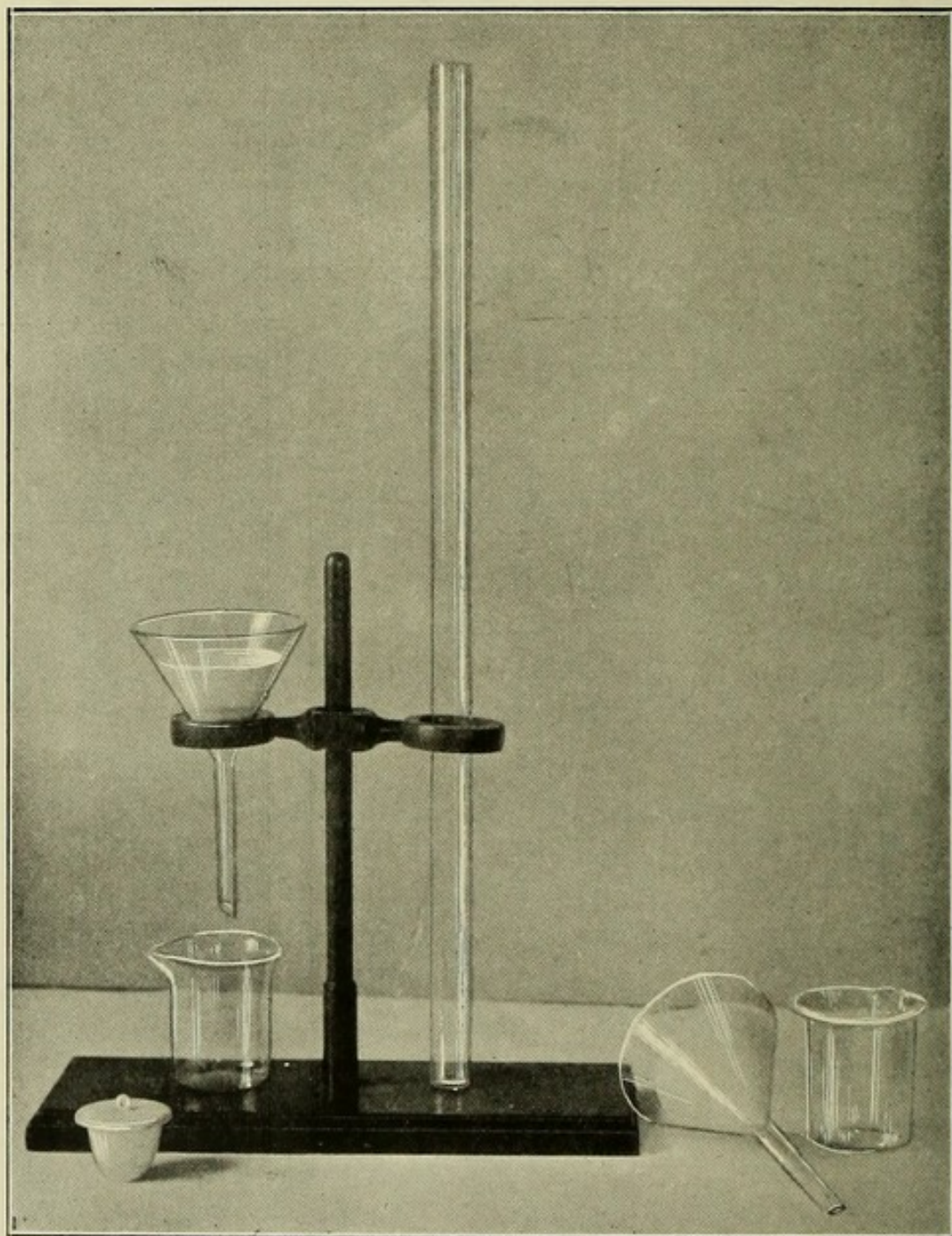


FIG. 3.—TWO-FOOT TUBE, FILTERING APPARATUS, AND CRUCIBLE.

should be passed over. River waters usually have a faint smell, due to a variety of causes, most often, perhaps, to vegetable organisms, some of which—for example, the well-known sewage fungus—are associated with the production of H_2S . The dead and

decomposing remains of plants and animals furnish a variety of odours, not only in river waters, but in cisterns, reservoirs, and mains. Of late years attention has been called to distinct species of lowly vegetable forms which produce disagreeable odours in water.

It is customary to obtain the sample of water for physical examination from the vessel containing that for the chemical examination, and something may now be said respecting the mode of collecting such samples. The so-called 'Winchester' quart bottle has long been used for this purpose, and when made of colourless glass answers the purpose admirably. The bottle should be thoroughly cleansed by rinsing with dilute HCl, and afterwards removing the last trace of acid with distilled water. Where it has to be sent by rail, etc., it is packed in a tightly-fitting wicker case, or wooden box fitted with padlock. Before filling, the bottle should be rinsed with a portion of the sample. A little air space should be left under the stopper to avoid cracking of the neck through rise of temperature. Procedure in collection will vary according to the object of the examination. If it is desired to ascertain whether, for example, lead is dissolved by a water in the house-pipes, it will be necessary to collect the first runnings from the taps in the morning. When a bacteriological examination is required, a special method must be pursued, which will be described later. Where the sample is to be taken from a river, cistern, etc., the bottle, prepared as above, is usually immersed some little distance below the surface, where the stopper is removed and the bottle filled. A small portion is poured out in order to procure the air space mentioned, and the stopper inserted. Various forms of apparatus have been devised for collecting samples under different conditions, but the circumstances will in all cases suggest the mode of procedure, if it be kept in mind that a fair sample of the water as it is usually found is the object desired.

A correct record of the sampling process, etc., should be made on the spot, and attached as a label—

1. Date, time, and place of taking sample.
2. Depth below surface, state of water-level—high, low, or average.
3. Particulars of rainfall and of geological strata of district.
4. Depth of water-level below ground-level.

5. Description of surroundings, possible sources of pollution, such as sewers, cesspits, cemeteries, etc.

In many cases it is well for the analyst to supply his own collecting-bottle, with instructions for taking the sample and filling up the label. The sender should be made to understand that the specimen must be of the same nature exactly as that actually consumed, and that it is desired to ascertain the maximum degree of pollution that may at any time obtain. All such particulars, as also the results of the analysis, should be transcribed into a book and preserved for future reference.

Taste.—Pure rain water well aerated has a fairly distinctive taste, more easily appreciated than described. So also have peaty waters, sea water, and chalybeate waters. The taste of a particular sample may be, however, everything to be desired, whilst the water is the foulest of the foul.

CHAPTER III

MODE OF PERFORMING THE PHYSICAL EXAMINATION

BEFORE proceeding further it may be well to state that in the physical examination, as also in the chemical, we form an opinion of the character of the water, not necessarily from the result of any one step, but from the collective evidence furnished by the entire examination.

Organic pollution will appear, as a rule, at many stages of the analysis, but the worst waters, if judged by only one or two tests, may escape detection.

Turbidity.—Place the Winchester on a white porcelain tile in a good north light, and examine it carefully with the naked eye. Much information regarding opacity, sediment, etc., may thus be gained by a practised eye.

As to opacity or turbidity, the sample may be described as brilliant (aeration good), clear, slightly turbid or opalescent, turbid, markedly turbid. If it be required to estimate the quantity of matter in suspension, 100 c.c. may be filtered through a hard filter and evaporated in a platinum dish to dryness. The difference between the weight of the residue dried at 100° C. and that of 100 c.c. of the unfiltered sample similarly treated will represent the desired result. Or, where a centrifugal machine is available, by means of small tubes the sediment may be read off quantitatively on a graduated scale. By instruments named turbidimeters a column of opalescent water mounted in a glass cylinder can be matched by the degree of illumination of a polarized light ray passing through a second similar glass cylinder containing no water; the degree of rotation of the Nicol of the eyepiece expresses the degree of turbidity.

Colour.—Clean thoroughly, and afterwards fill the 'two-foot' tube and place it likewise on the tile; then look down through the

column, noting the tint of colour, which may range from a pale sky-blue to a yellow or brown.

As to colour, for all ordinary purposes the naked-eye inspection is sufficient, but if for any reason great accuracy is required a tinto-

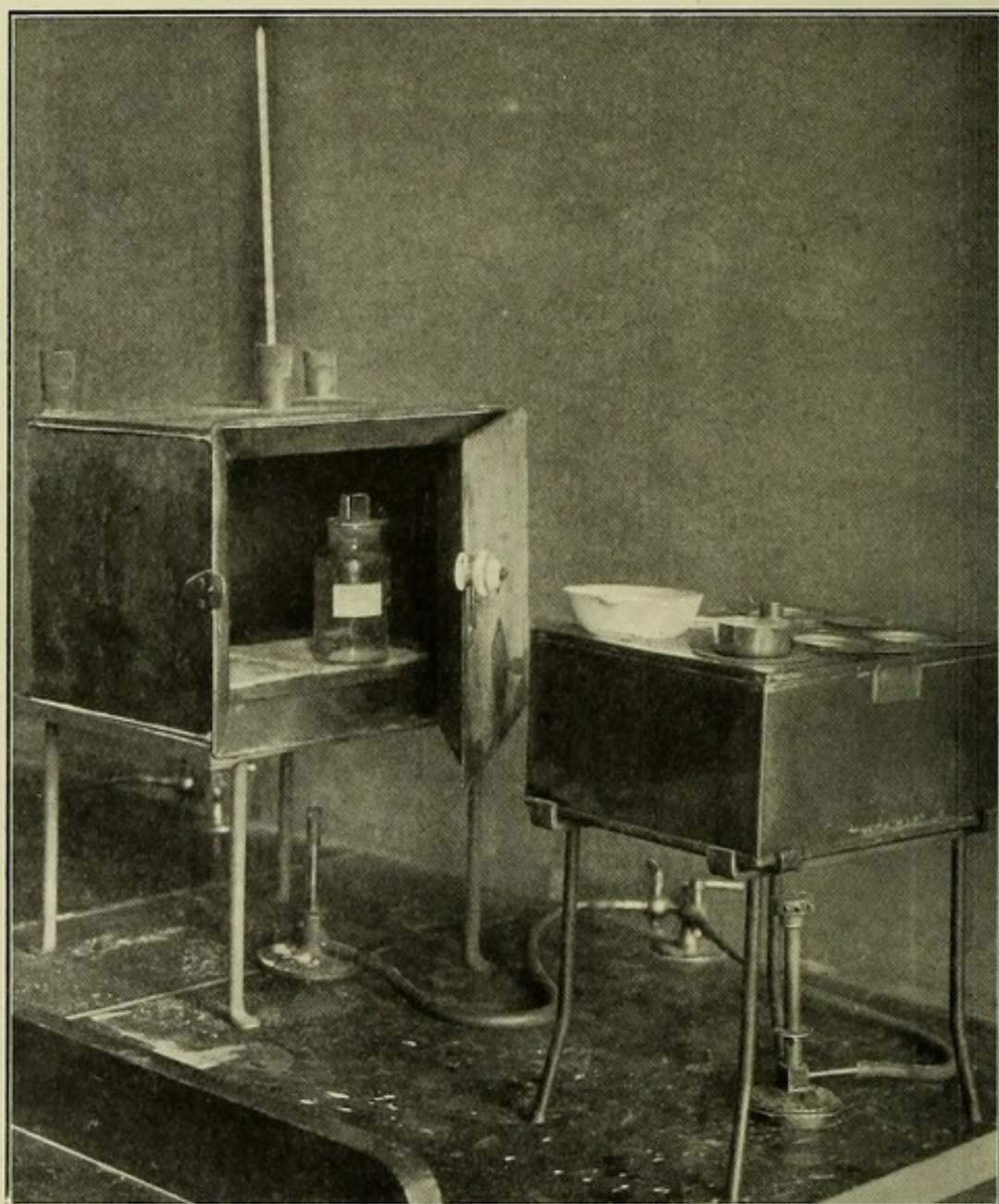


FIG. 4.—HOT-AIR OVEN SURROUNDED BY WATER-JACKET. WATER-BATH CARRYING PORCELAIN AND PLATINUM DISHES.

meter may be used. Two hollow glass wedges containing respectively dilute solutions of CuSO_4 , and a mixture of ferric and cobalt chlorides slightly acidified, are made to slide over each other in front of an empty tube, so that any desired combination of blue and brown tints can be obtained. Alongside is placed a similar

tube filled with the sample, and the wedges are arranged so that on looking down upon a white surface the colours exactly match. The prisms are graduated in millimetres, and the results are expressed in terms of millimetres of blue and brown.

Odour.—Place 200 c.c. in a stoppered flask, and heat to 100° F. in an air-bath. Remove the stopper and smell. It is generally sufficient to shake the sample well in the cold, rapidly remove the stopper, and smell. The variety of odours is infinite. Many odours are produced by organisms, either as products of their life-history or of their death and putrefaction. *Beggiatoa*, *Chara*, and certain species of *Crenothrix* produce an offensive odour of H_2S . It is believed that *Beggiatoa* during its life-cycle reduces sulphates, and produces under favourable circumstances large quantities of H_2S . *Crenothrix*, moreover, often produces abundance of colour, varying from brown to red.

Tabellaria, *Meridion*, and certain diatoms, as also the protozoon *Cryptomonas*, furnish a distinctly aromatic odour. A fishy odour is produced by *Volvox* and the protozoa *Glenodinium*, *Bursaria*, and *Uroglena*.

Taste.—Aeration produces in a good water its characteristic and pleasant taste. Taste, however, is of little service to the analyst, and not always to be recommended. Iron is about the only ingredient that can in this way be detected in very small quantities, being recognisable to the amount of $\cdot 5$ part per 100,000.

CHAPTER IV

THE CHEMICAL EXAMINATION

It will be well for the student from the first to fit up his own apparatus, and make his own standard solutions. He must learn to use properly the chemical balance, and a special demonstration is devoted to the mechanism, methods of adjusting and using this all-important instrument. Before commencing to weigh, he should see that the balance is accurately levelled, and that the index moves without effort over the whole field of the graduated scale, and comes to rest at zero. All weights, basins, etc., should be transferred to and from the scale-pans only when these are supported. It is customary to use three rows of weights: grammes (brass), decigrammes and centigrammes (platinum), and milligrammes (platinum). A rider of platinum applied to the beam also reads milligrammes. The right-hand pan should be used only for weights, and these should be placed methodically in three rows in front of the operator. By this means the total reading is most easily obtained and checked.

Immediately on finishing a weighing all weights should be transferred to the box, with the forceps used for the purpose, and the box and balance carefully closed.

The standard solutions in use in water analysis are of two types :

1. Normal, decinormal, etc.
2. Standards of such strength that a litre contains the equivalent of a gramme, or some submultiple of a gramme, of the substance to be estimated.

A normal solution of HCl , for example, contains the molecular weight in grammes dissolved in a litre of distilled water.

$$\begin{aligned} \text{H} &= 1 \\ \text{Cl} &= 35.35 \\ \text{molecular weight} &= 36.35 \end{aligned}$$

Therefore 36.35 grammes HCl per litre = normal HCl, written N.HCl.

So also N.NaOH = 40 grammes of this salt per litre.

One cc. N.HCl is equivalent to 1 c.c. N.NaOH.

Decinormal ($\frac{N}{10}$) solutions of the above would contain respectively 3.635 HCl, and 4 grammes NaOH per litre ;

and 1 c.c. $\frac{N}{10}$ HCl is equivalent to 1 c.c. $\frac{N}{10}$ NaOH.

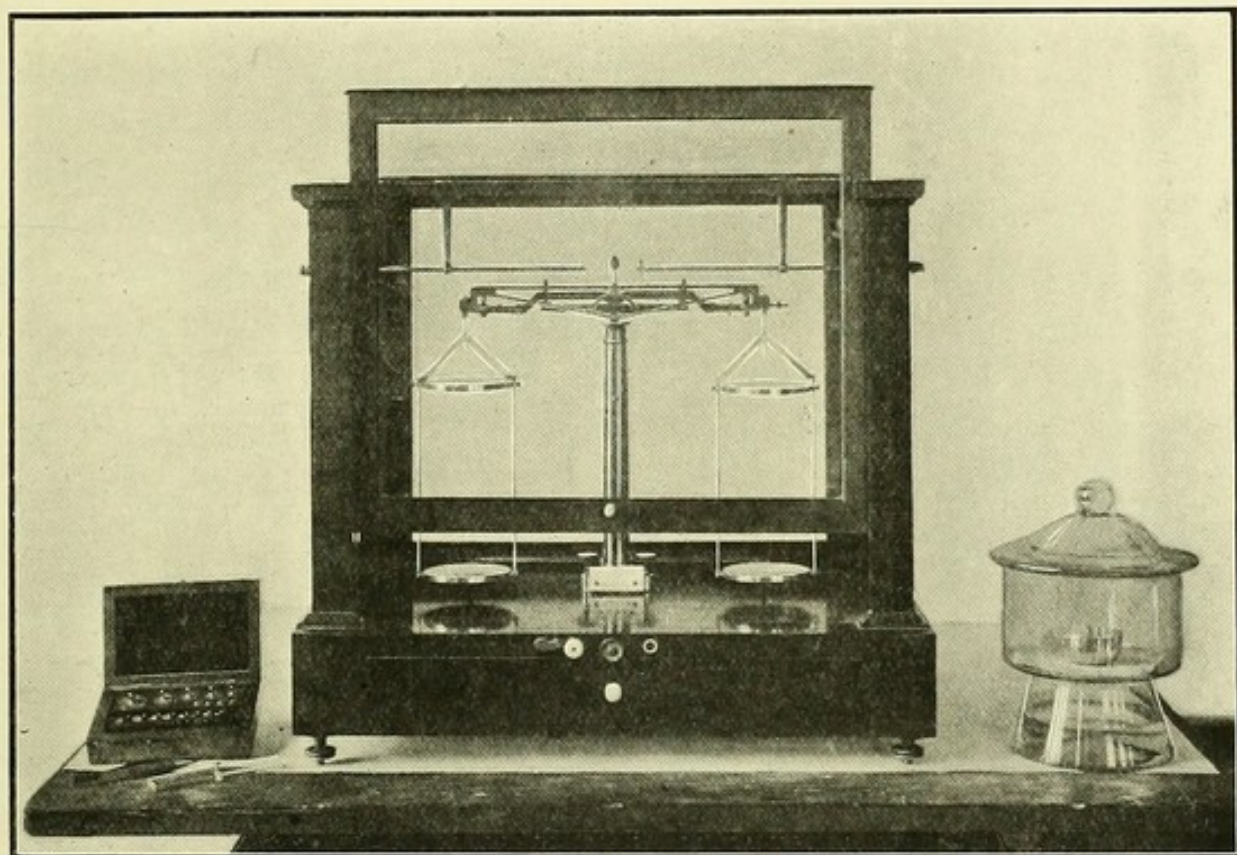


FIG. 5.—CHEMICAL BALANCE: WEIGHTS ON LEFT, DESICCATOR ON RIGHT.

In the case of bibasic acids, such as H_2SO_4 , half the molecular weight in grammes per litre of water forms a normal solution. One molecule of H_2SO_4 is equivalent to two molecules NaOH.

Molecular weight of $\text{H}_2\text{SO}_4 = 98$

\therefore 49 grammes per litre = normal solution,

and 4.9 ,, ,, = $\frac{N}{10}$ solution.

In the case of tribasic acids one-third of the molecular weight in grammes per litre equals a normal solution, and so on for acids of higher basicity.

The second type of standard solution used is constructed so that a minimum amount of calculation suffices in estimating results. Since it is customary to represent the various items of the analysis as parts by weight per 100,000 of the water, and since 1 c.c. of water weighs 1 gramme (1,000 milligrammes), 100 c.c. of water will weigh 100,000 milligrammes.

It is therefore convenient, when possible, to work on 100 c.c. of the water sample throughout the various estimations, and to use a standard solution that will give readings directly in the above terms.

Suppose we wish to estimate the quantity of Cl in a water, we use a solution of AgNO_3 of such strength that 1 c.c. is equivalent to 1 milligramme Cl. To make this solution we refer to the molecular weight of AgNO_3 , and the atomic weight of Cl.
 $\text{AgNO}_3 + \text{NaCl} = \text{AgCl} + \text{NaNO}_3$.

170 grammes AgNO_3 precipitate 35.35 grammes Cl.

\therefore dividing by 35.35, we find that 4.8 grammes AgNO_3 precipitate 1 gramme Cl.

If, then, we dissolve 4.8 grammes AgNO_3 in 1 litre of water we obtain a solution 1 c.c. of which precipitates 1 milligramme of Cl, and working with 100 c.c. of water, the number of c.c. of the silver nitrate solution used indicates the number of milligrammes of Cl in 100,000 milligrammes of the water, which is parts per 100,000.

Again, in estimating NH_3 a standard solution of NH_4Cl is used and prepared in the same way.

One molecule of NH_4Cl contains 1 molecule of NH_3 .

53.35 grammes	„	contain 17 grammes	„
and 3.14	„	„ 1 gramme	„

Therefore a litre containing 3.14 grammes NH_4Cl will contain 1 gramme NH_3 , and consequently 1 c.c. contains 1 milligramme. It is found convenient to dilute this 100 times, so that 1 c.c. = .01 milligramme NH_3 .

In reading a burette arrange it so that the lower convex line of the meniscus is in the same horizontal plane with the eye; the

division of the scale cut by the lowest point of this convex line is the reading.

In measuring small quantities of liquids much time may be saved by using a few plain 10 c.c. pipettes graduated to tenths of a c.c., and for quantities under a c.c. a 1 c.c. pipette graduated to hundredths. These can be easily and rapidly cleaned, and as easily and rapidly manipulated, and may often take the place of burettes. In weighing platinum and porcelain basins, crucibles, etc., it is very necessary to see that they are quite dry. To insure this, especially after heating, they should be placed for ten minutes in a desiccator immediately before going to the balance. It is also necessary to be certain that all such vessels are thoroughly clean. Accurate notes of all operations, measurements, weights, etc., should be made in the bench notebook, and considered as much a part of the work as the operations themselves. Without this notebook it is impossible to get on with analytical chemistry. Where possible it is well to write down the chemical equations representing decompositions. When in doubt in this matter refer to a work on chemistry. All colour matches are best made in glass cylinders standing on a white ground, as the operator faces a good north light.

The Reaction of Water.—This is an important item, and should form the first step in the routine examination. In addition to the use of red and blue litmus-papers, it is often well to use a more delicate indicator, such as phenol-phthalein, and to estimate the amount of acidity (when acid) in 100 c.c. by titrating with $\frac{N}{10}$ NaOH, or of alkalinity (when alkaline) with $\frac{N}{10}$ H_2SO_4 . An acid water dissolves lead, iron, and zinc; it also fixes ammonia, and so prevents its being distilled off. Some hold that neutral waters and those possessing very slight temporary hardness are capable of dissolving lead. It should be remembered, however, that sodium carbonate when present prevents this action. Houston has correlated the acidity and plumbo-solvency of a large number of moorland waters.

He causes the sample to percolate upwards through a column of specially prepared lead shot at a uniform rate. He then collects successive 50 c.c.'s, and estimates the amount of lead in each.

The following figures are taken from a report to the L.G.B.:

ACIDITY IN TERMS OF C.C.	PLUMBO-SOLVENCY.
$\frac{N}{10}$ Na_2CO_3 required to neutralize 100 c.c. of the Water.	Mgms. of Pb. in 100 c.c. of the Water after Filtration through Lead Shot.
·2	·28
·3	·25
·4	·4
·5	·66
·6	·92
·8	1·55
·95	2·66
1·5	2·8
1·7	5·6
2·2	8·6

Some waters not acid, and failing to dissolve lead, exert an 'erosive' action, forming an insoluble film of oxyhydrate upon the lead, which after a time may become detached, and produce in the water a degree of opacity.

Chlorides in Water.—Free Cl rarely occurs in water-supplies. Certain manufacturing effluents may on occasion contain small quantities of free Cl, but the quantity is so small and the occurrence so rare that this form of Cl may be practically ignored. The great bulk of Cl in drinking water is found as NaCl. All soils and subsoils contain this salt in large amounts. The water-bearing strata are rich in chlorides, especially NaCl, and consequently rain water (which itself may contain as much as ·5 part per 100,000 NaCl), as it percolates from the surface to the impermeable stratum on which it rests, dissolves these in considerable quantities. CaCl_2 and MgCl_2 are found in certain strata—chalk and limestone—in much smaller quantities, but MgCl_2 abounds in sea water, and in large quantity is distinctive of it. Wells, reservoirs, etc., to which sea water can obtain access will yield waters rich in MgCl_2 . Sources of water subject to much evaporation, especially if situated near the sea, exhibit large quantities of chlorides. The total Cl in sea water approaches 2,000 parts per 100,000, and if this figure be kept in memory it will explain the large estimations often found some considerable distance from the littoral. During the passage of water through the soil, subsoil, and strata, Cl is not likely to be diminished as are the organic matter and bacteria.

When we have accounted for all the Cl contributed by rain water, sea water, soil, subsoil, and strata, and trade effluents from chemical works, paper factories, etc., there may remain a surplus furnished by organic pollution of animal origin. This surplus is of some import to the analyst, as indicating sewage; but before it is returned as such all the possible sources of origin just mentioned must be rigidly excluded. Vegetable organic matter does not yield this surplus Cl. Attempts have been made in

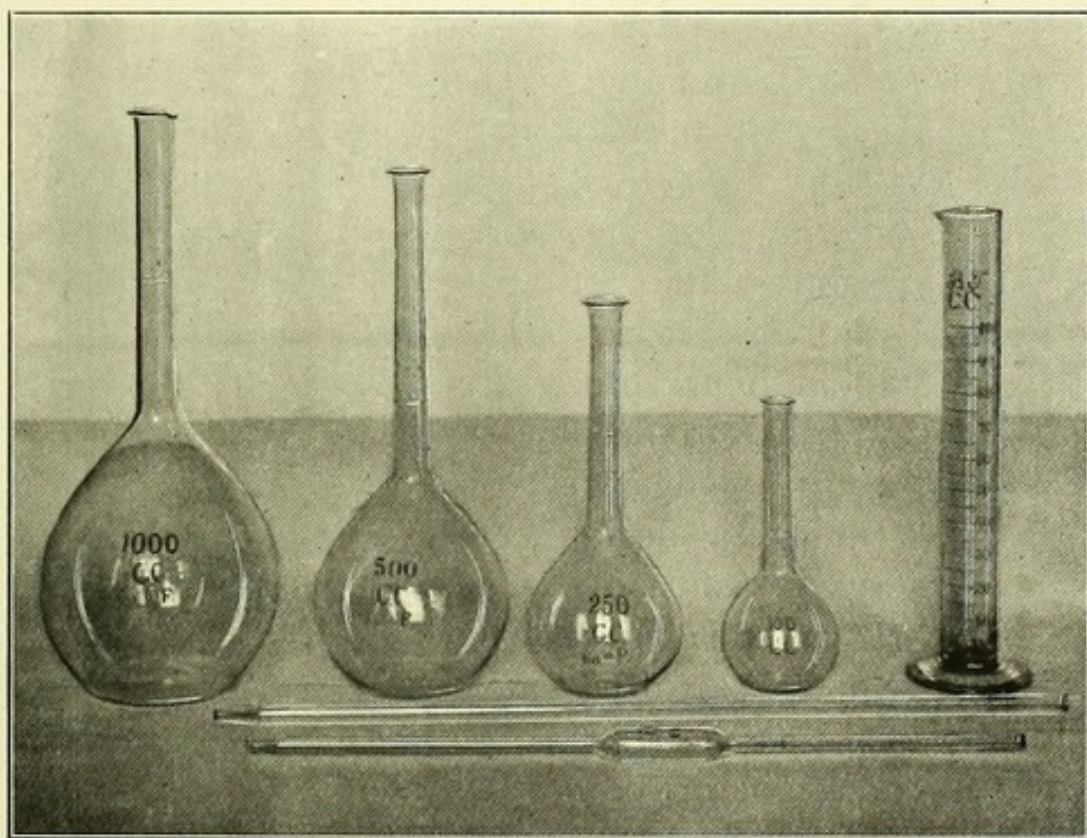


FIG. 6.—MEASURING-FLASKS, CYLINDER, AND PIPETTES.

U.S.A. to estimate and permanently record the Cl due to the natural causes named, so that sewage pollution may be readily detected. Maps have been constructed and points furnishing equal quantities of Cl joined by lines named 'isochlors.' In districts remote from the sea, and centres of population and land cultivation, such maps may be more or less reliable, but in this country they would be useless. Whilst it is true that animal pollution contains much Cl (urine about 1 per cent. chlorides), and that soils, strata, etc., in certain districts yield fairly constant quantities, still there are variations in many localities in these natural sources, and it is

only where large quantities of sewage have gained access to waters that we can rely on the surplus Cl as evidence of this accession. In the case of small amounts of sewage this surplus Cl figure is of little, if any, value. But in a water analysis the most important information lies very often not so much in the exact amount of a particular constituent as in the fact that its presence points to past pollution, and consequently to the possibility and even probability of a recurrence of such pollution. In this light Cl and nitrates play an important rôle. These afford unmistakable evidence of previous contamination; they are the distinct and unchangeable indications of previous pollution, now oxidized and harmless, but as to whether recent or remote they indicate nothing. Hence the necessity for further and different forms of examination. As to the amounts of chlorides that should condemn waters, it is difficult to speak, since there is such infinite variety in the quantities contained in different soils and strata. MgCl_2 and CaCl_2 render waters hard, so that more than 4 or 5 parts of either or both of these per 100,000 will cause a large destruction of soap, and these figures will in most cases form the limit for domestic waters. NaCl may go up to perhaps 50 parts per 100,000; above this it imparts a taste, and the water consequently will not be fit for drinking.

Estimation of Cl.

APPARATUS AND REAGENTS REQUIRED.

A white porcelain basin capable of holding 250 c.c.

A glass stirring-rod.

A burette charged with standard solution of AgNO_3 , of which 1 c.c. is equivalent to 1 milligramme Cl (4.8 grammes AgNO_3 to a litre of water).

A 5 per cent. solution of K_2CrO_4 .

Place 100 c.c. of the water in the porcelain dish.

Add 1 c.c. of the K_2CrO_4 solution, and stir.

Run in from the burette drop by drop the silver nitrate solution until the pale yellow colour remains permanently orange.

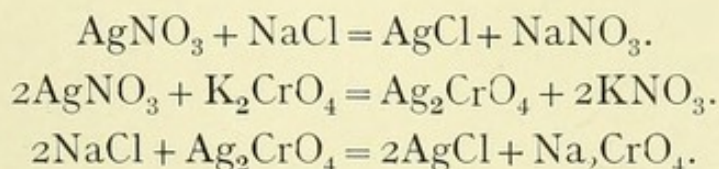
Take the reading.

The rationale of the process is as follows :

AgNO_3 , when added to a solution of chlorides, forms AgCl , a white curdy precipitate insoluble in HNO_3 , soluble in NH_4HO . Without a special indicator it would be impossible to determine when the whole of this white precipitate had been formed—when the whole of the Cl had been deposited.

K_2CrO_4 is also acted on by AgNO_3 , and Ag_2CrO_4 formed, which is red. But so long as any chloride remains ununited with Ag , this silver chromate is decomposed and AgCl formed; hence the disappearance of the red colour on stirring. Immediately the whole of the Cl is precipitated as AgCl the red silver chromate remains.

The reactions are represented by the equations :



It is obvious that the K_2CrO_4 should be free from Cl . Acidity in the water will dissolve Ag_2CrO_4 ; hence if a water is even slightly acid it must be neutralized. Freshly precipitated CaCO_3 is the best alkali to use, and it should be used only to the point of neutralization. If too little K_2CrO_4 is used the Cl reading will be too high, and if too much be used it is difficult to determine the end; 1 c.c., accordingly, is found a suitable quantity when the solution is of the above strength. It will be noticed that as the titration proceeds the red Ag_2CrO_4 disappears more slowly on stirring, until finally it ceases to disappear. This is explained by the continuous decrease in the original chloride. Whilst abundance of this undecomposed chloride remains in solution, the Ag_2CrO_4 is rapidly robbed of its Ag and the red colour discharged; but as the chloride diminishes and the end approaches, the decomposition of the Ag_2CrO_4 becomes slower and slower, until at the end of the reaction it ceases, and the red Ag_2CrO_4 permanently remains.

Since the colour-change from pale yellow to red is somewhat difficult to detect in daylight (it is more easily perceived by gas-light), a flat glass cell whose plates are $\frac{3}{8}$ inch apart should be filled with chromate solution of the same tint as that of the contents of the basin, and interposed between the eye and the basin during titration, when the appearance of the red silver chromate becomes strikingly manifest. The effect is to neutralize the yellow

and to cause the appearance of the basin to be the same as if it were filled with pure water. In working with turmeric, cochineal, etc., cells should be used filled with corresponding solutions of turmeric, cochineal, etc.

The number of c.c. of silver nitrate run in represents the number of parts of Cl per 100,000.

$$\begin{aligned} 100 \text{ c.c. water} &= 100,000 \text{ milligrammes,} \\ 1 \text{ c.c. AgNO}_3 &= 1 \text{ milligramme Cl;} \\ \therefore \text{ the number of c.c. AgNO}_3 \text{ used} &= \text{number of parts} \\ &\text{per 100,000.} \end{aligned}$$

Some operators subtract .1 c.c. from the AgNO_3 figure as the quantity required to form the slight permanent orange colour. Others add a small measured quantity of the water sample from a burette until the permanent orange tint departs, and reckon half of this with the AgNO_3 reading.

It is well always to do two careful estimations, and take the mean. When once an idea of the quantity of Cl present is obtained, two careful estimations can be performed very rapidly. A control basin containing 100 c.c. of the same water and 1 c.c. of K_2CrO_4 may assist in determining the end reaction.

Where small quantities of Cl are to be estimated, 250 c.c. or 500 c.c. of the water may be concentrated by evaporation to 100 c.c. Alkaline silicates, nitrates, and phosphates slightly affect the Cl estimation, but not to such a degree as to require correction.

Chlorine is sometimes returned in terms of sodium chloride. This figure is found by multiplying the Cl return by $\frac{35.35}{58.35}$, the ratio of the weight of Cl to NaCl. Where CaCl_2 , or MgCl_2 , or both, enter into the problem, corrections have to be made in accordance with the respective molecular weights and the quantities of each present.

In chalk and red sandstone waters 3 parts of Cl per 100,000 may occasion no suspicions of sewage, and 4 or 5 parts may be passed, unless organic pollution is indicated by other items of the analysis. Pure surface waters seldom contain more than 1 part per 100,000, whilst deep greensand waters may give rise to 15 to 20 parts per 100,000, and still be absolutely pure.

The following are a few examples of the Cl figures for different waters :

					Parts per 100,000.
A well in St. Pancras	-	-	-	-	4.5
Lambeth water-supply	-	-	-	-	1.9
" " " "	-	-	-	-	2.0
Southwark water-supply	-	-	-	-	1.85
A well in Devonshire	-	-	-	-	3.1
Thames water at Waterloo Bridge	-	-	-	-	103.2
Deep well near Hindhead	-	-	-	-	112.3
Sample of rain water taken from rain gauge in Herts	-	-	-	-	.3

CHAPTER V

HARDNESS

THE hardness or soap-destroying power of a water has perhaps little influence on health, but from an economic point of view is of some importance.

A soap is a chemical salt formed by the union of an inorganic base and a fatty acid. Some soaps, such as potassium and sodium, are soluble in water, and when shaken with it form a dense froth or lather. Others, such as calcium and magnesium soaps, are insoluble in water, and fail to form a lather. If a solution of a soluble soap be added to a water containing calcium or magnesium salts these will be completely precipitated in the form of insoluble calcium or magnesium soaps before a lather is produced. By using a standard soap solution an approximate estimate of the quantity of such soap-destroying bodies in a water can be made. The total quantity of these bodies, as measured by the standard soap solution, constitutes the total hardness.

CaCO_3 and MgCO_3 , especially the first, have by far the greatest share in rendering waters hard. These salts are held in solution by CO_2 dissolved in the water. On boiling such waters, CO_2 escapes, and the insoluble carbonates separate out as a precipitate. If the boiled water be filtered, made up to its original volume with distilled water, and again titrated with standard soap solution, the permanent hardness is obtained. The difference between the total and permanent hardness is the temporary hardness.

The soap test has been made to measure the quantity of CaCO_3 and other salts which produce hardness, but this is not accurate quantitative analysis. It should be clearly understood that the chemical action is multiple and indefinite, and altogether different from that which usually takes place, when in quantitative analysis

we titrate one definite compound against another. All that can be claimed for the soap process is that it indicates the amount of soap-destroying bodies present in a given water, but fails to form a measure for any in particular.

The following compounds produce hardness :

CaCO_3 , MgCO_3 , CO_2 in solution, CaSO_4 , MgSO_4 , Fe_2O_3 , and other Fe oxides, zinc salts, SiO_2 , $\text{Al}_2(\text{OH})_6$, chlorides, nitrates, phosphates, and free mineral and organic acids.

The temporary hardness, which is got rid of by boiling, is for the most part produced by CaCO_3 and MgCO_3 , held in solution by CO_2 . After these come small quantities of CaSO_4 and MgSO_4 , which are also thrown out immediately CO_2 is driven off, but the great bulk of these sulphates remains in solution. Lastly, in a few cases minute quantities of oxides of Fe, silica, and alumina are deposited. Phosphate of Ca, if present in appreciable quantity, may, under certain conditions, be deposited in very small amounts. On cooling some of the precipitated MgCO_3 , and to a less degree CaCO_3 , CaSO_4 , and $\text{Ca}_3(\text{PO}_4)_2$ will redissolve and go to form permanent hardness.

MgCO_3 destroys nearly 50 per cent. more soap than CaCO_3 , but is found in potable waters in very much less quantity.

The Estimation of Hardness.—Prepare standard soap solution, 1 c.c. of which shall precipitate 1 milligramme CaCO_3 , or its equivalent of other soap-destroying compounds, as follows : Weigh out 12 grammes castile soap, and dissolve in a litre of equal parts methylated spirit and water. Stand in a cool place for a day or two, and filter. Dry at 120°C . some powdered CaCl_2 (calcite) for half an hour, and weigh out 1 gramme into a porcelain basin. Add a few drops of HCl , and to avoid loss by spiriting cover the basin with a watch-glass. Evaporate to dryness. Redissolve in a few c.c. of water, to which add carefully the washings from the watch-glass, and again evaporate to dryness. Repeat the last step in order to get rid of final traces of HCl . Lastly, dissolve in 1 litre of water. Each c.c. of this solution contains Ca equivalent to 1 milligramme CaCO_3 —that is, the solution contains hardness to the extent of 100 parts per 100,000. Place 10 c.c. of this solution in a stoppered bottle of 200 c.c. capacity, and add 90 c.c. distilled H_2O , thereby reducing the strength to 10 parts per 100,000.

Run in from a burette the soap solution until the characteristic lather appears.

The quantity of standard soap solution used should be exactly 11 c.c. (10 c.c. to precipitate the equivalent of 10 milligrammes CaCO_3 , and 1 c.c. to produce the lather). If, for example, 9 c.c. soap solution be found sufficient to produce the characteristic lather, it is evident that the solution must be diluted with the aqueous spirit in the proportion of 9 to 11. Dilute, therefore, 900 c.c., or thereabouts, of the original litre to the volume— $\frac{11}{9} \times 900$ c.c. The remainder may be kept for fortifying the standard, as it is found that in time it loses in strength, especially if when on keeping it becomes turbid.

Should the soap solution prove too weak, it must have additional soap added, and be put through the same process of standardization until found correct.

The student should carefully prepare a number of lathers by shaking 100 c.c. distilled water and 1 c.c. standard soap solution in such a bottle as above mentioned, noting the time that the lather remains unbroken, its thickness, the character of the sound produced by shaking, and the number and appearance of specks of froth which slowly trickle down the sides of the bottle when laid in the horizontal. Having studied these phenomena, he should next estimate the hardness of different waters by working on like quantities—100 c.c.—and running in the standard soap solution 1 c.c. at a time, shaking vigorously after each addition of soap, until the characteristic lather is obtained.

When at any time in doubt as regards the end of the reaction, he should resort to a control experiment with distilled water. The same appearances exactly must be produced in the sample under estimation as in the control.

The following is an example of the determination of the hardness of a sample of a London (New River) water :

Take 100 c.c. of the water in a 200-c.c. stoppered bottle. Fill a 50-c.c. burette mounted on a stand with standard soap solution (1 c.c. = 1 milligramme CaCO_3). Run in the soap solution 1 c.c. at a time, shaking vigorously after each addition, until a permanent lather $\frac{1}{4}$ inch thick remains unbroken for three minutes when the bottle is laid on its side. As the end of the reaction approaches,

the hard metallic sound at first heard on shaking gives place to a dull thud, the froth which previously disappeared almost instantaneously remains, and adheres in specks to the sides of the bottle.

Twenty-one c.c. of standard soap solution were required in this case to complete the titration. Subtracting 1 c.c. used in producing the lather, we find that 20 c.c. were destroyed by the 100 c.c. of water.

$$\begin{aligned}\text{But each c.c.} &= 1 \text{ milligramme } \text{CaCO}_3; \\ \therefore 20 \text{ c.c.} &= 20 \text{ milligrammes } \text{CaCO}_3,\end{aligned}$$

and 100 c.c. of this water contains 20 milligrammes of soap-destroying substances, or a 'total' hardness equal to 20 parts per 100,000. In waters containing magnesium salts the lather is slowly produced, and of a dirty, granular appearance, very unlike the light frothy condition seen in hard waters destitute of Mg salts.

To obtain the 'permanent' hardness in the above example, place 100 c.c. in a small beaker on a porcelain ring over a Bunsen flame, and boil for fifteen minutes, or till one-third of the volume has evaporated. Filter into a clean 100 c.c. flask, and make up to the mark with distilled water. Transfer to the stoppered bottle and determine the hardness as above: this is 'permanent hardness.'

13.5 c.c. of the soap solution were required to lather the 100 c.c. of water prepared as described.

$$13.5 \text{ c.c.} - 1 \text{ c.c.} = 12.5 \text{ c.c.},$$

or 12.5 parts permanent hardness per 100,000.

The 'temporary hardness' = difference between 'total' and 'permanent' hardness.

$$20 - 12.5 = 7.5 \text{ parts temporary hardness per 100,000.}$$

Hard waters, whilst palatable, cause waste of soaps, and fail somewhat in cooking vegetables, meats, etc., and making infusions of tea and coffee. They are unsuitable for boilers, in that a deposit forms on the interiors which by reason of its low conductivity of heat wastes fuel, and from its divergent coefficient of expansion may lead to explosions.

This deposit or crust will consist of bodies representing both temporary and permanent hardness. Carbonates of Ca and Mg will fall out first, and be followed by their sulphates, together with salts of iron, silica, and alumina.

In this country the hardest waters arise from the chalk, dolomite, and new red sandstone strata, carbonates of Ca and Mg forming by far the largest proportions of soap-destroying compounds.

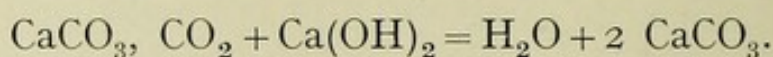
Where the hardness exceeds 20 parts per 100,000, it is well in performing the estimation to dilute the sample with an equal bulk of distilled water. The total hardness of a potable water should not exceed 25 to 30 parts per 100,000. Waters whose hardness falls below 10 parts are considered soft, whilst those containing 20 to 30 parts are hard, and upwards of 30 parts very hard.

Clark's scale of degrees represents hardness as grains per gallon (parts per 70,000).

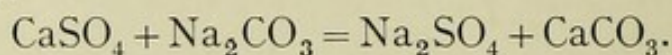
It is universally agreed that a good water should contain less than 10 parts per 100,000 of permanent hardness, and of this little should be due to magnesium salts.

Temporary hardness can be easily got rid of ; not so permanent.

In Clark's process lime is used for softening—in other words, for combining with the CO_2 in solution, thereby causing insoluble carbonates to separate out which were previously held in solution by the CO_2 . Care should be taken that no excess of lime is added.



A little softening of permanent hardness may be effected by the use of Na_2CO_3 :



As lime compounds act more rapidly on soap than magnesia, in dealing with unknown waters sufficient time should be allowed for the action of any magnesium salts they may contain. Where it is desirable to estimate the quantity of Mg present in a sample, the ordinary methods of quantitative analysis should be employed.

CHAPTER VI

SOLID RESIDUE

THE total solids in waters vary greatly in extent, ranging from 2 to 3 parts in rain water to over 3,000 parts in sea water per 100,000. From the purely health point of view perhaps little information will be derived from an estimation of the total solids. Occasions, however, arise in which it may be desirable to estimate the total solids, and also the quantities of certain constituents, such as Ca and Mg salts. Where these latter exist in large quantity in the form of sulphates, it is found that the waters are unfit for drinking, from their action on the alimentary tract. The incineration of the dry residue affords a check on some of the other portions of the analysis dealing with organic matter. On the whole, any useful information that can be obtained will, for the most part, centre round the quantities of Ca and Mg salts present, especially the sulphates.

Chalk waters contain little sulphates; limestone waters hold chiefly CaSO_4 , at times to the extent of 15 to 20 parts per 100,000; magnesium limestone (dolomite) generally contains much less CaSO_4 and considerable MgSO_4 . Sulphates in water are chiefly derived from strata; a very small amount is due to the oxidation of S in organic matter; a small quantity in the rain water of large towns has its origin in the solution of the oxides of S found in the atmosphere; whilst in exceptional cases an appreciable portion is due to the oxidation of metallic sulphides.

Phosphates in marked quantities indicate organic pollution, especially urine. The phosphates of the alkalies are those chiefly found in water. But, in that certain geological beds and organic matter of purely vegetable origin contain phosphates, no very

direct information is obtained from their estimation, and it is usually unnecessary to go beyond a qualitative examination.

In a few instances silica may require to be estimated: this compound lessens the plumbo-solvency of water.

In clear waters the solids are all in solution; in turbid waters they are partly in solution and partly in suspension. It is customary to estimate the solids in solution, but as this requires complete sedimentation it may be advisable in cases where time is limited to perform the estimation on the sample after thoroughly shaking. The method adopted, however, should be stated on the report.

Measure out 100 c.c. of the water, and place in a clean platinum basin on a water bath, 25 c.c. at a time, as evaporation proceeds. When dry, transfer the basin, after carefully wiping the outside, to an air bath at 100° F. for half an hour. Remove to a desiccator for ten minutes, and weigh. By drying at this low temperature no water of crystallization is lost, and no dissolution or other decomposition takes place. Further drying should be carried out, if necessary, until a constant weight is obtained. This weight, less that of the dish, represents the total solids.

With platinum-tipped tongs hold the dish over a Bunsen flame until thorough incineration is effected. After cooling in the desiccator, weigh again to obtain the non-volatile solids. The difference between this last and the previous weight represents the volatile solids. The degree of charring (organic matter) which occurs during incineration should be noted; also the smell—odour of burnt sugar indicates vegetable matter, burnt horn animal substance.

Ca.—Where it is deemed necessary to estimate the quantity of Ca salts, Mg salts, or both, 500 c.c. of the sample should be evaporated down to 200 c.c., and the Ca removed by precipitation with $(\text{NH}_4)\text{HO}$, NH_4Cl , and $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The precipitate of CaC_2O_4 when thoroughly washed, dried, ignited, and weighed, represents the Ca as CaCO_3 , 56 per cent. of which is Ca. The weight of the crucible and ash of filter-paper must be accurately known and accounted for. It is well to let the beaker or other vessel containing the mixture of precipitate and fluid stand for some hours in a warm place, by which filtration is rendered much more easy and thorough.

The student may be reminded that the addition of NH_4Cl holds Mg salts in solution.

Mg.—Concentrate the filtrate down to one-fifth its bulk or less. Add slight excess of sodium phosphate and stand aside in a warm place for some hours. Filter, wash the precipitate well with dilute $(\text{NH}_4)\text{HO}$, dry, ignite, and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$ (magnesium pyrophosphate). The Mg forms $\frac{8}{37}$ of this weight.

Phosphates.—It is rarely necessary to estimate phosphates. Where, however, required, proceed as follows :

Evaporate 200 c.c. of the water to dryness. Moisten the residue with a few drops of pure HNO_3 and evaporate again to dryness, in order to render insoluble any silica that may be present. Dissolve in dilute HNO_3 and filter. Add ammonium molybdate in slight excess ; keep, if possible, in a warm place over night, and filter. Wash the precipitate well with hot water, and dissolve in ammonia. Add a few drops NH_4Cl and slight excess of MgCl_2 , and filter. Wash the precipitate thoroughly with dilute ammonia. Dry, ignite, and weigh the $\text{Mg}_2\text{P}_2\text{O}_7$. The phosphates returned in the form of P_2O_5 will be represented by $\frac{71}{111}$ of this weight.

It is hardly necessary to say that a qualitative test for phosphates should be carefully performed before entering on the more lengthy quantitative estimation. For this test concentrate by evaporation a quantity of the water—say 200 c.c.—to one-tenth its bulk. To 10 c.c. in a test-tube add a drop or two of HNO_3 , 1 or 2 c.c. ammonium molybdate, and heat to a temperature somewhat below boiling, for several minutes if necessary. A greenish-yellow coloration indicates traces of phosphates, a canary-yellow colour an appreciable amount, and a yellow precipitate larger quantities.

Silica.—This compound generally exists in water, either as soluble silicates of the alkalies, or as insoluble silicate of alumina. Evaporate 300 c.c. of the water to dryness after acidulating with HCl . Treat the residue with strong HCl , and transfer by washing to a filter with boiling water. Dry, ignite, and repeat the foregoing treatment with acid and boiling water three or four times. Finally dry, ignite, and weigh as SiO_2 .

Sulphates are readily detected by concentrating to about one-tenth, and adding to the warmed sample a drop of HCl and a few

drops of BaCl_2 in solution, when a white insoluble precipitate of BaSO_4 is formed and rapidly sinks to the bottom of the test-tube. The insolubility of this precipitate should always be tested with sufficient strong nitric acid.

The Quantitative Estimation.—A measured quantity of the water is heated to boiling in a beaker ; a few drops of HCl are added, and sufficient hot solution of BaCl_2 to precipitate the whole of the sulphates dropped in. Time is given to the precipitate to settle, and a little more of the BaCl_2 allowed to fall into the supernatant clear solution. If no turbidity is produced the reaction is complete ; but if even the slightest turbidity occur more BaCl_2 must be added, and the mixture again allowed to settle, until the addition of a drop of BaCl_2 produces no turbidity. The white precipitate is collected on a filter-paper, the weight of whose ash is known, well dried, ignited in a crucible, and weighed as BaSO_4 .

The SO_3 is returned as $\frac{40}{233}$ of this weight.

Alkaline phosphates, sulphates, and chlorides may indicate animal organic matter, especially urine, but it is often difficult to attribute to these salts a source in recent pollution, as all are found in strata free from organic matter. Where marked excess is found, the composition of the geological strata accurately known, and where frequent analyses of pure waters from the same strata are made, an increase of any or all may be attributed to organic pollution. But it should be remembered that slight variation in amount of these salts is met with from time to time in waters arising in certain strata, where contamination is out of the question.

Nitrites, nitrates, and poisonous metals, when present, will be found in the dry residue forming the total solids. The metals are most easily detected in this residue.

CHAPTER VII

POISONOUS METALS

THERE are only a few metals whose compounds enter into water-supplies. Iron and lead are the chief, occasionally zinc is found, very rarely copper, and equally rarely chromium and tin.

A qualitative examination should be performed in all cases for each of these metals, and where a possibility of other metallic compounds derived from mines, industrial wastes, etc., exists, a further careful investigation will, of course, be necessary.

Iron.—Ferruginous waters are found in mountain limestone, chalk, Bagshot sands, and greensands. They are generally opalescent, and slightly yellow in colour. The metal occurs as a bicarbonate which is readily converted into an insoluble carbonate, and also oxidized into the well-known 'rust'—hydrated ferric oxide, $\text{Fe}_2\text{O}_3, \text{H}_2\text{O}$. Ferrous salts decompose nitrates, absorbing O and producing nitrites, which in turn are further reduced to NH_3 . This reducing action accounts for the free NH_3 often found in pure waters derived from the greensands and other strata.

Chalybeate waters may be quite clear when drawn, but as oxidation of the Fe proceeds they become turbid and more or less brown. The insoluble and highly oxidized particles dissolve on the addition of a little dilute acid. Such turbidity may have its origin in iron pipes, cisterns, etc., in addition to strata.

DETECTION AND ESTIMATION.—I. Put 50 c.c. or thereabout of the water in a white porcelain dish. Dip a clean glass rod in a fresh solution of $(\text{NH}_4)_2\text{S}$ and draw the rod through the contents of the dish. If Fe be present a dark coloration will be observed along the track of the rod, the depth of colour depending on the quantity of Fe. A corresponding appearance is seen in the case

of Pb ; in that of Cu the sulphide is slightly brown, except where an exceedingly large amount of a copper salt is present, when the colour is black. To the dark sulphide in the dish add a few drops of dilute HCl and stir ; the sulphide passes into colourless solution. Confirm this test by adding to a little water in a test-tube a drop or two of HCl and a like quantity of $K_4Fe(CN)_6$, when Prussian blue is formed.

The water may require to be concentrated, and this is advisable in all cases where the reaction is absent or doubtful.

A litre may be evaporated down to 100 c.c. on a water bath or over a flame, and in case of very small amounts of Fe the evaporation should be continued to 50 c.c. or less.

A quantitative estimation of the metal is rapidly performed as follows :

1. Place 50 c.c. of the water, diluted if necessary, in a Nessler glass on a white tile ; add a drop or two of $(NH_4)_2S$, sufficient to produce the maximum precipitate of sulphide. In a similar Nessler glass place 50 c.c. distilled water and the same number of drops of $(NH_4)_2S$, and carefully run from a burette a standard solution of Fe_2Cl_6 (1 c.c. = .1 milligramme Fe) until the colour matches that of the water sample. Mix well after each addition. Perform three or more estimations and take the mean.

Note the quantity of standard solution used, and a simple calculation will determine the number of milligrammes of iron in the 50 c.c., the double of which will represent parts per 100,000.

The least quantity of $(NH_4)_2S$ capable of precipitating the whole of the metal should be determined and used ; and in the second Nessler glass, containing distilled water and the standard iron solution, exactly the same quantity of $(NH_4)_2S$ must be placed, otherwise the match will not be reliable.

2. To 50 c.c. of the water in a Nessler glass add 1 c.c. dilute H_2SO_4 (20 per cent.) and a few drops HNO_3 to oxidize any ferrous iron to ferric. Heat if necessary. Add 1 c.c. $K_4Fe(CN)_6$, when a blue tint will be produced in solutions containing as little as .01 part per 100,000. The quantitative estimation is made by matching the above tint in a second Nessler glass with distilled water, using the same quantities of dilute H_2SO_4 and $K_4Fe(CN)_6$, and sufficient Fe_2Cl_6 (1 c.c. = .1 milligramme Fe) to make a match.

Where the colour is dark blue the sample must be sufficiently diluted to admit of accurate matching of tints.

Lead.—Waters possessing an acid reaction, such as those derived from peaty moorlands, in which organic acids (ulmic, geic, etc.) are formed by certain micro-organisms, dissolve lead. The primary action of water on lead is an oxidation. In alkaline and strictly neutral waters the coating of oxide remains intact, but in acid waters it dissolves. Hard waters containing abundant carbonates form an insoluble oxycarbonate; hence hard waters lack the property of dissolving lead. Houston distinguishes between the solvent action of acid waters, and the 'erosive' action of neutral waters containing dissolved oxygen. Acid waters should be cut out of public supplies, if they cannot be passed through chalk, limestone, etc., so as to be completely neutralized. Four parts of CaCO_3 or MgCO_3 per 100,000 are necessary to eliminate plumbo-solvency.

The effects of acid moorland waters on lead have been only too clearly seen in certain districts of Yorkshire and Lancashire, where the inhabitants have suffered from anæmia, constipation, colic, wrist-drop, depression, gout, renal disease, and other classical effects of lead-poisoning. The lead is dissolved out of materials of joints, block-tin pipes, house pipes, cisterns, etc.

Whilst carbonates and sulphates in water diminish plumbo-solvency, nitrates favour it, as lead nitrate is the most soluble salt of the metal. A rise in temperature up to 48° to 50° C. increases plumbo-solvency.

DETECTION AND ESTIMATION.—To 10 c.c. of the water, concentrated if necessary, add a drop of neutral KCrO_4 . If Pb be present an opalescence occurs, which in case of large quantities of the metal appears as a yellow precipitate.

A few drops of a freshly-saturated solution of H_2S produces a dark colour or dark-coloured precipitate, insoluble in HCl and insoluble in KCN .

Place 50 c.c. of the water to be examined in a white dish and draw a glass rod moistened with $(\text{NH}_4)_2\text{S}$ through the fluid. The slightest dark coloration will be seen against the white ground, as in the case of iron. The addition of a few drops each of HCl and KCN leaves the colour or precipitate undischarged.

The quantitative estimation is performed in the same manner as that described for iron, using a standard solution of lead acetate (1 c.c. = .1 milligramme Pb).

Copper.—Through 50 c.c. of the water, placed in a porcelain dish, draw a glass rod dipped in $(\text{NH}_4)_2\text{S}$, as in the cases of Fe and Pb. If Cu be present a dark colour is produced, removed by KCN, but unchanged by the addition of HCl.

Acidulate 50 c.c. of the water in a Nessler glass, placed on a white tile, and add a drop or two of $\text{K}_4\text{Fe}(\text{CN})_6$; a brown colour (copper ferrocyanide) indicates copper.

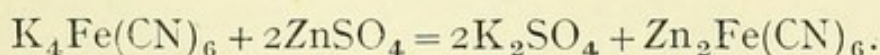
In a clean platinum basin place 50 c.c. of the water acidulated with HCl, and a polished strip of steel, so that one end rests on the bottom of the dish and the other projects over the edge. In half an hour a deposit of Cu will have formed on the steel if a copper salt be present. The coating of copper can be rendered more evident by holding the strip for a second or two in bromine vapour.

Quantitative Estimation.—To 50 c.c. of the water in a Nessler glass add a few drops of dilute HCl, and sufficient $\text{K}_4\text{Fe}(\text{CN})_6$ to produce the maximum colour. Match this in a second Nessler glass containing 50 c.c. distilled water with the necessary amount of a standard solution of CuSO_4 (1 c.c. = .1 milligramme Cu), as in the previous examples.

Zinc.—When no darkness is produced in the water by the addition of $(\text{NH}_4)_2\text{S}$, and it is desirable to test for zinc, to 10 c.c. of the water in a test-tube add $(\text{NH}_4)\text{HO}$ till alkaline, a few c.c. $(\text{NH}_4)\text{Cl}$ solution, and boil. Then add a few drops of $(\text{NH}_4)_2\text{S}$, when, if zinc be present, a characteristic white sulphide is formed of a peculiar flocculent gelatinous appearance. Confirm this in another portion of the sample by boiling with $(\text{NH}_4)\text{HO}$, filtering, and adding $\text{K}_4\text{Fe}(\text{CN})_6$, to obtain a white gelatinous precipitate of zinc ferrocyanide.

Quantitative Estimation.—The zinc sulphide obtained as above from a measured quantity of the water may be collected on a filter, well washed with dilute $(\text{NH}_4)_2\text{S}$, dried, ignited at a bright red heat, cooled, and weighed as ZnO . $\text{ZnO} \times .8 = \text{Zn}$. A quantitative estimation may be approximately made, in the manner already described, by matching the turbidity produced in a measured volume of the water by a drop or two of potassium

ferrocyanide, with distilled water, and a standard solution of ZnSO_4 (1 c.c. = .1 milligramme Zn). A volumetric estimation of zinc may be performed thus : Concentrate at least $\frac{1}{2}$ litre of the sample to 50 c.c. Transfer this to a white basin, and add a drop of a solution of CuSO_4 . Run in a standard solution of $\text{K}_4\text{Fe}(\text{CN})_6$ until a permanent brown colour is produced. Read the amount of $\text{K}_4\text{Fe}(\text{CN})_6$ used (1 c.c. = .07 milligramme of the salt) and calculate the amount of Zn present from the equation :



The brown $\text{Cu}_2\text{Fe}(\text{CN})_6$ is not permanent until all the zinc has been formed into $\text{Zn}_2\text{Fe}(\text{CN})_6$.

Chromium.—Evaporate a litre of the water to be tested to dryness, and fuse the ash with solid potassium nitrate and sodium carbonate to produce yellow K_2CrO_4 , which in neutral solution produces a purple precipitate with excess of AgNO_3 . Or a few c.c. of a largely concentrated sample may be dropped on a thin layer of ether which has been floated on a dilute solution of H_2O_2 acidified with H_2SO_4 . Upon slight agitation the blue colour which forms in the lower solution passes to the ether.

Quantitative Estimation.—See Fresenius' 'Quantitative Analysis' and Sutton's 'Volumetric Analysis.'

Tin.—Evaporate a litre of the water to dryness. Dissolve out the tin by warming with a little pure HCl . Dilute and boil for a considerable time with pure metallic Cu, in order to convert all stannic compounds to the stannous form. Filter and add to the filtrate excess of mercuric chloride, when a shining opalescence of mercurous chloride is produced. Now add a few drops each of pure ferricyanide of potassium and pure ferric chloride to obtain Prussian blue. In the presence of HCl and stannous salts ferricyanide is reduced to ferrocyanide. This reaction is extremely delicate where no other reducing agents are present.

Into the stannous solution pass some H_2S , to obtain a dark-brown precipitate of stannous sulphide, soluble in KOH .

Quantitative Estimation.—See works referred to under chromium.

CHAPTER VIII

ORGANIC MATTER IN WATERS

ALL water which falls on inhabited districts must come in contact with organic matter—living and dead animal and vegetable substances. As vegetable organic matter, with the exception of the pathogenic micro-organisms, has little significance from the sanitary point of view, attention is almost entirely directed to animal matter in the form of sewage. It is not proved that animal organic matter *per se* in the quantities found even in dilute sewage is hurtful to health ; its importance lies rather in the fact that pathogenic microbes, especially those of intestinal origin, accompany it. Wherever, then, faecal matters, in quantity large or small, are met with danger exists.

The complex remains of dead animals and plants are slowly changed to simple inorganic compounds in the superficial layers of the soil under the action of manifold ferments, the products of micro-organisms in association with favourable quantities of heat, moisture, and oxygen. The sum total of these changes is spoken of as an oxidation, since the end products are oxides of carbon, nitrogen, etc. ; but there is no doubt that, as in the case of the various fermentations which take place in the alimentary canal of animals, known collectively as digestion, reductions frequently alternate with oxidations. There is some evidence to show that these ferments or enzymes, metabolic products of aerobic and anaerobic bacteria, act along certain lines which are intimately co-related. The specific action of one enzyme furnishes the necessary conditions for the opposed functions of a succeeding enzyme.

Such enzymes readily pass from soils into waters, and the existence of organic matters in the latter excites instant activity amongst the enzymes, evident to the eye in impaired transparency and to

chemical tests, as in the case of the nitric ferment, by the production of nitrates.

Whilst an accurate qualitative or quantitative estimation of organic matter in a potable water is impossible, still there are certain chemical tests of value in directing us towards the source of the organic matter, which source may ultimately be discovered by other means.

A rough differentiation of animal from vegetable matter may be effected by a consideration of the ratio of 'organic carbon' to 'organic nitrogen,' which ratio forms the basis of Frankland's well-known method of estimating organic matter. The process is only suitable for experienced chemists and laboratories equipped with apparatus for gas analysis. But in skilled hands it is simple and direct. A measured volume of water is carefully evaporated to dryness; the residue is introduced into a hard glass tube along with some oxide of copper, and the tube is heated in a furnace until combustion of the organic matter is complete. The gaseous products of combustion—carbon dioxide, nitric oxide, and nitrogen—are severally collected and weighed, as 'organic carbon' and 'organic nitrogen.' If in surface waters the proportion of organic carbon to organic nitrogen be as low as 3 : 1 the organic matter may be considered as of animal origin, while if it be as high as 8 : 1 it is chiefly vegetable. In certain fresh peaty waters the ratio of C : N has been found as high as 12 : 1. In fresh sewage the proportion of C : N may be 2 : 1. Frankland held that the smaller the proportion of organic carbon and organic nitrogen in a water, and of these constituents the larger the proportion of C : N, other things being equal, the better is the quality of the water. He divided waters into four classes, based on the quantities of organic C and N in parts per 100,000.

				Upland Surface Water.	Other Waters.
Class 1.	Water of great organic purity	under	'2	under	'1
" 2.	" " medium "	" "	'2 to '4	"	'1 to '2
" 3.	" " doubtful "	" "	'4 to '6	"	'2 to '4
" 4.	Impure water		over '6		over '4

Such classification is of little value in the light of present knowledge, since a water of great organic purity may convey the organism of enteric, and waters which would be classed impure may be harmless.

A method devised by Wanklyn for the estimation of the 'albuminoid' ammonia as distinguished from the 'free and saline' ammonia is perhaps the most generally useful in affording information concerning soluble organic matter. During those fermentative changes in organic bodies commonly known as putrefaction NH_3 is formed and evolved.

If we follow this NH_3 as it escapes, say, from a dung-heap in solution into the soil, we shall find that in the presence of the 'nitrous' organisms nitrous acid is formed, which, in conjunction with several bases, rapidly becomes nitrites. Later, under the action of the 'nitric' organisms, nitric acid is formed which rapidly becomes nitrates. These three stages in the oxidation processes, or purification of organic matter, stand out as landmarks, and afford considerable information to the water analyst.

For example, if A be a source of organic pollution—say a manure-heap—on the surface of the ground, and B a well sunk near it, the water of B will contain abundance of NH_3 .

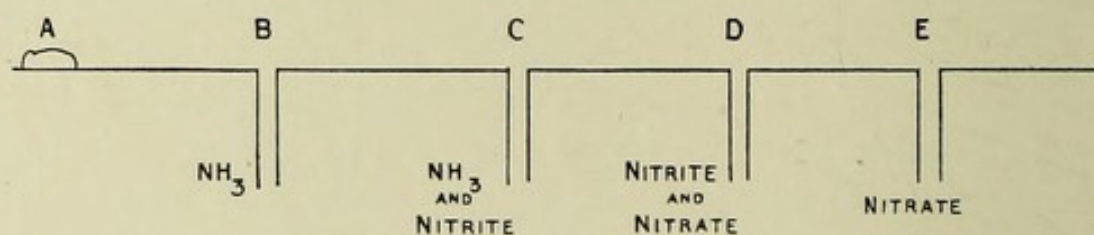


FIG. 7.

If a second well, C, be sunk at some distance, the purification processes will have advanced to the stage of nitrous acid and nitrites, and this water will contain less NH_3 and some nitrites. The water from D has travelled a much greater distance through the soil, and has consequently undergone further purification, so that NH_3 has disappeared and nitrites and nitrates are found. At E purification is complete, in that N is completely oxidized to nitric acid, and this water contains no NH_3 , no nitrites, but only nitrates.

The opportunities for purification offered to water bearing organic matter in solution from A to B are not sufficient to carry the oxidation changes beyond the stage of NH_3 ; whereas the journey from A to E is of such length that the entire changes have been completed. At intermediate points the corresponding intermediate stages in the purification are observed.

From the consideration of a single instance of this kind no conclusions as to the distance a well must be removed from a source of contamination in order to be safe can be drawn, since the factors in the problem of safety are numerous and variable. The distance between A and E, if the water in E is to be completely purified, would require to be much greater if the slope from A to E be considerable, or E would need to be much deeper. On the other hand, if the slope of the ground water descended from E to A, it is possible that the water of B may be free from all organic matter. The porosity of the soil, conditions of heat and moisture necessary to vigorous growth of purifying organisms, direction of slope of ground water, geological features of subsoil and underlying strata, rainfall, and a number of other factors, all influence this question of safe distance of well waters from foci of contamination. Each case must be worked out on its own merits, and here the chemical examination renders useful service. A sample of water from E may be pure to-day — that is, contain no organic matter as such, no NH_3 , no nitrites, but only nitrates ; to-morrow, owing to increased rainfall, whereby more organic matter than usual is washed into the soil, or to some other condition by which the powers of the soil for purification are lessened, this same water may contain, besides nitrates, nitrites, NH_3 , and even undecomposed organic matter. It should ever be borne in mind that the machinery by which organic matter is purified in the soil is liable at any point to break down, and in too many instances, although just sufficient for the work, is nearing breaking-point. The question, therefore, should be, not how near to a focus of contamination may it be safe to procure water, but rather how far from the focus is it possible to acquire it. Chemical analysis, if frequently and regularly performed, will, in most cases, discover such breakdown in the purification machinery, although a single analysis, unaccompanied by further information as to source and surroundings, may be quite useless. It is the comparative information regarding a water acquired by systematic and repeated analyses that is of value.

Wanklyn's Process.

Prepare a standard solution of NH_4Cl , 1 c.c. of which equals .01 milligramme NH_3 .

Prepare also Nessler's Reagent.

Dissolve 35 grammes KI in about 100 c.c. ammonia-free distilled water. Dissolve 16 grammes HgCl_2 in about 250 c.c. hot distilled ammonia-free water, and cool. Dissolve 200 grammes NaOH in stick in a litre of the same ammonia-free water.

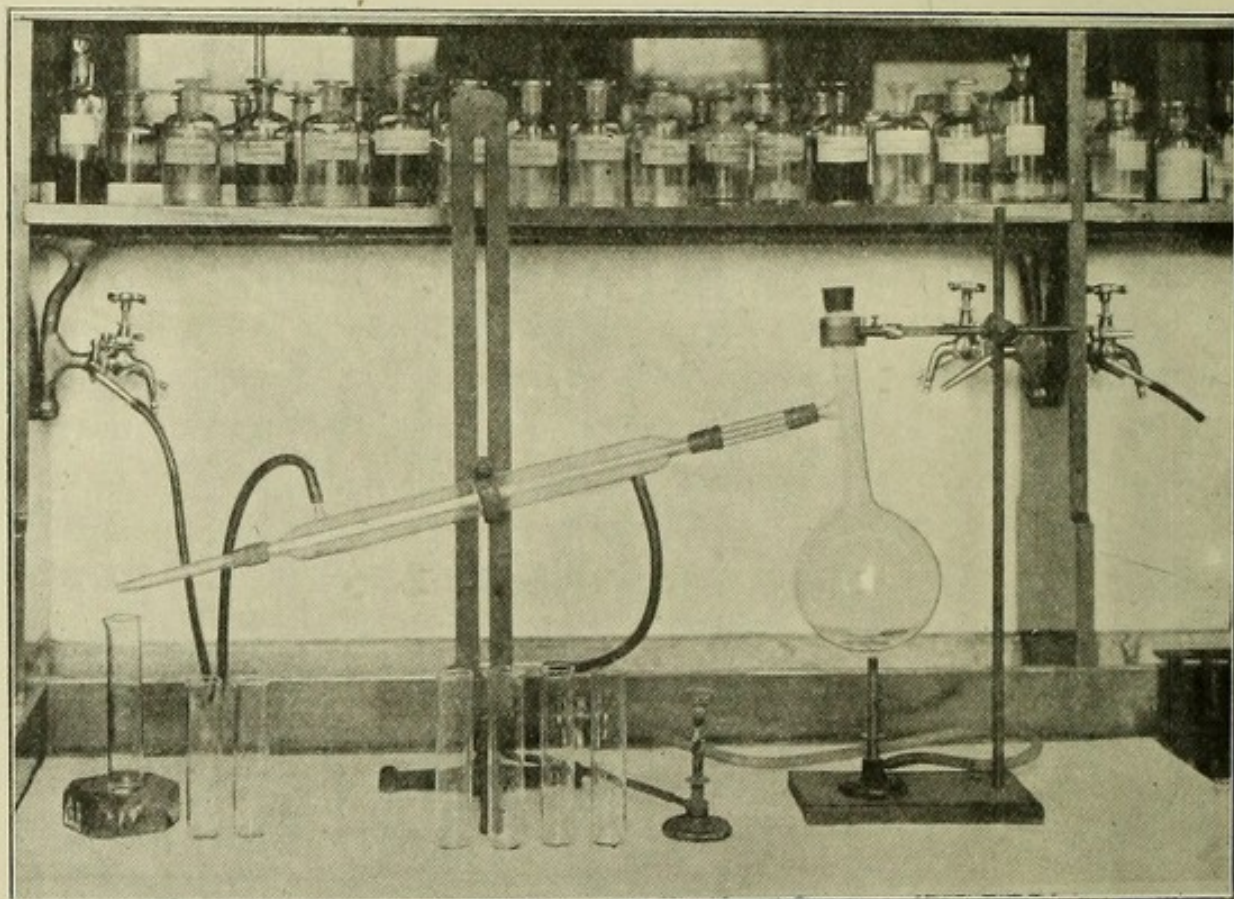


FIG. 8.

Into the solution of KI run the perchloride solution until a permanent precipitate of HgI_2 is formed.

Make this up to a litre with the NaOH solution, and add further sufficient perchloride solution to produce again a permanent precipitate. Let settle for several hours, and use the clear fluid

without disturbing the sediment. The sensitiveness of Nessler's reagent depends on its being saturated with HgCl_2 , and when this is the case it is of a very pale yellow colour. It may be necessary to add a few drops of HgCl_2 at times to restore lost sensitiveness.

Arrange a distilling flask and condenser, as in the figure. Into the flask pour 500 c.c. of the sample of water, and add a pinch of pure sodium carbonate; if the water is acid, a little more Na_2CO_3 will be required to render it faintly alkaline. The least acidity will fix NH_3 ; hence the necessity for Na_2CO_3 . Arrange a Bunsen burner, and distil over three Nessler glasses (50 c.c. each). Wanklyn found that the whole of the free and saline NH_3 comes over in 150 c.c. distillate. The boiling should be briskly effected, and it is generally useful to add a piece of pumice to the contents of the flask in order to prevent bumping. As each Nessler glass is filled, it should be covered until Nesslerization is accomplished.

Nesslerization is one of a number of colorimetric methods of volumetric analysis in which the amount of a substance is estimated by adding to it a second body capable of forming a characteristic colour with it. The same conditions are accurately fulfilled in a similar vessel, using distilled water and such quantity of the substance sought, in standard solution, as will match the colour of the first when the same quantity of the second body is added. In order that slight differences in tint may be appreciated and matched, it is necessary to work with dilute solutions of the body to be estimated and the standard reagent, and at times it will be necessary to largely dilute the water under examination.

Having collected the three 50 c.c.'s of distillate, Nesslerize each separately. Stand the Nessler glass on a white tile in a good north light, and by its side place a second Nessler glass of similar shape containing distilled ammonia-free water, and that quantity of standard solution of $(\text{NH}_4)\text{Cl}$ deemed necessary to match the first. Into each deliver 2 c.c. of Nessler's reagent, and carefully mix. In a few minutes the yellow colour will have fully developed, and its depth can be gauged by looking down through the column. Should there be some discrepancy in the tints, rapidly add to another Nessler glass containing distilled ammonia-free water a little more or a little less of the standard solution, as the case may be, until an exact match is produced. In all such colorimetric work every

condition should be exactly similar in the two cases—length of time reagents are in contact, order in which reagents are added, shape and size of containing vessels, etc. The standard solution of NH_4Cl must be added to the second Nessler glass before the Nessler's reagent, as this occurred in the Nessler glass containing the distillate. If the standard solution be added after the Nessler reagent an opacity is likely to form which prevents to some degree an exact match being made. Several trials may be necessary before an accurate result is reached.

The second and third 50 c.c. of the distillate are treated in the same way, and the sum of the results in terms of c.c. of the standard solution noted.

Wanklyn found that the whole of the free and saline NH_3 was contained in 150 c.c. distillate, and that the first 50 c.c. contained three-fourths of the total.

Example.

First Nessler glass matched by 3.00 c.c. NH_4Cl (1 c.c. = .01 milligramme NH_3)

Second " " " " .75 " " " "

Third " " " " .25 " " " "

Total $\text{NH}_3 = 4.00$ " " " "

But each c.c. standard $\text{NH}_4\text{Cl} = .01$ milligramme NH_3 ;

∴ 4 c.c. = .04 " "

And in 500 c.c. of the water under examination there is .04 milligramme NH_3 . In 100 c.c. there will be .008 milligramme NH_3 , or, since 100 c.c. water = 100,000 milligrammes, this water contains free and saline NH_3 to the extent of .008 part per 100,000.

Whilst the Nesslerization of the free and saline NH_3 is going on, 50 c.c. of alkaline potassium permanganate (composed of 800 grammes KOH , 8 grammes permanganate, to a litre of water) should be boiled, so as to expel any ammonia that it may contain, and to heat the liquid in order to prevent cracking the retort when pouring it in. This is a strongly-oxidizing reagent, and rapidly converts undecomposed organic matter into NH_3 . By this moist combustion process a degree of oxidation is effected in the course of half an hour or so in the laboratory that would require weeks or months by the natural processes outside.

When the alkaline permanganate is ready, the cork of the retort is removed and the hot solution poured in.

This portion of the distillation should be carried out more slowly, as organic matter is slowly decomposed, and the distillate should be collected as long as any NH_3 comes over. No relation exists between the number of the Nessler glasses collected and the total NH_3 , as in the case of the free and saline portion. Moreover, the second Nessler may contain as much NH_3 at times as the first.

The student should fit up his apparatus himself, and see that all connections are water-tight and air-tight, as the case may be. Corks should be carefully bored and made to fit flasks and condenser tubes, and indiarubber corks are preferable to wood. The distilling-flask should be thoroughly cleansed with weak acid and rinsed out with distilled water until all traces of acid have disappeared. It is well to distil some pure ammonia-free water through the condenser in order to get rid of any traces of NH_3 that it may contain before starting the distillation of a sample. A large and constant stream of water running through the condenser is necessary throughout the entire process. A long-stem funnel is to be used for delivering water, etc., into the retort, and this is especially necessary for the introduction of the hot alkaline permanganate, so that none of the reagent may enter the central tube of the condenser and foul the distillate.

Seeing that the atmosphere of an ordinary chemical laboratory contains quantities of NH_3 , it is well to have a separate room for water analysis.

In very rare instances a potable water may not yield the entire free and saline NH_3 to the first 150 c.c. of the distillate. In such cases it will be necessary to distil over and Nesslerize a fourth or fifth 50 c.c.

It is possible that the 'free' ammonia exists in water in conjunction with some acid, which, on being boiled in the presence of carbonates, yields up the ammonia in the form of $(\text{NH}_4)_2\text{CO}_3$.

It is well before commencing the process to ascertain roughly the quantity of NH_3 present by Nesslerizing 50 c.c. of the water. In a fairly good sample the colour furnished in 50 c.c. by 2 c.c. Nessler reagent should be the faintest tint of yellow; if the tint is well marked the sample is bad, and dilution must be made before distilling.

In the second part of the process, the distillation of the albu-

minoid ammonia may require to be carried to a point at which the volume of fluid in the flask becomes dangerously small; this should never be allowed, but ammonia-free distilled water should be added to the flask as required, so that the volume may be kept up.

With regard to the amounts of 'free and saline' and 'albuminoid' ammonia which may be allowed in different potable waters, there is some little difference of opinion. All observers agree that the two ammonias must be considered together, and most agree that in drinking waters if the 'albuminoid' reach $\cdot 005$ part per 100,000 the 'free and saline' should not be more. If the 'albuminoid' be small—say less than $\cdot 002$ part per 100,000—the 'free and saline' may be allowed to slightly exceed $\cdot 005$.

Much 'albuminoid' and little 'free and saline' ammonia indicate vegetable matter; whereas much 'free and saline' and little 'albuminoid' indicate animal matter. These indications must not be too literally relied upon.

As a general rule, it may be stated that where a water has been contaminated with sewage the high free and saline ammonia figure will be supplemented by an increase in chlorides, phosphates, and oxidized nitrogen. Whilst accepting the principle that animal pollution is indicated by a relatively larger figure for 'free and saline' ammonia than for 'albuminoid,' and that vegetable matter produces much 'albuminoid' ammonia, with little or no 'free,' it must be borne in mind that these relations are liable to be upset. Peaty waters, whilst producing albuminoid ammonia in quantity, should not produce any 'free'; still, there are such waters met with at times which give rise to a small quantity of 'free' ammonia although no animal matter can be traced.

Good spring waters rarely contain 'albuminoid' ammonia above $\cdot 002$ part per 100,000. Upland surface waters, as a whole, should not produce 'free' ammonia beyond $\cdot 001$ part per 100,000.

The degree of initial dilution necessary to produce the best colour-tint for matching on Nesslerization can only be discovered by experience, and here, as in all matters practical, the student should ever appeal to experiment. Scores of waters must be patiently worked out in all details before he can expect to acquire even an elementary knowledge of the subject.

Much 'free' ammonia in the absence of 'albuminoid' may be

accounted for by the water passing through strata rich in ammonium salts, portions of which are carried away in solution ; water-bearing strata containing nitrates and subsalts of iron afford ' free ' ammonia by the reduction of the nitrates through the intermediate phase of nitrous acid to NH_3 ; rain water falling through the atmospheres of towns abounding in ammoniacal fumes will yield appreciable quantities of ' free ' ammonia, and at times small quantities of ' albuminoid ' also from the organic matter in suspension in the air.

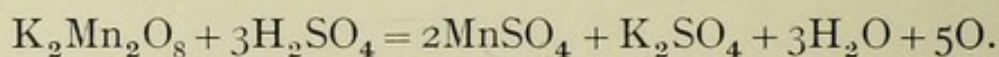
It may be noted that, although the Wanklyn process does not decompose urea, the most important and abundant nitrogenous constituent of urine, nor recover NH_3 from a few other bodies in sewage, still it is of the greatest value in dealing with the contamination of water by organic matter, from the comparative results afforded, so long as the determinations are carried out under similar conditions.

CHAPTER IX

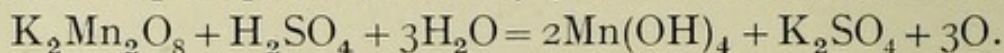
OXIDIZABLE ORGANIC MATTER IN WATER

FORCHAMMER applied to water analysis his knowledge of the experimental fact that organic matter in the presence of an acid can rob $K_2Mn_2O_8$ of a portion of its oxygen. This process was slightly modified by Tidy, and is usually known in this country in connection with his name. It is not a reliable test of either the quality or quantity of organic matter present, but, in that pure waters absorb practically no O from permanganates of potassium, and foul waters a great deal, the process has some value as corroborative evidence of the presence of organic matter. It should be noted that other bodies beside organic matter, such as ferrous salts, nitrites, sulphides, etc., abstract O from $K_2Mn_2O_8$, and when these are present they must be accounted for before drawing a conclusion as to the amount of organic matter dealt with. The quantity of O absorbed varies with the time of contact, the temperature, and, to less extent, with the acidity, and light admitted during digestion.

Potassium permanganate in contact with organic matter and H_2SO_4 furnishes 5 atoms of O and colourless sulphates of manganese and potassium.



If sufficient acid be not added, the hydrated peroxide falls as an opaque brown precipitate, and only 3 atoms of O are set free.



During the digestion the reaction should be carefully watched, to see that the fluid remains transparent throughout. If much organic matter be present, it may be necessary to add further quantities of permanganate from time to time. Ferrous salts, nitrites, etc., abstract O rapidly from the permanganate, whilst organic matter acts much more slowly.

Various times and temperatures have been employed in this process for digesting the sample of water with the acid and permanganate, some analysts recommending four hours at 80° F., others two hours, three hours, or fifteen minutes, at higher and lower temperatures. In a laboratory where an incubator is kept at blood-heat (37° C.) it is convenient to use it, and four hours is a sufficient length of time. In examinations two hours at room-temperature may be found most convenient.

Prepare a standard solution of potassium permanganate (1 c.c. = .1 milligramme of available O) by dissolving .395 gramme of the pure crystal in a litre of distilled water. Make a fresh 10 per cent. solution of KI, and a fresh solution of sodium thiosulphate, 1 gramme to a litre of water. Lastly, prepare a boiled solution of starch and test its delicacy with water containing the merest trace of free iodine.

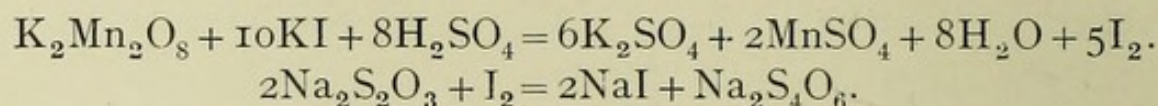
Clean two Erlenmeyer flasks (capacity 300 c.c.), and into one measure 100 c.c. of the water sample. Mark it 'Sample' with a wax pencil. Into the second, marked 'Control,' measure 100 c.c. distilled water. Now carefully pipette into each 10 c.c. of the standard solution of $K_2Mn_2O_8$, and with another pipette run in to each also 10 c.c. of a 25 per cent. solution of pure H_2SO_4 . Stopper and set aside in an air oven or incubator, as the case may be, at the temperature chosen, for a period of two or four hours. Should the amount of organic matter in the water be large, the whole of the permanganate may be decomposed and become colourless; in such case a second 10 c.c. of the standard solution is added, and should this be decolourized a third, and so on. Account of the further additions will be taken in the calculation at the end of the experiment.

When the time allowed has expired, and a portion of the permanganate remains undecomposed, as demonstrated by the red tint still remaining, a few drops of the KI solution are added to the flask containing the water sample, when free iodine is liberated in quantity proportional to the amount of undecomposed $K_2Mn_2O_8$ remaining. A very few drops of the KI solution will contain an excess of iodine. This liberated I—the measurer of the undecomposed $K_2Mn_2O_8$ remaining in the flask—is titrated with thiosulphate solution from a burette until completely oxidized, the end reaction

being definitely ascertained in the presence of a few c.c. of the boiled starch solution by the disappearance of the blue colour of the iodide of starch.

The same procedure exactly is carried out with the control, and here, as no $K_2Mn_2O_8$ has been decomposed, but the whole of the 10 c.c. remains intact, we obtain a figure in terms of c.c. of thio-sulphate solution which represents this amount, or which represents 1 milligramme available O. When it is remembered that the thiosulphate is a most unstable body, changing in strength from day to day, the necessity for standardizing the permanganate and for the control experiment is at once obvious.

The following equations represent the liberation of free I and its subsequent oxidation by sodium thiosulphate :



Example.—The distilled water and intact 10 c.c. standard solution of permanganate liberated iodine that required for its oxidation 27 c.c. of the thiosulphate solution. The sample of water and undecomposed portion of the 10 c.c. of standard permanganate liberated iodine that required for its oxidation 23.2 c.c. of thiosulphate. From this it is plain that the amount of permanganate solution decomposed by the organic matter (assuming that no nitrites, sulphides, etc., were present) is represented by $27 - 23.2$ c.c. thiosulphate. But 10 c.c. standard permanganate or 1 milligramme O = 27 c.c. thiosulphate ;

$$\therefore 27 : 27 - 23.2 :: 1 \text{ milligramme} : x ;$$

$$x = \frac{27 - 23.2}{27} = \frac{3.8}{27} = .14.$$

There is, therefore, in 100 c.c. of this water organic matter capable of absorbing from permanganate of potassium O to the extent of .14 milligramme, or .14 part per 100,000, under the conditions of time and temperature named.

CHAPTER X

OXIDIZED NITROGEN—NITRITES AND NITRATES

DURING the early stages of putrefaction of organic matter much free N escapes in gaseous form, and the rest unites with H to form NH_3 . As has been already stated, certain bacteria in the soil and elsewhere convert NH_3 into HNO_2 , which latter combines with various bases to form nitrites. Of the so-called 'nitrous' organisms a few species have been studied, one of which is the *Nitrosomonas* of Winogradsky. Nitrites, therefore, represent chemically the intermediate stage in the process of oxidation or purification. Under certain conditions, to be presently mentioned, they also represent an intermediate stage in the reduction of nitrates to NH_3 . The presence of nitrites in a water indicates more remote contamination in point of time or space, or of both, than does NH_3 .

In like manner 'nitric' organisms, such as the *Nitrobacter* (Winogradsky), transform HNO_2 into HNO_3 , which readily becomes nitrates. This class of bacteria has no action on NH_3 , and the previous class is unable to carry the oxidation of NH_3 further than HNO_2 , so that two distinct and independent types of organism are necessary to the complete oxidation of NH_3 .

It will be readily seen that the detection and estimation of nitrites and nitrates are of considerable importance in the investigation of the problem of organic pollution.

The presence of nitrates alone in a water indicates previous pollution that has been oxidized and rendered harmless. But if the quantity of nitrates be great, purified sewage may be suspected, which, through a breakdown at any moment in the machinery of purification, may become most dangerous sewage. Moreover, in view of the fact that sewage effluents contain almost as many micro-organisms as crude sewage, no effluent, however high its degree of

purification may be chemically, should ever be allowed to come in contact with drinking water. In all waters possessing a high nitrate figure this possibility of the presence of purified sewage should be borne in mind.

When nitrates, which form the end of the purification of organic matter, occur alone, it is obvious that no indication of the date of the previous pollution is given.

In determining the true significance of nitrates in potable waters it is necessary to consider (1) whether they arise from geological strata (chalk, lias, oolite, sandstones) through which the water has percolated, in which case the evidence of organic pollution supplied by the other steps of the analysis—such as the free and saline NH_3 , organic NH_3 , O absorbed from permanganate of potassium, etc.—will be negative; (2) whether they are due to purified sewage, in which case the quantity will be much too great, as also that of Cl; (3) whether they represent a small amount of organic matter (for the most part animal) that has undergone complete oxidation, and is to be considered harmless. In this case the quantity will be small—in rain and upland surface waters not exceeding .1 part per 100,000—and all the other items of the analysis employed to discover organic matter will afford negative evidence.

In the few cases where strata alone contribute soluble nitrates the quantity will rarely exceed .5 part per 100,000, but no figures can be laid down as an accurate standard, and each case must be worked out in connection with the rest of the analytical data.

In a few instances strata containing nitrates (in particular the lower greensand) contain also reducing minerals, such as proto-salts of iron, which reduce HNO_3 to HNO_2 , and the latter to NH_3 . The same reduction can be effected by denitrifying micro-organisms. Free NH_3 , due to reduction of nitrates and nitrites, will be identified by the absence of organic NH_3 , and all other evidence of organic pollution.

Nitrites are very unstable, and in the presence of available O rapidly become nitrates. In the early stages of the oxidation of large quantities of animal organic matter they are mostly found in company with NH_3 , but a foul water may at a particular moment fail to furnish any nitrites. They are significant of recent contamination, except in those cases just mentioned, where they are

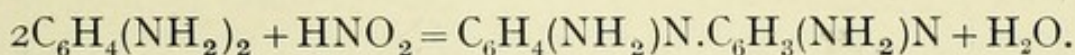
due to the reduction of nitrates in strata. Nitrites, then, which in deep-well waters may be merely the products of reduction of nitrates by iron in strata, iron pipes, etc., and consequently quite harmless, will in shallow wells and surface supplies condemn the water.

All the inorganic N—apart from strata—found in nitrates, nitrites, free and saline NH_3 , after deducting that present in rain water, may be regarded as due to previous sewage contamination.

Detection and Estimation of Nitrites.

Potassium, Iodide and Starch.—To 10 c.c. of the water in a test-tube add 1 c.c. of a clear and boiled starch solution and a drop of KI. Mix and add a little dilute H_2SO_4 , when immediately a blue colour is produced if nitrites be present in considerable amount. On standing, nitrates give this reaction also. Pure sulphuric acid should be used, and it is found that, owing to the instability of KI, ZnI gives better results. This test can be made a quantitative colorimetric one by operating on 100 c.c. of the water in a Nessler glass, and in a second Nessler 100 c.c. of a mixture of distilled water and the amount of a standard nitrite necessary to form a colour match. When the proportion of nitrites in a sample is 1 in 10,000,000, the blue colour is formed in a few minutes; when 1 in 100,000,000, in twelve hours; and when 1 in 1,000,000,000, in forty-eight hours.

Griess's Method.—Make a 5 per cent. solution of metaphenylene-diamine in water. Decolourize with animal charcoal, and render slightly acid with H_2SO_4 . Much acid must not be used. To 100 c.c. of the water to be tested in a Nessler glass add 1 c.c. of the reagent, cover, and set aside in a warm place for twenty minutes. A yellow to orange colour is produced, according to the quantity of nitrites present. The reagent should be made at the time of use. When metaphenylene-diamine (diamido-benzol) reacts with nitrous acid, triamido-azo-benzol (Bismark brown) is produced; hence the colour.



By using a standard solution of potassium nitrite, the colour produced in the 100 c.c. of water may be matched in the same

quantity of distilled water. A series of trials must be made, in which the reagent is added to the contents of the two cylinders at the same moment, and the cylinders covered and set aside in a warm place for twenty minutes. The standard nitrite is prepared thus: Dissolve .406 gramme of AgNO_2 in boiling water; add slight excess of KCl . Silver chloride is formed, and gradually falls to the bottom. Make up to a litre and allow to settle. When clear, decant off the supernatant fluid, and dilute each 100 c.c. up to a litre. It should be kept in the dark and in small bottles filled to the stopper, so as to protect it from the air.

$$\begin{aligned} 1 \text{ c.c.} &= .01 \text{ milligramme } \text{N}_2\text{O}_3. \\ &= .0037 \quad \quad \quad \text{N.} \end{aligned}$$

Detection and Estimation of Nitrates.

Brucine Test.—To 10 c.c. of the water in a test-tube add 1 c.c. of a saturated solution of brucine, and shake. Incline the test-tube and pour down the side 2 c.c. of pure H_2SO_4 . Carefully bring the test-tube to the vertical against a white ground. A pink zone is formed at the junction of the acid and supernatant mixture, which lasts for a few seconds, and then changes to brownish yellow. When nitrates are in large quantity, the colour changes very rapidly. Where the reaction is doubtful, a fresh layer of the mixture can be brought in contact with the acid by imparting to the test-tube a slight centrifugal motion.

Or, 10 c.c. of the water may be evaporated to dryness in a platinum dish, a drop of pure H_2SO_4 added, and a small crystal of brucine dropped on the contents, when a pink colour will appear, even where the quantity of nitrates is so small as .01 part per 100,000.

Diphenylamine Test.—Mix about 10 milligrammes of diphenylamine with 1 c.c. pure H_2SO_4 in a porcelain basin, and carefully run $\frac{1}{2}$ c.c. of the water over the mixture. A blue colour develops in the presence of nitrates; the depth of the tint is roughly proportional to the amount of nitric acid. This reaction is not simulated by any other constituent of potable waters.

Quantitative Estimation of Nitrates.

1. **Crum's Method.**—This method consists in shaking up the residue obtained from the concentration of a measured quantity of the water with metallic mercury and pure H_2SO_4 , when nitric oxide is produced, which is afterwards conducted to a gas analysis apparatus and measured. It requires some experience in collecting and measuring gases, but in the hands of a skilled operator is one of the most exact methods known. The nitric oxide produced represents the N of nitrites and nitrates. To obtain the N due to nitrates alone, that obtained for nitrites by Griess's method is subtracted from the total. This method may be used for the estimation of nitrous and nitric N in sewage effluents.

2. **Copper-Zinc Couple Method.**—This method estimates nitrous and nitric N as NH_3 . In calculating the nitric N, it is plain that from the amount of NH_3 obtained in the process deductions must be made for original NH_3 in the water as well as that derived from nitrites.

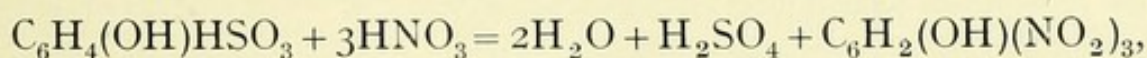
When zinc is immersed in CuSO_4 solution, a spongy deposit of Cu is precipitated upon it, and in this condition it is capable of bringing about various decompositions in which H is liberated. The H is occluded by the spongy copper, and when thus occluded reduces nitrates to nitrites, and nitrites to ammonia. The reaction is hastened by the presence of traces of NaCl and other salts, rise of temperature, and any condition which increases the electrolytic action of the couple.

Take a piece of clean zinc-foil and cover it with 3 per cent. CuSO_4 solution until a copious, firmly-adherent coating of black spongy Cu has been deposited. This deposition should not be pushed too far, otherwise the Cu will be so easily detached that it cannot be washed. When sufficient deposit has accumulated, the CuSO_4 solution is removed and the couple carefully washed with distilled water, when it is ready for use. A clean, wide-mouthed, stoppered bottle is selected and washed out with some of the water to be tested. The coated foil is inserted, and a measured quantity—say 100 c.c.—of the water poured in so that the foil is completely covered. The bottle is tightly stoppered and set aside in a warm place for some hours. If the bottle be properly closed, the tempera-

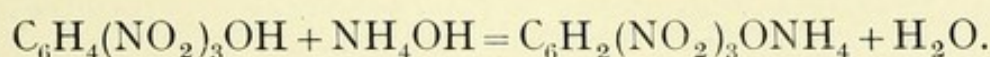
ture may be raised to 28° or 30° C. without fear of losing NH_3 . When it is desirable to hasten the reaction, a little NaCl may be added to the water ($\cdot 1$ gramme to 100 c.c.), or CO_2 may be passed through the water before it is placed in the bottle. In calcareous waters lime may be removed by the addition of some pure oxalic acid previous to digestion with the couple. Nitrous acid remains in the solution until the reaction is complete, so that it is necessary to test a small quantity of the water from time to time by Griess's reagent for the presence of this body. Metaphenylenediamine easily detects 1 part of nitrous acid in 10,000,000 of water. When the last trace of nitrous acid has disappeared, the water is poured off the couple into a clean, stoppered bottle, and if turbid allowed to subside. A portion of the clear fluid, diluted if necessary according to the degree of concentration of the nitrates in the water, is transferred to a Nessler glass and the NH_3 estimated in the usual manner. In the case of coloured waters, or those containing magnesium and other salts that interfere with the Nessler reagent, a measured quantity of the water poured off the couple should be put in a retort, a little Na_2CO_3 added, and Nesslerization performed on the distillate. It has been found that about half a square decimetre of zinc-foil should be used for each 100 c.c. of a water containing 5 or less parts of nitric acid per 100,000. A larger proportion of foil should be used for waters richer in nitrates and for sewage effluents. The couple, if carefully washed after use, may be used for at least three estimations. It is convenient in most laboratories to digest overnight. Where accurate results are required, and in the hands of the inexperienced, it is advisable to distil the water removed from the couple and estimate the ammonia in the distillate. From the total N found as NH_3 deduct that due to inorganic NH_3 found by Wanklyn's process, and that due to nitrites found by Griess's process; the remainder is the N due to nitrates in the water.

3. Sprengel's Phenol Method.—This is a much less accurate method (the error is one of under estimation), but can be performed in a limited time. It estimates the N of nitrates alone, and is chiefly applicable to waters containing small quantities of nitric acid. The method has for its basis the facts that when phenol

sulphonic acid reacts with nitric acid, picric acid (trinitro-phenol) is formed.



and the ammonium salt of picric acid being yellow, this body lends itself to quantitative colorimetric estimation.



The solutions required are :

Standard potassium nitrate, containing .7215 gramme KNO_3 in a litre of water. One c.c. of this solution = 0.1 milligramme N. A dilution of 100 c.c. to a litre should be made for the analysis, in order to avoid the possible error resulting from measuring 1 c.c. One c.c. will then contain .01 milligramme nitric N.

Phenol Sulphonic Acid.—The phenol sulphonic acid used should be the pure disulphonic acid ($\text{C}_6\text{H}_3(\text{OH})\text{H}_2\text{SO}_3$), which, with HNO_3 , gives, according to Kekulé, picric acid even in the cold. Three grammes pure phenol and 37 grammes (20.1 c.c.) pure H_2SO_4 , specific gravity 1.84, are mixed in a beaker and heated for six hours on a water bath at 100°C . Should the acid thus formed crystallize out on standing, it may be brought into solution by reheating for a short time.

Process.—Place 10 c.c. of the water in a porcelain basin on a water bath and in a similar basin 10 c.c. of the standard nitrate ; when just dry, add to each 1 c.c. of the phenol sulphonic acid and allow to remain for a few minutes on the bath. Now transfer to two Nessler glasses the contents of the dishes, and wash out with 25 per cent. ammonia solution the last trace of material from the dishes ; add further ammonia to the Nessler until all effervescence ceases and a small excess of ammonia is found in each. Spirting may be prevented by washing out the contents of the basins into the Nessler glasses with a small quantity of distilled water, and adding the ammonia solution afterwards. Make up to 50 c.c. in both cases with distilled water, and let stand for fifteen minutes.

In performing the estimation, take a third Nessler glass and pipette into it from the more deeply-coloured cylinder (which is generally that containing the standard nitrate) a quantity deemed

necessary to match the tint of the cylinder containing the water sample. Make up to 50 c.c. with distilled water, and compare the two cylinders when placed on a white tile. The exact match can be effected in a few trials.

Suppose that 20 c.c. from the standard solution match the water sample, the latter contains $\frac{20}{50}$ of the N as nitrates contained in the standard. Each c.c. of the standard contains .01 milligramme N.

\therefore 10 c.c. = .1 milligramme N, but $\frac{20}{50}$ of .1 = .04 ;

\therefore 10 c.c. water under examination = .04 milligramme N ;

\therefore 100 „ „ „ „ = .40 „ „

or this water contains .4 part nitric N per 100,000.

In the case of very good waters 20, 50 or more c.c. should be evaporated to dryness as above, and only 5 c.c. of the standard nitrate taken.

The amount of sulphonic acid used, so long as there is enough, is of little import. In comparing the colours, the best results are obtained when the intensity of the colour does not exceed that produced by 1 c.c. of a water containing about .05 part N per 100,000. The colour produced by .1 part per 100,000 is difficult to match accurately. The loss of N during evaporation is less when the evaporation is made to take place rapidly in an open dish at 100° C. Slow evaporation at a lower temperature causes more loss, and the dry residues, if further heated, lose N. Chlorine does not interfere if present in less quantity than 2 parts per 100,000. If it exceed 7 parts, it should be removed before evaporation by Ag_2SO_4 . This process does not estimate the N as nitrite, as the action of nitrous acid results in the formation of nitroso-phenol, $\text{C}_6\text{H}_4(\text{NO})\text{OH}$, which is colourless in dilute solutions.

CHAPTER XI

GASES IN WATER

WATER dissolves gases in quantities depending on temperature, pressure, and solubility of the gas. The principal gases found in potable waters are N, O, CO₂, and occasionally CH₄, H₂S, and NH₃. Of these O and CO₂ are alone worthy of estimation. As organic matter in water throughout all its stages of change lays hold of dissolved oxygen, the presence or absence of this gas may afford valuable information regarding such organic material. These remarks apply equally to sewage effluents.

From a hygienic point of view the subject of gas extraction from waters is not sufficiently important to warrant the expenditure of time and labour inseparable from accurate gasometric work. Nor is the information gained even when the work is most exactly performed of constant or certain value.

Estimation of O Dissolved in Water (Thresh).

When sulphuric acid is added to a mixture of KI and a nitrite, iodine is set free. If O be carefully excluded, this free iodine rapidly reaches its maximum, and remains constant. But if O be admitted, the amount of iodine liberated varies with the time of exposure, and has no relation to the amount of nitrite present. Thresh concluded that the NO produced acted as a carrier of O, forming N₂O₃, which liberated more iodine and was again transformed into NO, and that this action continued as long as any free dissolved O remained in the water.

1. $\text{NaNO}_2 + \text{H}_2\text{SO}_4 = \text{HNO}_2 + \text{NaHSO}_4.$
2. $2\text{HNO}_2 + 2 \text{KI} = \text{I}_2 + 2\text{NO} + 2\text{KOH}.$
3. $2\text{NO} + \text{O} = \text{N}_2\text{O}_3.$
4. $\text{N}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{KI} = \text{I}_2 + 2\text{NO} + 2\text{KOH}.$

In the above reactions it will be noted that free nitrous acid is first formed, and that this liberates I. KOH is neutralized by H_2SO_4 , which is in excess.

If now the total amount of I liberated be determined, and the amount of I theoretically liberated by the nitrite be calculated, the difference will represent the I liberated by the O dissolved in the water.

The estimation is carried out as follows (see Fig. 9) :

Into a wide-mouthed glass bottle A, of 500 c.c. capacity, is fitted an indiarubber cork, with four perforations. The stem of a separator funnel B, holding about 300 c.c. of the water, is pushed through the cork. Through another perforation is run a piece of glass tube attached by rubber tubing to the lower end of a 100 c.c. burette C, graduated to tenths of a c.c. Through the remaining two perforations are run pieces of glass tubing bent at right angles, one D, connected by rubber with a gas-tap, and the other E, by similar tubing with a short piece of glass tube thrust through an india-rubber cork, which fits the top of the separator funnel. The funnel B is filled with water to the top, and the glass stopper inserted, displacing a small quantity of water. The contents are accurately measured once for all, and the capacity of the funnel noted.

The funnel is now filled with the water to be examined. The burette C is charged with thiosulphate (1 c.c. = .25 milligramme O), made by dissolving 7.75 grammes of crystalline sodium thiosulphate in a litre of distilled water. Having thoroughly cleaned and dried the bottle A, the cork is inserted and the tube connected with the lower end of the burette C, fixed in position. The funnel B is filled up to the top, and the stopper inserted; the stopper is now taken out and 1 c.c. of a solution of sodium nitrite and potassium iodide (sodium nitrite .5 gramme, KI 20 grammes, distilled H_2O 100 c.c.) poured in from a 1 c.c. pipette. From a second 1 c.c. pipette is run in 1 c.c. H_2SO_4 (25 per cent.). The higher specific gravity of the nitrite mixture and of the H_2SO_4 solution causes these to sink rapidly to the bottom of B, and when the stopper is replaced a negligible quantity, if any, of the reagents just added is lost in the small amount of water which overflows; in this way the entry of air is excluded. The funnel is inverted a

few times, so as to effect a uniform admixture, and its nozzle pushed through the cork. The tube D is joined up with a gas-tap, and gas rapidly passed through the bottle. When all the air has been

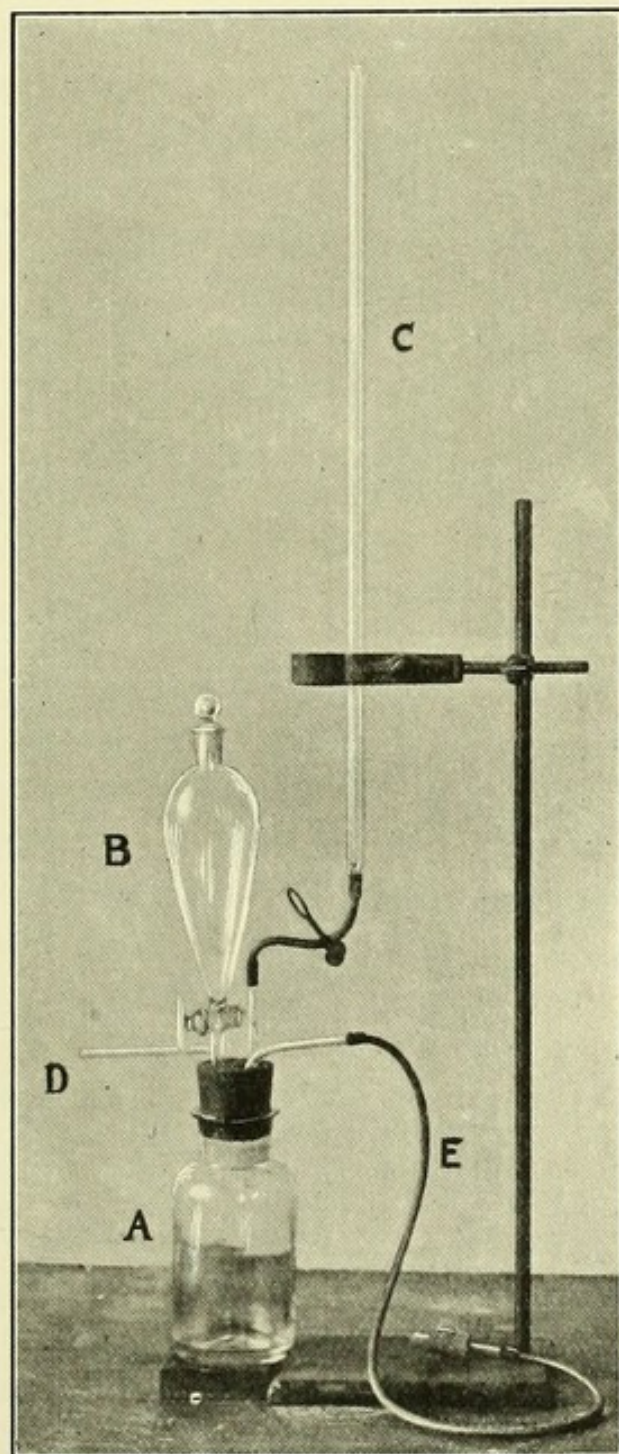


FIG. 9.

expelled the gas may be lighted at the end of E, where it will burn quietly. The stopper of B is removed, and having rapidly extinguished the flame at the end of E, the cork of the latter is fixed

in B, after which the tap is turned, and the mixture of water and nitrite solutions is discharged into A. The tap of B is now turned off, the cork at the end of E removed, and the gas relighted and turned down to a small flame. Thiosulphate is then run in slowly from C until the brown colour produced by the liberated iodine is nearly removed. About 3 c.c. of a fresh starch solution is poured into B, and 1 c.c. of this carefully run through the tap into A, in order to definitely fix the end of the reaction. As the blue colour returns in most instances after a few seconds, it is well to wait for a little and add a further drop or two of thiosulphate to complete the decolorization.

The amount of thiosulphate used will represent :

- (1) The oxygen dissolved in the water used.
- (2) The oxygen annexed by the HNO_3 formed from the nitrite.
- (3) The oxygen annexed by the HNO_2 of any nitrite present in the water.
- (4) The oxygen dissolved in the reagents added.

The value of (1) can obviously be determined by subtracting the sum of the values (2), (3), and (4) from the total.

The values of (2) and (4) can be easily determined by making a blank experiment, using five times the amounts of nitrite-iodide solution, sulphuric acid, and distilled water in lieu of the thiosulphate, as it may be assumed that the oxygen in distilled water is equal to that in thiosulphate. The number of c.c. of thiosulphate solution divided by 5 gives the joint values of (2) and (4). In order to estimate (3) the nitrous acid in the sample must be very carefully determined, and as 94 parts by weight of the acid are equivalent to 16 of O, the calculation is easily made.

For a given piece of apparatus, the values of (2) and (4) having been once determined, it is unnecessary to repeat the process, granted that the same quantities of reagents are always used. In (3) the nitrous acid may be estimated by Griess's method.

A simpler method for the estimation of O dissolved in water is that of **Winkler** :

In collecting the sample of water, care must be taken to avoid agitating it and exposing it for any length of time to the air. It is transferred with similar precautions by syphoning to a stoppered bottle of known capacity—about 350 c.c. One c.c. of strong manganous chloride solution (40 grammes $\text{MnCl}_2 \cdot \text{H}_2\text{O}$ to 100 c.c.)

is added, followed by 2 c.c. of a solution containing 33 per cent. KOH and 10 per cent. KI. The bottle, which must be full of liquid, is now closed with the stopper without including any air-bubble, and the liquids are mixed by several times inverting the bottle. The manganous hydroxide precipitate which forms will be more or less discoloured by higher hydroxide, according to the proportion of O which was dissolved in the water sample. As the oxidation of the manganous hydroxide is not immediate, and the result is influenced by light, the bottle is put aside in a dark cupboard for fifteen minutes; 2 to 3 c.c. of pure strong H_2SO_4 are added, which cause the precipitate to disappear, and leaves the liquid coloured with dissolved iodine. The iodine is titrated with standard thiosulphate, of which the oxygen value should be known, so as to give the amount of oxygen directly. It is usual, however, to determine the amount of thiosulphate required by the same volume of fully aerated pure water of similar character, or of distilled water, and then to calculate the percentage of the possible amount of oxygen present in the polluted water directly from the amounts of thiosulphate which equal volumes of the two samples require. The manganous chloride must be free from iron, and all the reagents must be free from nitrites.

CO_2 in Water.

Carbon dioxide may exist in solution in water in the free state, or as a bicarbonate or a carbonate.

Estimation of Total CO_2 (free CO_2 , CO_2 in bicarbonates, CO_2 in carbonates).—Solutions and apparatus required :

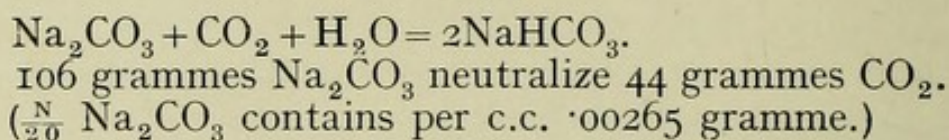
BaCl_2 solution, 10 per cent. H_2SO_4 , baryta-water, flask of capacity about 300 c.c., fitted with a perforated bung through which three holes are bored, one carrying a funnel tube provided with a stop-cock, to hold H_2SO_4 ; a second carrying a glass tube almost to the bottom of the flask, and connected outside to a bottle containing baryta-water; and a third carrying a glass tube connected with a CaCl_2 tube and a weighed potash bulb containing 50 per cent. solution of KOH.

Process. — Measure into the flask 200 c.c. of the water to be examined, and 50 c.c. baryta-water, together with 5 c.c. BaCl_2 . Shake, and allow to settle for twenty-four hours. Decant off as

much of the clear fluid as possible without disturbing the sediment. Should there be a scum on the surface, rapidly run the fluid through a filter-paper, and drop the filter into the flask. Replace the bung and run in slowly the H_2SO_4 , which decomposes the carbonates. The $\text{Ba}(\text{OH})_2$ has previously precipitated as carbonates all the free CO_2 and that existing as bicarbonate. The total CO_2 evolved by the action of H_2SO_4 is absorbed by the KOH in the bulb. Weigh the bulb, and difference in weight represents this CO_2 .

When during the experiment the CO_2 ceases to come off, the flask should be gently heated in order to assist the evolution, and air drawn through in order that all the CO_2 may reach the KOH .

Estimation of Free CO_2 .—Measure into a porcelain basin 100 c.c. of the water; add a few drops of phenolphthalein, and run in from a burette a solution of $\frac{\text{N}}{20}$ Na_2CO_3 until a faint red colour is developed. The sodium carbonate forms with the CO_2 sodium bicarbonate (NaHCO_3), and immediately all the CO_2 is used up the bicarbonate turns the indicator red. The amount of Na_2CO_3 used measures the quantity of CO_2 present.



1 c.c. of the sodium carbonate therefore neutralizes $\frac{44}{106} \times .00265$ gramme $\text{CO}_2 = .0011$ gramme.

If in an estimation it is found that 2.2 c.c. $\frac{\text{N}}{20}$ Na_2CO_3 are required to neutralize the CO_2 in 100 c.c. water, the amount of CO_2 in this water will be $2.2 \times .0011$ gramme = .00242 gramme = 2.42 milligrammes = 2.42 parts per 100,000.

Estimation of Free CO_2 and CO_2 as Bicarbonate.—If to 100 c.c. of the water a little BaCl_2 be added to precipitate carbonates, sulphates, and phosphates of any alkalies which might be present, and which would precipitate the barium from the baryta-water; and, further, if a little saturated ammonium chloride be added to prevent the precipitation of magnesia (MgCO_3 would precipitate BaCO_3 from $\text{Ba}(\text{OH})_2$), the CO_2 existing free and as bicarbonate may be neutralized by $\text{Ba}(\text{OH})_2$, and the loss in alkalinity of a measured quantity of $\text{Ba}(\text{OH})_2$ solution may be estimated by titration with standard oxalic acid, as carried out in Pettenkofer's method of estimating CO_2 in the air.

CHAPTER XII

WATER SEDIMENT

THE biological examination of a water sediment may throw much light on the problem of its origin and the nature and mode of its contamination. A $\frac{2}{3}$ -inch and $\frac{1}{6}$ -inch objectives of the ordinary English microscopes furnish good fields for this work. The number of possible organic forms—animal and vegetable—that may contaminate a water is so great that no expert could be expected to recognise all. But in the search for sewage pollution a number of unmistakable objects may be seen that will clinch the diagnosis. The micro-chemical examination of mineral particles, such as iron compounds, carbonates, oxalates, etc., is in certain cases of some import; but the investigation of animal and vegetable matter is much more likely to lead to positive evidence of sewage and other organic forms of pollution.

In this chapter a few, and only a few, general remarks will be made on the biological examination, and the student will do well to consult such works as Cooke's 'British Desmids,' 'Fresh-water Algæ,' by the same author, Whipple's 'Microscopy of Drinking Water,' and other writers on the Infusoria, Rotifera, Fungi, etc. A necessarily limited number of illustrations are given, but it is hoped that these will be sufficient to introduce the beginner to the microscopic study of water sediments, which in every examination should be faithfully carried out.

Much has been written on methods of procuring the sediment. Where a centrifugal machine is at hand it is most satisfactory to use it, and where none can be had the ordinary conical urine glass suffices in every respect. In using the latter, the water should stand overnight. The clear fluid is carefully syphoned or poured away, and the sediment at the bottom is removed by a fine pipette,

and dropped in single drops on a series of microscopic slides. Some workers use well-slides. Should there be a scum on the surface of the water in the conical glass, this is removed separately and transferred in like manner to slides. Cover-glasses are applied, and the slides carefully examined, first by the low and afterwards by the higher objective.

Certain biological forms inhabit only foul water, and disappear when it becomes purified. Where a supply usually satisfactory develops colour, turbidity, or odour, a microscopical examination alone may elucidate the causes. A satisfactory water should be free from all suspended matter, and especially from all living and dead animal and vegetable matter. Certain animal and vegetable growths may occur in storage reservoirs and cisterns through the admission of light to the water: plants containing chlorophyll (green algæ, diatoms, etc.) grow in light. The different seasons bear different forms and amounts of animal and vegetable life, therefore a systematic microscopical examination is necessary. Vegetable growths may take place at dead ends in mains. Much dead organic matter will be found in the form of unrecognisable débris, but amongst it much that is recognisable, as epithelium, striped muscle, cotton, silk, and linen fibres, starch granules, dotted vegetable ducts, wool, hair, ova of intestinal worms, and numerous other bodies, all distinctive of sewage. It will thus be seen that a knowledge of the fauna and flora of water will enable workers to recognise certain organisms, alive or dead, which produce odours in water, others which live only in pure waters, and whose presence excludes gross pollution, and those which live in polluted waters, and consequently point to sewage or other contamination. Fishy odours, according to Whipple, are produced by *Endorina*, *Volvox*, *Pandorina*, and other *Chlorophyceæ*, *Uroglena*, *Bursaria*, and other *Protozoa*. Aromatic odours are created by numerous diatoms—*Tabellaria*, *Meridion*, *Diatoma*, etc.—and *Protozoa*. Grassy odours are produced by *Rivularia*, *Anabæna*, *Cælosphærium*, and other *Cyanophyceæ*.

In river water and unfiltered supplies possessing odours the organisms are likely to be found in the supply; whilst in filtered waters they mostly grow on the filters. The foul odour and reddish colour of the Cheltenham water some years ago was shown to be

due to a species of *Crenothrix* growing in the reservoirs and on the filters. In deep-well and spring waters any low forms, animal or vegetable, indicate insufficient protection from light, such as storage in uncovered reservoirs. The so-called sewage fungus, *Beggiatoa alba*, including *Carchesium Lachmanni*, and other forms, occurs in effluents from sewage-farms and bacteria-beds. *Beggiatoa* also occurs in river beds and stagnant waters containing H_2S . Winogradsky holds that it does not produce the S which it contains in the dried state, but that this S is derived from the H_2S by other means. Cohn states that it produces S from sulphates and albuminous bodies.

The organisms forming the slimy superficial layer (*Schlammdecke*) of a sand-filter are innumerable, and vary with the source of the water and other factors.

When a sand-filter is first set to work, it acts merely as a strainer. In the course of a few days a slimy organic layer consisting of green and blue algæ, fungi, zooglæa masses of bacteria, diatoms, and a multitude of other organisms, makes its appearance, and true filtration then commences. The source of the water, season of the year, etc., determine the presence of specific forms. Certain green algæ are produced in the spring, blue algæ in the summer, and their colouring matter may be liberated at any time and remain on the surface long after the organisms have died.

The matter obtained as sediment from a centrifugal machine, conical glass, or surface scum, when examined microscopically, may be found to contain (1) living animal forms, (2) dead animal forms, (3) living vegetable forms, (4) dead vegetable forms, (5) mineral detritus, and (6) unrecognisable débris, requiring micro-chemical and other methods of investigation.

The differentiation of some lowly animal and vegetable organisms is frequently a matter of no little difficulty, but careful search should be made for these, as their presence has special significance.

FIG. 10.

1. Wood cells.
2. Cotton fibre.
3. Linen fibre.
4. Hemp fibre.
5. Algal zoospore.
6. Particles of sand.
7. Paramœcium.
8. Amœba.
9. Encysted Infusorian.
10. Algal zoospore.

FIG. 11.

1. Fresh-water Hydra.
2. Scale of insect.
3. Egg of *Tænia solium*.
4. Egg of *Trichocephalus dispar*.
5. Egg of *Ascarus lumbricoides*.
6. Paramœcium.
7. Amœba.
8. Wool fibre.
9. *Euplotes Charon*.
10. Diatoms.

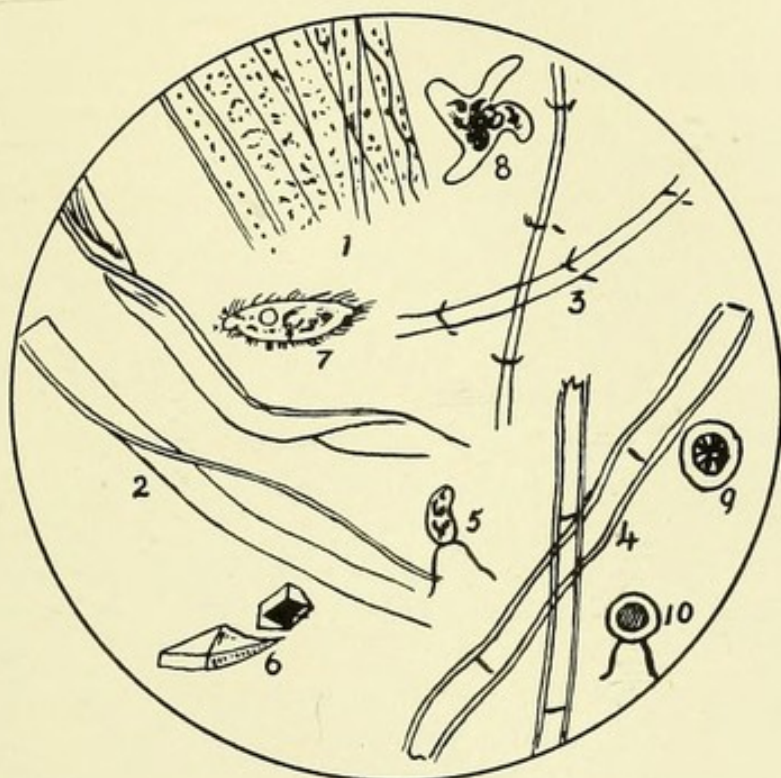


FIG. 10.

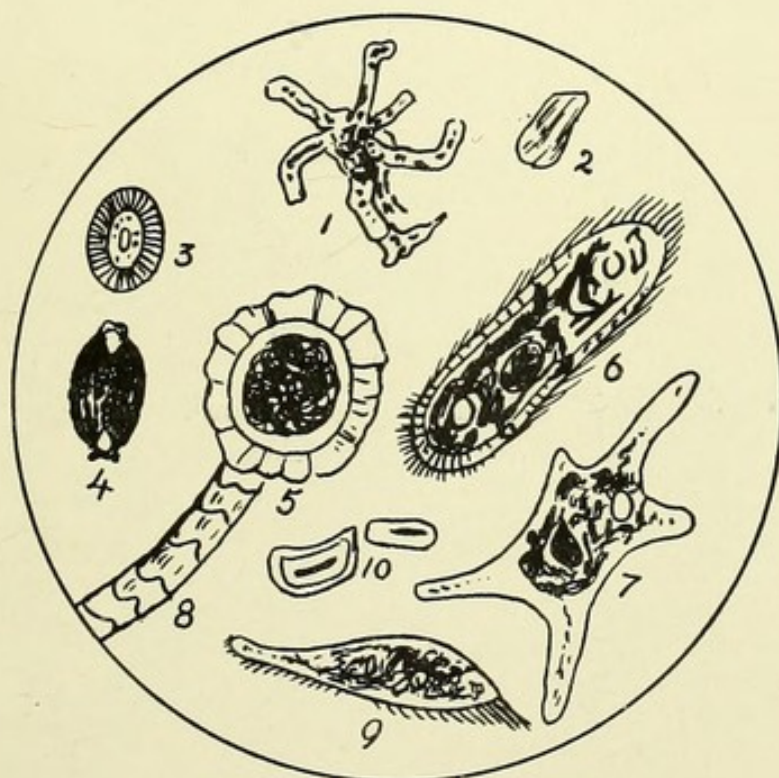


FIG. 11.

FIG. 12.

1. Pleurococcus (Algæ).
2. Amœba (Protozoa).
3. An Infusorian.
- 4 and 5. Diatoms (Algæ).
6. A Desmid (Algæ).
7. Hair of insect.
8. Vegetable tissue.
9. Fibre of wool.
10. Ulothrix (Algæ).

FIG. 13.

1. Anguillulæ (Nematoda).
2. Ulothrix.
3. Zooglæa of micrococci.
4. Anabena.
5. Cryptomonas.
6. Chara fragilis.
7. Diatom (Synedra).
8. Uroglena.
9. A Desmid (Cosmarium).
10. Encysted Infusorian.

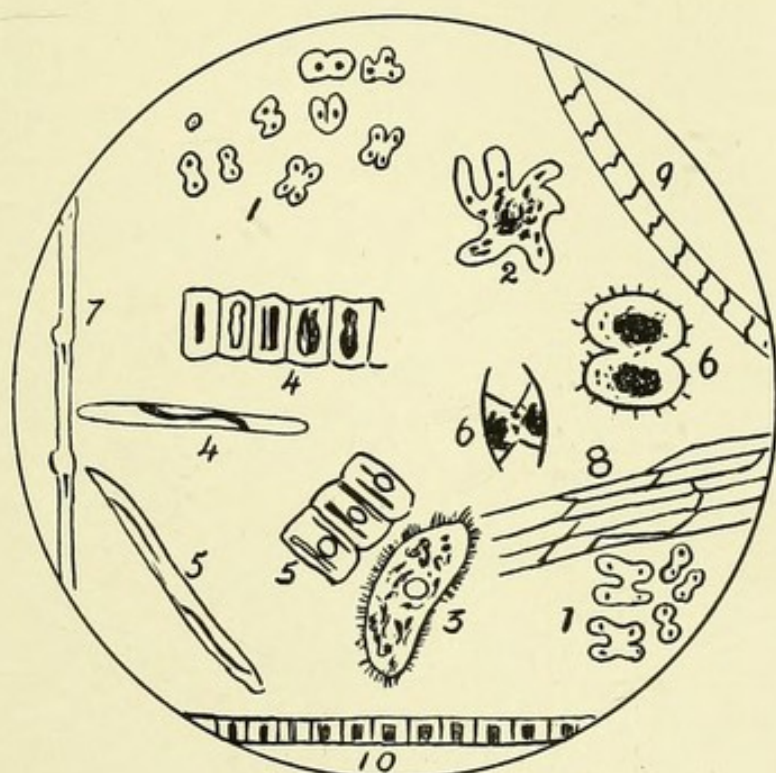


FIG. 12.



FIG. 13.

FIG. 14.

1. Vorticella.
2. Spirogeira.
3. Sphærotilus natans.
4. Beggiatoa.
5. Daphnia.
6. Crenothrix polyspora.
7. Volvox globator.
8. Tabellaria.
9. Species of Nostoc.
10. Melosira.

FIG. 15.

1. Rotifer (Annuloida).
2. Paramœcium (Protozoa).
3. Animal spine.
4. Wing scale of an insect.
5. Vegetable débris.
6. Crystals of calcium sulphate
7. Algal filaments.
8. Not identified.
9. Bacteria.
10. Diatom.

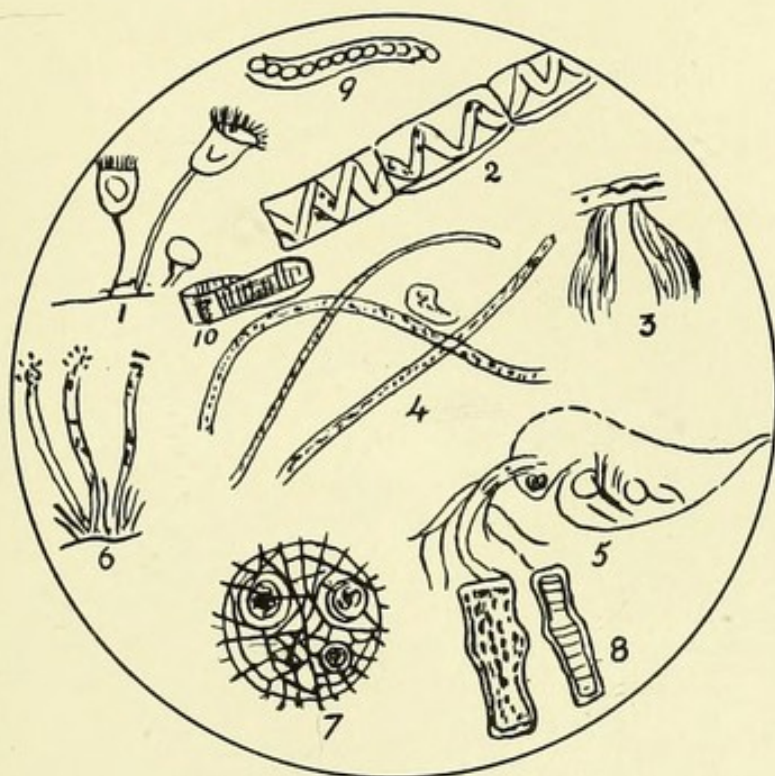


FIG. 14.

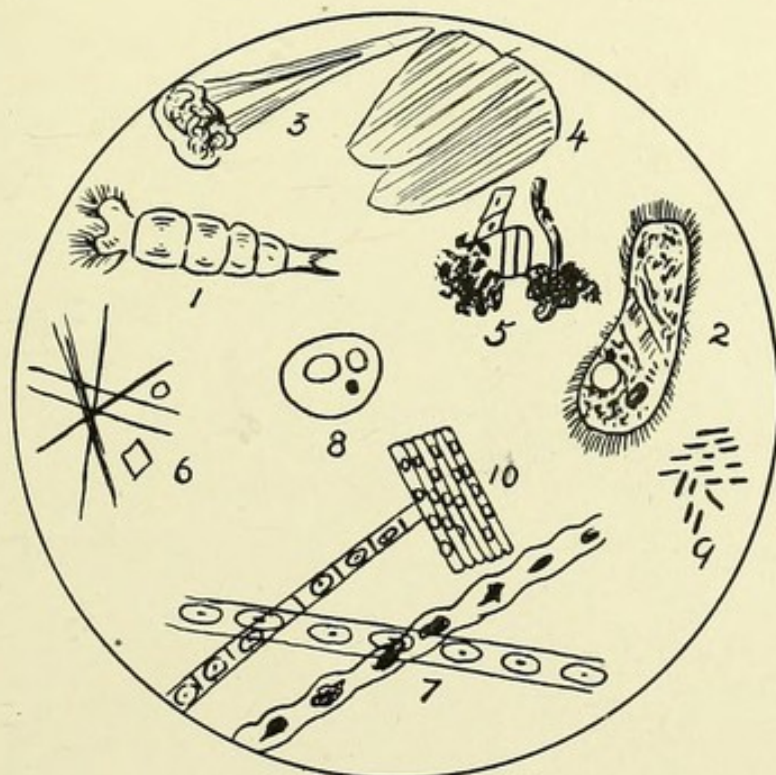


FIG. 15.

FIG. 16.

1. Oscillatoria.
2. Small Infusorian.
3. Free-swimming Vorticella.
4. Cotton fibres.
5. Navicula (Diatom).
6. Confervoid Alga (*Synura uvella*).
7. A Heliozoon.
8. Egg of an Entozoon.
9. Pith cells partially covered with vegetable débris.
10. Wood of a Conifer.

FIG. 17.

1. *Leptomitrus lacteus* (from impure river).
2. *Carchesium Lachmanni* (from water polluted with sewage).
3. *Conferva bombycina* (pond water).
4. Fresh-water Alga (*Lyngbya*).
5. *Bursaria gastris*.
6. *Hydrodictyon* (fresh-water Alga).
7. Sand particles.
8. Algal filament.
9. Hypha of fungus (sporing).
10. Encysted Protozoon.
11. Water bear.

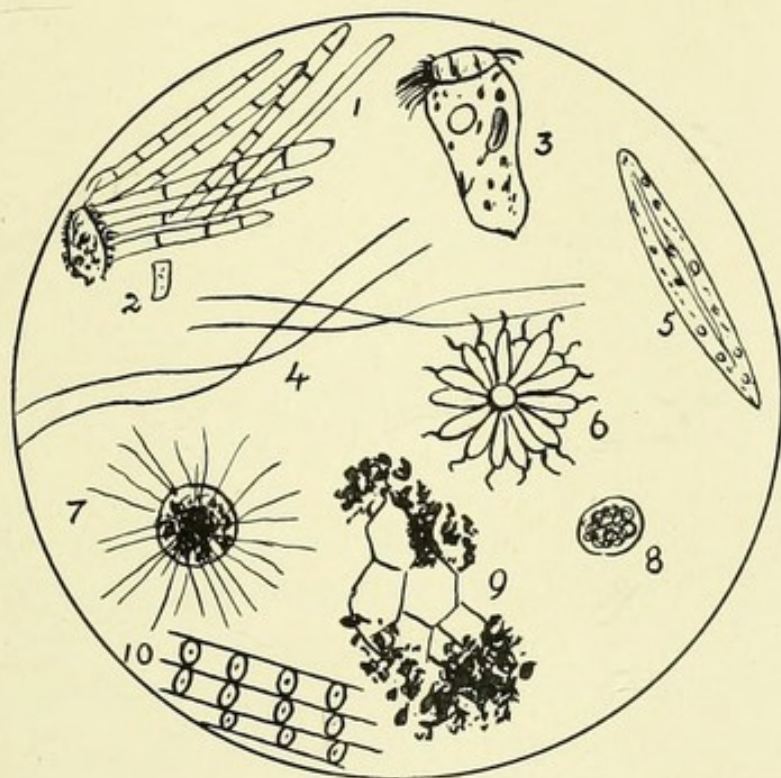


FIG. 16.

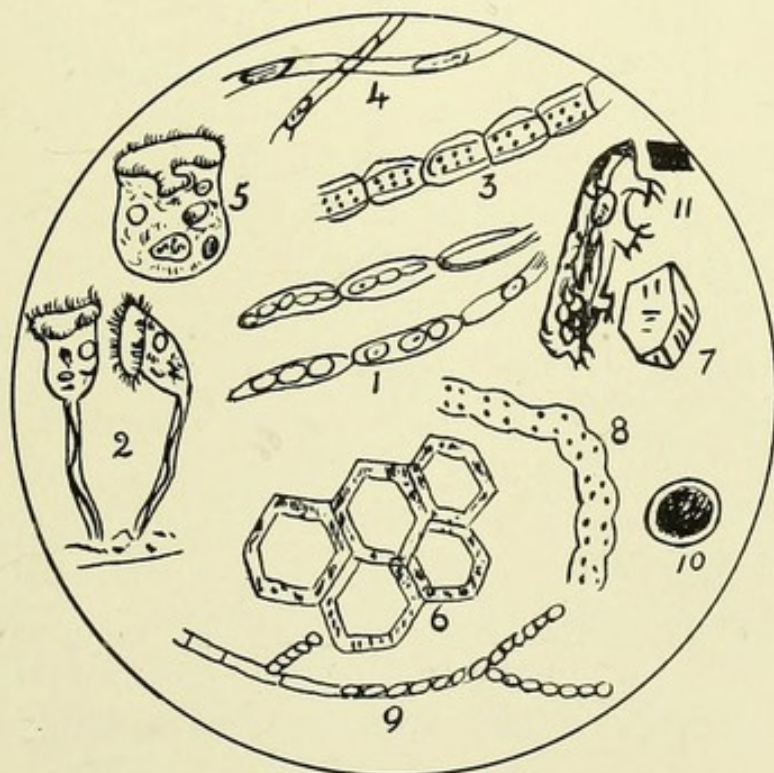


FIG. 17.

CHAPTER XIII

BACTERIOLOGICAL EXAMINATION OF A WATER SAMPLE

It is assumed that the student who attempts to bacteriologically examine water (as also air, soil, food, etc.) is familiar with the morphological, tinctorial, and cultural characters of the principal micro-organisms dealt with in pathological and hygienic bacteriology. He should be capable of rapidly and accurately passing a particular organism through the usual routine tests: hanging drop, simple stain, Gram's stain, special stains—such as Ziehl-Neelsen's for *B. tuberculosis* and other acid-fast bacteria, Neisser's for *B. diphtheriæ*, Van Ermengem's for flagella—stains for spores and capsules, etc. He should be able to carry out a Durham-Gruber reaction. He should be intimately conversant with the results obtainable by growing the more commonly occurring organisms aerobically and anaerobically in the various fluid and solid media, and particularly with the products of fermentation created by them in the different carbohydrates in use. He should know how to perform inoculation experiments, and to recognise characteristic effects. His experience should be such that in each of these tests he can intelligently decide when a positive and when a negative result is obtained.

The sample of water should be collected in a clean, tightly-stoppered bottle, sterilized by heat; and if taken from a river, reservoir, or pond, the bottle should be filled at a level one foot below the surface; if from a tap, the water should be let flow for a few minutes in order to obtain an average portion. The examination should be carried out forthwith, as organisms multiply rapidly. If the sample has to be sent some distance to the laboratory, it should be packed in one of the well-known ice-chests. The total number of organisms per c.c. which should condemn a water has not been settled by

bacteriologists, but most workers assume with Koch that a good water should not contain more than 100, and the bulk of these will be chromogenic and non-liquefying, and will grow at 22° C.

The chief advantages of a bacteriological examination are (1) it often demonstrates directly infective organisms, (2) it indirectly detects small quantities of sewage pollution not to be found by the chemical examination.

The organisms found in surface waters—rivers, ponds, shallow wells, etc.—are, with the exception of a few *sarcinæ* and *micrococci*, mostly chromogenic and liquefying bacteria, which grow at 22° C. and not at 37° C. In waters polluted with sewage the number of organisms is greatly increased, whilst many liquefy gelatin and develop at blood-heat; also, members of the colon group appear. Deep-well waters when pure are remarkably free from organisms. Storage in reservoirs diminishes the number of organisms through sedimentation, and sand-filtration, provided the 'surface scum' has properly developed, may cut off 95 per cent. of the total bacteria. The process of softening and precipitation of iron, through the addition of lime and alum, largely reduces the number of organisms.

The examination consists in estimating the number of organisms present in 1 c.c., the number of liquefying organisms, the number growing at 37° C., and the searches for the *colon* bacillus, the *B. enteritidis sporogenes*, and *s'reptococci*.

To determine the **total number of organisms** present and the **ratio of liquefiers of gelatin to non-liquefiers**, take three Petri dishes and with a 1 c.c. pipette graduated to .01 c.c., run in .5 c.c., 2 c.c., and 1 c.c. respectively, and then pour from test-tubes gelatin of a neutral or very slightly alkaline reaction, and melted at 40° C. Incubate at 22° C. and examine daily for several days. The number of colonies represents approximately the number of organisms present in the water. The liquefiers rarely exceed 10 per cent. of the total.

To estimate the number of **organisms growing at 37° C.**, prepare three agar plates with 3 c.c., 2 c.c., and 1 c.c. of the water, and incubate in the inverted position at 37° C. for twenty-four hours.

The **B. coli** is sought for by inoculating three bile-salt-lactose-agar plates with 3 c.c., 2 c.c., and 1 c.c. of the water respectively,

and incubating at 42° C. for forty-eight hours. Neutral red and glucose formate are used in this examination, as also the medium of Conradi and Drigalski for the differentiation of *B. coli* from *B. typhosus*. A routine examination for *B. typhosus* is not usually undertaken. If growth appears on the plates, subcultures should be made in gelatin plates containing .05 per cent. carbolic acid, and incubation effected at 22° C., and also with bile-salt broth and incubation carried out at 42° C. for forty-eight hours; or the original water may be inoculated on carbol-gelatin plates and in bile-salt broth. No drinking water should contain *B. coli* in 250 c.c.

The Search for the Enteritidis Sporogenes.—Concentrate by passage through a Pasteur-Chamberland filter 1 litre of the water, and suspend the deposit in 5 c.c. of sterile distilled water. Inoculate three milk-tubes with 1 c.c. each of the suspension. Heat to 80° C. for fifteen minutes and incubate anaerobically for forty-eight hours. Confirm by inoculating 2 c.c. whey into a guinea-pig. This organism is absent from all good waters.

Examination for Streptococci.—Concentrate and make suspension of the deposit as above. Make surface-plates with .1 c.c., .05 c.c., and .005 c.c. of the suspension, and incubate at 37° C. Examine all minute colonies, and, if necessary, subculture in broth. Streptococci indicate recent contamination. Some difference of opinion exists as to the significance of streptococci, both in the matter of the date of the pollution and its danger, but there can be no doubt that where streptococci accompany the *B. enteritidis sporogenes*, sewage has recently had access to the water, and it is accordingly to be condemned.

CHAPTER XIV

INTERPRETATION OF RESULTS OF CHEMICAL ANALYSES

As previously indicated, judgment should be exercised at all times in expressing an opinion on a water without a personal inspection of the source, etc.; but many instances will arise in which no doubt can exist as to the foulness of the sample. Positive results in the search for sewage contamination are much more easily dealt with than negative. The liability to such pollution should ever be kept before the mind of the analyst. Deep springs and wells for the most part afford the purest waters. Upland surface waters may be also quite pure. But subsoil waters and waters from cultivated lands, as also most river waters, are rarely free from pollution. Waters collected from the surfaces of the more impervious rocks, destitute of animal and vegetable life, are extremely pure. These rarely contain any appreciable NH_3 , and rarely more than 1 part chlorine, .1 part nitric N, 5 parts hardness, and 10 parts total solids per 100,000. Waters collected from rocks covered with peat will present high figures for organic ammonia, and O absorbed by organic matter, and their acidity will be great. Such waters are plumbo-solvent, and should be neutralized before distribution to the consumer. Waters from mountain limestone are moderately hard, with high total solids and neutral or faint alkaline reaction. The mineral residue is chiefly composed of carbonate and sulphate of calcium and magnesium. Great variety in composition is found amongst waters originating in the lias, magnesian limestone, red sandstone, and oolite; total solids may range from 10 to 15 parts; total hardness 10 to 15; chlorine 1 to 2; and nitric N .1 to .2. Alluvial strata furnish waters of high total solids (50 to 100); and waters from cultivated soils vary within very wide limits in total solids, hardness, chlorine, and nitric N.

Hard waters are derived from the chalk, limestone, magnesian limestone, oolite, and dolomite.

Chalk waters are mostly bright, transparent, and charged with CO_2 . When the CO_2 is driven off, these waters are almost universally alkaline, although before boiling the reaction to litmus may be distinctly acid. Chlorine varies from 2 to 3 parts, nitric nitrogen from .2 to .4, total hardness 15 to 30 (the hardness is chiefly temporary, and may be nearly all due to carbonates of Ca), and total solids from 25 to 50 parts.

Waters from oolite closely resemble those from chalk, with the exception that they contain a little more permanent hardness. Limestone waters contain more total solids and more permanent hardness (due principally to calcium and magnesium sulphate). Waters from dolomite strata occupy an intermediate position between chalk and limestone waters in points of hardness and total solids. Greensands, in that they frequently contain much nitrates and variable quantities of ferrous iron, furnish, through the reduction of the nitrates by the iron, quantities of free NH_3 . The intermediate stage of nitrites may be occasionally demonstrated. The lower greensand furnishes water collected at great depth—often many feet below the chalk—and accordingly the total solids are high, often 80 to 100 parts per 100,000. Hardness is very variable, and much is permanent. Chlorine may run to 10 or 12 parts per 100,000, and nitric N to as much as .5 or .6. These waters are very free from organic matter. Where water is procured from lias clays much permanent hardness may be expected (CaSO_4 and MgSO_4), 20 parts or more, and total solids may range from 200 to 300.

A water containing over 30 parts of total hardness may be considered unsuitable for domestic purposes, unless it can be largely softened.

Waters containing more than 20 parts of permanent hardness are not suitable for washing and cooking.

Deep wells, if sufficiently steined, are for the most part pure. Very occasionally a well in the chalk may tap a hidden reservoir of unpurified sewage which has leaked through fissures from a cesspool.

Sewage derives the bulk of its Cl from urine, which contains, as above mentioned, about 1 per cent. chlorides, but although it contains

this large amount of Cl, it is obvious that deadly pollution by sewage may occur in such small amounts as are wholly incapable of detection by chemical methods ; the chlorine figure, therefore, will be chiefly of diagnostic value in those cases where the soil, subsoil, and water-bearing strata are of constant composition and beyond the reach of contamination by cultivated land. If after a series of analyses the Cl figure is found fairly constant, a particular rise of $\cdot 5$ to 1 part per 100,000 may justly arouse a suspicion of sewage pollution.

Considering the varieties in source and surrounding conditions from source to distribution, it is quite impossible to erect standards of purity for waters in this country. An inspection of the source and surroundings is of the utmost importance in all cases.

In considering the 'free and saline' NH_3 , the merest trace should be considered of import if not suspicious, except in those cases where reduction of nitrates has taken place, such as occurs in the greensands. As previously stated, if the 'albuminoid' ammonia be very small (less than $\cdot 002$), the 'free and saline' may be allowed to exceed slightly $\cdot 005$. In peaty waters, where the 'albuminoid' ammonia may reach $\cdot 01$, the 'free and saline' should be negligible. In a deep-well water the O absorbed from permanganate in two hours at 80°F . should not exceed $\cdot 01$ or $\cdot 02$. In a peaty water free from animal pollution this figure may exceed $\cdot 1$.

In passing judgment on river waters, analyses, in addition to inspection, should be made of all tributaries, lest evidence of present or past pollution be overlooked. The search for poisonous metals should be carefully carried out, and when any of these is found a quantitative estimation should invariably be made. Lead to the extent of $\cdot 025$ part per 100,000 is sufficient to condemn a potable water. Present or recent sewage pollution may be more or less accurately differentiated from past and remote, in that, whilst high Cl and nitrate figures obtain in both, in the present or recent contamination there will be marked free and organic NH_3 , whereas in the past and remote little or no free or organic NH_3 will be found. Further animal pollution may be more or less accurately differentiated from vegetable by contrasting the two ammonias, oxygen absorbed by Tidy's process, Cl, and nitrates. All these figures are high in cases of marked animal pollution ; whilst in vegetable pollution free NH_3 is low, organic NH_3 high,

Cl and nitrates are low, and in the last two no increase if the water is drawn from below the surface. Where much vegetable matter exists the water is usually coloured, as in the various peaty waters, and the solid residue chars on ignition. Sulphates and phosphates occur in larger quantities in water polluted with animal matter than in those contaminated with vegetable material. Little has been said of nitrites, because, although they are easily formed by oxidizing and reducing agents, they are rarely present in natural waters. They are found in purifying sewage, but, unfortunately, as they may be formed from other sources than ammonia (such, *e.g.*, as nitrates in contact with iron, zinc, and lead pipes or cisterns), it is not always possible to locate their origin. The faintest trace, however, of nitrites should condemn a water, except in the single instance of a pure water containing nitrates undergoing reduction by metallic or other inorganic compounds, and not by organic matter.

The solids impart different properties to waters according to their composition, so that no strict limit can be set to their amount. Sulphates should not exist in larger quantity than 8 parts SO_2 per 100,000. Magnesium salts, especially MgSO_4 , should be very small, if at all present, in a good water. And perhaps, all forms of mineral matter considered, the total figure should not nearly reach 100.

The various items of the analysis are recorded in some such form as the following:

Sample of water from Date

Labelled

Brief particulars of source

Physical characters :

Turbidity

Colour

Odour

Reaction

Free and saline NH_3 parts per 100,000.

Organic NH_3

Cl.

Nitrous N

Nitric N

Hardness (total)

„ (permanent)

„ (temporary)

O absorbed at in hours

Metals

Solids (total)

„ (volatile)

„ (fixed)

Appearance on ignition

Microscopic examination of sediment

Bacteriological Examination

EXAMPLES OF WATERS FROM VARIOUS SOURCES

RESULTS EXPRESSED AS PARTS PER 100,000.

	No. 1. A Pure Water.	No. 2. Rain Water Collected on Grass Land.
Physical characters - - -	Excellent	Good
Reaction - - - - -	Faint alkaline	Faint alkaline
Free and saline NH_3 - - -	001	012
Organic NH_3 - - - - -	001	000
Cl - - - - -	1200	200
Nitrous N - - - - -	Nil	Nil
Nitric N - - - - -	010	010
Hardness (total) - - - -	8500	600
" (permanent) - - - -	3000	600
" (temporary) - - - -	5500	000
O absorbed at 80° F. in two hours	013	002
Metals (Zn, Pb, Fe, Cu) - - -	Nil	Nil
Solids (total) - - - - -	11500	2500
" (volatile) - - - - -	2500	1000
" (fixed) - - - - -	9000	1500
Appearance on ignition - - -	Nil	Nil
Microscopic examination of sediment	Nil	Nil
Bacteriological examination - -	20 non-liquefying saprophytes per c.c. Intestinal organisms absent	Not performed

	No. 3. Foul.	No. 4. Chalk Water from Deep Well.
Physical characters - - -	Excellent	Excellent
Reaction - - - - -	Alkaline	Alkaline
Free and saline NH_3 - - -	030	005
Organic NH_3 - - - - -	020	006
Cl - - - - -	5000	4500
Nitrous N - - - - -	050	Nil
Nitric N - - - - -	600	300
Hardness (total) - - - -	20000	22000
" (permanent) - - - -	12000	12000
" (temporary) - - - -	8000	10000
O absorbed at 80° F. in two hours	150	060
Metals (Zn, Pb, Fe, Cu) - - -	Nil	Nil
Solids (total) - - - - -	30500	38000
" (volatile) - - - - -	10500	12000
" (fixed) - - - - -	20000	26000
Appearance on ignition - - -	Marked charring	charring
Microscopic examination of sediment	Objects indicating sewage pollution	Nil
Bacteriological examination - -	<i>B. coli</i> found in 50 c.c.	Not performed

Sample No. 2, although it possesses a high 'free' NH_3 figure, is good. Rain water in towns is generally impure; it is slightly acid from SO_2 , and contains NH_3 .

Sample No. 3 has had a small amount of untreated sewage admitted to it.

Sample No. 4 is an average chalk water with low total solids. This figure may be allowed to go up to 200 or over. The hardness of chalk waters varies considerably.

Sample No. 5.—The saline NH_3 , chlorine, and nitrates are high, and nitrites are present. These items in general point to animal

	No. 5. Deep-well Water from the Lower Greensand.	No. 6. Deep-well Water from Chalk near the Sea.
Physical characters - -	Good	Saline taste, greenish colour, no odour
Reaction - - -	Alkaline	Alkaline
Free and saline NH_3 - - -	·035	·000
Organic NH_3 - - -	·001	·003
Cl - - -	12·250	115·000
Nitrous N - - -	·020	·000
Nitric N - - -	·320	1·000
Hardness (total) - - -	16·000	47·000
„ (permanent) - - -	10·000	—
„ (temporary) - - -	6·000	—
O absorbed at 80° F. in two hours	·020	·035
Metals (Zn, Pb, Fe, Cu) - -	Nil	Nil
Solids (total) - - -	105·000	260·500
„ (volatile) - - -	20·000	35·500
„ (fixed) - - -	85·000	225·000
Appearance on ignition - -	Nil	Slight darkening
Microscopic examination of sediment - - -	Nil	Mineral particles
Bacteriological examination - -	Excellent	Excellent

pollution; that they are not due to this cause here is shown by the low organic NH_3 and O absorbed. Reduction of nitrates by iron salts is going on, as demonstrated by the high saline NH_3 and presence of nitrites.

Sample No. 6 is contaminated by sea water. Before contamination Cl was 3, and total hardness 20. Much MgCl_2 is present, and the water is unfit for domestic use.

Sample No. 7 contains much acid, and could not be allowed to traverse lead pipes. Its organic NH_3 and O absorbed are not so high as in many peaty waters.

	No. 7. Surface Water, Peaty.	No. 8. Surface Water, not Peaty.
Physical characters - - -	Colour brownish ; slight taste	Almost colourless, no taste
Reaction - - -	Acid	Neutral
Free and saline NH_3 - - -	·001	·002
Organic NH_3 - - -	·030	·003
Cl - - -	·600	·800
Nitrous N - - -	Nil	Nil
Nitric N - - -	·010	·030
Hardness (total) - - -	3·000	3·000
„ (permanent) - - -	3·000	2·500
„ (temporary) - - -	·000	·500
O absorbed at 80° F. in two hours -	·150	·050
Metals (Zn, Pb, Fe, Cu) - - -	Nil	Nil
Solids (total) - - -	9·000	4·000
„ (volatile) - - -	2·000	1·000
„ (fixed) - - -	7·000	3·000
Appearance on ignition - - -	Charring	Faint darkening
Microscopic examination of sedi- ment - - -	Vegetable debris	Nil
Bacteriological examination - - -	No intestinal or- ganisms	No intestinal or- ganisms

Samples Nos. 9 and 10 were taken from the same house. The analysis of 10, carried out a month after that of 9, shows some slight variations, which are to be expected, when it is remembered that the composition of river water varies, with its varying powers of

	No. 9. New River Water from the Lea.	No. 10. New River Water from the Lea.
Physical characters - - -	Excellent	Excellent
Reaction - - -	Slightly alkaline	Slightly alkaline
Free and saline NH_3 - - -	·000	·001
Organic NH_3 - - -	·002	·003
Cl - - -	1·900	1·860
Nitrous N - - -	Nil	Nil
Nitric N - - -	·160	·210
Hardness (total) - - -	20·500	21·500
„ (permanent) - - -	11·500	13·500
„ (temporary) - - -	9·000	8·000
O absorbed at 80° F. in two hours -	·017	·023
Metals (Zn, Fe, Pb, Cu) - - -	Nil	Nil
Solids (total) - - -	32·600	28·560
„ (volatile) - - -	10·200	10·000
„ (fixed) - - -	22·400	18·560
Appearance on ignition - - -	Nil	Nil
Microscopic examination of sedi- ment - - -	Nil	Nil
Bacteriological examination - - -	—	—

self-purification, with the nature of the strata in which its springs of origin occur and of the strata over which it flows, and with the

	No. 11. Peaty Water.	No. 12. Well Water.
Physical characters - - -	Colour light-brown	Excellent
Reaction - - -	Acid	Neutral
Free and saline NH_3 - - -	·005	·000
Organic NH_3 - - -	026	·001
Cl - - -	1·500	3·8
Nitrous N - - -	Nil	Nil
Nitric N - - -	·220	·362
Hardness (total) - - -	3·500	26·000
„ (permanent) - - -	3·500	12·300
„ (temporary) - - -	·000	14·000
O absorbed at 80° F. in two hours -	·146	·008
Metals (Zn, Fe, Pb, Cu) - - -	Nil	Nil
Solids (total) - - -	12·300	38·260
„ (volatile) - - -	8·300	8·500
„ (fixed) - - -	4·000	29·760
Appearance on ignition - - -	Charring	Nil
Microscopic examination of sedi- ment - - -	Vegetable débris	Nil
Bacteriological examination - - -	Negative	Nil

nature of the soils and subsoils of its basin, especially in regard to cultivation, density of population, and the presence of sewage and industrial waste.

	No. 13. Lambeth Supply.	No. 14. Chelsea Supply.
Physical characters - - -	Excellent	Excellent
Reaction - - -	Faint alkaline	Neutral
Free and saline NH_3 - - -	·000	·000
Organic NH_3 - - -	·005	·002
Cl - - -	1·850	1·740
Nitrous N - - -	Nil	Nil
Nitric N - - -	·086	·009
Hardness (total) - - -	18·600	18·400
„ (permanent) - - -	8·500	8·400
„ (temporary) - - -	10·100	10·000
O absorbed at 80° F. in two hours -	·043	·023
Metals (Zn, Fe, Pb, Cu) - - -	Nil	Nil
Solids (total) - - -	26·400	26·720
„ (volatile) - - -	6·800	6·400
„ (fixed) - - -	19·600	20·320
Appearance on ignition - - -	Nil	Nil
Microscopic examination of sedi- ment - - -	Nil	Nil
Bacteriological examination - - -	Nil	Nil

Sample No. 11 is plumbo-solvent, and is slightly polluted with animal matter, in that free and saline NH_3 , Cl, and nitric N, are too high for a peaty water.

Sample No. 12 is a pure water from a deep well in Kent.

Samples Nos. 13 and 14 are fair specimens of filtered Thames water.

In the 'nil' returns of the bacteriological and sediment examinations, it is to be understood that nothing was found indicative of animal pollution.

A DORSET WATER-SUPPLY.

Three samples selected from a series of thirteen investigated at the same time by the writer, and showing the changes effected by treatment with chalk and filtration. These waters, derived from Bagshot sands, covered with peat, are acid and ferruginous.

	(A) Before Treatment with Chalk.	(B) After Treatment with Chalk.	(C) After Filtration.
Physical characters—	2.5 1.5		
Colour, smell, turbidity - - -	Good	Good	Excellent
Chemical reaction - - -	Acid	Acid	Acid
	Acidity = } 2.190 HCl }	.500	.350
Free and saline NH_3 - - -	.018	.022	.001
Organic NH_3 - - -	.016	.010	.001
O absorbed in two hours at 80° F. - - -	.040	.020	Nil
Total solids - - -	12.300	11.500	11.500
Hardness (total) - - -	2.500	2.500	2.700
„ (temporary) - - -	—	—	—
„ (permanent) - - -	2.500	2.500	2.700
Chlorine - - -	2.500	2.000	2.500
Nitric N - - -	.100	.100	.010
Iron in solution - - -	.325	.220	.110

As the filtered water still contains acidity, it may not be passed through lead pipes.

Sea water contains in 100,000 parts nearly 2,000 parts Cl, and between 3,000 and 4,000 parts total solids. Hardness ranges between 500 and 600 parts. Lime and magnesia together form about 240 parts, and the ratio of the first to the second is about 1 : 6.

The following is an estimation :

							In 100,000 pts.
Free and saline NH_3	-	-	-	-	-	-	·006
Total solids	-	-	-	-	-	-	3,380·000
Lime	-	-	-	-	-	-	35·000
Magnesia	-	-	-	-	-	-	205·000
Silicia	-	-	-	-	-	-	·450
Hardness	-	-	-	-	-	-	580·000
Chlorine	-	-	-	-	-	-	1,875·000

The table below represents the comparative figures for the principal chemical constituents of a well-filtered river water, delivered to a town of some 40,000 inhabitants, and the sewage of the same town before treatment :

	Water.	Sewage.
Free and saline NH_3 - - -	·000	6·800
Organic NH_3 - - -	·002	2·000
O absorbed in two hours at 80° F. -	·020	4·080
Chlorine - - -	1·850	11·800
Nitric N - - -	·120	·000
Total solids - - -	28·500	160·000

CHAPTER XV

SEWAGE EFFLUENTS

AN average sample of the day's working should in all cases be obtained, and the analysis performed forthwith.

It is usual to estimate the organic NH_3 , O absorbed from permanganate, total solids, and total suspended matter, nitrous N, and nitric N.

The physical characters may be noted, and incubation at 80°F . for forty-eight hours may be effected in order to determine the presence or absence of further fermentation, as indicated by odour.

The analysis is frequently required for the determination of the degree of purification at a particular stage, or the comparative value of a certain method of treatment. It is usual to record the purification as percentages of the figure for albuminoid NH_3 . If, for example, before treatment the albuminoid figure is $\cdot 6$ part per 100,000, and after treatment $\cdot 15$, it is clear that purification has taken place to the amount of $\cdot 45$ part per 100,000, or 75 per cent. of the original albuminoid NH_3 has been oxidized.

The albuminoid NH_3 is estimated by the Wanklyn method described under water, but a large dilution of the effluent is necessary. Ten c.c. may be made up to 1,000 c.c. with distilled water, and in some instances 5 c.c. in the same volume will be convenient.

The O absorbed from permanganate is estimated by Tidy's process, and care should be taken that sufficient permanganate is added from time to time, and that the flask is frequently shaken. A convenient dilution is 10 c.c. in a litre.

Total solids are estimated by evaporating 100 c.c. of the sample in a platinum dish on a water bath. When dry, the dish is transferred to an air bath, and dehydration continued at 100° to 110°F . It is then passed through a desiccator, and weighed. The difference

between this weight and that of the dish represents the 'total solids.'

The solids in suspension are found by passing 100 c.c. of the sample through two folds of filter-paper, whereby the solids in solution alone pass through. The filtrate is evaporated to dryness, further dehydrated, desiccated, and weighed. The difference between this weight and that of the total solids represents the 'solids in suspension.'

Nitrous N is estimated thus: Dilute the liquid with distilled water (free from nitrite) to a convenient strength. Take 100 c.c. in a Nessler glass, add 1 c.c. metaphenylene-diamine and 1 c.c. H_2SO_4 (1 in 3). Match by treating in a similar manner a standard solution of potassium nitrite made up to 100 c.c. Stand for twenty minutes before comparing.

The nitric N is estimated by Crum's method or by the copper-zinc couple, as described under water analysis. A convenient dilution must be made. Where time is an item, as in examinations, the less accurate phenol sulphonic acid method may be used.

If raw sewage is to be analyzed, weaker dilutions should be used.

In the working out of Tidy's process it should be noted that various bodies besides organic matter absorb O from permanganate, such as nitrites, sulphites, sulphides, sulpho-cyanates, numerous dyes, and various coal-tar products.

In the distillations carried out in Wanklyn's process the volume of the boiling fluid should never be allowed to fall below 100 c.c. Hot, ammonia-free distilled water when necessary should be added.

Griess's test should be rapidly performed, and if the fluid is not transparent it should be filtered before adding the reagents.

Estimation of the total N by Kjeldahl's method is a much more accurate index of the organic pollution than that by Wanklyn's process for albuminoid ammonia. The latter usually gives less than half the N figure obtained by the former.

With a little practice Kjeldahl's method can be carried out rapidly and accurately as follows:

In a 100 c.c. boiling-flask put 10 c.c. sewage effluent and 1 c.c. H_2SO_4 , and evaporate on a water bath to half the bulk. When

cool, add about 10 c.c. oil of vitriol, and carefully bring to the boiling-point under a hood in a draught-chamber. Add from time to time a small crystal of permanganate of potassium until the colour slowly disappears. Continue the boiling until the solution is a pale, transparent yellow colour. Cool and wash out into a distilling-flask. Make up to 500 c.c. with ammonia-free distilled water; add excess KOH and a piece of ignited pumice-stone, and distil over nearly 400 c.c. Nesslerize the ammonia collected, and subtract from the result the amount of free and saline ammonia previously estimated by Wanklyn's process. The difference is the NH_3 due to organic nitrogen. The reagents used should be free from NH_3 .

Ammonium sulphate is first formed, and later ammonia through the action of KOH.

The purification of sewage has little influence on the amount of its chlorine, which in average samples reaches 10 or 11 parts per 100,000.

The composition of sewage is constantly varying.

A sewage effluent should be colourless and without odour.

The albuminoid NH_3 should not exceed .1 part per 100,000, nor the O absorbed in four hours at 80°F . 1 or 1.2 parts. There should be no solids in suspension. It is unfortunate that no standards exist, and that the degree of purity insisted on in many localities is far too low.

It may be laid down as a minimum requirement that a sewage effluent after incubation at 80°F . for seven days should present no evidence of putrefaction.

It has been shown that the presence of nitrate in an effluent may prevent putrefaction of a certain amount of organic substances occurring in another effluent with which the nitrate effluent has been mixed.

Little that is definite can be said regarding the area of filtration-beds required to deal satisfactorily with given quantities of sewage. The factors engaged in sewage purification are so variable, and the composition of the sewage itself is so changeable, even in the same district, that all possibility of discovering uniform figures for the size of filter-beds is out of the question. It has been stated that, where solid matters have been thoroughly dealt with, either by

precipitation as sludge or liquefaction in the septic tank, and where the composition of the resulting liquid is reasonably constant, 4,000,000 gallons can be treated in this climate per day on an acre of coke-bed of a depth of 6 feet to such a degree as to allow of the effluent being cast into a river not used for potable water-supply. This area of filter-bed is perhaps too little, and under certain conditions much too little.

CHAPTER XVI

ANALYSIS OF SOILS

THE analysis of soils is a large subject, and requires for its proper execution a special training in chemistry. For public health purposes, however, very few estimations are required, and these are of a simple kind. The powers which a soil possesses for absorbing and retaining moisture are of some importance, but direct examination of the soil and subsoil in position in a given locality will furnish more valuable information than laboratory tests.

The capacity for absorbing moisture may be estimated by the method of Fuelling, in which, by means of a percolator and attached burette, a quantity of dried soil (say 100 grammes) is flooded with water for two hours, and allowed to drain for four hours. The difference in the reading of the burette before and after the operation gives the number of c.c. of water absorbed by 100 grammes, or the absorption per cent.

Perhaps a simpler method is the following :

One hundred grammes of dried soil are saturated with water in a cylinder. Sufficient time is allowed for saturation, which in the case of clay soils may be several hours. The water is drained off through a muslin filter, and the soil is reweighed. The increase in weight represents the percentage absorption.

The determination of the size of the particles of a soil is carried out by using a series of sieves possessing meshes of 2 millimetres, 1 millimetre, and .5 millimetre respectively.

One hundred grammes of dried soil are pulverized with the fingers. The larger pebbles, roots, etc., are removed and weighed. The residue is transferred to the 2 millimetre sieve, and when all has passed that will, the remainder is further rubbed between the fingers, and once more shaken on the sieve. What remains on this sieve is

weighed. In like manner the amounts left on the other sieves are weighed. Finally, the soil which passes the .5 millimetre sieve is weighed, and the results are collected as (a) coarse masses removed by hand, (b) masses kept back by the 2 millimetre sieve, (c) sand retained by the 1 millimetre sieve, (d) fine sand retained by the .5 millimetre sieve, and (e) fine soil passing the .5 millimetre sieve.

The specific heat of soils is sometimes determined. This requires a sensitive calorimeter. The specific heat ranges from .2 to .5, and is greatest in peaty soils.

The determination of the porosity of a soil is effected by finding the real and apparent specific gravity of the soil, and dividing the latter by the former.

The real specific gravity is obtained by placing in a 50 c.c. specific gravity bottle 10 grammes of the soil dried at 100° C. to constant weight, rinsing the last particles into the bottle with distilled water, and making up with distilled water to the mark. The whole is weighed at 15° C. The weight of the water displaced by the 10 grammes of soil is thus easily calculated.

The apparent specific gravity is obtained by filling a 1,000 c.c. cylinder with soil, introduced in small quantities at a time, and thoroughly settled in the cylinder by tapping from time to time on the bench. When full the cylinder is covered with a glass plate and weighed. From this weight the apparent specific gravity is obtained.

The real specific gravity of a sample was found to be 2.46, and the apparent 1.36; the porosity is therefore $\frac{1.36}{2.46} = .55$, or expressed as a percentage = 55 per cent.

The differentiation of the constituents of soils into sand, clay, and organic matter is of some importance in connection with certain public health subjects.

Sand consists of the coarser particles which rapidly sink in water; clay of the fine particles which remain for a time in suspension.

The estimation of sand and clay may be performed thus: Take 10 grammes of dried soil in a beaker. Moisten the soil with a little distilled water and a few drops of a solution of NH_4Cl . When moist add 80 to 100 c.c. distilled water, and stir. Allow to settle for five minutes, and pour off the fluid into a tall cylinder. Another

100 c.c. of water is added, and the soil well stirred. After settling again for five minutes the fluid is poured off into the cylinder. These manipulations are repeated until the overlying fluid is quite clear.

The sand is turned on to a filter-paper, well washed, dried, weighed, and recorded as sand.

The cylinder is set aside for twenty-four hours, and when fully settled the upper portion of the fluid is run through a filter-paper without disturbing the sediment. When nearly all the water has been drained off, the sediment is stirred and poured on the filter. The last traces of clay are washed from the cylinder, and the entire contents now on the filter are thoroughly washed, dried, weighed, and recorded as clay.

Clay soils contain over 30 per cent. clay; brick clay contains at times 95 per cent. Sandy soils contain as little as 1 or 2 per cent. A loam contains 10 per cent.

In order to determine the amount of organic matter in a soil, take 10 grammes of a dried sample in a platinum dish, and heat it at a temperature a little over 100° C. until a constant weight is obtained. Oxidize over a flame at a low red heat, transfer to desiccator, and weigh. The loss in weight gives roughly the amount of organic matter.

CHAPTER XVII

AIR ANALYSIS

A CHARACTERISTIC property of gases is the invariable ratio that exists between their volume and pressure. According to Boyle's law this fact is expressed as, '*the volume of a gas is inversely proportional to the pressure when the temperature is constant.*' Another characteristic is the relation which exists between volume and temperature. The law of Charles states that '*the volume of a gas is directly proportional to its absolute temperature when the pressure is constant*'; when temperature and pressure vary, $V = \frac{T}{P}$.

The absolute zero of the Centigrade scale is -273° ; the corresponding reading on the Fahrenheit scale is -459° , or 491° below freezing-point (32°). These temperatures have been arrived at from consideration of the fact that all gases expand $\frac{1}{273}$ part of their volume for each degree of increase of temperature on the Centigrade scale, and $\frac{1}{491}$ part of their volume on the Fahrenheit scale.

Water vapour is not a gas, and consequently not subject to these laws.

All work on gases and vapours requires a thermometer and barometer. The student will remember that there are three thermometric scales in use—Celsius or Centigrade, Fahrenheit, and Réaumur; that the freezing-points in the three are respectively 0° , 32° , and 0° , and the boiling-points 100° , 212° , and 80° . The conversion of degrees from one scale to another is simple when it is remembered that $180^{\circ} \text{ F.} = 100^{\circ} \text{ C.} = 80^{\circ} \text{ R.}$ (the number of degrees between freezing and boiling points in each case). When reducing degrees F. to other scales 32 must first be subtracted, and when reducing other scales to F. 32 must be finally added.

Barometers are used for recording the pressure of the atmosphere, and may be constructed of mercury, water, and other liquids. The mercury barometer is the only one in general use, and consists of a glass tube $\frac{1}{8}$ inch in diameter and about 3 feet long, closed at one end and filled with mercury. The length of a mercury column supported by the atmosphere is about 30 inches. This tube is inverted, and placed in a cistern containing mercury which is exposed to the atmosphere. All air, moisture, etc., must be rigidly excluded from the tube, otherwise the column would be subject to a pressure opposed to the atmosphere, and the reading accordingly too low. The tube is graduated in inches, tenths, and twentieths of an inch, or in millimetres. There are two patterns of barometer in use—the 'Fortin' and the 'Kew.'

When the atmospheric pressure increases the mercury in the cistern is depressed, whilst that in the tube rises. This pressure is measured by the height of the column in the tube above the level of the mercury in the cistern. In the Fortin barometer the level of the surface of the mercury in the cistern when screwed up to exactly meet the tip of the fixed ivory point constitutes the zero of the scale. Hence, in taking a reading it is necessary to adjust the surface of the mercury in the cistern to the level of the point. In the Kew barometer no adjustment of the surface of the mercury in the cistern is made, but the graduations are shorter than true inches, being calculated from the relative diameters of the tube and cistern.

Four corrections are usually made of a barometric reading : (1) index error, (2) capillarity, (3) temperature, (4) altitude. The index error consists in the inaccuracy in the divisions of the scale, and in the Fortin barometer in the difference between the fixed 'fiducial' point and the true zero of the scale. Capillarity is always negative for mercury and glass. These two corrections are ascertained during standardization, and when taken together afford an inclusive figure, which is usually supplied with the instrument.

All barometric readings are reduced to freezing-point (32° F. or 0° C.) in order that comparisons may be made. When, therefore, the temperature is not freezing a correction must be made for the expansion or contraction of the mercury in the tube. Moreover,

the brass index is subject to variations in volume, due to changes in temperature. If it be taken that the mercury is correct in volume at 32° F., the brass scale is correct at 62° F., and in exact work the coefficient of expansion of brass at 62° F. is determined.

The volume of the mercury is proportional to the height of the column.

If H be the observed height of the mercury at t° F., and a the coefficient of expansion of mercury at 32° F., the correct height H^1 will be found from the formula :

$$H^1 = \frac{H}{1 + a(t - 32)}.$$

If b represent the coefficient of expansion of brass at 62° F., the combined correction for mercury and brass will be given by :

$$H^1 = \frac{H}{\{1 + a(t - 32)\} \{1 + b(t - 62)\}}.$$

All barometric readings for comparison must be reduced to sea-level (mean water height at Liverpool).

The barometer falls as the atmosphere is ascended, and since the atmosphere becomes rarer and rarer as higher altitudes are reached, it follows that the barometer will fall less for a given space traversed at a higher altitude than at a lower. In order, therefore, to compare two or more readings at different levels, they must be corrected—that is, they must be subjected to similar conditions as regards total pressure. If it be assumed that in the lower regions of the atmosphere a column of 900 feet supports 1 inch of mercury, the following formula will roughly give the correction :

$$H^1 = H + \frac{a}{900} \text{ inches ;}$$

where

H^1 = corrected reading,

H = observed reading,

a = height in feet above sea-level.

A sliding-scale known as a vernier is attached to the principal scale of the barometer. Verniers are of different lengths, and contain variable numbers of divisions. A common form is $1\frac{1}{3}$ inches long, divided into twenty-five parts, which correspond in length with twenty-four divisions of the principal scale.

A division on the principal scale is therefore greater than one on the vernier by

$$\begin{aligned} & \left(\frac{1}{24} \times 1\frac{1}{5} \text{ inches} \right) - \left(\frac{1}{25} \times 1\frac{1}{5} \text{ inches} \right) \\ &= \frac{25 - 24}{600} \times 1\frac{1}{5} \text{ inches} \\ &= .002 \text{ inch.} \end{aligned}$$

To read the vernier adjust its lower edge with the top of the meniscus, when two very small triangles of light will appear, one

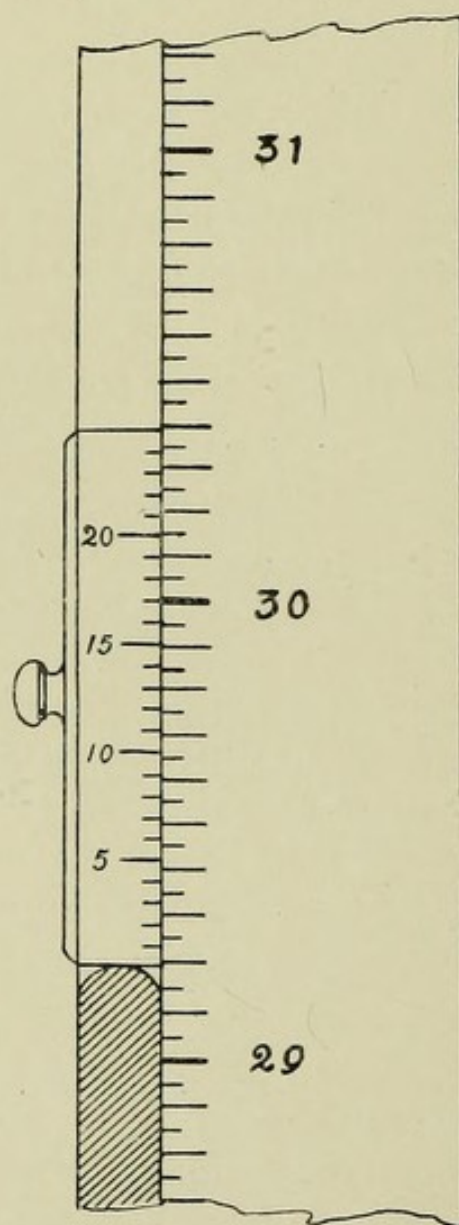


FIG. 18.

on either side. If the lower edge of the vernier correspond with a division of the principal scale, this is the reading; but if not, it is evident that the interval between the surface of the mercury and the division of the principal scale next below is equal to the difference between the lengths of the divisions of the vernier and

principal scales (.002 inch) multiplied by the number of vernier divisions which intervene between the lower edge (zero of vernier) and that division which exactly corresponds with a division on the principal scale.

Suppose in a given example that the lower edge of the vernier cuts the principal scale between 29.15 and 29.2 inches, and when the vernier scale is examined it is found that its thirteenth division corresponds with a division of the principal scale, the reading will be :

$$\begin{aligned} & 29.15 \text{ inches} + 13 \times .002 \text{ inches} \\ & = 29.15 \text{ inches} + .026 \text{ inch} \\ & = 29.176 \text{ inches.} \end{aligned}$$

Altitudes are calculated from barometric readings either (1) by Laplace's formula, or (2) by Apjohn's formula.

Laplace's formula is :

$$D = 18,363 (\log P - \log p) \left(1 + \frac{2t + t'}{1,000} \right),$$

where D = difference in altitude in metres of the two stations.

P = barometric pressure in mm. Hg at lower station.

p = " " " " higher "

t = temperature in °C. at lower station.

t' = " " higher "

Apjohn's formula is :

$$D = \frac{16,000 (P - p)}{P + p} \times \left(1 + \frac{2t + t'}{1,000} \right),$$

where D = difference in altitude in metres of the two stations.

P = barometric pressure in mm. Hg at lower station.

p = " " " " higher "

t = temperature in °C. at lower station.

t' = " " higher "

In estimating the weight of volumes of air and aqueous vapour at varying temperatures and pressures, it is necessary to understand aright the meaning of 'density,' 'specific gravity,' and 'relative density.' Density is defined as the mass of unit volume (mass being the amount of matter as measured by inertia); specific gravity is the ratio of the weight of a certain volume at a given temperature and pressure to the weight of an equal volume of a standard substance at the same temperature and pressure. Since

the unit volume is 1 c.c., and the unit mass 1 gramme, it follows that water is the standard substance whose density is unity. When the density of oxygen is spoken of as 16, it is meant that the specific gravity of oxygen is 16, hydrogen being taken as the standard; the real density (mass of 1 c.c. O) is .0014 gramme. It is preferable to use the phrase 'relative density' of oxygen, etc., and consider it as meaning the same thing as specific gravity when air or hydrogen is the standard. The atomic weights of gaseous elements such as H, N, etc., represent their relative densities, whilst the relative densities of compound gases are represented by half their molecular weights. The relative density of O is 16, that of CO₂ 22, H being the standard. The relative density of air referred to the same standard is 14.47.

In hygiene it is customary in calculating the weights, etc., of gases to take air as the standard. The relative density of H is, therefore, $\frac{1}{14.47}$; of O, $\frac{16}{14.47}$; of CO₂, $\frac{22}{14.47}$; and of water vapour, $\frac{9}{14.47}$.

In the metric system the weight of a litre of H at 0° C. and 760 millimetres Hg = .0896 gramme.

In English measure the weight of a cubic foot of air at 32° F. and 30 inches Hg = 266.86 grains.

The pressure of water vapour increases with its temperature until at boiling-point it equals that of the atmosphere (30 inches Hg).

The following figures are extracted from a table of vapour tensions:

32° F.	= .181	inch pressure.
33° F.	= .188	„ „
34° F.	= .196	„ „
42° F.	= .267	„ „
43° F.	= .277	„ „
44° F.	= .288	„ „
50° F.	= .361	„ „
52° F.	= .388	„ „
53° F.	= .403	„ „
54° F.	= .418	„ „
62° F.	= .556	„ „
63° F.	= .576	„ „
64° F.	= .596	„ „

Example.—Find the weight of a cubic foot of aqueous vapour at 62° F.

At this temperature the tension or pressure is .556 inch. As the relative density of aqueous vapour (air being the standard) is $\frac{9}{14.47}$, or .622, it is necessary to find the weight of a cubic foot of dry air at 62° F. and .556 inch pressure, and multiply the result by .622.

The weight of a cubic foot of dry air under these conditions of temperature and pressure will be given by finding the fourth term x of the proportion :

$$\begin{array}{l} 521 : 491 :: 566.86 \text{ grains} : x \\ 30 : .556 \end{array}$$

$$x = \frac{491}{521} \times \frac{.556}{30} \times 566.86 = 9.9 \text{ grains,}$$

and this multiplied by .622 = weight of aqueous vapour = 6.16 grains.

The pressure of aqueous vapour is constant for a given temperature, whether it is *in vacuo* or mixed with a gas or gases, and varies directly, as has already been stated, as the temperature.

Two other types of problem arise in connection with this subject—namely, (1) finding the weight of a volume of air saturated with vapour at a given temperature and pressure; and (2) finding the weight of a volume of air partially saturated with vapour at a given temperature and pressure.

Example 1.—Find the weight of a cubic foot of air saturated with aqueous vapour at 62° F. and 30 inches Hg.

By the table of vapour tensions it is seen that 62° F. corresponds with .556 inch Hg. As the total pressure of air and vapour is 30 inches, the pressure exerted by the air alone must be 30 - .556, or 29.444 inches. The problem, therefore, resolves itself into finding the weight of a cubic foot of dry air at 62° F. and 29.444 inches, and that of a cubic foot of aqueous vapour at 62° F. and .556 inch.

$$\frac{491}{521} \times \frac{29.444}{30} \times 566.86 = 524.32 \text{ grains (weight of dry air).}$$

$$\frac{491}{521} \times \frac{.556}{30} \times 566.86 \times .622 = 6.16 \text{ grains (weight of aqueous vapour).}$$

∴ the cubic foot of saturated air

$$= 524.32 + 6.16 \text{ grains} = 530.48 \text{ grains.}$$

Example 2.—Find the weight of a cubic foot of air partially saturated with aqueous vapour at 62° F. and 30 inches, dew-point being 50° F.

The dew-point is the temperature of complete saturation of the atmosphere. If the atmosphere be raised in temperature its capacity for holding aqueous vapour will be increased; if lowered this capacity will be diminished. When the temperature is lowered below the dew-point vapour is deposited in the fluid form.

Vapour tensions in the above table correspond with temperatures of complete saturation or dew-points, hence in problems of the type under consideration, if the dew-point be not given, it must be found. This may be done directly by such instruments as Daniell's or Regnault's hygrometers, or indirectly by Glaisher's formula, which determines the dew-point from the reading of the wet and dry bulb thermometers. Dew-point = $D - G(D - W)$ where D = temperature of dry bulb, G = Glaisher's factor for reading of dry bulb, and W = temperature of wet bulb; or by Apjohn's formula :

For temperatures above 32° F. :

$$P = p - \left(\frac{d}{87} \times \frac{h}{30} \right).$$

For temperatures below 32° F. :

$$P = p - \left(\frac{d}{90} \times \frac{h}{30} \right).$$

Where

P = pressure of aqueous vapour at dew-point.

p = pressure of aqueous vapour at temperature of wet bulb.

d = difference in degrees F. between dry and wet bulbs.

h = height of barometer in inches.

Returning to the problem, when the dew-point 50° F. has been found, the pressure of the aqueous vapour $\cdot 361$ inch is obtained from the table of vapour tensions.

The problem is resolved as before into two portions—viz., the weight of dry air at 62° F. and pressure $30 - \cdot 361$ inches, and the weight of vapour at 62° F. and pressure $\cdot 361$ inch.

$$\frac{491}{521} \times \frac{29\cdot639}{30} \times 566\cdot86 = 527\cdot8 \text{ grains.}$$

$$\frac{491}{521} \times \frac{\cdot 361}{30} \times 566\cdot86 \times \cdot 622 = 3\cdot98 \text{ grains.}$$

$$527\cdot8 + 3\cdot98 = 531\cdot78 \text{ grains.}$$

Relative humidity represents the ratio between the weight of aqueous vapour present in a given volume of air and the weight of vapour which would be required to saturate the same volume of air under similar conditions of temperature and pressure, and is expressed as a percentage.

Consider the last example, in which the temperature is 62° F. and the dew-point 50° F. :

Relative humidity =

$$\frac{\text{pressure at } 50^{\circ} \text{ F.} \times \frac{30}{30} \times \frac{491}{521} \times 566\cdot86 \times \cdot 622}{\text{pressure at } 62^{\circ} \text{ F.} \times \frac{30}{30} \times \frac{491}{521} \times 566\cdot86 \times \cdot 622} = \frac{\text{pressure at } 50^{\circ} \text{ F.}}{\text{pressure at } 62^{\circ} \text{ F.}}$$

$$= \frac{\cdot 361}{\cdot 566}; \text{ or expressed as a percentage, } \frac{361 \times 100}{566} = 64\cdot9\%.$$

Air.—The atmosphere contains a number of gases, three of which occur in the following fairly constant proportions : O = 20·96, N = 79, CO₂ = 0·04 per cent. In addition, aqueous vapour is present in variable quantities, and under certain conditions traces of NH₃, HNO₃, O₃ are found. The new gases—argon, krypton, xenon, neon—discovered by Rayleigh and Ramsay are included with N in the above percentages. Nitrogen is practically unalterable in quantity, whilst O and CO₂ vary, owing to the circulation carried on through the respiration and transpiration of animals and plants.

The composition of the air expired from the lungs contrasted with ordinary air demonstrates the invariable nature of the N and the limits of variation of O and CO₂.

	Ordinary Air.	Expired Air.
O - - - -	20.96 per cent.	16.4 per cent.
N - - - -	79.00 „	79.0 „
CO ₂ - - -	.04 „	4.6 „

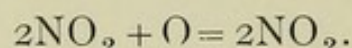
The practically uniform composition of the air all over the earth is maintained by variations of temperature leading to variations of volume and pressure, with resulting air-currents, diffusion of gases, the above-named circulation effected by the respiration and transpiration of animals and plants, rain, etc.

Oxygen is the most important constituent of the air, in that it is a prime necessity to life. Its quantity is diminished by respiration, putrefaction, combustions of all types, and at high altitudes.

The estimation of O may be readily carried out in the following ways :

1. The nitric oxide (NO) method.

This method, although it has been adversely criticised, yields, in careful hands, excellent results. The reaction is



The NO₂ is soluble in water. There is a contraction of three volumes of the mixture for every one volume of O, therefore one-third of the contraction represents the O.

To a sample of air in a gas burette excess of nitric oxide is added. The mixture is passed into an absorption pipette charged with water. The ruddy fumes of NO₂ are rapidly absorbed, and after passing the gas backwards and forwards a few times the reading becomes constant. One-third of the contraction represents the O.

2. Hempel's gas burette and absorption pipette.

In the figure the mounted tube—the gas measurer—next to the bulbs is graduated into c.c. and tenths ; the other—the levelling-tube—is plain.

The absorption pipette used is a double one, consisting of four bulbs ; the first and largest contains alkaline pyrogallic acid

(15 grammes acid and 50 KOH to the litre) ; the second and fourth are empty ; whilst the third contains water. This arrangement is necessary to seal off the atmosphere. The reagent in the first bulb absorbs O and CO₂. The graduated burette is supplied at

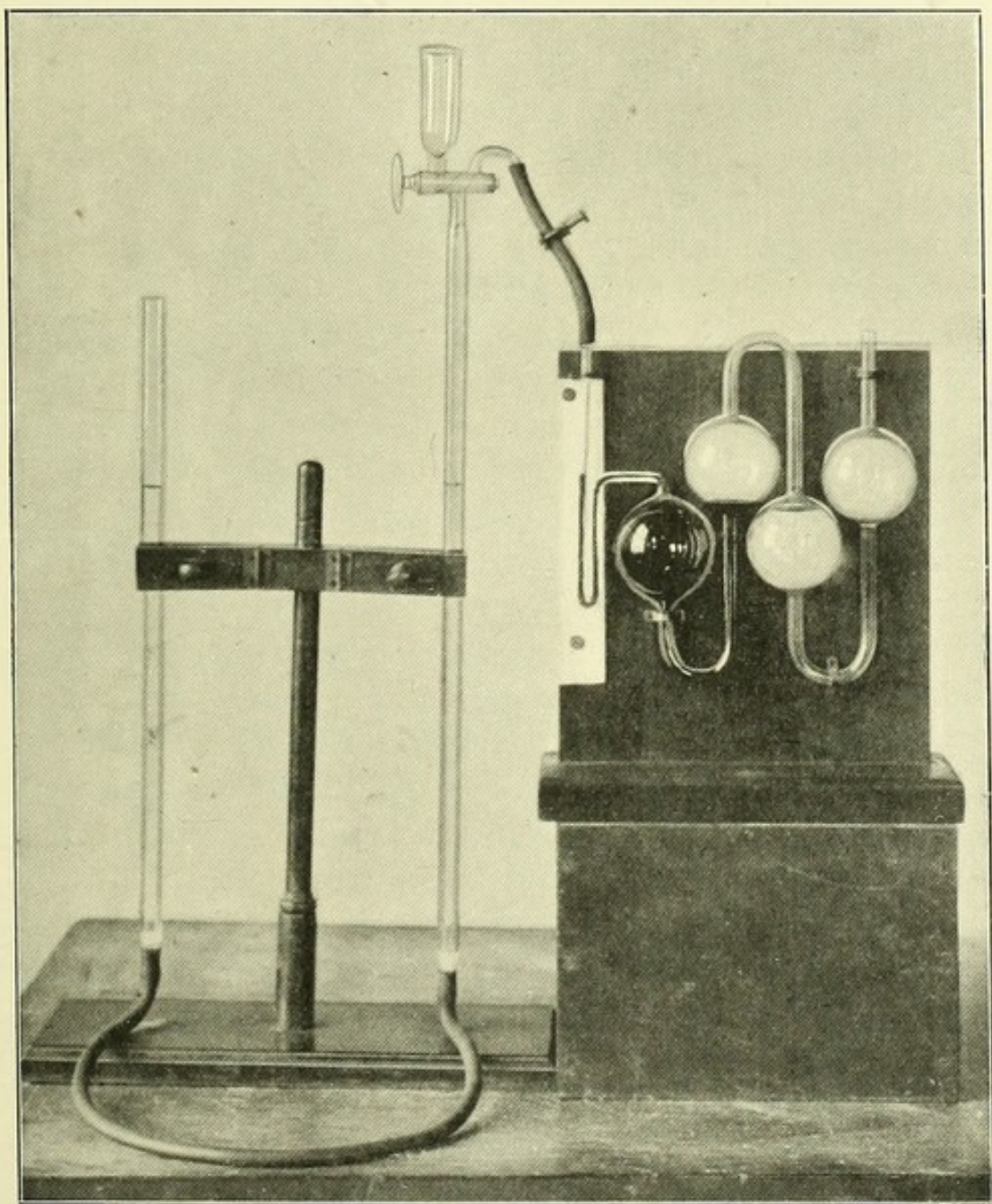


FIG. 19.—HEMPEL'S GAS BURETTE AND ABSORPTION PIPETTE.

the upper end with a two-way stopcock and a short piece of fine pressure tubing (carrying a screw clip) which connects it with the small manometer U-tube of the bulbs. In order that this piece of tubing may be as short as possible, the bulbs are raised on a

block, so that the end of the manometer-tube is near to the burette. The burette and the levelling-tube are connected at their lower ends by a piece of rubber tubing, and water is poured into the levelling-tube until it and the burette are half full.

In making an estimation, first mark on the ivory slip the height at which the coloured liquid stands in the capillary U-tube, turn the tap so that connection is made between the burette and bulbs, then raise the levelling-tube until all the air is driven over out of the burette into the bulbs. Now connect the atmosphere with the burette, and lower the levelling-tube until a definite quantity of the particular atmosphere (say 25 or 50 c.c.) is admitted. Then make connection with the bulbs, and raise the levelling-tube until this quantity of air is driven over into the absorption apparatus. Turn the tap halfway, screw down the clip, and unfasten the bulbs from the burette. Shake carefully for ten or fifteen minutes, reunite with burette, and bring back the air by lowering the levelling-tube. Repeat these manipulations until a constant volume is obtained, when the liquid stands at the original mark in the U-tube and the burette is levelled. The decrease in volume is due to the O and CO₂ absorbed. Deduct the CO₂ obtained by Pettenkofer's method, and the remainder represents the O. This volume of O may be reduced to standard temperature and pressure.

Since the temperature should not vary during the operation, the burette must not be handled. The absorption reagent in the first bulb, the water in the third, and the water in the burette, should all be saturated with air before commencing the estimation. It is to be noted that the pyrogallic solution will absorb besides O other gases, such as H₂S, SO₂, HCl, etc.

3. Where accurate estimations are required, the combustion method of Dumas may be used.

A measured volume of air is drawn through KOH to free it from CO₂, and thence over ignited spongy copper in a combustion-tube. The copper fixes the O, and the amount of the latter is estimated from the difference in weight of the copper and copper oxide.

Carbon Dioxide.—Carbon dioxide may vary in an atmosphere from .02 to .7 or .8 per cent. The quantity ordinarily found in a pure atmosphere ranges from .035 to .04 per cent.

The atmosphere of London during a fog often contains .08 per cent. In a living-room lighted by coal-gas the CO_2 may reach .2 per cent., and a higher figure where gas-stoves are used, when an appreciable amount of CO is often found.

Carbon dioxide arises from (1) animal respiration; (2) combustion of all kinds of fuel; (3) organic combustion, in the form of putrefaction, fermentation, etc. Its special significance lies in the fact that as a product of respiration it can be made a fairly accurate measure of the organic impurities which accompany it.

Carbon dioxide *per se*, in the quantities commonly found, may be considered harmless. It is generally agreed that the amount furnished by respiration may not exceed .02 per cent. Taking .04 per cent. as the average quantity found in the air, .06 per cent. (.02 + .04) will represent the limit of CO_2 allowable in any atmosphere contaminated by respiration.

The number of cubic feet of fresh air required to dilute the CO_2 of a room, so that this limit may be preserved, will be found by the formula :

$$\frac{\text{cubic feet CO}_2 \text{ added} \times 100}{.02}$$

The quantity of CO_2 added to the air through respiration is roughly .6 cubic foot per head per hour. Substituting this figure in the formula, it is found that 3,000 cubic feet fresh air per head per hour must be admitted to living rooms if the CO_2 is to be kept within the limit named.

The Estimation of CO₂ in the Atmosphere — Pettenkofer's Method.—When CO_2 is shaken up with baryta-water, Ba(OH)_2 , insoluble BaCO_3 is formed, and the alkalinity of the fluid is lessened.

Take a 5 litre air-jar, cleansed and filled with water, into the apartment in which the estimation is to be made. Pour out the water, so that the air may enter the jar, and stopper carefully.

Prepare baryta-water by adding about 5 grammes Ba(OH)_2 to a litre of distilled water, and accurately estimate, in terms of standard oxalic acid solution, the alkalinity of 25 c.c., using phenolphthalein as indicator. The acid is prepared by dissolving 2.82

grammes of the crystals in a litre. This solution is of such strength that 1 c.c. is equivalent to .5 c.c. CO_2 at standard temperature and pressure.

Now add 50 c.c. of the clear barium hydrate solution to the contents of the jar, and roll it round the interior for some time. When, in say twenty minutes, the whole of the CO_2 is absorbed

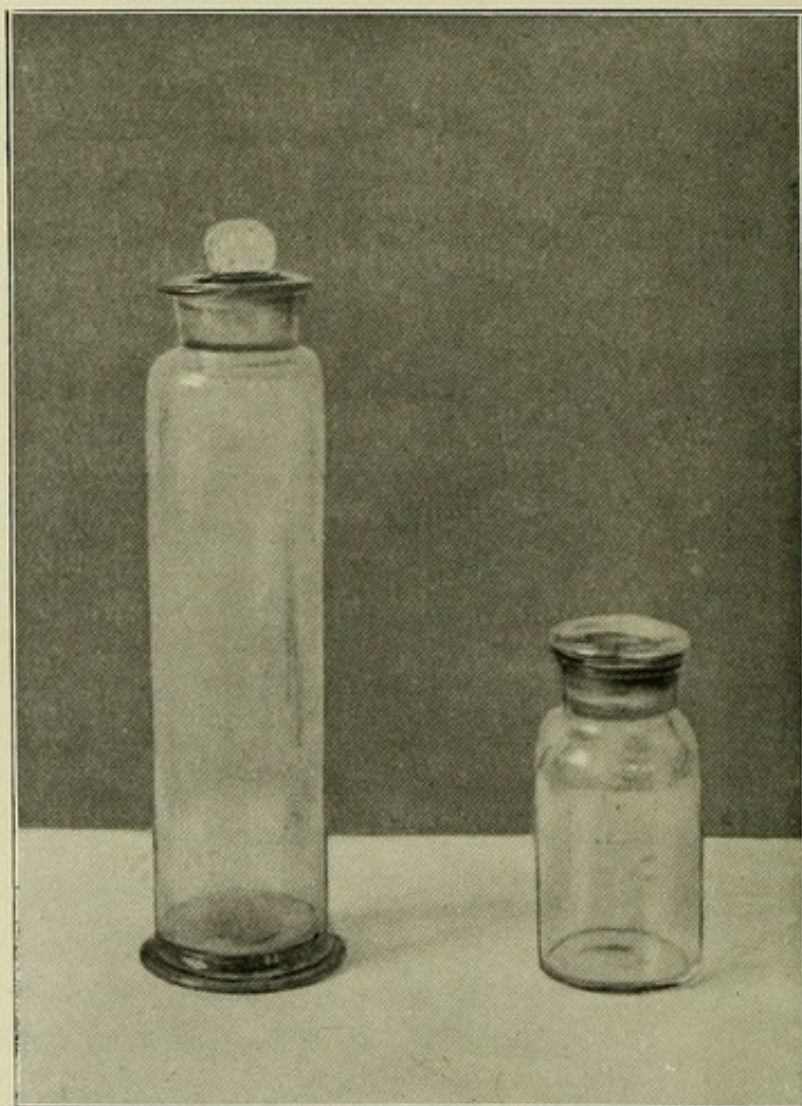


FIG. 20.—LARGE AIR-JAR.

SMALL AIR-JAR.

and neutralized, take out 25 c.c. of the solution with a pipette and rapidly titrate it with the standard oxalic acid, delivered from a burette. The difference in alkalinity of this and the original 25 c.c. multiplied by 2 is equivalent to the CO_2 in the jar. This result is to be recorded as CO_2 at standard temperature and pressure.

The following is an example: Temperature 15°C. , pressure

750 millimetres. Twenty-five c.c. of the freshly-prepared $\text{Ba}(\text{OH})_2$ were measured by pipette into a porcelain basin, a few drops of phenolphthalein added, and standard oxalic acid run in until the pink colour just disappeared after thorough stirring; 21.5 c.c. of the standard acid were used.

Fifty c.c. $\text{Ba}(\text{OH})_2$ were run into the jar, and after complete absorption of the CO_2 had taken place, 25 c.c. were removed and titrated with acid; 19.9 c.c. standard acid were used. $21.5 - 19.9 = 1.6$ c.c.; and $1.6 \text{ c.c.} \times 2 = 3.2$ c.c., the total amount of CO_2 in the jar, or 3.2 c.c. in 4,950 c.c. (5,000 c.c. — 50 the volume displaced by the $\text{Ba}(\text{OH})_2$). The volume of this 4,950 c.c. at 0°C . and 760° millimetres =

$$\frac{4950 \times 750}{760 \times \{1 + (.0036 \times 15)\}}$$

(in the C. scale $\frac{1}{273}$ or .0036 = coefficient of expansion of gases per degree) = 4,635 c.c.

3.2 c.c. CO_2 in 4,635 c.c. air = .06 per cent.

Baryta-water is best prepared fresh, but if it must be kept, it should be stored in a vessel shut off from the atmosphere by a hollow tube filled with pumice moistened with KOH. $\text{Ba}(\text{OH})_2$ has a slight action on glass, but any error that might arise through liberated alkalies is so infinitesimal, that it may be neglected, especially when a jar has been used a few times.

Angus Smith's 'household test' consists in running $\frac{1}{2}$ ounce of clear lime-water into a $10\frac{1}{2}$ ounce bottle. No turbidity will be found so long as the CO_2 in the air does not exceed the limit allowed—viz., .06 per cent.

Lunge and Zeckendorf's Method.—A bottle of 70 c.c. capacity and an indiarubber pump of the same capacity are connected so that air can be pumped into the bottle. A weak standard solution of NaOH is prepared and tinted with phenolphthalein, by adding 2 c.c. $\frac{\text{N}}{10}$ NaOH containing 1 per mille phenolphthalein, to 100 c.c. ammonia-free distilled water. The ball of the pump is squeezed until the bottle is filled with the air to be tested. Ten c.c. of the $\frac{\text{N}}{500}$ NaOH are now placed in the bottle, and the stopper, through which the delivery tube of the pump and an exit tube pass, inserted. The ball is then gently pressed, causing air to bubble through the

liquid, and the bottle is carefully shaken after each addition of air until the colour is discharged.

The number of times the ball is emptied indicates the amount of CO_2 , according to the following table, compiled by Lunge from estimations made by Pettenkofer's method :

Per cent.					Per cent.				
2	-	-	-	·3	16	-	-	-	·071
3	-	-	-	·25	17	-	-	-	·069
4	-	-	-	·21	18	-	-	-	·066
5	-	-	-	·18	19	-	-	-	·064
6	-	-	-	·155	20	-	-	-	·062
7	-	-	-	·135	22	-	-	-	·058
8	-	-	-	·115	24	-	-	-	·054
9	-	-	-	·10	26	-	-	-	·051
10	-	-	-	·09	28	-	-	-	·049
11	-	-	-	·087	30	-	-	-	·048
12	-	-	-	·083	35	-	-	-	·042
13	-	-	-	·08	40	-	-	-	·038
14	-	-	-	·077	48	-	-	-	·030
15	-	-	-	·074					

When, from respiration, CO_2 rises above ·06 per cent., a certain unpleasant odour is experienced in rooms, due to the accompanying organic exhalations, and when much above this figure headache and even faintness may supervene.

A cubic foot of coal-gas yields on combustion ·6 cubic feet CO_2 . It is obvious that when CO_2 is due solely to the combustion of coal-gas the quantity may be allowed to exceed considerably the above-named limit.

Carbon Monoxide.—This odourless gas possesses a special affinity for hæmoglobin, displaces oxygen from it, and thus destroys the oxygen-carrying function of the blood and ultimately life, by cutting short internal respiration. When hæmoglobin is saturated to the extent of 30 per cent., symptoms of poisoning set in, and 70 per cent. saturation is fatal. Coal-gas contains by volume nearly 10 per cent. CO, and when imperfectly burnt leaves small quantities in the flue ; but greater danger attaches to the escape of the gas from ill-constructed taps and joints. The use of coke, especially in cast-iron stoves, is a fruitful source of CO. As CO_2 passes over hot coke it is reduced according to the equation $\text{C} + \text{CO}_2 = 2\text{CO}$.

The carbon of the hot cast-iron acts in the same manner, reducing CO_2 to CO . Solid particles of organic matter floating in the atmosphere become charred on the exterior of the stove, and this partial oxidation results in the formation of CO .

The characteristic cherry-red colour of CO -hæmoglobin serves as an excellent test for the presence of carbon monoxide. If a few drops of fresh mammalian blood be diluted with water down to about 2 per cent., and the solution shaken up with CO , the distinctive colour is at once formed. If dilution be extended to .2 per cent., and HbCO formed by shaking with the gas, the characteristic spectrum consisting of two bands occupying nearly the same position as those of HbO_2 , but differing in that they do not disappear on the addition of reducing agents, such as $(\text{NH}_4)_2\text{S}$ or H_2S , may be readily seen.

The estimation of CO in the air may be performed by (1) Haldane's hæmoglobin percentage saturation method, or (2) by the cuprous chloride method for large quantities.

1. The following is Haldane's account of his method :

' A solution of about 1 of normal blood to 100 of water is made ; also a solution of carmine dissolved with the help of a little ammonia and diluted till its depth of tint is about the same as that of the blood solution. Two test-tubes of equal diameter (about $\frac{1}{2}$ inch) are then selected. Into one of these 5 c.c. of the blood solution are measured with a pipette ; into the other about an equal quantity is poured. Ordinary lighting gas is then allowed to blow into the second test-tube through a piece of rubber tubing for a few seconds. The test-tube is then quickly closed with the thumb before the gas has time to escape, and the blood solution thoroughly shaken up with the gas for a few seconds. The hæmoglobin is thus completely saturated with carbonic oxide, and the solution has now the characteristic pink tint. The carmine solution, which has a still pinker tint, is now added from a burette to the 5 c.c. of normal blood solution in the other test-tube until the tints are the same in the two test-tubes. Not only, however, must the tints be equal in quality, but they must also be sensibly equal in depth. If the carmine solution is too strong or too weak, the latter will not be the case, and the solution must be diluted or made stronger accordingly. It is usually easiest to make the carmine a little

too strong at first, so that on adding both carmine solution and water equality can be established. From the amount of water which is required to be added it is easy to calculate the extent to which the original carmine solution needs to be diluted. The solutions are now ready for use, and the actual analysis is made as follows: 5 c.c. of the solution of normal blood are measured into one of the test-tubes, and a drop of the suspected blood placed in the other test-tube and cautiously diluted with water till its depth of tint is about equal to that of the normal solution. If carbonic oxide be present in the hæmoglobin, a difference in quality of the tints of the two solutions will now be clearly perceptible. Carmine solution is then added from the burette to the normal blood, and water, if necessary, to the abnormal blood, till the tints are equal in both quality and depth. The carmine is added by about .2 c.c. at a time, the points being noted at which there is just too little and just too much carmine, and the mean being taken. The solution of normal blood is then saturated with coal-gas, and the addition of carmine to the other test-tube continued until equality is again established and the amount of carmine noted. The percentage saturation with carbonic oxide of the abnormal blood can now be easily calculated, since we know how much carmine solution its saturation represented as compared with what complete saturation represented.

'The method of calculation is illustrated by the following example: To 5 c.c. of normal blood solution 2.2 c.c. of carmine is required to be added to produce the tint of the blood under examination, and 6.2 c.c. to produce the tint of the same blood fully saturated. In the former case the carmine was in the proportion of 2.2 in 7.2, and in the latter of 6.2 in 11.2. The percentage saturation (x) of the hæmoglobin with carbonic oxide is thus given by the following proportion sum:

$$\frac{6.2}{11.2} : \frac{2.2}{7.2} :: 100 : x.$$

x is therefore = 55.2. As the compound of carbonic oxide and hæmoglobin is, to a slight extent, dissociated when the blood is diluted with water, the value found is a little too low. The corrections needed are as follows: Add .5 if 30 per cent. saturation

be found, 1.1 if 50 per cent., 1.6 if 60 per cent., 2.6 if 70 per cent., 4.4 if 80 per cent., 10.0 if 90 per cent. Thus, in the above example we must add 1.3, so that the true saturation is 56.5 per cent. In comparing the tints, the test-tubes should be held up against the light from a window, but bright light should be avoided as much as possible, as it increases the dissociation. Failing daylight, an incandescent burner, with a chimney of blue glass and an opal globe, may be used as the source of light.

‘Hæmoglobin brought into intimate contact with air containing .07 per cent. of CO will finally reach a state of equilibrium in which it is saturated to an equal extent with CO and oxygen. If the percentage of CO or oxygen in the air be increased or diminished, there will be an exactly corresponding increase or diminution of the relative share of the hæmoglobin which either gas obtains. Air containing $2 \times .07 = .14$ per cent. of CO will, for instance, produce two-thirds saturation with CO, and one-third saturation with oxygen, and so on. In the living body the proportion of CO taken by the hæmoglobin from respired air containing a given percentage of CO is not so large as outside the body, about 1 per cent. of CO in the air breathed being necessary to produce half saturation of the hæmoglobin. The general law of absorption is, however, much the same, and it follows that there is a certain maximum of saturation for each percentage. With less than .05 per cent. of CO in the air this maximum does not exceed 33 per cent. saturation, and the corresponding symptoms are scarcely appreciable, except on muscular exertion. With more than about .2 per cent. the maximum exceeds 60 per cent. saturation.

‘The detection and determination of small percentages of CO in the air was formerly a matter of great, and often almost insuperable, difficulty. I have recently, however, introduced a simple and, I think, very satisfactory method, depending on the already described action of CO on blood solution in presence of air. The sample of air is collected in a clean and dry bottle of about 4 ounces capacity. The cork of the bottle is removed in the laboratory under a .5 per cent. solution of blood, and about 5 c.c. of the air allowed to bubble out, a corresponding volume of the blood solution entering. The cork is then replaced, covered with a cloth to keep off the light, and shaken continuously for about ten minutes, when

the hæmoglobin will have reached the point of saturation corresponding to the percentage of CO present. The solution is then poured out into a test-tube, and the saturation is determined with carmine solution in the manner described above. It is evident that as in each case the saturation found corresponds to a definite percentage of CO in the air, it is easy to calculate this percentage. If p be the percentage required, and s the percentage saturation found, p is calculated from the following formula :

$$p = \frac{s \times .07}{100 - s}.$$

Thus, if $s = 60$, p is $.105$. This method may also be used for the direct determination of carbonic oxide in lighting-gas. The latter must, however, be first diluted to $\frac{1}{100}$ (or with carburetted water-gas to $\frac{1}{100}$) with air. As it is quite easy to make this dilution with perfect accuracy, the method is an exact one, and is not only rapid, but avoids the difficulties and sources of error connected with the ordinary method of determination by cuprous chloride, or by explosion.'

2. The cuprous chloride method.

Cuprous chloride is prepared from copper turnings, copper oxide, and strong HCl, and dissolved in distilled water. This solution absorbs CO.

The air to be treated is first freed from O and CO₂ by passage through Hempel's burette. The residue is slowly and repeatedly passed into a second absorption pipette containing cuprous chloride in solution. The bulb containing the copper salt should be large, the time for absorption long, and the transference from burette to pipette and *vice versa* as often repeated as necessary to procure a constant reading. The loss in volume, assuming that ethylene, acetylene, etc., are absent, represents the CO present. This method is by no means reliable ; it will not furnish accurate results below .1 per cent.

Ammonia is found in traces in all atmospheres. It is a product of putrefaction, and although in small quantities it seems to be harmless, it should be regarded with suspicion, by reason of the noxious bodies which accompany it. It is found in larger quantity in air in immediate contact with peat. It may be collected and

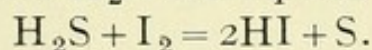
estimated by aspirating a known volume of air through ammonia-free distilled water, and afterwards distilling and Nesslerizing.

Sulphur dioxide, ammonium sulphide, and sulphuretted hydrogen are all present in the atmospheres of cities, and are hurtful to health and vegetation. Sulphur dioxide abounds where impure coals are consumed, and H_2S where organic decomposition takes place. It is stated that .06 per cent. H_2S in an atmosphere is dangerous to life, and fatal accidents in sewers have been attributed to this gas.

SO_2 may be estimated by aspirating a large and known volume of air through bromine water, and precipitating the H_2SO_4 thus formed with BaCl_2 . From the weight of the BaSO_4 obtained the weight of SO_2 is calculated.

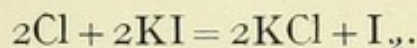
Sulphuretted hydrogen may be detected by exposing to the air strips of filter-paper moistened with lead acetate, and estimated quantitatively by aspirating a known volume of air through a solution of decinormal iodine containing a little starch paste. Immediately the blue colour departs the aspiration is stopped.

1.7 milligrammes H_2S correspond with 1 c.c. $\frac{\text{N}}{10}\text{I}$.



The violet colour produced by the interaction of $(\text{NH}_4)_2\text{S}$ and sodium nitro-prusside may be utilized for matching a standard solution with another containing an unknown quantity of $(\text{NH}_4)_2\text{S}$.

Chlorine may be absorbed in 10 per cent. KI solution, and the liberated I estimated with $\frac{\text{N}}{10}$ sodium thiosulphate. Bromine may be estimated in the same way :



3.5 parts by weight Cl = 12.6 parts I, or 7.9 parts bromine.

Nitrous, nitric, and hydrochloric acids may be estimated by absorption in water, and employing the methods described in water analysis.

The vapour of CS_2 found in the air of indiarubber works is estimated by passing it into strong alcoholic potash. This solution is then acidified with acetic acid, and finally neutralized with CaCO_3 . It is now diluted to twice its volume with water and titrated with standard iodine solution (1.66 milligrammes I per litre) and starch

paste. One c.c. I = 1 milligramme CS_2 . The reaction is complete when a faint blue tint appears.

Chlorine and bromine are injurious to human beings in dilution of $\cdot 1$ part per 100,000, and the following as noted :

Iodine	-	-	-	-	-	$\cdot 5$ part per 100,000.
SO_2 and HCl	-	-	-	-	-	1.0 „ „
H_2S and NH_3	-	-	-	-	-	10.0 parts per 100,000.
CO	-	-	-	-	-	20.0 „ „

Ozone.—Ozone, an allotropic modification of oxygen, O_3 , is a gas possessing an odour of phosphorus and an irritating action on the cells of the respiratory and conjunctival mucous membranes. It is produced by electric discharges over the sea, and to a greater extent at night than in the day. It is stated that more ozone is found in the winter (especially after snowstorms) than in the summer. It is absent from the air of towns, living rooms, and foggy atmospheres.

Detection and Estimation of Ozone.—Pieces of blotting-paper are soaked in a solution of KI and starch, and dried. These are then suspended in a cage, which protects them from direct sunlight, dust, and rain for twelve or twenty-four hours; where ozone is present, it liberates I , which forms a blue colour with the starch. It should be remembered that N_2O_3 , H_2O_2 , and Cl act in the same way; that free iodine may be partially volatilized, or in part form iodide or iodate of potassium, instead of blue iodide of starch; and that constant results cannot be expected owing to the variability in the conditions of temperature, light, and moisture.

Houzeau's test consists in moistening faintly red litmus-papers with a solution of KI and exposing them to the air. If ozone be present I is liberated, and alkaline KOH is formed, which renders the paper blue. Ammonia and hydrogen peroxide are the only other two gases which could produce this result. As H_2O_2 is practically never present, NH_3 is the only other gas to be considered. If, therefore, a second piece of litmus-paper untreated by KI is exposed at the same time, and if the entire colour is not due to NH_3 , the difference in the shades of the two papers must be furnished by ozone.

The intensity of colour created by ozone acting on papers exposed

to the atmosphere may be matched with one of a series of ten papers forming a standard scale. Each paper is exposed to a known quantity of ozone. Measured quantities of air should be aspirated over the papers in tubes. If instead the papers are suspended in the atmosphere, wind currents, etc., by bringing unequal quantities of air into contact with the papers, will vitiate the results.

Suspended Matter in the Air.—Solid animal, vegetable, and mineral particles float in the atmosphere, and tend to settle on objects as favourable conditions occur. In factories and workshops the amount of such matter may be so great as to be positively dangerous to health. Pathogenic micro-organisms adhere to dust and are carried with it.

The collection and microscopical examination of dust is effected by aspirating large quantities of air over gelatin, etc., or through water. In the first case the microscope will detect mineral and dead organic matter, and where living bacteria are present these will grow and produce colonies which can later be subcultured and studied at length. In the second a few drops of the water are evaporated on a slide and the sediment microscopically studied.

Pouchet's aeroscope and Hesse's apparatus are simple instruments in which known volumes of air are aspirated over transparent substances, such as glycerin, whereby the intercepted particles can afterwards be studied microscopically.

The dust in the atmosphere of towns commonly exceeds 10 milligrammes per cubic metre, or from 10,000 to 200,000 particles per c.c. On the top of a lofty mountain there may be no dust, or only a few particles per c.c.

As to the nature of the particles forming dust, it is sufficient to say that they are derived from every conceivable substance with which we have to do that is capable of existing in particulate form. The most important substances, from a health point of view, are solid particles capable of irritating the various internal channels in man, and bacteria and their spores.

Sewer air contains less oxygen and more CO_2 than that of the atmosphere. Ammonia, ammonium sulphide, and various compound ammonias emitting foetid odours, sulphuretted hydrogen, and marsh-gas, are present in ever-varying quantities. Ground air is very rich in CO_2 , especially in the autumn season of the year.

Ground air should be excluded from all living rooms, not only because of its own impurity, but because where it is allowed entrance, other more dangerous gases, such as coal-gas, sewer-gas, etc., may often enter too.

A sample of ground air may be collected for examination thus : A hollow, sharp-pointed steel cylinder, with many perforations, is pushed into the soil for a distance of 4 to 6 feet. The upper end of the cylinder is connected with an air-jar, and this in turn with an aspirator. The jar being shut off from the cylinder, is first emptied by the aspirator ; connection is then made, and the sample collected.

Besides CO_2 , which may reach 5 or 6 per cent., small quantities of NH_3 , CH_4 , H_2S are usually found.

Qualitative Examination of Air for Noxious Gases in Large Amounts.

Where air contains noxious gases qualitative examination is readily performed by aspirating large quantities of the air through pure water or other suitable solvent. Where, however, the gases are in considerable quantities tests may be applied direct to samples of the air in jars. Occasionally the atmosphere surrounding chemical works, etc., contains such large quantities of Cl , HCl , SO_2 , etc., that this direct method of examination may be adopted.

The following gases may be readily recognised by a few simple chemical tests :

HCl , CO_2 , N_2O_3 , HNO_3 , H_2S , SO_2 , Cl , CO , CS_2 , NH_3 , $(\text{NH}_4)_2\text{S}$.

1. Having collected a sample in an air-jar, remove the stopper and smell the gas. Replace the stopper quickly. Cl has a characteristic odour. HCl has a faint odour of chlorine. SO_2 has a characteristic odour, so also have NH_3 , $(\text{NH}_4)_2\text{S}$, H_2S , CS_2 .

CO_2 , CO , N_2O_3 , HNO_3 have no odours.

2. Take the reaction by moistening a red and blue filter-paper with water and rapidly inserting them in the jar, fixing the ends between the neck and the stopper. If doubt exist as to the effect on the litmus-papers the reaction may again be taken when the gas is dissolved in a small quantity of distilled water.

HCl, CO_2 , N_2O_3 , HNO_3 , SO_2 are acid.

NH_3 , $(\text{NH}_4)_2\text{S}$ are alkaline.

H_2S , CO , CS_2 are neutral.

Cl first reddens blue litmus-paper and afterwards bleaches it.

3. Dissolve the gas in 10 c.c. of water by vigorous shaking, and if the reaction be acid, to 2 or 3 c.c. of the solution add a drop or two of AgNO_3 solution. A white precipitate indicates

(a) HCl. Acidity marked; precipitate marked and soluble in $(\text{NH}_4)\text{HO}$; insoluble in HNO_3 .

(b) CO_2 . Acidity slight; precipitate slight. Addition of $\text{Ba}(\text{OH})_2$ produces turbidity, increased on further addition of a drop or two of $(\text{NH}_4)\text{HO}$.

(c) SO_2 . Odour characteristic; acidity marked; precipitate marked, soluble in HNO_3 . Two or three c.c. of the solution from the jar added to iodide of starch will decolourize it. If 2 or 3 c.c. of the same solution be heated with a drop of HCl a granule of $\text{Zn}, \text{H}_2\text{S}$ will be formed, which will darken lead acetate paper.

(d) No precipitate, HNO_3 . Perform the brucine test.

(e) No precipitate, N_2O_3 (now HNO_2). Test for nitrous acid with KI, starch, and H_2SO_4 ; or perform the meta-phenylene-diamine test.

4. If the reaction be alkaline the gas is either

(a) NH_3 . Odour characteristic. To 2 or 3 c.c. of the solution from the jar add a drop or two of Nessler's reagent, and the well-known yellow colour is developed. Or

(b) $(\text{NH}_4)_2\text{S}$. Odour characteristic. Nessler's reagent causes a black colour when mixed with the solution from the jar. To a few c.c. add a drop or two of sodium nitroprusside, and a violet colour rapidly appears.

5. If the reaction is neutral one or other of the following is present:

(a) H_2S . Odour characteristic. Lead acetate paper is darkened. Solutions of salts of iron, lead, and copper produce the dark-coloured sulphides of these metals.

(b) CS_2 . A liquid at ordinary temperatures. Set alight a drop on a porcelain slab, and note the yellow deposit of sulphur left behind.

6. The only gas which first reddens blue litmus-paper and then slowly bleaches it is Cl.

Odour characteristic. Suspend a moist KI paper in the jar. Free I will be liberated and darken the paper ; later the darkened paper will be bleached. Chlorine added to a mixture of ferrous sulphate and potassium sulphocyanide produces a red colour.

Note the differences between H_2S and $(NH_4)_2S$. H_2S has a neutral reaction, odour of rotten eggs only, and forms no colour with nitro-prusside of sodium. $(NH_4)_2S$ has an alkaline reaction, odour of rotten eggs and NH_3 , and produces a violet colour with sodium nitro-prusside.

7. CO is distinguished by absence of odour, no reaction with litmus, and by the characteristic colour and spectrum when shaken with blood.

Bacteria in the Air.—The great bulk of bacteria found in the air are chromogenic saprophytes, yeasts, and spores of moulds. They are distributed in the dry condition alone—hence the danger of dust contaminated with tubercle bacilli and typhoid bacilli. The number of organisms varies with the altitude, date and amount of recent rains, and a number of other factors.

The estimation of the number of air organisms may be carried out by one or other of the following simple methods :

1. *Hesse's Method.*—A 2-inch glass cylinder, 30 inches long, is covered at one end by a rubber sheet perforated by a $\frac{1}{4}$ -inch hole in the centre. This sheet is in turn covered with a non-perforated sheet. The other end receives a rubber cork carrying a piece of glass tubing plugged with cotton-wool. The apparatus is sterilized, and when ready for use, 50 c.c. of sterile gelatin are made to coat the interior of the cylinder. The instrument is then levelled on a tripod, and connected by the glass tube and a piece of indiarubber tubing, with an aspirator consisting of two flasks so arranged as to form a reversible syphon. Into one of the flasks is poured a litre of water. The outer sheet of rubber is removed, and by lowering the second flask a litre of air is aspirated through the tube. The second flask is then connected with the tube, and by repeating the operation a number of times a corresponding number of litres of air are drawn through. The rate of aspiration should

not exceed a litre in two and a half minutes, and this is controlled by a screw-clamp on the rubber connecting-tube. When 10 or 15 litres have been drawn through, the aspirator is disconnected, the sheet of rubber replaced, and the cylinder incubated. The number of colonies, liquefying and non-liquefying, are afterwards counted at the end of periods of twenty-four, forty-eight, seventy-two, etc., hours.

2. *Frankland's Method*.—In this method a tube 5 inches long and $\frac{1}{4}$ inch in diameter is plugged with cotton-wool at one end. One inch from the open end a slight constriction is made to support a plug of glass-wool inserted through this end. At a distance of $2\frac{1}{2}$ inches from this plug a second constriction occurs to support a second plug of glass-wool and fine cane-sugar supported before and behind by glass-wool plugs. A number of these tubes are made sterilized at 130° C. for two hours and packed for use in a tin box. When required, one is removed, horizontally clamped, and connected by rubber tubing with aspirating-flasks of the type described in the last paragraph. When the requisite quantity of air has been drawn through, the tube is disconnected and placed in another tin box. Several tubes can in this way be made to control one another in a given determination. When brought to the laboratory, a file is drawn across the centre of each tube, and the contents shaken out into a sterile flask of 300 c.c. capacity. About 15 c.c. of sterile nutrient gelatin are poured into the flask; the sugar dissolves, the glass-wool disintegrates, and a roll culture is made on the interior of the flask, which is incubated at room-temperature. After a definite time the colonies are counted.

3. Sedgwick and Tucker use a specially-constructed tube, one half wide and the other narrow, plugged at both ends. Glass-wool and cane-sugar are inserted in the narrow portion, and when the desired quantity of air has been aspirated through, the sugar and glass-wool are shaken into the wide portion, gelatin poured in, and a roll culture made. The tube is incubated and the colonies counted.

4. *Simple Plate Exposure*.—Agar and gelatin plates are prepared in Petri dishes in the usual way. These plates are then exposed for certain periods ranging from ten to twenty minutes to the air under investigation, care being taken that no undue agitation

of the air is produced, and that dust from the operator's clothing does not fall on the plates. The dishes are then covered and incubated at room- and blood-temperature as the case may be, and the colonies counted. Some investigators return their results in terms of the number of organisms falling on a square foot in a minute. In accurate hands this simple method yields as good results as any other.

CHAPTER XVIII

MILK

SINCE the milk of the cow is used to a much greater extent than that of any other mammal, its composition and properties have been much more thoroughly studied. Its liability to early decomposition and the fact that it forms an excellent bacterial culture medium render it necessary that the strictest attention should be paid to its production, collection, and distribution.

Composition of cow's milk :

				Per Cent.
Water	87.0
Proteids	4.6
Lactose	4.0
Fat	3.7
Ash7

Our knowledge of the proteids of milk is still very incomplete. The application of ordinary and crude chemical methods to the investigation of vital products necessarily leads to unsatisfactory results. The preparation of pure proteids is a most difficult task, and the probabilities are that in most cases where it is thought that a pure product has been isolated it is contaminated by reagents.

The proteids of the milks of different animals vary considerably. On the addition of an acid to cow's milk or goat's milk a curd or clot composed of casein is formed, and it is believed that in these cases the casein is chemically combined with the phosphates of the alkaline earths. In human milk and the milk of the ass and mare no such clot is produced on the addition of acid. Here it is believed that the proteid is not combined with phosphates. Besides casein, a second proteid (lactalbunin) is found in all milks. Storch describes a muco-proteid which he holds forms a gelatinous envelope

round the fat globules. Amylolytic and proteolytic ferments are said to occur in milk.

The proteid molecule is highly complex, as evidenced by its indiffusibility. Through the action of enzymes in the presence of acids and alkalies these complex bodies are hydrolized, passing through various intermediate stages (varieties of albumoses) into diffusible peptones.

The number of proteids in the milk of the cow has been variously stated. Duclaux maintains that there is only one—casein, existing in two forms, coagulable casein and non-coagulable casein. Hammarsten describes two—casein, corresponding to Duclaux's coagulable casein, and lactalbumin, corresponding to Duclaux's non-coagulable casein. This observer admits that lactalbumin has the properties of a true albumin, and closely resembles serum albumin; but holds that, owing to differences in certain physical constants, it is a distinct body. Hammarsten's casein and Halliburton's caseinogen are doubtless the same body under different names. Sebelein describes a globulin in milk.

Casein.—When pure, this is a white, non-crystalline, odourless, and tasteless body, insoluble in water, weak acids, alcohol, and ether. It is soluble in stronger acids and weak alkalies. It appears to possess a peculiar affinity for calcium phosphate, as it is almost, if not quite, impossible to free it from this salt. Casein contains less sulphur than either globulin or albumin, but much more phosphorus. In solution in weak alkalies it is lævo-rotatory on polarized light. Béchamp holds that it is a weak dibasic acid, forming two types of salts, and his view is confirmed by Söldner. This body is prepared by diluting milk about five times and adding acetic acid until the solution contains .1 per cent. The precipitate formed carries down the fat with it. This precipitate is well washed on a filter, dried by pressure, and dissolved in the least excess of ammonia. By this means the fat rises to the surface and the underlying solution can be syphoned off. It is again precipitated by acetic acid, washed, dried, and redissolved in ammonia. After three or four such precipitations the casein is rubbed up with alcohol in a mortar. The alcohol is poured off, and the residue treated in the same manner with ether. It is afterwards extracted with ether in a Soxhlet apparatus to remove the fat. The treat-

ment with alcohol and ether is repeated a number of times. It is finally dried at 100°C . If dried whilst containing water it forms a hard, horny mass.

Söldner showed that two lime compounds exist (CaO and 2CaO) to one molecule of casein ($\text{C}_{170}\text{H}_{268}\text{N}_{42}\text{SPO}_{51}$).

Lactalbumin.—This proteid coagulates at 70°C ., although the precipitation is never complete. Like other albumins, it is not precipitated by saturating its solutions with MgSO_4 . It is precipitated, like other albumins, by saturating its solution with Na_2SO_4 . Its rotatory power is $[\alpha]_D = -67.5^{\circ}$.

It can be prepared by saturating milk with MgSO_4 , filtering, and adding to the filtrate acetic acid until 25 per cent. of the solution is reached, when lactalbumin is precipitated. It is redissolved in water, again saturated with MgSO_4 , and reprecipitated with the same strength of acetic acid. This treatment is repeated three or four times. The solution of lactalbumin is next dialyzed to remove salts. Finally, when the salts have been got rid of, the solution is precipitated with alcohol and ether, and dried at a low temperature. The result is a tasteless white powder completely soluble in water.

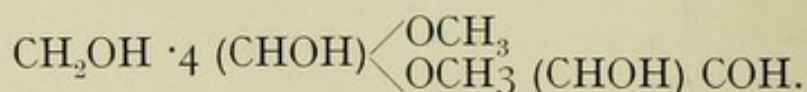
Lactoglobulin.—This proteid is not coagulated by rennet, but is coagulated by heat and neutral sulphates. It occurs in very small quantities in milk, and it is doubtful whether it is distinct from serum globulin.

Muco-proteid of Storch.—This body is insoluble in dilute ammonia and weak hydrochloric acid. It is partially soluble in the hydroxides of potassium and sodium, undergoing at the time of mixture considerable increase in bulk. It gives the characteristic proteid reactions with the xantho-proteic and Millon's tests. On gently heating with dilute sulphuric acid it yields a reducing sugar. When washed with alcohol and ether, and dried at the ordinary temperature of the atmosphere, it forms a light grayish powder which is very hygroscopic.

It may be prepared by centrifugalizing separated milk and washing the deposit with weak ammonia-water. The resulting mass is then well washed with alcohol and ether, and dried. Or it may be prepared from cream. Storch has, by means of benzene, alcohol, and ether, separated it from butter.

Milk contains traces of extractives and colouring matters. Its characteristic white appearance is held to be due to the interference with the passage of light rays by casein in pseudo-solution, a state in which particles exist in the solution not of sufficient size to settle under gravity, but which interfere with the passage of light. These particles can be separated by a current of electricity. There is no sharp line of division between crystalloids and colloids in solution, substances in pseudo-solution, and bodies in suspension. In milk, fat is in suspension, casein in pseudo-solution, albumin in solution as a colloid, and lactose in solution as a crystalloid. The variety in size of the particles, or masses of molecules, probably determines the presence of one or other of these states in a given case.

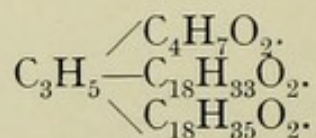
Lactose.—Lactose ($C_{12}H_{22}O_{11} \cdot H_2O$) is an aldose, and exhibits the constitution of a galactose-glucoside in that on hydrolysis by acids it produces a mixture of galactose and glucose. The aldehyde group of the galactose has been eliminated in lactose, whilst the glucose remains. Emil Fischer gives it the constitutional formula :



Several modifications of milk-sugar are known, distinguishable from each other chiefly by their action on polarized light. Lactose, like other aldoses and ketoses, reduces alkaline solutions of $CuSO_4$, forming cuprous oxide, the well-known Fehling's reaction. Each sugar effects a definite amount of reduction, and this affords an excellent method of distinguishing them. Lactose differs from other sugars in that its osazone forms an anhydride.

Fat of Milk.—The fat of milk consists of a mixture of ethereal salts of glycerol, and exists as small globules ranging in size from $\cdot 001$ millimetre to $\cdot 01$ millimetre.

It is highly probable that there are three separate acid radicles combined with each glycerol group, thus :



A compound of the acid radicles of butyrin, olein, and stearin with glyceryl.

Milk-fat has the following composition :

				Per Cent.
Butyrin	3.90
Caproin	3.45
Caprylin50
Caprin	1.85
Myristin	20.30
Laurin	7.50
Stearin	2.00
Palmitin	25.50
Olein	35.00

In addition to the above fats, traces of certain extractives, such as urea, lecithin, cholesterin, together with colouring matters, exist in the fat of milk.

The vexed question of the presence or absence of a definite membrane round the fat globule will not be discussed in this work. It may be stated in a word that Béchamp, from his studies of the appearances found on mixing ether with milk and of the behaviour of milk towards certain stains, has concluded that an endosmotic membrane exists; whilst Storch, by his observations, is led to believe that, instead of a definite membrane, a muco-proteid capsule encloses the fat globule, and insensibly shades off into the surrounding fluid.

The Ash.—Phosphates of calcium, magnesium, potassium, and sodium are found; also chlorides and sulphates of these metals, and salts of certain organic acids.

The P and S of the milk proteids produce phosphoric and sulphuric acids. Carbonic acid is formed by the combustion of organic carbon. The ash does not truly represent the inorganic constituents. It is computed that at least 8 per cent. of the phosphoric acid arises from the P of the casein. Bases predominate over acids in milk, and unite with proteids to form soluble proteid salts, and with citric acid to form citrates.

Composition of ash :

				Per Cent.
Lime	19.3
Phosphoric acid	28.3
Potash	27.7
Chlorine	13.9
Soda	6.7
Ferric oxide3

				Per Cent.
Magnesia	2.7
Carbonic acid	1.0
Sulphuric acid1

A probable composition for the salts as they exist in milk has been theoretically calculated :

				Per Cent.
NaCl	10.62
KCl	9.16
KH_2PO_4	12.77
K_2HPO_4	9.22
$\text{K}_3(\text{C}_6\text{H}_5\text{O}_7)$	5.47
MgHPO_4	3.71
$\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)$	4.05
CaHPO_4	7.42
$\text{Ca}_3(\text{PO}_4)_2$	8.90
$\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$	23.55
Lime combined with proteids	5.13

Human milk has the following composition :

				Per Cent.
Water	88.2
Fat	3.3
Casein	1.0
Albumin5
Lactose	6.8
Ash2

The fat globules are smaller than those of cow's milk, ranging from .009 to .0009 millimetre. Its composition varies much more than that of cow's milk. It contains small quantities of citric acid. It is almost always alkaline.

When milk is allowed to stand for a time a series of well-known changes succeed each other. The fat, the lightest portion, rises to the surface as cream. After a variable period, depending on the temperature, presence of certain micro-organisms, and other factors, the milk becomes acid and separates into solid curd and liquid whey. The principal agent in this reaction is the *B. lacticus*, which converts lactose into lactic acid. Other micro-organisms, such as the *B. butyricus*, *B. coli communis*, etc., are also capable of forming acid, and thereby curdling milk. Rennet is used artificially for bringing about the same change. The curd consists of precipitated proteids with entangled fat, and the whey of water,

lactose, and salts. The cream of ordinary milk forms about 10 per cent. by volume of the whole.

The variations in the composition of milk, even from the same animal, are due to a number of factors, such as the health of the animal, the age—young animals secrete less milk and a product of poorer quality—the time that has elapsed from the last milking, the stage of milking, the breed of the animal, the time that has elapsed since the previous parturition, the nature of the food eaten, etc.

There are, however, limits to these variations, and all good milks at all times fall within these limits. Fatty solids may range from 2 to 7 per cent., non-fatty solids from 8 to 11 per cent., ash from .6 to .9 per cent., cream from 2 to 25 per cent., specific gravity from 1,027 to 1,037.

But it is rare that the fatty solids fall below 3 per cent., and the non-fatty solids below 8.5 per cent., and these figures are insisted upon by law.

Comparative analyses of various milks are represented in the following table :

				Water.	Proteids.	Fat.	Lactose.	Ash.
Cow	87.2	3.5	3.7	4.7	.7
Human subject	88.2	1.5	3.3	6.8	.2
Goat	86.0	4.3	4.6	4.2	.7
Mare	89.8	1.8	1.1	6.9	.3
Ass	90.1	1.6	1.2	6.5	.4
Ewe	79.4	6.7	8.6	4.3	.9

In cattle-plague and foot-and-mouth disease marked changes occur in the milk of the animals affected. The quantity is diminished, the curd separates out quickly on heating, from a pale-blue whey, and blood and pus corpuscles are generally present. In tuberculosis the milk is not markedly affected, except in those rare cases in which the udder is extensively diseased.

The Analysis of Milk.

A chemical analysis is of service, from a public health point of view, in detecting the removal of fat, the addition of water, or both, and the presence of artificial colouring matters and preservatives. A bacteriological examination is often necessary in the investiga-

tion of milk-borne epidemics—such as enteric, diphtheria, etc.—and for the detection of tubercle bacilli.

For chemical analysis the milk must be fresh, as after standing for a time the lactose is transformed into lactic acid, and the non-fatty solids consequently diminished.

Reaction.—The reaction is mostly alkaline, sometimes amphoteric when litmus is used as an indicator. This is due to the presence of NaH_2PO_4 and Na_2HPO_4 , the first turning blue litmus red, and the second red litmus blue.

Estimation of Total Acidity—Lactic Acid.—Place 100 c.c. of the milk in a beaker, add 5 c.c. of a .1 per cent. phenolphthalein solution, and titrate with $\frac{N}{10}$ NaOH until a faint pink tint appears.

It will be found that generally 20 c.c. of $\frac{N}{10}$ NaOH is required ; each c.c. of the decinormal alkali represents 1 degree of acidity.

Freshly-drawn milk has a distinct acidity, so that it is probable that the total acidity is not wholly due to lactic acid. If litmus be used as indicator instead of phenolphthalein a smaller figure will be obtained, as the salts of milk and carbonic acid are not sensibly acid to litmus-paper ; for this reason litmus may be used in roughly determining the quantity of lactic acid. There is no good method for quantitatively estimating lactic acid. When milk is boiled its acidity is diminished.

Specific Gravity.—Specific gravity is the weight of unit volume, and may be determined in two ways : first, by finding the weight of a known volume, and second, by finding the volume of a known weight. The first method may be used by taking the weight of liquid which fills a vessel of known volume—example, specific-gravity bottle, or Sprengel's tube. This method may also be used by immersing a plummet of known volume in the liquid, and noting the loss of weight due to the displacement of the same volume of liquid—example, Westphal's balance. The second method is applied by immersing a float of known weight in the liquid, and noting the volume immersed, which will be equal to a volume of the liquid of the same weight as that of the float—example, hydrometers, of which the lactometer is a special form employed in testing milk.

In using the specific-gravity bottle, which is perhaps the most exact method, care should be taken that the bottle is clean. It is well to observe the ritual of subjecting the bottle to cleansing with

weak acid, alcohol, and ether on each occasion before use, and to weigh it direct from a desiccator. The bottle is first weighed. It is then filled with milk, the stopper is gently let in, and its hollow channel is filled to the top with the fluid. Any superfluous milk is carefully wiped away with a clean and dry duster, and the bottle is again deposited in the desiccator for a short period before weighing a second time. The temperature should remain constant and at 15° C. during the entire process.

The second weight minus the first is equal to the weight of the milk contained in the bottle. This weight divided by the weight of the same volume of distilled water at the same temperature is the specific gravity. Most specific-gravity bottles have the weight of distilled water which they contain at 15° C. marked on their surface, so that it is unnecessary to take this weight.

Taking the specific gravity of H_2O at 15° C. as 1,000, that of milk is about 1,032. It is obvious that the removal of fat, which is the lightest constituent of milk, raises the specific gravity, and its addition lowers it. The addition of water also lowers the specific gravity. So, therefore, a low specific gravity may mean either abundant fat or added water.

If the quantity of cream as measured in a cream-tube reading percentages be the normal 10 per cent. after standing twenty-four hours, and the specific gravity be found low, it is clear that water has been added.

The Westphal balance consists of a graduated swinging arm resting on a knife-edge, and a glass plummet suspended from a hook attached to one end of the arm. The other end of the arm is drawn out to a point, which, when the balance is adjusted and the plummet hangs in air, should rest exactly opposite a similar point on the frame. Three riders are used on the graduated arm: their weights are wholly empirical, and indicate hundreds, tens, and units respectively.

The milk or other fluid is poured into a glass cylinder; the arm is raised or lowered by means of a screw in the upright support until the plummet is just completely immersed, and the riders are so placed on various divisions of the scale that the points come to rest exactly opposite each other. Supposing that in the case of a milk the largest (as must be) is suspended from the hook carrying

the plummet, the tenth division of the scale, and the tens and units riders rest on the scale divisions 3 and 2 respectively, when the point of the swinging arm comes to rest at zero the specific gravity will be $100 \times 10 + 10 \times 3 + 1 \times 2 = 1,032$.

Lactometers, special forms of hydrometers, are less accurate in estimating specific gravities.

The specific gravity of milk varies between 1,013 and 1,039.

By removal of all the cream from a milk of specific gravity 1,032, the figure is raised to 1,036. On the other hand, by adding 4 per cent. fat to the same milk, the specific gravity is reduced to 1,028. The specific gravity test is not an absolute one, but a useful preliminary test. Like most substances, milk alters in specific gravity with change of temperature. It does not share, however, the peculiarity which water possesses of attaining its maximum specific gravity at 4° C. It decreases in specific gravity from freezing-point (-0.5° C.) upwards. Tables of corrections for temperature have been constructed when the determination is made at temperatures above or below 15° C.; but it will be sufficiently exact to add or subtract 1 degree of specific gravity for every 6 degrees of temperature registered above or below 15° C.

The Fat.—Of the many methods at present in use for the estimation of fat the following two are to be recommended, and the first is preferable to the second :

1. ADAMS'S PROCESS.—In this gravimetric method the solvent used for the extraction of fat is ether, convenient on account of its low boiling-point and heat of volatilization, its high solvent power for fat, and its miscibility with water.

When milk is dropped on blotting-paper it spreads out to a much greater degree than when placed on glass or in a dish, and Adams considered that extraction of the fat by ether would accordingly be much more complete. After passing through various stages of evolution, the process is now carried out somewhat as follows :

A strip of Schleicher and Schüll's fat-free paper is hung up by one end. The other end is held in the fingers so that the surface of the strip is as nearly as possible horizontal, and 5 c.c. of the sample of milk carefully measured in a pipette are distributed over the paper. The weight of this volume is determined by running into a convenient weighing vessel 5 c.c. of the same sample at the

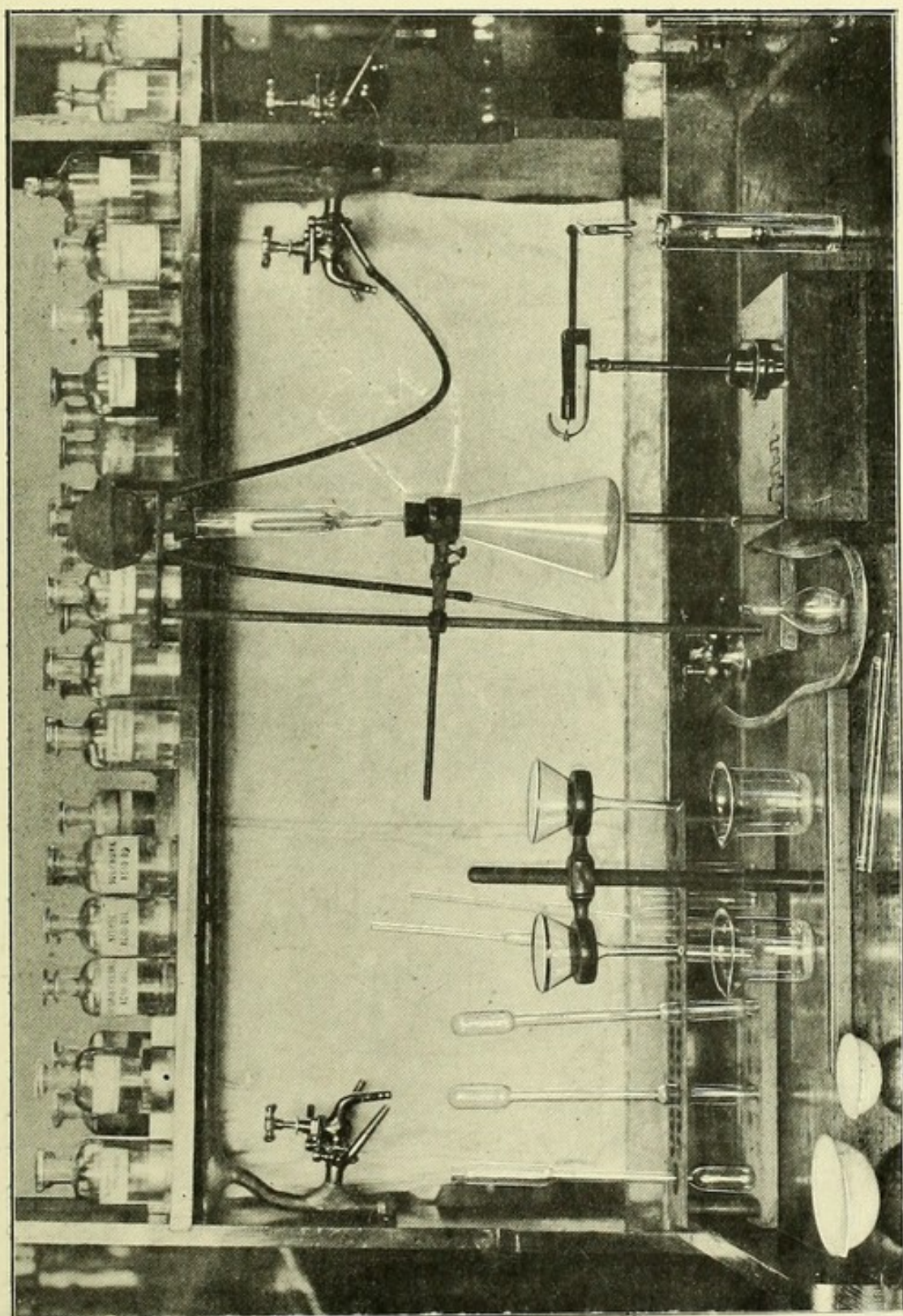
Westphal's
balance.Soxhlet apparatus with ball
condenser, for Adams's process.Filtering
apparatus.Stokes' tubes for
Schmidt's process.

FIG. 21.

same rate as it was run on to the paper. The paper is allowed to hang until dry, and must be protected from flies and all other disturbing influences. When dry, the paper is rolled up into a loose coil of a diameter such that it will easily pass into the Soxhlet extractor (say $\frac{3}{4}$ inch). A blank coil containing no milk should be dried and rolled up in the same way, and both further dried at 100° C. for an hour. Each coil is then placed in a Soxhlet extractor, arranged in an upright position, and connected with vertical condensers. Small weighed flasks, of 150 c.c. capacity, containing dry ether in sufficient quantity to fill the extractor well above the upper portion of the syphon, are attached to the lower end of the Soxhlet apparatus, and the ether is made to boil by immersing the flask in water at 55° to 60° C. Extraction should be continued for two to three hours, although many analysts are satisfied with twelve to eighteen syphonings.

The flasks containing ether and dissolved fat are then disconnected, the ether is driven off by evaporation, and the flasks dried and weighed.

The difference in weight represents the fat ; the small amount of extract derived from the paper of the blank experiment is finally subtracted from the weight of fat found for the sample, and the difference represents the fat contained in 5 c.c. The weight of 5 c.c. has been determined ; accordingly the percentage of fat is readily calculated.

Sour milk may be operated on if the acidity be neutralized by $\frac{N}{10}$ NaOH, using litmus as indicator.

It is advisable to put a small piece of blotting-paper in the mouth of the open tube at the top of the condenser so as to limit the entrance of moist air which would slightly wet the ether. In driving off the ether from a flask, it is well to lay the flask on its side in one of the openings of the water bath, and afterwards, when the drying is being completed in an air oven, the flask should be rotated from time to time, and air blown in every five minutes, to remove ether vapour.

Dry ether is prepared by washing commercial ether with water, shaking the washed ether with calcium chloride, and, after allowing it to stand over calcium chloride for a day or two, distilling. Sufficiently dry ether may also be obtained for most purposes by

distilling the commercial variety and rejecting the first fractions which pass over below 34.3°C ., and the last above 34.8°C .

If at any time doubt exists as to the completion of the extraction process, a second weighed flask containing fresh ether should be affixed, and the process continued for some time. This flask after evaporating the ether and drying at 100°C . should not increase in weight.

2. THE WERNER-SCHMIDT METHOD.—The specific gravity of the sample is ascertained. Fifteen c.c. are pipetted into a boiling-tube and a like measure of pure hydrochloric acid added. The mixture is shaken up and gently boiled until the contents appear dark

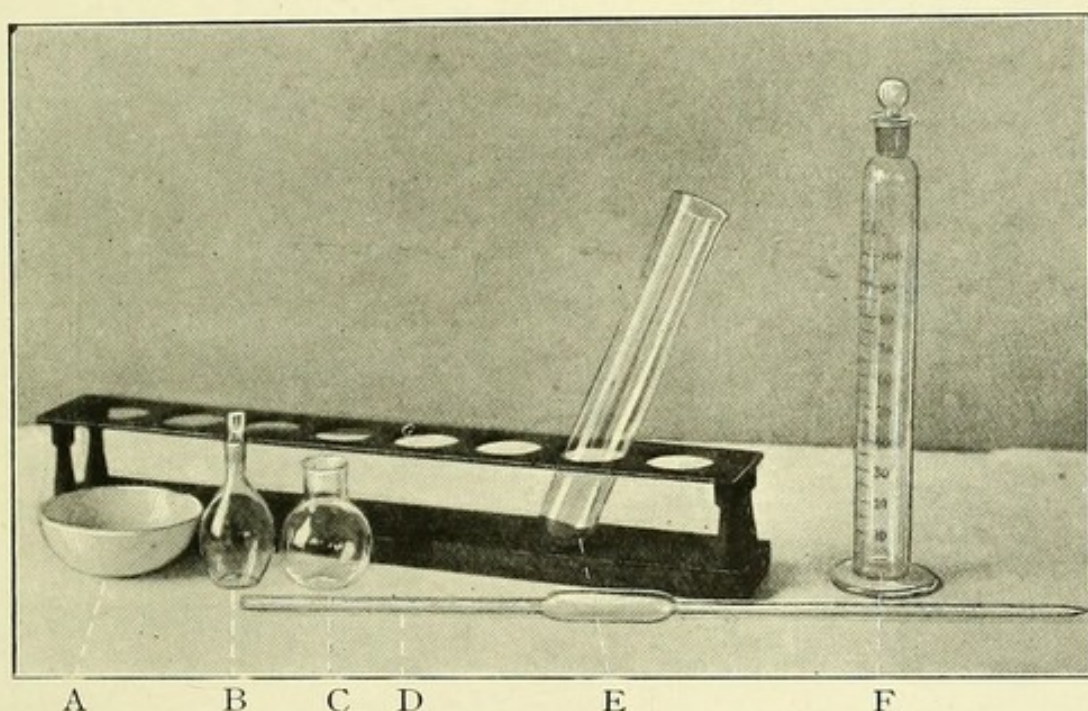


FIG. 22.

A, evaporating basin; B, specific-gravity bottle; C, fat flask; D, pipette; E, boiling-tube; F, 100 c.c. stoppered cylinder.

brown in colour. The boiling must not be continued too far, as certain bodies soluble in ether are liable to be formed from sugar. The process is not suitable for milks containing cane-sugar. Boiling with acid renders the casein soluble, and so eliminates the hindrance which, in the solid condition, it offers to the extraction of fat.

When cold, add some ether to the tube, and pour the whole into a graduated and stoppered 100 c.c. cylinder. Wash out the boiling-tube with more ether, and finally make the column in the cylinder up to 75 c.c. with ether. Invert the cylinder several times, and put aside to settle. Read the height of the ethereal column, including

three-fourths of the fluffy layer of casein. Draw off an aliquot part of this column and evaporate; dry, and weigh the residual fat in a small flask, in the manner described in Adams's process.

Stokes's tube, a specially graduated tube prepared to treat 10 c.c. of milk, is sometimes employed. After completing the boiling with 10 c.c. of HCl, and cooling, ether is added until the surface of the column reaches the 50 c.c. mark. An aliquot portion of this column is afterwards drawn off, evaporated, dried, and the residue weighed as above. The special tube is not to be recommended, as the narrowed central portion offers resistance to the free escape of hot air during boiling, and the consequent explosive action frequently causes loss of the contents.

The process is much more rapid than that of Adams, and in skilled hands almost as accurate.

The student will remember that, owing to the low boiling-point of ether, it should never be added to a hot solution, and will accordingly always cool the boiling-tube before adding ether to it. This may be rapidly done by holding it under a water-tap. In drying and weighing the fat it is essential that the last trace of ether vapour be got rid of by blowing dry air into the flask, and by ascertaining that two successive weighings, separated by half an hour's heating at 100° C., are the same.

Example.—A milk whose specific gravity is 1,032 is subjected to the Adams process, and the fat collected in a flask weighing 16.056 grammes. The weight of the flask and fat is 16.236 grammes. The weight of the fat is therefore .180 gramme.

5 c.c. of specific gravity 1,032 = 5.16 grammes.

If now 5.16 grammes of milk yield .18 gramme fat, what is the percentage of fat?

$5.16 : 100 :: .18 : \text{the percentage.}$

Percentage therefore = 3.5 nearly.

The same sample subjected to the Werner-Schmidt process yielded practically the same result.

15 c.c. of the milk yielded .542 gramme fat;

but 15 c.c. of specific gravity 1,032 = 15.48 grammes;

$15.48 : 100 : 1.542 : 3.5.$

The Leffmann-Beam process is a rapid one, but not nearly so accurate as the preceding two.

A centrifugal apparatus carries test-bottles of capacity about 30 c.c., and provided with an elongated graduated neck, each division of which represents 1 per cent. by weight of fat. To 15 c.c. of the milk placed in the bottle are added 3 c.c. of a mixture of equal parts of strong hydrochloric acid and amyl alcohol, and 9 c.c. of strong H_2SO_4 . The contents are now thoroughly mixed, and the neck is filled to the zero with 50 per cent. H_2SO_4 . If one sample only is tested, a second bottle filled with water is put on the other side of the horizontal arm in order to balance the apparatus. Four samples (two on each side) may be readily examined at the same time. Rapid rotation is maintained for two minutes, and the bottle is removed and set in a warm place for a short period. The percentage of fat in the neck is then read off.

Estimation of Cream.—This is one of the oldest methods of determining the amount of fat in milk. A cream-tube or creamometer provided with a short scale at its upper part, each division of which reads 1 per cent. of the capacity of the tube up to the highest line (zero), is filled to the zero with the milk to be tested, and set aside for six, twelve, or twenty-four hours, and the volume of cream measured. A good milk should throw up 10 per cent. of cream in eight hours. The method is by no means accurate, as the same milk under different conditions of setting may show very marked differences in the quantity of cream formed.

Total Solids.—Pipette into a clean, weighed, platinum dish 10 c.c. of the milk, and reweigh to obtain the weight of the milk used. Heat in a water bath, breaking up occasionally the film that forms on the surface, in order to hasten evaporation. After an hour's drying, the dish is removed to a tray, carrying two or three layers of blotting-paper to remove moisture, and the tray is placed in an air oven at a temperature of $95^{\circ} C.$, and provided with sufficient draught; here the drying is completed. It may require two to three hours in the oven to produce a constant weight. Platinum basins are preferable to porcelain, as they cool much more rapidly, and thus require less time in the desiccator. As milk solids are highly hygroscopic, no time must be lost in con-

veyance from the desiccator to the balance, nor in the process of weighing.

Supposing that the specific gravity of the milk is 1.032, the weight of 10 c.c. will be 10.32 grammes. Further supposing the difference in the first and second weighings of the dish to be 1.3 grammes, the percentage of total solids will be found from the proportion :

$$10.32 : 100 :: 1.3 : x ;$$

$$x = \frac{100 \times 1.3}{10.32} = 12.5.$$

The Ash is obtained by ignition at a low heat over an argand burner. The last trace of dark, separated carbon must disappear and the residue consist of a grayish-white mass before the dish is removed from the flame. Cooling, weighing, and percentage calculation are carried out as in the case of total solids.

Solids not Fat.—This item of the analysis is calculated by finding the difference in weight between the total solids and the fat. The solids not fat have been found to vary between 5 and 10 per cent. The law fixes 8.5 as the lower limit for whole milk, and 9 for skim-milk.

In case it is necessary to determine the percentage of proteids in milk, the best method is to employ the following modification of Kjeldahl's method for the estimation of total nitrogen, and multiply the result by 6.38. To obtain the total nitrogen, weigh 5 grammes of milk into a Jena flask of about 150 c.c. capacity, and add 20 c.c. pure H_2SO_4 . Place over a small flame in the fume-chamber, and heat till thoroughly charred. Remove the flame, and add 10 grammes bisulphate of potash and about a gramme of CuSO_4 . Place a pear-shaped bulb in the neck of the flask and apply the flame, increasing its size as frothing ceases. The liquid becomes colourless in thirty minutes or thereabout. Cool, dilute largely with water, and transfer to the copper distillation-flask provided with perforated cork carrying a dropping funnel with stopcock, and a wide tube with one or more bulbs blown in it, which are loosely packed with asbestos. One end of the tube is connected with a condenser, and the other is made to dip below the surface of 50 c.c. $\frac{\text{N}}{10} \text{H}_2\text{SO}_4$.

Through the dropping-funnel pass about 100 c.c. of a 20 per cent.

solution of NaOH and 10 c.c. of the alkaline tartrate solution used in estimating dextrose. Shake well by a rotatory motion. Apply a flame to the distilling-flask and collect about 200 c.c. of the distillate. Take care that the condenser remains throughout quite cold. Titrate with $\frac{N}{10}$ NaOH, using litmus as indicator. Subtract the number of c.c. $\frac{N}{10}$ NaOH solution used from the 50 c.c. sulphuric acid, and the remainder represents the acid neutralized by the ammonia distilled over. From this deduct the figure obtained in a blank experiment in which all the factors are exactly the same, except that milk is eliminated.

Each c.c. of the $\frac{N}{10}$ H_2SO_4 neutralized by ammonia is equal to .0014 gramme of N, which, when multiplied by 6.38, is equal to the total proteid.

Colostrum is a term applied to the first milk secreted after parturition. Houdet describes two forms—a viscous, brownish product, and a non-viscous lemon-yellow liquid; the earlier milkings furnish the first, and the later the second; the two co-exist often in the same animal. The fat differs somewhat from that of ordinary milk, in that its melting-point is high ($42^\circ C.$) and its Reichert-Wollny figure low (6 to 7). The most characteristic feature of colostrum is the presence of the *corps granuleux* of Donné, consisting of cells clustered together like bunches of grapes, and measuring in diameter from .005 to .025 millimetre. The specific gravity of colostrum averages 1.068.

Estimation of Citric Acid in Milk.—Prepare acid nitrate of mercury by dissolving mercury in twice its weight of HNO_3 (specific gravity 1.42), and adding an equal volume of water.

With this reagent precipitate the proteids of the milk, and filter until the filtrate is clear. To a measured volume of the filtrate add dilute caustic soda solution until the neutral point is reached (phenolphthalein to be used as indicator). Filter off the white precipitate of calcium phosphate, calcium citrate, and mercury; wash well with water; remove from the filter and suspend in water to which a little dilute HCl has been added. Pass H_2S through the fluid until all the mercury comes down as HgS . Filter again, and boil the filtrate to remove H_2S . Add a little calcium chloride and cool. Carefully neutralize a second time with dilute caustic soda, and filter off the calcium phosphate. Concentrate the

filtrate to small bulk. This contains the citric acid as calcium citrate. After thorough boiling, filtering, and washing the precipitate with boiling water, ignite it, and add to it excess $\frac{N}{10}$ HCl. Titrate back the excess with $\frac{N}{10}$ NaOH (methyl orange to be used as indicator). Each c.c. $\frac{N}{10}$ HCl used = .0064 gramme citric acid.

Action of Heat on Milk.—When heated to 70° C., the albumin of milk, although not precipitated, is so changed that it is readily precipitated by acids and $MgSO_4$. At 80° C. a further unknown change occurs in certain organic constituents, recognisable by the fact that they cease to evolve a gas from H_2O_2 , and to produce a blue colour with para-di-amido-benzene, and with H_2O_2 . At 100° C. calcium citrate is deposited, and a reduction in the rotatory power of milk-sugar takes place.

When milk is heated in contact with air a proteid film, probably an oxidation product, is formed on the surface, which has been variously classified.

It has been claimed that boiled milk is more easy of digestion than the raw secretion, and perhaps this is true. The much-discussed question of boiled milk producing symptoms of scurvy has not been settled; there is no reliable evidence from which a conclusion may be drawn.

An important product of milk in connection with the artificial feeding of infants is milk-sugar. Its estimation may be carried out as follows:

To 50 c.c. distilled water add 6 grammes of finely-powdered milk-sugar, and stir with a thermometer for ten seconds; allow to settle for twenty seconds, and read the fall in temperature. Filter, and fill a polariscope tube with the clear filtrate. Take readings every minute until the specific rotatory power begins to diminish. When the polarized solution is kept at a temperature of 15° C., several readings can be obtained which are nearly constant; the mean of these is the *initial* rotation. After twenty-four hours, polarize again at the same temperature to obtain the *normal* rotation. The $\frac{\text{initial rotation}}{\text{normal rotation}}$ is the 'birotation ratio.'

The amount of sugar may be estimated in 100 c.c. of the above solution by dividing the normal rotation reading in angular degrees by 1.106.

Genuine commercial milk-sugar crystallized from water gives :
Not more than .05 per cent. ash.

Solubility at 15° C. = 7.0 grammes per 100 c.c. (with an increase of .1 gramme per 100 c.c. for each degree of increase of temperature).

Fall of temperature, .5° C.

Birotation ratio, 1.6.

Amount of milk-sugar, 99.5 to 99.9 per cent.

Milk-sugars are adulterated with cane-sugar, maltose, dextrose, and various mineral matters. Cane-sugar can be detected by treating a solution with yeast at 55° C. for six hours. Milk-sugar is unchanged in specific rotatory power, whilst the addition of as little as 1 per cent. cane-sugar produces a marked change. Maltose is detected by a decrease in the birotation ratio ; dextrose by an increase in this ratio and a decrease in the fall of temperature.

Adulteration of Milk.—The principal adulterations are the addition of water and the abstraction of cream.

The estimation of the water added is made from the solids not fat, as these solids, in different samples, do not depart so far from the mean as the fat. The legal limit is 8.5 per cent.

Example.—A milk yields 3 per cent. of fat by one of the foregoing processes of estimation, and 11 per cent. of total solids. The solids not fat amount to $11 - 3 = 8$ per cent.

On the assumption, therefore, that 8.5 per cent. represents 100 per cent. pure milk, 8 per cent. will represent 94.1 per cent. pure milk.

$$(8.5 : 8 :: 100 : 94.1).$$

In other words, 5.9 per cent. of water has been added to this sample.

It may be urged that, since a few animals produce milk containing less than 3 per cent. of fat and less than 8.5 per cent. of solids not fat, it is unfair to the dairyman to enforce these figures as legal limits. But the number of animals in a herd producing milk below these standards is so small in proportion to the whole number, that the mixed milks should in all cases not only reach but surpass the standards.

Cane-sugar, starch, dextrin, and other bodies have been added

to mask the addition of water by raising the solids not fat ; these may be detected by the sweet taste, deficiency in total nitrogen, and by the ash. Starch is denoted by the blue colour formed with iodine. Common salt has been added, and is detected in the ash by increase of Cl. Chalk, carbonate and bicarbonate of soda, borax, fluorides, etc., may be found. Of these, borax and boracic acid are used as preservatives. The employment of preservatives—bodies such as boric acid, formalin, etc.—that prevent the growth of micro-organisms has been much discussed. Some hold that it is better to add these bodies than to allow the milk to decompose ; whilst others advocate the exclusion of all such reagents.

There does not appear to be any experimental evidence to show that small quantities of preservatives like boric acid and its compounds exert an injurious effect upon healthy adults, or even upon healthy children ; but in the case of weakly infants there is a strong feeling in favour of excluding all such bodies from their food. Salicylic acid holds a somewhat different position. In quantities necessary to prevent the growth of micro-organisms this drug is likely, in certain cases, to produce injurious effects. Besides, it inhibits the action of the digestive enzymes of the alimentary tract. Its use as a preservative has been rightly forbidden in France. Formalin, formal, or formol is a 40 per cent. solution of formaldehyde in water, and in the strength of 1 per cent. has been much used of late as a milk preservative. It produces a very decided change in casein, rendering it insoluble in the digestive juices. A patented process exists in Germany for converting casein, by the action of formalin, into a substance resembling celluloid. This preservative should be rigorously excluded from all foodstuffs. The question of the addition of preservatives to milk has another aspect. All purchasers of milk expect to get a thoroughly fresh article. Any procedure allowed the dairyman by which he can retain milk for a number of days puts a premium on the sale of a stale substance. Milk should be consumed on the day on which it is drawn from the animal. Its constitution is such that, apart from sterilization, which can only be legitimately performed by heat, it rapidly decomposes and becomes unfit for consumption. If dairy-men were compelled to keep their churns scrupulously clean, and the temperature of the milk during transit sufficiently low, there

would be no need for preservatives, and we should hear little of decomposed milk.

It is stated that a mixture of boric acid and borax is more efficacious in preserving milk than either alone, and that 35 grains of this mixture are required to preserve a gallon of milk.

Detection of Boric Acid or Borax.—*The Turmeric Test.*—Evaporate 100 c.c. of the milk, which has been made alkaline with caustic soda (.5 gramme), to dryness; incinerate. Take up a portion of the ash in water, and the remainder in weak HCl. Add to each portion a few drops of freshly-prepared turmeric solution, and evaporate to dryness. When boric acid or borax is present, the residue assumes a brownish-pink colour, which changes to dark-green on the addition of a solution of sodium bicarbonate. If the watery extract gives no reaction, whilst the acid extract reacts strongly, it may be concluded that borax is present; if the two reactions are of equal intensity, boric acid has been added; and if the reaction produced by the acid extract is stronger than that produced by the watery extract, it is probable that a mixture of the two is present.

Turmeric paper dipped in oxalic acid and dried is said by some to be a more delicate test than ordinary turmeric.

If the ash be moistened with dilute H_2SO_4 , methylated spirit added, and the mixture thoroughly stirred and set on fire, a green border will appear on the flame when boric acid is present.

Estimation of Boric Acid.—The following method is recommended by R. T. Thompson: To 100 c.c. milk add 2 grammes caustic soda and evaporate to dryness in a platinum dish. Char the residue thoroughly, and heat with 20 c.c. water. Add HCl drop by drop till all but carbon is dissolved. Transfer to a 100 c.c. flask, and add .5 gramme dry $CaCl_2$. Run in a few drops of phenolphthalein, and then a 10 per cent. solution of caustic soda till a permanent pink colour is perceptible, and finally 25 c.c. lime-water. The phosphoric acid is all precipitated as calcium phosphate. Make up to 100 c.c., mix, and filter through a dry filter. To 50 c.c. of the filtrate (representing 50 c.c. of the milk) add normal sulphuric acid till the pink colour is gone, then a few drops of methyl orange, and continue the addition of acid until the yellow is just changed to pink. Next add $\frac{N}{3}$ NaOH till the liquid

assumes a yellow tinge, avoiding excess of soda. All acids likely to be present at this stage exist as salts neutral to phenolphthalein, except boric acid, and a little carbonic acid, which latter is expelled by a few minutes' boiling. Cool the solution, add a little more phenolphthalein, and as much glycerine as will form 30 per cent. of the solution, and titrate with $\frac{N}{5}$ NaOH till a permanent pink is produced. Each c.c. of $\frac{N}{5}$ NaOH is equal to .0124 gramme crystallized boric acid (= .007 gramme boric anhydride).

Phosphoric acid can be separated from boric acid by precipitation as calcium phosphate, if not more than .2 per cent. of crystallized boric acid be present.

It is necessary not to carry the charring further than that required to produce a colourless solution, as excessive heating drives off boric acid.

Formalin.—*Detection.*—To 10 c.c. of milk add an equal volume of HCl (specific gravity 1.2), and a drop of dilute ferric chloride solution; heat the mixture, stirring vigorously the while, to just below the boiling-point. A violet colouration indicates the presence of formalin.

Hehner's Test.—To 10 c.c. of milk in a test-tube add 1 drop ferric chloride solution, and dilute the milk to about 30 c.c. To a portion of this in another test-tube add concentrated H_2SO_4 , by cautiously pouring it down the side of the tube so as to form a layer at the bottom of the milk. A violet blue ring will be formed at the junction of the liquids.

A few c.c. of the milk may be curdled by dilute sulphuric acid, and a little Schiff's reagent added to the filtrate in a test-tube, which is corked and allowed to stand. In a short time a violet-pink colour is produced in the presence of an aldehyde. Schiff's reagent is a solution of rosanilin carefully bleached with sulphurous acid, avoiding excess of the acid.

Estimation of Formalin.—An approximate estimation, which must be made early, as the aldehyde rapidly disappears, may be carried out by the following method: Reagents required: a normal solution of H_2SO_4 , a few 100 c.c. bottles, with close-fitting rubber stoppers, and a boiler, in which they may be immersed to the neck, a solution of methyl orange, and an approximately normal solution of ammonia. Place in each bottle 25 c.c. of the ammonia solution,

and to half of them add a sample containing .5 gramme formaldehyde. Stopper tightly, place the bottles in the boiler, fill with water to the neck, and boil for one hour. Cool slowly, and titrate with the sulphuric acid, using methyl orange as indicator. The differences in the readings of the blanks and the samples represent the ammonia consumed in normal c.c. Each c.c. = .0601 gramme formaldehyde. Any acid that may be present must be accounted for.

A more accurate but lengthier method is that described in "The Detection and Estimation of Preservatives in Milk," by Meredith Wynter Blyth, *Analyst*, xxvi., 503.

Salicylic Acid.—Precipitate the proteids from 50 to 100 c.c. of milk by the addition of mercuric nitrate, and filter. Shake up the filtrate with half its volume of a mixture of equal parts ether and petroleum ether, and stand aside until the ether separates out. Pipette off the ether, and evaporate to dryness in a clean flask. Dissolve the residue in a few drops of hot water, and add to a portion of the solution a drop of a 1 per cent. ferric chloride solution; in the presence of salicylic acid a violet or purple colour is produced. Add to a second portion of the solution a little bromine water: salicylic acid produces a curdy, yellowish precipitate. Evaporate the third portion of the solution to dryness with strong HNO_3 , and take up the residue in a few drops of water. If salicylic acid be present, a yellow colouration is produced on adding ammonia.

It should be borne in mind that carbolic acid and other hydroxy-benzene derivatives act in a somewhat similar manner to salicylic acid.

A further test consists in evaporating a part of the ethereal extract to dryness, placing a minute portion of the residue in the subliming cell, and comparing the crystalline sublimate with one obtained from pure salicylic acid. The melting-point of pure salicylic acid is 155° to 156°C .

Benzoic acid is but very occasionally found in milk. It is detected as follows: Render alkaline with baryta-water 200 c.c. milk, and evaporate down to one-fourth. Mix the residue with CaSO_4 to form a paste, and dry on the water bath. Powder, moisten with dilute H_2SO_4 , and extract with cold 50 per cent.

alcohol. Neutralize the alcoholic extract with baryta-water, evaporate to small volume, acidulate with dilute H_2SO_4 , and extract with ether. On evaporating the ether, any benzoic acid will be found sufficiently pure for testing. Make a watery solution of the benzoic acid, and add a little sodium acetate; now add a drop or two of ferric chloride to obtain a reddish-yellow colour.

Skimmed and separated milk must contain 9 per cent. of total solids. Most samples of separated milk contain less than .2 per cent. of fat.

Condensed milk contains, as a rule, a large percentage of sugar, as much in some cases as 40 per cent. Condensed whole milk ought to contain 10 per cent. fat, 25 per cent. solids not fat, and 2 per cent. of ash.

Harmless colouring matters are added to milk to give it a rich yellow colour. Amongst these are annato, turmeric, saffron, and yellow coal-tar dyes.

Annato, obtained from the seed of *Bixa orellana*, is largely used as a colouring agent. Like saffron and turmeric, it is readily soluble in alcohol, but not in water. If the solution be evaporated down to dryness, and a drop of strong H_2SO_4 be placed on the residue, a dark blue colour is produced, changing to green in the presence of annato and saffron. In the case of saffron, a final reddish brown is produced. Turmeric produces a violet-red, turning brown on the addition of an alkali.

Milk reduced to a powder by drying at a temperature of 240°F. , or over, is sterile, of pleasant odour, contains the whole of the original proteids in a thoroughly digestible form, and most of the fat. This is the best form in which to preserve milk, as it keeps indefinitely. By mixing the powder in proportional quantities with water—say 1 part to 8.5 parts—a solution resembling the original milk is produced, on the surface of which swims the fat, in a free and more easily-digestible form than cream. A little care is necessary in the manipulation. A thin paste is made in warm water, and when thoroughly rubbed up, cold water is slowly added, whilst the mixture is vigorously stirred.

Bacteria of Milk.

Owing to its excellent nutrient properties, milk develops micro-organisms in the greatest abundance. One c.c. may contain from one to twenty millions, or thirty millions in the case of cream.

Two methods are employed to free milk from infective organisms—pasteurization and sterilization.

Pasteurization consists in heating to 68° C. for half an hour. There seems to be doubt in the minds of some bacteriologists as to the exact temperature necessary to destroy tubercle bacilli, but most are agreed that 68° C. is sufficiently high for this purpose. Spores are not killed at this temperature, and sterilization, which consists in heating to boiling-point for five or six hours at ordinary pressure, or for a shorter period in steam under pressure, is the safer course, as all bacteria and their spores are destroyed. The deterioration of milk from the nutritive aspect produced by boiling exists, perhaps, more in imagination than in reality.

Various bacteria set up fermentation in milk-sugar, resulting in the production of lactic acid, butyric acid, alcohol, etc.

Some act specially on proteids, producing acid and precipitation of casein; others precipitate and digest casein without production of acid; whilst a few digest the proteids without precipitation of casein.

Certain saprophytes exert no particular action on milk, and others produce pigments.

The organisms which produce lactic acid from lactose, thereby souring milk, form a large class. Their *optimum* temperature is about 35° C., and they are easily destroyed by heat.

Many micro-organisms cause butyric fermentation without the primary development of acidity; the precipitated casein is re-dissolved, a bitter taste is produced, and butyric acid formed. Where lactic acid is previously formed, this fermentation does not readily take place. Many of the organisms producing butyric acid—*e.g.*, *B. subtilis*, potato bacillus, etc.—curdle milk without acidity, and redissolve the curd.

Alcoholic fermentation is produced in small quantities by a great variety of organisms, but a few species of saccharomyces convert most of the lactose into alcohol. Ordinary yeasts, *Saccharomyces cerevisiæ*, do not ferment milk-sugar.

Various moulds are found in sour milk. White mould (*Oidium lactis*), by its hyphæ and mycelium, forms a thick covering on the surface. Green mould (*Penicillium glaucum*) is found in sour milk, and forms the green colour of Gorgonzola cheese.

Blue milk is caused by the growth of *B. cyanogenus* in milk containing lactic acid. Yellow milk is produced by the *B. synxanthus*, an organism which precipitates the casein and redissolves it to form a yellow liquid. There are probably several organisms of this class all possessing proteolytic functions.

Red milk is occasionally found, and may be due to the *B. prodigiosus*. A pink colour is produced by *Micrococcus rosaceus* and *Sarcina rosea*.

Pathogenic Organisms.—*B. tuberculosis*.—If a cow suffer from tuberculosis of the udder, the bacillus will pass into the milk. Unless the disease affects the udder, no bacilli are found in the milk. It has been stated that in Berlin and Copenhagen, where cows are examined by veterinary experts, 16 per cent. of the cattle are found to suffer from the disease.

Typhoid, cholera, scarlet fever, and diphtheria have all been shown to be conveyed by milk. There are two ways by which the infection in each case is introduced: first, through the presence of the disease in those handling the milk, and their families; and, second, through the presence of organisms in the water used to wash utensils or adulterate the milk.

The enumeration of the number of organisms in milk is of importance in affording information concerning the amount of contamination to which the milk has been subjected. Under clean conditions, milk after it has been drawn from the cow should not yield in cold weather much more than 20,000 organisms per c.c., or in hot weather 30,000. If kept at a temperature below 10° C., these figures will not increase to much more than double in twenty-four hours. But the conditions of collection and distribution are not generally such as to produce these results, hence the number of organisms per c.c. in milk may reach millions.

In determining the total number of bacteria, the addition of preservatives must be taken note of. The milk should be collected in sterile bottles, and if the examination cannot be commenced at once, packed in ice.

Gelatin and agar plates are used, as in the bacteriological examination of water, the only difference in procedure being the employment of weaker dilutions of milk, owing to the great rapidity with which organisms multiply in the latter. The dilutions may be made to 1 milk in 1,000 sterile distilled water, 1 in 10,000, and 1 in 100,000.

For the detection of tubercle and diphtheria (which rarely occurs in milk), the inoculation of animals is necessary. Morphological examination in both cases is insufficient, by reason of the various pseudo forms which exist.

The search for *B. typhosus* in milk is about as unsatisfactory as in water.

By heating 10 c.c. of milk in a test-tube to 80° C. for ten minutes, and afterwards incubating anaerobically, the characteristic appearances of *B. enteritidis sporogenes* may be directly obtained, when this organism is present.

The detection of streptococci and staphylococci is of importance as indicating suppuration of the udder, in which case there will also be a large increase of leucocytes and the presence of pus cells.

The detection of *B. coli communis* in milk is effected by methods similar to those described under water.

CHAPTER XIX

BUTTER

BUTTER is produced from milk or cream by churning. The agitation causes the fat globules to coalesce to form granules of a fine spongy nature. When butter is collected and worked it assumes a more homogeneous appearance.

The mean composition of butter made from ripened cream according to Storch is :

				Per Cent.
Fat	82.97
Water	13.78
Proteids84
Milk-sugar39
Ash16
Salt	1.86

The composition of different butters varies considerably in the constituents.

If butter be churned at a higher temperature than 13° to 18° C., according to the season, rapidity of churning, etc., it will contain more water than at medium temperatures. Very low temperatures and rapid churning produce an article containing too much water.

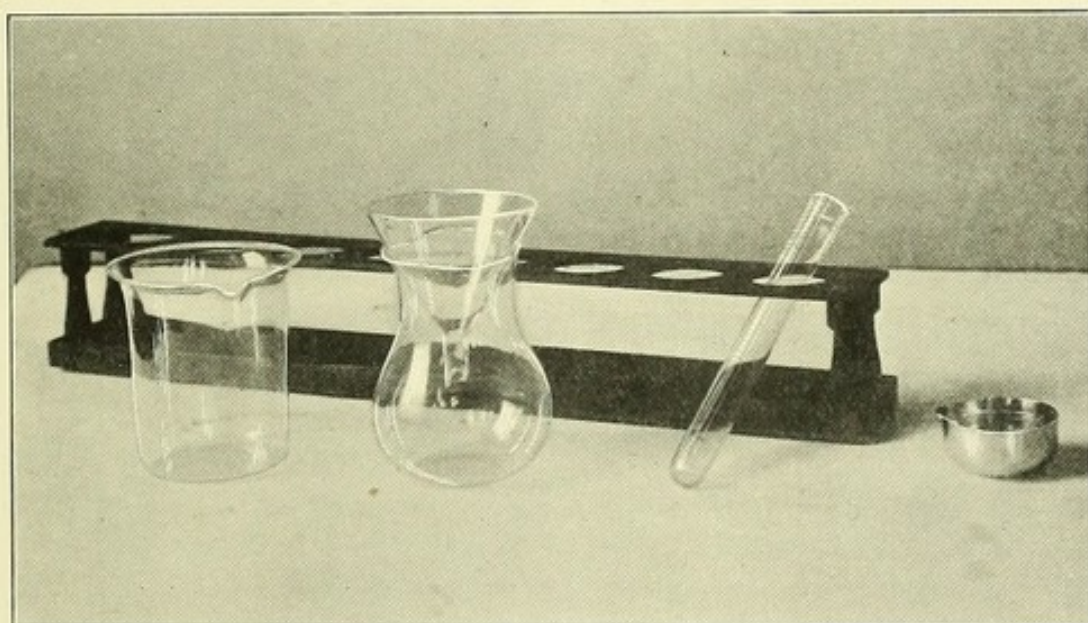
Butter is adulterated with various foreign fats, animal and vegetable, under the name of margarine, which, as a rule, are very little inferior in nutritive qualities to the fat of milk. In the production of margarine, animal and vegetable fats are melted, filtered through coarse filters, and worked up with milk, to look and smell very like pure butter.

It is stated that margarine, as prepared for the market, is not quite so digestible as butter. Whether or not this be true, it is illegal to substitute margarine for butter, and the principal object

of a butter analysis is to determine the presence or absence of foreign fats.

The odour and taste of butter are characteristic, and excellent tests of its purity. By heating it to 25° C. any unpleasant taste that it may possess becomes more apparent.

Adulteration.—Foreign fats are the chief item of adulteration. Colouring matters, especially annato, are frequently employed. Water is sometimes worked into butter for the purpose of increasing its weight; but, as the addition of water renders butter liable to decomposition, it is only possible to escape detection in cases where



Beaker for melting
crude butter.

Bottle beaker with funnel
for filtering butter-fat.

Graduated test-tube
for Valenta test.

Platinum
basin.

FIG. 23.

the butter is rapidly disposed of. The addition of pepsin, rennet, etc., to milk before churning aims at increasing the yield of butter by securing an increase of contained water.

The Estimation of Water.—At present butter is allowed to contain 16 per cent. of water. The following two methods readily determine the amount of water; the second is the more accurate.

1. Weigh out 10 grammes of butter into a small platinum or porcelain basin provided with a piece of glass rod which acts as a stirrer. Heat on a sand bath or over a small flame, and carefully stir until all frothing ceases. It is necessary to regulate the temperature so that the curd is not appreciably browned during the heating, and

that there is no loss by spirting. The basin with its contents is cooled in a desiccator and weighed. The loss of weight represents the water in 10 grammes.

2. Fill a small platinum or porcelain basin with pieces of pumice that have been recently washed and ignited. Select portions of butter from three different regions of the sample (water is not always equally distributed throughout the mass of butter), and place them in a clean, wide-mouthed, stoppered bottle. Melt at as low a temperature as possible, and shake vigorously until the mass is solid. Place 5 grammes of this mass in the porcelain basin, and heat in a drying-oven with good draught at 100° C. for an hour. Cool and weigh. Replace in the oven for a further half-hour, and again cool and weigh. Repeat the heating and weighing until a constant weight is obtained. The difference between the lowest weighing and that of the original butter is taken as water.

The following table represents the variations of water in Danish butters :

Percentage of Water.					Number of Samples.	
					Summer.	Winter.
9	to	10	1	1
10	„	11	16	8
11	„	12	136	20
12	„	13	335	138
13	„	14	534	431
14	„	15	512	562
15	„	16	287	447
16	„	17	124	205
17	„	18	39	95
18	„	19	13	20
Above 19		4	3
Average		14.03 per cent.	14.41 per cent.	

Butters containing 13.5 per cent. of water are said to have the best flavour.

Estimation of Curd and Salt.—The residue from the determination of water is taken and melted at a low temperature. Ether is added, and the whole well stirred and set in a warm place until the ether is quite clear, when the fluid is decanted into a small weighed flask. Fresh ether is poured on the residue, and when clear poured off. This treatment, repeated three or four times, removes the whole of the fat. A little practice and ordinary care

will prevent any of the non-fatty solids being poured away with the solvent. The residue is dried in the hot-air oven to constant weight, and represents salt and solids not fat.

The Salt.—To estimate the salt, the residue from the last determination is treated with hot water and filtered. The filter with its contents is well washed, and the filtrate, when cold, is titrated with standard nitrate of silver, using a 5 per cent. solution of neutral potassium chromate as indicator. The amount of sodium chloride is easily calculated. The silver nitrate should be standardized on pure sodium chloride.

The Fat.—This item is best estimated by subtracting the combined weights of water, salt, and solids not fat from 100. As a control the ether may be evaporated, and the fat residue weighed.

Curd.—The estimation of the proteids is best effected by carrying out Kjeldahl's process for the estimation of total N on the residue left after estimating the fat, and multiplying the N by 6.38.

Preservatives.—Besides salt, several substances are used as preservatives, such as boric acid, borax, formalin, salicylates, sulphites, and nitrates. These are all estimated in the watery fluid which separates out underneath the fat on heating the butter.

The estimation of boric acid is best carried out by Thompson's method described in the chapter on milk (p. 145), using the watery solution. The titration may be performed on this solution without any treatment, as butter is free from phosphates.

Formalin cannot be estimated with any degree of exactitude, as it enters into combination with the proteids, so that the uncombined formalin alone reacts, and this gives no information as to the amount originally added.

Nitrates may be estimated by the copper-zinc couple method, or Crum's method as described under water.

Sulphites.—A portion of the watery liquid is distilled with dilute HCl, and the gas evolved is passed into $\frac{N}{10}$ I solution, which in turn is titrated with sodium thiosulphate. Sixty-four parts of SO_2 are converted into sulphuric acid by 254 parts of I. Or the SO_2 gas may be passed into bromine water, and the H_2SO_4 formed, estimated as BaSO_4 . Sixty-four parts SO_2 represent 233.5 parts BaSO_4 .

Butter Fat: Preparation of Fat for Analysis.—A portion of the sample of butter is placed in a beaker and heated at a temperature of 45° to 48° C. in an air-oven. In a little time three layers separate out in the beaker. The largest, the butter-fat, containing a few particles of curd in suspension and a few drops of water underneath the surface film, on the top; a grayish-white layer, the curd, near the bottom; and underneath a small quantity of water. If the sample be genuine butter the melted fat is quite transparent, whereas if mixed with margarine, melted, and re-emulsified, churned at a high temperature, or rancid, it is generally turbid.

The fat is poured on a dry filter kept at a temperature above the melting-point of butter, and is now free from the other constituents, except about .1 per cent. of water, and a trace of lactic acid. These manipulations are readily carried out by placing the beaker containing the melted butter, and a second beaker (carrying a funnel and filter-paper) in which the fat is received, on the top of an air-oven whose inner temperature approaches but does not exceed 50° C. After filtration the fat is rapidly cooled so as to prevent partial solidification, and to obtain a homogeneous mass.

Butter-fat contains considerable quantities of the glycerides of the fatty-acid series $C_nH_{2n+1}COOH$, of low molecular weight. The lowest and most important is butyric acid. Acids of the oleic series are also present.

The various foreign fats which are admixed with butter, such as beef and mutton fats, lard, cotton-seed oil, and other vegetable oils, present several important physical and chemical differences.

The Melting - point.—A little of the fat as prepared above is taken on a platinum wire and placed in a beaker of cold water near to the bulb of a thermometer. This beaker with its contents is placed in a larger beaker of water, which is slowly heated. The temperature at which the particle of butter becomes translucent is the melting-point. Butter fat melts at about 33° C. Foreign fats have different melting-points, some of which lie very near to that of butter-fat, so that this test is of little practical value in distinguishing pure butter from margarine. Artificial butters are made to melt at the same temperature as butter.

The Refractive Index: Oleo - Refractometry.—The oleo-refractometer measures the refraction which a ray of light undergoes in passing through a layer of butter. It is found more convenient to read the angle of total reflection. The butter-fat to be tested is poured warm into the prism of the instrument, and the deviation noted at a temperature of 45° C. Pure butter gives a deviation of about 30° to the left. Certain forms of margarine give deviations much less— 15° and 20° —whilst cocoa-nut oil gives over 55° .

The butyro-refractometer of Zeiss is a modification of the Abbé refractometer, and gives rapid readings in scale divisions which by reference to a table can be read off as refractive indices.

Density of Butter - fat.—On account of the glycerides of low molecular weight which it contains, butter-fat has a greater density than the fats used to adulterate it. As it is more convenient to take the specific gravity of a fluid than a solid, and as Skalweit found that at, or around, the temperature 38° C. there is the greatest difference between the specific gravities of butter and foreign fats, this temperature is usually adopted for the taking of specific gravities.

Fill the pycnometer with water at 38° C. and weigh it. Remove the water and dry the flask in an air-oven through which a good current of air passes. Now fill it with fat, and place it in water at 38° C. till the volume is constant. Weigh again rapidly, and the weight of the fat divided by the weight of water gives the specific gravity at 38° C. The limits of specific gravity for pure butter-fat at 38° C. are $\cdot 914$ and $\cdot 909$. The fats usually added as adulterants have a mean specific gravity of $\cdot 903$.

The density may also be determined by a hydrometer or by Westphal's balance at 38° C.

Microscopic Examination.—When examined microscopically, butter-fat presents a collection of small round refractile globules, together with a few larger globules, fairly uniform in size, and in the number present in a single field. Margarine presents a mass of small globules much less distinct in outline and more crowded together. The larger globules occur in relatively greater numbers, and present much more diversity in size.

Examination under Polarized Light.—A small particle of butter is placed on a clean microscopic slide, and a cover-glass affixed. The slide is placed on the stage of a microscope provided with crossed nicols, and examined with a course objective. In order to shut out light from the upper surface a short black tube is laid on the slide in such a manner that the objective dips into it. When pure butter-fat, which is non-crystalline, is examined, it presents a uniformly dark field. On the other hand, when margarine is examined, certain portions of the field are bright, and crystalline masses are dimly perceived. These may be critically studied by uncrossing the nicols.

Iodine and Bromine Absorption.—Von Hübl's method: Oleic, linolic, and linolenic acids contain unsaturated bonds, and consequently unite under certain conditions with iodine and bromine. The following solutions are required: 25 grammes of iodine dissolved in $\frac{1}{2}$ litre of 95 per cent. alcohol; 30 grammes HgCl_2 dissolved in the same volume of the above alcohol; filter. A decinormal thiosulphate solution is prepared by dissolving 25 grammes of pure sodium thiosulphate and 1 gramme of salicylic acid in a litre of water. Stand aside for a few days and filter. The solution is then standardized against a known weight of I dissolved in potassium iodide. Equal volumes of the iodine and mercuric chloride solutions are mixed a day or two before use.

Weigh out $\frac{1}{2}$ gramme of fat in a 100 c.c. flask; add 10 c.c. chloroform and 20 c.c. of the mixed iodine and mercuric chloride solutions, and mix thoroughly. Prepare a blank experiment by putting in a similar flask 10 c.c. of CHCl_3 and 20 c.c. of the mixed iodine and corrosive sublimate solutions, and stand all the flasks aside in darkness for three hours.

At the end of this time add to each flask 10 c.c. of potassium iodide solution, and transfer to a stoppered bottle, washing out the last trace of the contents. Run into this bottle standard thiosulphate solution with continuous shaking until the iodine has almost disappeared. Finish the reaction by the aid of a little starch paste. The same procedure is carried out in the control. The volume of thiosulphate used for the sample subtracted from that used for the blank experiment corresponds with the iodine

absorbed. This, multiplied by the strength of the solution, will give the weight of the iodine :

$$\frac{\text{weight of I} \times 100}{\text{weight of fat}} = \text{percentage of iodine absorbed.}$$

Bromine dissolved in chloroform may be used instead of iodine and mercuric chloride solutions, and the titration may be performed at once.

Valenta's Test.—Valenta demonstrated the fact that there is a considerable difference in the temperatures at which various fats dissolve without turbidity in acetic acid.

Weigh out 2.75 grammes of butter-fat into a test-tube ; add 3 c.c. 99.5 per cent. acetic acid ; insert a thermometer, and gently heat with vigorous shaking until the mixture becomes transparent. Now cool down gradually, stirring with the thermometer until the first trace of opacity makes its appearance, generally as a fine tail in the fluid at the extremity of the thermometer's bulb. This is the required temperature. The glycerides of the saturated fatty acids are deposited as the acetic acid cools. The temperature corresponding with pure butter-fats runs from 29° C. to 39° C., and that for margarine falls between 94° C. and 97° C. A standard sample of butter may be tested against a weaker acid giving a temperature of turbidity of, say, 60° C. Margarine then gives 100° C. or over. This is a very good preliminary test for the differentiation of pure butters from margarine.

Reichert-Wollny Process.—The history of the development of the Reichert process, and the modifications introduced by Meissl, Hansenn, Kreiss, and many others, form an interesting chapter in the chemistry of butter. Wollny published an able paper on the errors of Meissl's modification, and his process, known as the Reichert-Wollny process, is almost universally accepted at the present time.

The whole of the volatile acids (butyric acid, etc.), contained in butter are not recovered by this method, but a fairly constant fraction, and the constancy of this fraction when the same sample is distilled under standard conditions constitutes the real value of the method.

Into a round Jena flask of 300 c.c. capacity are placed 5 grammes

butter-fat, together with 2 c.c. of a 50 per cent. NaOH solution and 10 c.c. 96 per cent. alcohol. The flask is heated for thirty minutes on a water bath under a reflux condenser. Between the condenser and the flask is inserted a T-piece which is closed, the limb being turned upwards. At the expiration of thirty minutes the limb of the T-piece is opened and turned downwards, while the alcohol is distilled off during fifteen minutes. The use of the

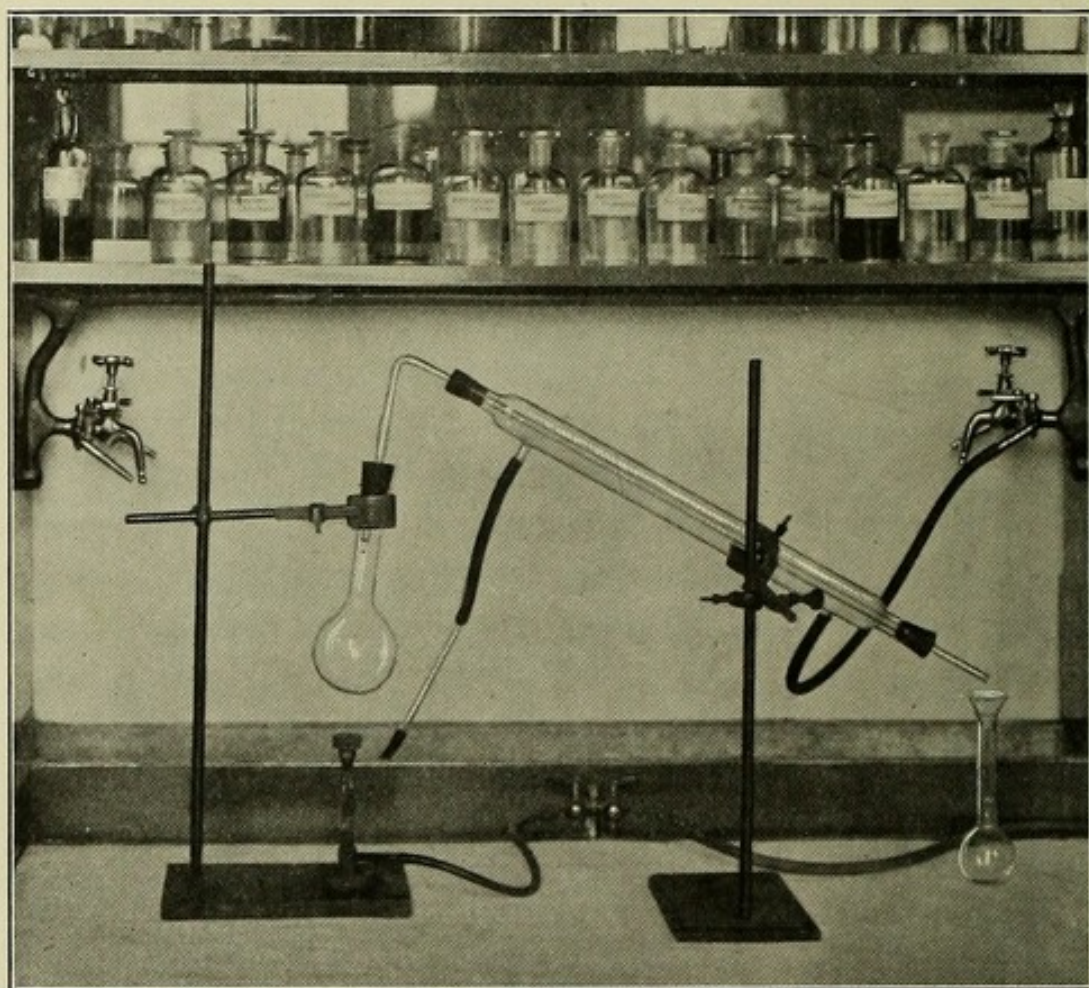
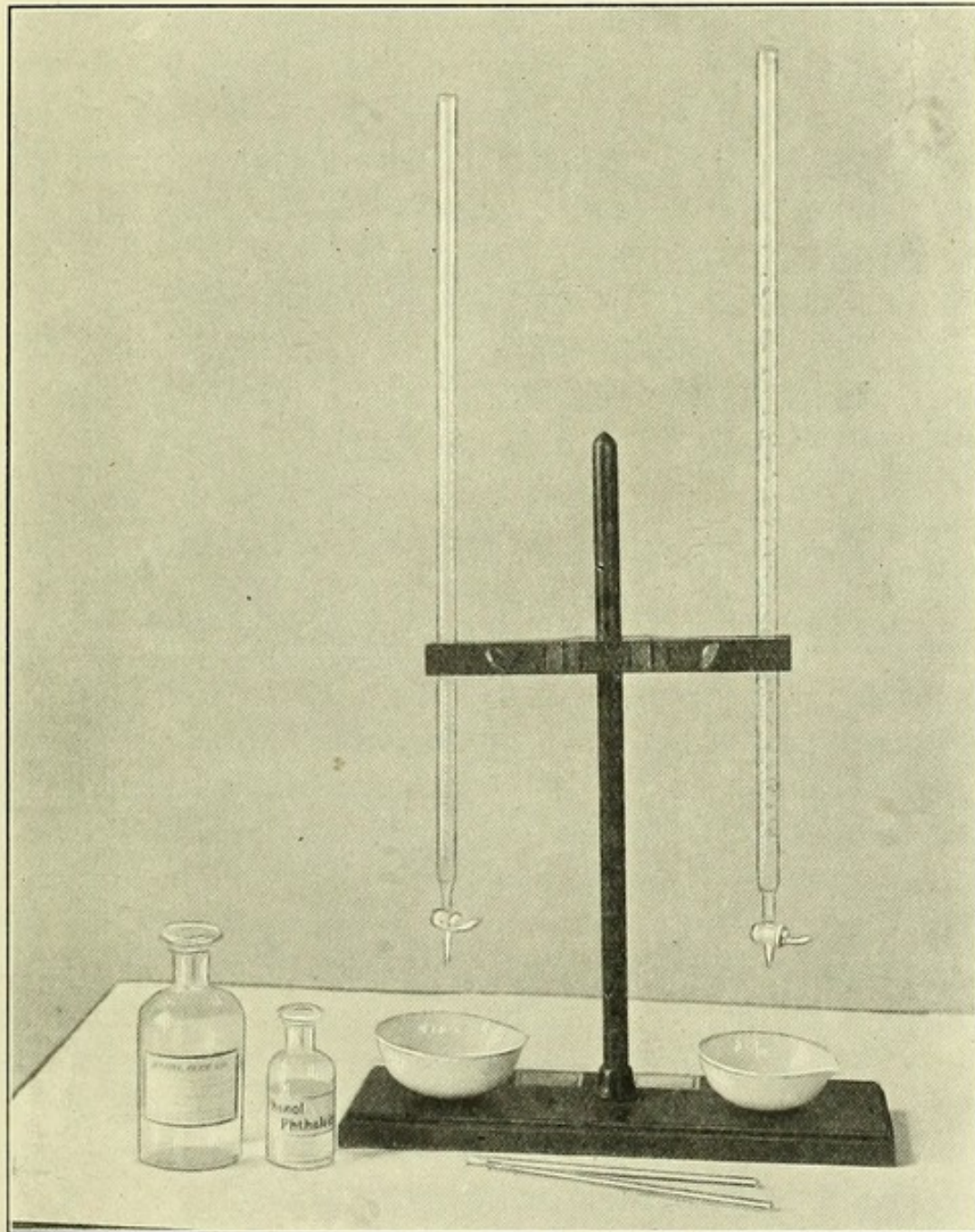


FIG. 24.—REICHERT-WOLLNY DISTILLATE BEING COLLECTED THROUGH FILTER-PAPER.

T-piece prevents the exposure of the contents of the flask to the CO_2 of the air. One hundred c.c. of hot distilled water are added through the T-piece, and the whole gently heated on the water bath with occasional shaking until the soap is completely dissolved. The solution is allowed to cool to 50°C. , and 40 c.c. of dilute sulphuric acid (25 c.c. to a litre) and two pieces of pumice are added. The flask is connected with a condenser by a specially

curved tube carrying a bulb, or by a simple tube, as in Fig. 24, and gently heated until all the fatty acids are melted. The flame is then turned up and 110 c.c. distilled over in thirty



Decinormal soda. Phenolphthalein. Burettes, etc.

FIG. 25.

minutes. The distillate is well mixed, and 100 c.c. filtered through a dry filter. One c.c. of a .05 per cent. phenolphthalein solution in 50 per cent. alcohol is added, and the solution titrated with $\frac{N}{10}$ baryta solution. To the result obtained one-tenth is added,

and the figure found by a blank experiment with the alcoholic soda solution made at the same time and under similar conditions is deducted; this latter should not exceed .3 c.c. of the $\frac{N}{10}$ baryta. The number obtained is known as the 'Reichert-Wollny number.' Five grammes of pure butter-fat give a figure ranging from 24 to 34, but not less than 24. Margarine gives 1 or 2, but never more than 3. In order to prevent fraud, not more than 10 per cent. of butter-fat is permitted in margarines, which will produce a Reichert-Wollny number of 4.

Example.—In a mixture of margarine and butter-fat the Reichert-Wollny figure is 16; find the percentage of butter-fat.

Taking 3 as the highest possible figure for margarines, and 24 as the lowest for butter-fats, 21 (24 - 3) will represent 100 per cent. of pure butter-fat.

$$21 : 16 - 3 :: 100 : x.$$

$$x = \frac{13 \times 100}{21} = 62 \text{ nearly.}$$

This sample, therefore, contains 62 per cent. of butter-fat, and consequently 38 per cent. of margarine.

To Detect Cotton-seed Oil in Butter.—To the melted fat add an equal volume of a saturated solution of lead acetate, and a smaller quantity of ammonia, and stir. On standing for a little time the superficial layers turn orange-red.

Bechi's Silver Test.—Dissolve 1 gramme AgNO_3 in 100 c.c. of 95 per cent. alcohol; add 20 c.c. ether and a drop of HNO_3 , and thoroughly mix. To 10 c.c. of the sample of fat add 2 c.c. of this reagent. Mix and stand the test-tube in boiling water for fifteen minutes. The mixture assumes a considerably darker tint in the presence of cotton-seed oil. These tests are best performed in the presence of blank tests on pure butter-fat.

Sesame Oil.—Fats containing this oil give a red colour when heated with stannous chloride on a water bath. The colour is not discharged by moderate dilution with water, thereby differing from the colour produced by turmeric.

Colouring Matters.—Annato, turmeric, and some coal-tar products have been used to increase the yellow tint of butter. These colouring-matters are, for the most part, vegetable, and harmless.

They are all, as a rule, soluble in alcohol, and this property readily distinguishes them from the harmful mineral matters, such as salts of lead, arsenic, copper, chromium, cobalt, mercury, antimony, iron, etc., which are insoluble in alcohol.

The presence of annato, turmeric, etc., may be detected by shaking up 5 grammes of the melted butter-fat with 25 c.c. of a mixture of 30 parts of methylated spirit and 5 parts CS_2 . The fat is dissolved in the CS_2 , and the colouring-matter in the alcohol which floats to the top. If the alcohol be decanted off and evaporated down, and the residue mixed with a drop of sulphuric acid, annato and saffron, when present, turn dark blue changing to green. The green in the case of saffron changes further to brown. Turmeric produces a violet-red, turning to brown on the addition of KOH. Mineral colouring-matters are not usually added to butter.

CHAPTER XX

MEAT

THE flesh of different animals, when killed according to present-day customs, differs materially in appearance. Veal, mutton, and pork are lighter in colour than beef. The method of slaughter has something to do with this, as in those cases where free bleeding takes place the flesh is of a lighter hue through loss of hæmoglobin. The flesh of young animals, containing, as it does, less hæmoglobin, is also lighter in tint.

There is a widespread feeling in this country, not by any means founded upon knowledge, that the carcass of an animal which has died of any disease should not be used as food. In certain cases this is obviously correct, but in others there is no evidence to show that the edible parts are in any way deteriorated as food materials.

Flesh containing infective parasites, and flesh which is in a state of putrefaction, including 'high' game, should be rigorously excluded from human consumption.

Fresh meat possesses certain well-recognised characters which are easy of detection. It should be firm and somewhat elastic to the touch, pointing to the fact that rigor mortis is well developed. It should be practically dry on section, of a clear red colour, and acid reaction. A section through the whole thickness of a joint should present a uniform appearance. The odour of fresh meat is known to all, and may be well obtained by running a clean wooden skewer down to the bone, and then withdrawing and smelling it. The fat should be firm, and not too yellow in colour. Old animals and those fed on oil-cakes exhibit fat of a deep yellow colour. The bone-marrow should be bright red, and should coagulate within twenty-four hours.

The lymphatic glands should be of normal size, colour, and consistence.

The ash of meat should contain a normal quantity of phosphoric acid and salts of potash.

When cooked, meat should not lose more than 30 per cent. of its weight, and when dried on a water bath to constant weight it should not lose more than 75 per cent.

Bad meat may present several evil characters. A deep purple colour points to acute septicæmia, pulmonary disease ending in asphyxia, or when found in patches to hypostatic congestion. The odour may be that of advanced putrefaction, or it may be urinous, as in uræmia. There is absence of elasticity in a section when pitted with the finger; some parts are softer than others, and the flesh may be generally sodden and dropsical. The fat is highly coloured, soft, and perhaps hæmorrhagic. The juice expressed from unsound meat is alkaline in reaction from the formation of ammonias. At later stages the meat becomes green, and even black, when no critical examination is required to establish its condition. Certain chemical tests have been devised to detect putrefaction in the early stages, but none of them can convey more reliable information than that obtained by well-trained eyes and noses.

The carcasses of animals that have died of anthrax and allied conditions, pyæmia, and septicæmia, present congested, ecchymosed, and hæmorrhagic tissues. In all cases where one or other of these diseases is suspected those internal organs and other portions known collectively as the offal, should be seen and carefully examined.

Parasites of Animal Flesh used as Food.—*Cysticerci cellulosa*.—In the muscles of the pig, and more rarely in the dog, monkey, and man, affected by this parasite, are seen small, round, or oval cysts about the size of a small pea. Each cyst contains a bladder-worm which, when taken into the alimentary canal of a second host, develops into a tape-worm—*Tænia solium*—which is easily recognised by its square head surmounted by four suckers, and a central rostellum carrying a double row of hooklets. In those cases where the cysts are calcified, or desiccated and indistinct, the addition of a little weak acid assists in rendering them visible. The muscles

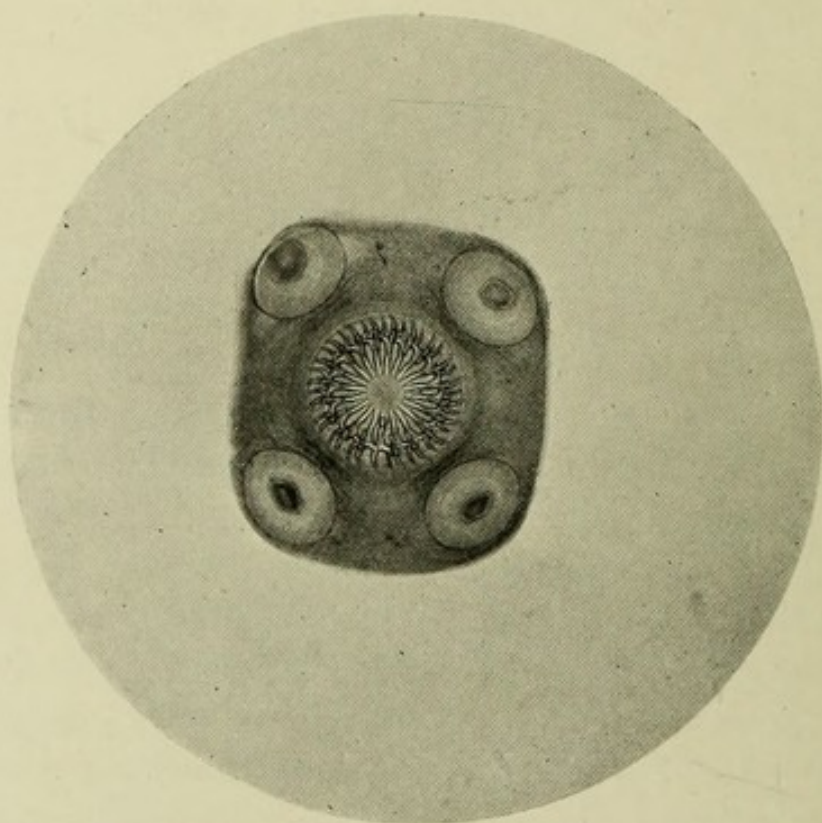


FIG. 26.—HEAD OF CYSTICERCUS. $\times 20$.

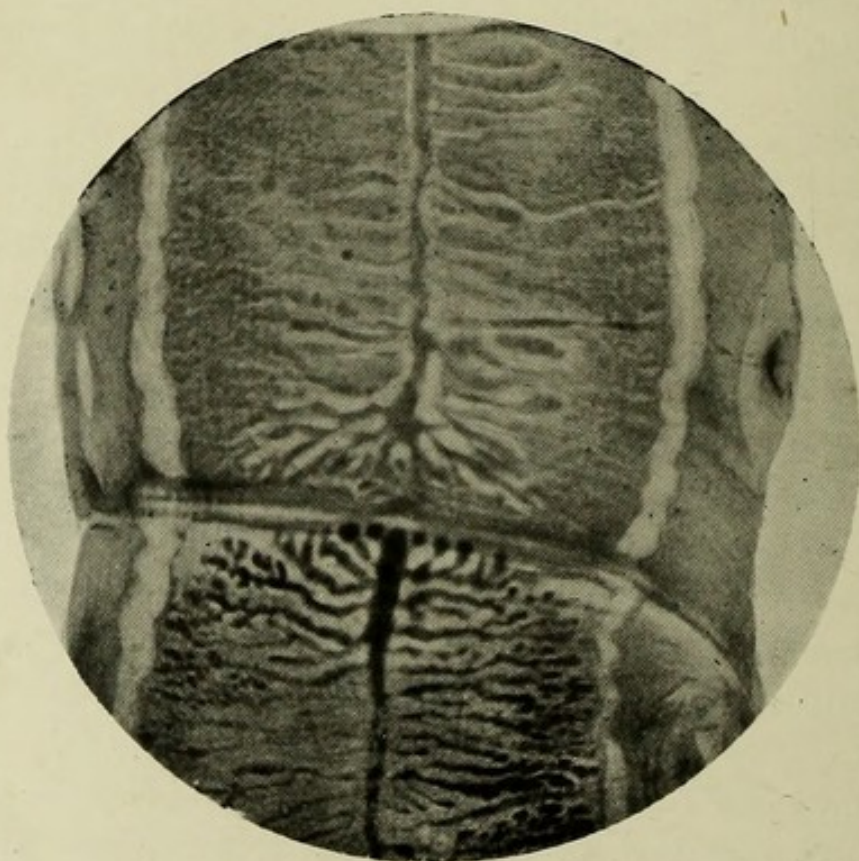


FIG. 27.—TÆNIA SOLIUM. $\times 4$.

of the back, loins, and shoulders are chiefly affected; the cysts are sometimes found in the liver.

Cysticercus bovis is found in the flesh of the ox. It develops into the adult *Tænia mediocanellata*, which is somewhat longer than *T. solium*. This worm possesses a flat head surmounted by four suckers, but devoid of hooklets.

Bothriocephalus latus, a larger tape-worm than either of the preceding, infects man through imperfectly cooked fish. It is not found in a cysticercus form.

Tænia echinococcus is a small tape-worm of about four segments found in the dog. It exists in the encysted form as 'hydatids' in the liver, lungs, and other organs of sheep and cattle, and is sometimes met with in this form in man. These cysts are found as vesicular bodies growing from the internal epithelial lining of a larger fibrous capsule, and floating in a clear liquid free from albumin. Secondary cysts (daughter cysts) form within these; tertiary and further generations may develop, and thus a huge number of embryonic parasites inhabit a small area in an organ. Microscopic examination of the fluid almost always detects hooklets.

Trichina spiralis is mostly found in pigs. It is a nematode which becomes encysted in muscle. The female worm is about $\frac{1}{8}$ inch long, and the male about half this length. The cysts are, as a rule, oval in shape, and arranged with the long diameter parallel with the muscle fibrillæ. As the cyst walls frequently become calcified the parasite may escape if cooking is performed imperfectly. The diaphragm is a favourite situation for *Trichinæ*, and where there is the least suspicion of the presence of the parasite it should be carefully examined. The affected muscle is pale and frequently œdematous, and on careful inspection small white specks are seen scattered throughout it. To the naked eye these specks appear somewhat less in size than a pin's head. They should be examined by a low power of the microscope, when their characteristic appearance will be readily seen. A strip of muscle may be treated with a weak solution of caustic potash, which renders it semi-transparent, and brings into prominence the coiled parasite lying in its capsule. Where the capsule contains more calcareous material than usual, a few drops of dilute hydrochloric acid may be

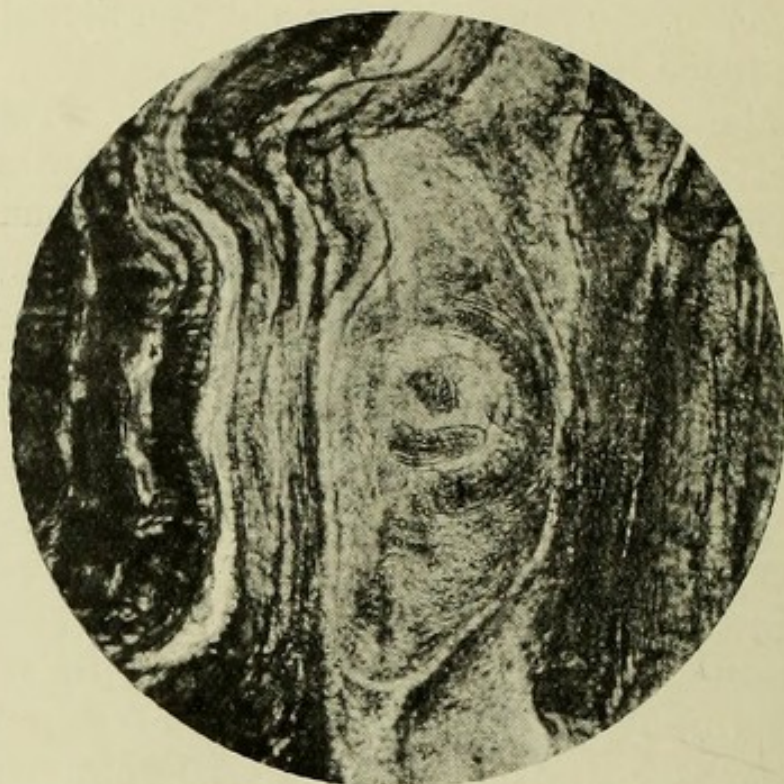


FIG. 28.—*TRICHINA SPIRALIS*. $\times 100$.

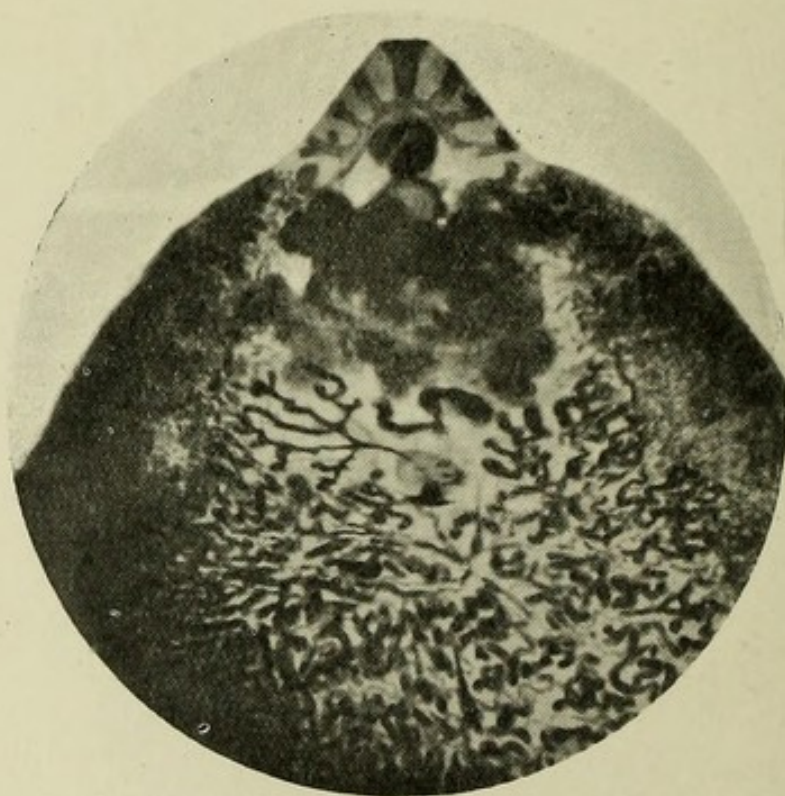


FIG. 29.—HEAD OF *DISTOMA HEPATICUM*. $\times 4$.

required to bring the enclosed nematode into view. In the early stages of the condition those muscles nearest to the intestinal tract, from whence the parasite proceeds, are usually the only muscles attacked, but later in the disease any muscle in the body may become the seat of deposit of capsules.

Psorosperms, known as Rainey's capsules, consisting of semi-transparent elongated masses of cells embedded in the muscle substance within the sarcolemma, should not be confounded with *Trichinæ*.

The *Actinomyces*, or ray fungus, is found in the tongue, lower jaw, and lungs of the ox. In the lungs it has frequently been confounded with tubercle. The thread-like elements and rosettes of clubs, when stained by Gram's method, exhibit an unmistakable picture of this fungus.

Distoma Hepaticum.—This trematode is frequently found in the liver of the sheep. It averages in length 1 inch, and in breadth $\frac{1}{2}$ inch. It is provided with two suckers, one at the anterior broad end, and the other in the median line one-third of the length of the parasite from the anterior end.

The life-cycle of *Tænia solium*, an intestinal parasite of man, is fairly representative of the *Tænia* as a class. Fully matured proglottides shed, say, from the human intestine are swallowed by pigs, or the ova may escape from the segments and become scattered upon the ground or in water, but finally enter the stomach of the pig or some other animal. The gastric juice dissolves the shell, and the liberated embryo pierces the stomach or intestinal wall, and afterwards comes to rest in some part of the body. Here it increases in size, loses its hooklets, and later develops a head provided with four suckers and a circle of small hooklets. This is the stage of bladder-worm, or *Cysticercus cellulosæ*, in which the parasite may remain for a considerable time or die if not swallowed by a flesh-eating animal. On reaching the stomach of such host the bladder is dissolved by the gastric juice, and the worm takes on a rapid development, reaching maturity in a few weeks, and ready to enter upon a new cycle.

The ova of *T. echinococcus* are usually shed in the fæces of the dog, and may infect sheep, pigs, and the human subject through water and raw vegetables.

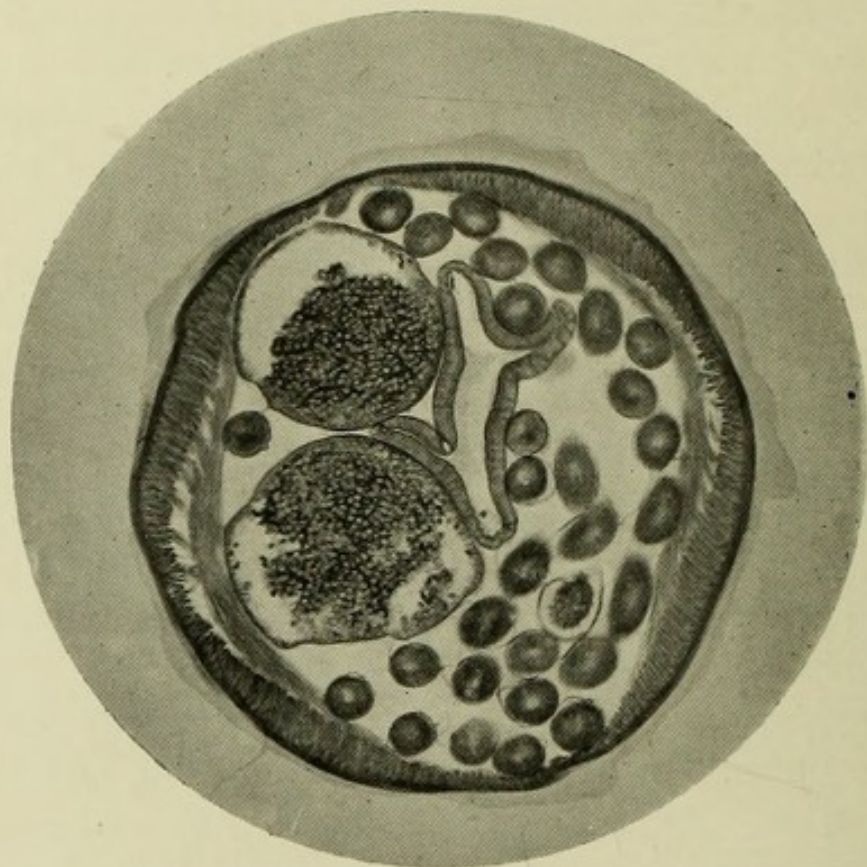


FIG. 30.—ASCARUS LUMBRICOIDES. $\times 7$.



FIG. 31.—OXYURIS VERMICULARIS. $\times 20$.

In addition to *Trichinæ spiralis*, a number of nematodes are found inhabiting the human alimentary canal, of which the more commonly occurring are: *Ascaris lumbricoides*, *Oxyuris vermicularis*, *Tricocephalus dispar*, *Eustrongylus gigas*, *Schlerostomum duodenale*, and *Filaria medinensis* (Guinea worm). The complete life-cycles of some of these have not yet been described.

CHAPTER XXI

CHEESE

CHEESE consists, for the most part, of proteids and fat. It may be prepared (1) by adding rennet to milk, whereby the casein clots and entangles most of the fat; and (2) by allowing the milk to become sour through the formation of lactic acid, or by the addition of a dilute acid, such as vinegar, when the cheese contains little fat.

The characters of different cheeses depend on the kinds of milk used, the methods of preparation employed, and the types of micro-organism admitted to the original milk or to the cheese whilst ripening. During the ripening of cheese a partial digestion of proteids is effected, resulting in the production of the so-called primary products of digestion—albumoses and peptones. Later, secondary products of ripening are found—viz., amido-compounds, ammonia, and nitrates.

Whether during these changes fat is increased at the expense of proteid, as was once believed, is doubtful. The relative proportions of this digestive work carried out respectively by milk enzymes and by enzymes of added bacteria are unknown. The flavour of a particular cheese is doubtless due to the micro-organisms growing in it during ripening. The old idea that a particular cheese, such as Stilton, can be made only in one locality is exploded. Magnificent Stiltons are now made in Hampshire by the agency of a 'cheese mould' carried to that county from Leicester.

Soft cheeses, such as Brie and Camembert, are produced by clotting milk with rennet at temperatures below 30° C., and using little pressure. Hard cheeses, like Stilton, Cheddar, Gorgonzola, and Gruyère, are clotted at higher temperatures—30° to 35° C.—and submitted to greater pressure. Soft cheeses contain much water, and therefore fail to keep long.

Percentage Composition of a Few Soft Cheeses :

			Water.	Proteids.	Fat.	Ash.
Camembert	50.9	18.6	27.4	3.1
Brie	50.0	18.3	27.6	4.1
Stracchino	39.2	29.3	27.7	3.8

Percentage Composition of a Few Hard Cheeses :

			Water.	Proteids.	Fat.	Ash.
Cheddar	27.2	36.6	32.0	4.2
Cheshire	30.4	36.1	28.7	4.8
Stilton	28.6	35.6	31.8	4.0
Gruyère	32.0	35.1	28.1	4.8

The ripening of cheese has been somewhat differently explained by Freudenreich, Duclaux, and Babcock and Russell. When the curd is thrown down by rennet it carries with it most of the bacteria of the milk. Freudenreich believes that the lactic acid organisms, which develop early and rapidly, are the chief factors in the process of ripening. Duclaux holds that, since the ripening proceeds after the lactic acid organisms have considerably diminished, the active agents are enzymes secreted by a variety of organisms, which he names *Tyrothrix*. Babcock and Russell accept the view that ripening is effected by an enzyme originally present in milk.

Moulds in Cheese.—Green mould (*Penicillium glaucum*) is found in Roquefort and Gorgonzola. *Aspergillus glaucus* produces the appearance known as blue mould, whilst red mould is accounted for by the growth of *Sporendonema casei*. The common mould (*Mucor mucedo*) is found in more than one variety of cheese.

Of animal parasites found in cheese, the two most frequently met with are 'the cheese mite' (*Acarus domesticus*), and 'cheese maggots' (larvæ of *Piophilæ casei*).

Adulteration in Cheese.—The principal adulterations in cheese are the use of skimmed milk for whole milk, and the addition to skimmed milk of foreign fats. Mineral adulterants, such as chromate of lead, used to tint the rind, and sulphate of zinc ('cheese spice'), used to prevent gas formation from fermentation, are rarely met with.

In a whole-milk cheese the ratio $\frac{\text{fat}}{6.37 \text{ total N}}$ is greater than 1 (generally 1.25 to 1.5). In a skimmed-milk cheese this ratio is less than 1. The fat is estimated by extraction with ether, petroleum ether, carbon bisulphide, etc. Foreign fats are detected by the Reichert process. In genuine cheese the Reichert figure exceeds 18, whilst foreign fats taking the place of cream produce a figure generally below 6. The total N is obtained by Kjeldahl's method.

In determining the amount of water in cheese, it is convenient to grind 2 grammes with 10 grammes of clean and dry sand, and to slowly heat the mixture in an oven possessing good draught, at a temperature of 60° C., until a constant weight is obtained. The loss in weight represents the water in the cheese.

The ash is obtained by weighing out 2 grammes of the sample into a platinum dish and igniting. The salt can be estimated from the ash by titration with standard silver nitrate solution, using neutral chromate of potassium as indicator.

The estimation of individual proteids and products of ripening is outside the scope of this work.

The digestibility of cheese in the stomach is less than that of meat, on account of its proteids being covered with fat. Cheese should therefore be well masticated, or, better, thoroughly grated before being used. Its digestion in the small intestine is effected without difficulty. Owing to the small quantity of water contained in cheese compared with that in beef, it has a higher nutritive value than the latter. The energy derivable from cheese, as measured by calories, is about three times that of beef. Moreover, the fact that the proteid of cheese is chiefly casein, and accordingly purin-free, should highly recommend it as an article of diet to those who are in any way troubled by uric acid.

CHAPTER XXII

DISINFECTANTS

THE rapid development of preventive medicine during the last quarter of a century, following closely in the wake of the still more rapid growth of the modern science of bacteriology, has greatly modified our ideas of the meaning of the word disinfectant. Until comparatively recent years no very marked distinction was made between disinfectants, antiseptics, and deodorants; and this statement applies not only to the lay public, but also to sanitarians. The explanation is, that through lack of definite and exact experimental knowledge concerning the physical and chemical nature of the work to be done in disinfection, and of the agents employed therein, quite erroneous views were held upon both. Prior to the days of origin of bacteriology, a disinfectant included, besides certain physical conditions, any body capable of destroying infective or putrefactive matter, especially the noxious odours connected with putrefaction. The disposal of dead and putrefying animal and vegetable substances, more especially the bodies of dead animals and the human subject, has been a matter of special interest to man from his earliest days, as witnessed by the manner in which it is interwoven with the most sacred religious rites of the oldest nations. That important evils in the form of disease arose from lack of proper attention to such disposal was understood, but of the mode of production of such conditions nothing was truly known until the bacteriologists demonstrated the existence of putrefactive and pathogenic micro-organisms, and also of certain bodies, to which reference shall be made later—products of their life-histories—possessed of profound potentialities for good or ill.

In 1854 Schroeder pointed out that in order to maintain a flask containing hay infusion sterile, it was only necessary to plug the

mouth of the flask with cotton-wool. The air as it passed through the wool was filtered free from bacteria. Pasteur in 1862, in response to an offer of the Paris Academy of Science of a prize for 'an attempt by means of suitable experiments to throw new light on the question of spontaneous generation,' demonstrated the possibility of sterilizing any substance whatsoever. Numbers of workers all over the world have confirmed those experiments, and finally settled the theory of heterogenesis.

The resistance offered by some micro-organisms to heat whilst in the state of spores was observed by Tyndall, who worked out a method of fractional heating for their destruction. During the first exposure all the bacteria were killed; the spores which escaped were by this heat rapidly transformed into bacteria; on second exposure these also perished; a third heating completed the destruction of any microbes that might have possibly escaped. In 1881 Koch published a means of isolating pure cultures by the celebrated plate method. Having separated several species, and shown that the same organism was constantly found in a given disease, he proceeded to demonstrate the causal relationship between the organism and the disease, and in the next year (1882) settled the question of the cause of tuberculosis, by (1) his discovery of the tubercle bacillus, and (2) production of the disease in animals by inoculation of a pure culture of the organism which had been grown on an artificial medium.

In the light of the knowledge afforded by this and further bacteriological work, the mode of action of disinfectants became plain. Heat, whether dry or moist, destroyed the life of the infecting agent; the problem of the resistance of spores was cleared up; and a significant distinction was drawn between antiseptics which merely inhibited the growth of microbes without destroying them, and disinfectants which killed the organisms outright. Deodorants, in that they only mask or absorb odours, possess neither the properties of disinfectants nor of antiseptics.

Recent discoveries in bacteriology have stimulated afresh chemical inquiry into the nature of enzymes and enzymotic action, and it is known that in infectious diseases the ultimate cause is not the mechanical action of the specific microbes, but the enzymes, known as toxins—metabolic products of the organisms—produced as

secretions, and thrown off either during their life or after their death into the tissue fluids of the host. The modern doctrine of immunity, constructed on a large mass of experimental evidence obtained by Ehrlich, Gruber, Bordet, and many others, assumes that under certain conditions these toxins call into existence antagonistic bodies—antitoxins—which neutralize the toxins and render them harmless. The antitoxins are products of metabolism of the body cells, specifically produced in response to stimulation by the toxins. But too frequently an unequal warfare is waged by these opposing forces in the animal body, and often before sufficient antitoxins can be produced it succumbs to toxic action. Safety in a given case can only be guaranteed by complete and early destruction of the whole of the organisms. When it is recollected how rapidly some bacteria reproduce themselves—under favourable conditions a single organism may produce a progeny of more than a million in half an hour—the enormous importance of lapse of time before commencement of treatment will be at once obvious. A rapid and complete destruction of all such micro-organisms constitutes the work of true disinfectants. Here it may be seriously inquired, How many of the disinfectants in use conform to these requirements?

It will now be clear that in order to intelligently and successfully carry out this work, the source, life-histories, and individual properties of the infective agent must be thoroughly known, as also the nature and mode of interaction obtaining between it and the disinfectant. Until very recently the merest empiricism has characterized the use of disinfectants. In the domain of pharmacology it has been found that only in those cases where drugs form actual chemical combinations with tissue cells can definite and constant results be procured, such, for example, as occur in the case of strychnine. Between this drug and the cells of the central nervous system there exists a special affinity; when strychnine is introduced into the body, it passes by all other cells to attach itself to nerve-cells only, and so produces its well-known effects. In the same manner, although at present we are only on the threshold of the subject, there seems to be some evidence of selective action displayed by action disinfectants for certain micro-organisms.

A Few Varieties of Chemical Disinfectants.

Salts of Mercury.—Of these the perchloride (corrosive sublimate) has been and still is largely used. That it is a powerful germicide there is no doubt, but as an ideal disinfectant it has few claims. The toxicity of HgCl_2 is high; it rapidly coagulates albumin, whereby it destroys microbes; its action on the skin and on metals detracts from its claims to a high place amongst disinfectants. It dissolves in about 15 parts of water, and in less alcohol and ether. Doses of .2 gramme per diem rapidly produce poisoning. This excludes it from intestinal use, and even makes its external application dangerous. A solution of 1 in 1,000, when properly applied, is sufficient to destroy the most resistant organism; spores require a stronger solution, as it has been shown that anthrax spores were not killed, but only inhibited in their growth for a period, by treatment with a 1 per mille solution, and regained their powers of reproduction on injection into an animal. The disinfecting power of mercuric chloride seems to vary with the degree of dissociation and concentration of metallic ions in the solution. If the degree of dissociation be reduced by the addition of a salt such as sodium chloride, its powers of disinfection are likewise diminished, and this is more marked in concentrated solutions, since in dilute solutions the free 'ions' are more numerous. The American Public Health Association recommends that a solution of 1 in 1,000 be used for all non-spore-forming bacteria, and 1 in 500 for spores.

Mercuric iodide is also used for disinfection in medical and surgical practice, and is said to possess twice the bactericidal power of corrosive sublimate, whilst it is less poisonous. It is insoluble in water, but readily soluble in excess of potassium iodide, forming the well-known double salt, potassio-mercuric-iodide. Other salts of mercury in use are mercuric cyanide, zinc-mercuric cyanide, mercuric carbolate, mercuric salicylate, and mercuric thymolate—all poisonous, difficult of solution, and, by reason of coagulating albumin, unable to penetrate deeply organic bodies containing micro-organisms in their substance.

Chloride of Lime.—The halogens, especially chlorine, have long been known as disinfectants. The latter body, contained in

bleaching-powder, has been before the public for a much longer period than warranted by its merits. Bleaching-powder, or so-called 'chloride of lime,' is a combination of calcium chloride and calcium hypochlorite, of the formula CaCl_2O , which, on solution in water, breaks up into these two bodies. The hypochlorite is alkaline, and unites with the CO_2 of the air to form CaCO_3 and hypochlorous acid. When hypochlorous acid is brought in contact with organic matter, it forms hydrochloric acid and free oxygen, which last body acts as a disinfectant. If chlorine is to be liberated from hypochlorites, strong acids must be used. Whilst the chemistry of disinfection by bleaching-powder looks well—perhaps even impressive—on paper, there is no shadow of doubt that in the great majority of cases in which it is ordinarily used this reagent is little better than a deodorant. The small quantity of oxygen liberated under the conditions mentioned is a poor remedy with which to fight a virulent pathogenic organism, such, for example, as anthrax.

Theoretically, bleaching-powder should yield nearly 35 per cent. of chlorine, but in reality this rarely occurs. Moreover, the body is only of value when fresh and dry, but frequently old and worthless material is alone to be met with in the market. Chlorine, under certain conditions, is a good germicide, but its action on linen, silk, and cotton fabrics, on the respiratory mucous membrane, and on plants, detracts largely from its value as a disinfectant. Formalin in recent days has somewhat taken its place as a gaseous disinfectant.

Hermite Solution.—Much has been written on the hermite solution as a disinfectant for sewage. This solution is obtained by the electrolysis of sea-water, and may be regarded as a combination of magnesium chloride and hypochlorite—the magnesian equivalent of bleaching-powder solution. In comparative experiments on the action of bleaching-powder and hermite solution on sewage, it was found that bleaching-powder acted more slowly, but, by reason of its greater stability, the results were much more satisfactory in the end. The fact remains that the inconstant composition and variable manner in which these disinfectants are used shuts out all possibility of quantitative results being obtained.

In the struggle against infection, which is often synonymous

with the struggle against death, we require as disinfectants bodies of known and constant composition, whose germicidal capacities are not only sufficiently powerful, but above any suspicion of variability, so that in forecasting the issues in a given case, no element of doubt regarding the disinfectants need be entertained. This is the condition of things to be accomplished ; at present we are very far from it.

With respect to the disinfectant action of gaseous bodies and metallic salts upon albuminoid masses containing in their substance pathogenic bacteria, it must ever be borne in mind that the surface layers of such masses are alone affected. In the case of advanced pulmonary tuberculosis, in which pellets of lung tissue are being expectorated, it is useless to treat the sputum with small quantities of perchloride of mercury or formalin, as in such case the superficial layers only are disinfected by a process of coagulation, which forms an envelope round the mass, whilst the interior of the pellet retains numberless organisms untouched ; and not only that, but most excellently preserved from all fear of destruction by this layer of coagulated albumins. Here the bacilli remain for indefinite periods, sometimes extending to years, until, in process of time, they are liberated by the disintegration of the enclosing capsule. It is clear that the disinfectants named are not suitable for this kind of work, and equally clear that what is required is a solution incapable of coagulating albumin, and at the same time powerfully destructive to tubercle bacilli.

Chlorine, Iodine, and Bromine.—It has been stated that the halogens Cl, I, and Br have disinfectant properties proportional to their atomic weights, which means that, in order to perform the same work by these three bodies, solutions will require to contain 35.35, 80, and 127 parts by weight respectively. This is the merest myth, a figment of imagination associated with arithmetical conceptions of atoms. Whether Cl employed as a fumigation is really valuable or not, there is no unequivocal experimental evidence on which to base an opinion. As to the other two bodies, their use as disinfectants on a large scale is quite impracticable. Certain halogen compounds have obtained reputation as germicides. Chloroform (CHCl_3) in weak solutions acts as a mild antiseptic ; to produce reliable disinfection, a strength of more than

1 per cent. is necessary. Its volatility, insolubility, and soporific effects render it unsatisfactory. Bromoform is less satisfactory still. The only halogen compound which has achieved a name worth bearing, perhaps, is iodoform, and its reputation is far in advance of its merit.

Oxygen.—Oxygen and the oxygen group (ozone and hydrogen peroxide) have been exploited from time to time with the zest worthy of a modern company promoter. That these bodies are under certain conditions antiseptics, and in some instances disinfectants, there is no doubt; but that any one of them— H_2O_2 not excepted—should be regarded as a reliable disinfectant is almost incredible. Of the oxides of N there is little to say further than that, like the previous group, they do not lend themselves to the work in question.

In future discrimination will be used in selecting a suitable type of disinfectant for a particular form of work, and in order to obtain the best results all the conditions attaching to the work to be done must be intimately known, as also all the properties, active and potential, of the substances employed. For medical and surgical disinfection the ideal is a substance readily soluble in water, non-metallic, non-toxic, capable of destroying all pathogenic bacteria, but incapable of coagulating albumin.]

For the disinfection of sewage very different requirements are to be met, according to the phase in which the sewage is found at a particular moment, and it is not yet clear whether future successful methods of disposing of sewage shall not avoid disinfection altogether. Our knowledge of what actually takes place in the so-called biological treatment of sewage is so limited that it is impossible even to guess whether any advantage may at any point be gained by destroying bacteria.

A prime necessity of the biological method is that, previous to submitting organic matter to the action of aerobic bacteria on the filters, such organic material should be wholly in solution, for the reason that aerobic organisms can only rapidly digest albuminoid matter when in complete solution. In sewage purification on the large scale the time required for oxidation is one of the most important factors, for where the work is not done rapidly—as filters are at present constituted—it is not done at all. The surface layers

of filters upon which the microbes grow should therefore be composed of materials incapable of precipitating albumins and albumoses from solution. No department of municipal work requires the strictest application of modern science so much as does the treatment of sewage, that of physiological chemistry.

Boric Acid.—Boric acid, in common with all free acids, even in weak solution, retards the growth of bacteria, and some say that the borates exercise a direct physiological action upon microbes. Boric acid has been, and still is, largely used for preserving milk, and there has been much controversy regarding its action, in this connection, upon the public health. On one side it is argued that not only is boric acid and the borates harmless in the quantities used, but a necessity in hot weather for the prevention of milk becoming sour. On the other side, the use of boric acid is condemned as possibly harmful to many members of the community, and especially to weakly children and infants, who live almost exclusively on this article of diet. In the case of infants it is most difficult to exclude toxic action. Moreover, as has already been stated, it is not necessary to add anything to milk for the purpose of preserving it. All milk should be distributed on the day on which it is drawn from the animals, under which condition very rarely, if ever, would anything in the nature of a preservative be required, even in the hottest weather experienced in this climate. The preservation of an old milk with boric acid, like the greening of inferior peas with copper sulphate, should be condemned on this, if on no other ground, that by allowing dealers to tamper with food-stuffs a premium is put on adulteration and the sale of inferior articles.

To-day a bewildering multitude of disinfectants crowd the market. With one or two exceptions no scientific credentials vouch for the efficiency of any. Clamorous advertisement alone recommends them. There is no fixed standard by which their efficiency, nay, rather, their glaring inefficiency, can be measured. They are wholly uncontrolled. Many of them are of doubtful composition and utterly useless; this applies to a large number of proprietary articles related to coal-tar, and to a few related to certain essential oils.

It is curious to note the state of affairs in this matter. Whilst the man in the street is carefully protected against water in his

milk and foreign fats in his butter, no obstacle is put in the way of his buying the most hopeless compound as a disinfectant. Typhoid may rage in his home, and the sanitary authority which guards his water-supply so jealously that a single *B. typhosus* may not enter, supplies him with Condyl's fluid of such strength that its powers of destroying bacteria are equal to those possessed by the same volume of distilled water.

Coal-tar has been the gold-mine of the serious organic chemist, as it has also been the happy hunting-ground of the commercial quack. It contains, amongst a multitude of things, a mixture of aromatic compounds derived from benzene (C_6H_6) and its homologues, from which an enormous number of so-called disinfectants have been in one way or another prepared. By well-known methods these tars can be separated into (1) basic bodies of the nature of ammonias; (2) hydrocarbons of the benzene series; (3) phenols.

Phenol, known also as carbolic acid, as prepared in the crude state, is a brown, oily liquid, containing higher homologues—cresols, etc.—and neutral tar-oils. Pure phenol is crystalline, of constant melting- and boiling-points, very hygroscopic, and fairly soluble in water. It has held for a long period a high place as a disinfectant. Many years ago Koch showed that in solution of 1 in 850 phenol prevented the growth of anthrax spores, and in this dilution classed it as an antiseptic. In order to thoroughly destroy spores, it has been found since that a solution of at least 5 per cent. is necessary. Phenol is useless as a deodorant, as it is incapable of absorbing gases such as ammonia and sulphuretted hydrogen. Its odour, which is very persistent, and out of all proportion to the quantity used, rather discounts its application to domestic disinfection; in surgical disinfection it is in many cases superior to corrosive sublimate, especially in its penetration of the skin. Commercially, it is combined with an almost infinite number of inert substances to form solutions, powders, pastes, ointments, etc., many of which contain but traces of phenol. It is useless in the treatment of sewage. Cresols and the higher phenols may be regarded as derivatives of phenol, in which one or more of the H atoms in the benzene ring have been replaced by fatty radicles (methyl, ethyl, etc.). These substitution homologues increase in density and boiling-point and decrease in solubility, as the scale is ascended.

One of these latter compounds—**Lysol**—has been a favourite disinfectant in England and on the Continent for some years. It is a brown syrup, containing 50 per cent. of higher phenols, but no carbolic acid. It is prepared by dissolving that portion of tar-oil which boils between 190° and 200° C. in a neutral fat, and afterwards saponifying the solution. Like phenol, it has a penetrating action on the skin, and in 2 per cent. solution forms an excellent antiseptic.

Izal, a reddish-brown liquid insoluble in water, is derived from the oil produced during the carbonization of coke in close ovens. Chemically, it differs considerably from the coal-tar phenols. It is non-caustic and non-toxic to higher animal life. It mixes with water in all proportions, forming a milk-like emulsion. It has been carefully tested by a number of reliable observers, all of whom agree that it is a valuable disinfectant, though somewhat slow in action. For the disinfection of fluids and fluids containing some solids, a copious solution, at least 5 per cent. in strength, should be applied for half an hour.

Creolin, of which there have been from time to time several preparations, and which is now known as **cyllin**, was originally a compound of cresols and neutral tar-oils in emulsion. The latest production—**cyllin**—is composed of a number of oxidized hydrocarbons exquisitely emulsified. Its toxicity in the dilutions and volumes necessary for disinfection in medical and surgical practice is so small that it may be ignored. It has been prepared in accordance with the knowledge that compounds containing a di-phenyl nucleus are less poisonous, but more strongly disinfectant, than those containing a single phenyl nucleus, and also that an emulsion of cresols is much more strongly disinfectant than a solution. It is an excellent attempt at the construction of a disinfectant on scientific principles, and appears as an encouraging ray of light in the abysmal darkness which surrounds the multitude of empirical preparations at present abroad. A form known as **cyllin (medical)** is intended for use as an intestinal disinfectant, and recently a third form—**cyllin (inhalant)**—prepared for use in a vaporized state in the treatment of tubercular lungs, has been put on the market.

With the appearance of these bodies is associated a second

encouraging feature—viz., the plea for a method of standardization and State control of disinfectants, initiated by Rideal and Walker, in a paper read by them upon a new method of bacteriologically standardizing disinfectants at the Congress of the Sanitary Institute in 1903. At that meeting a resolution was proposed and carried that the Sanitary Institute should appoint a committee to inquire into the desirability of establishing a standard bacteriological method for determining the efficiency of disinfectants, and to take such steps as may be necessary for insuring the legal control of disinfectants. Up till then the bacteriological tests applied by most competent observers had little in common in the matter of methods, and accordingly results were extremely divergent. Too much attention had been paid to the quantity of chemically active principle present in a disinfectant, whilst the form in which it existed was mostly ignored; chemical analysis accordingly was regarded as the main criterion by which the value of a compound was estimated. In this connection it is well to bear in mind that a chemical analysis can demonstrate nothing of the germicidal powers of any disinfectant.

In the Rideal-Walker method, which has been carefully tested by a number of competent observers, it is first shown that the glaring discrepancies attaching to investigations by different bacteriologists are not so much due to the personal equation as to different modes of procedure. Uniformity of procedure in every step of an investigation is therefore laid down as a *sine qua non* where results are to be compared.

In bacteriology, as in all sections of biology, the estimation of effects produced on any unit or set of units by external conditions involves the careful consideration of a number of variable factors. If, therefore, in a given series of experiments on disinfection, one observer considered the time of application of the agent the only important factor, a second the proportion of culture to disinfectant, and so on throughout, no two results would be comparable. The above authors hold that all details of procedure must be agreed on beforehand, and that in selecting any particular process to be employed as a standard; the following factors must be considered: time, age of culture, choice of medium and reaction of medium, temperature of incubation, temperature of medication, varia-

tions in vital resistance of same species, variations in vital resistance of different species, proportion of culture to disinfectant. The standard disinfectant recommended is pure phenol, and the method of procedure is roughly the following :

A particular dilution of the disinfectant is made in distilled water, and to 5 c.c. of this 5 drops of a twenty-four hours' culture of the organism in broth at 37° C. are added. The mixture is shaken, and sub-cultures made into broth every two and a half minutes up to fifteen minutes. These are incubated for forty-eight hours at 37° C. Four different dilutions of the disinfectant and one standard control may be tested on the same culture, under strictly comparable conditions, allowing thirty seconds for the manipulations necessary for each act of medication, and the same time for the making of each sub-culture. The efficiency of the disinfectant is expressed in terms of phenol performing the same work. In other words, that dilution of the disinfectant which performs the same work as the phenol dilution is divided by the latter, and a ratio is obtained, which the authors call the 'carbolic acid co-efficient.' The subjoined table represents the manner of expressing results :

B. TYPHOSUS, 24 HOURS' BROTH CULTURE AT 37° C.

ROOM TEMPERATURE, 15°-18° C.

Sample.	Dilution.	Time Culture exposed to Action of Disinfectants—Minutes.						Sub-cultures.	
		2½	5	7½	10	12½	15	Period of Incubation.	Temperature.
Cyllin -	1 : 700	•	•	•	•	•	•	48 hours	37° C.
„ -	1 : 900	×	•	•	•	•	•	„	„
„ -	1 : 1100	×	×	×	•	•	•	„	„
„ -	1 : 1300	×	×	×	×	•	•	„	„
Phenol -	1 : 100	×	×	×	•	•	•	„	„

$$\therefore \text{Carbolic Acid Co-efficient} \frac{1100}{100} = 11.0.$$

Of the two methods of analysis of disinfectants—the chemical and the bacteriological—the latter is alone universally reliable.

For example, an emulsion of cresols is three times as strong a disinfectant as a solution; and an emulsion at 37° C. is very much stronger than at 18° C.

As it becomes recognised that a disinfectant can only be tested by direct application to the particular organism to be destroyed, and as the various disinfectants are in this way referred to a standard, a large number of worthless articles will of necessity disappear.

It has been shown that the 'carbolic acid co-efficient' of certain disinfectants is different for individual organisms. In working with cyllin and the *Vibrio cholerae asiaticæ* the writer found the ratio to be 32 : 3, whilst for *B. typhosus* it was 11.

The following table, compiled from a few recent papers on the subject, shows that with the same organism the 'carbolic acid co-efficient' for each disinfectant cited is different from that of all the others :

Disinfectant.	Organism Used.	Carbolic Acid Co-efficient.
Phenol, 98 per cent. - -	<i>B. typhosus</i>	1·0
Formalin . - - -	"	·3
Izal - - - -	"	8·0
Liquor carbonis detergens -	"	·1
Cyllin - - - -	"	11·0

The issues of this advance in sanitary science must be plain to every thoughtful mind. Whether or not Parliament take up the matter in the near future and enforce a State control of disinfectants, as the knowledge of the relative values of disinfectants spreads, the ordinary laws of economics, under which the worthless article in time disappears, will justly dispose of the problem.

Much has been written on methods of estimating available chlorine in bleaching-powders, crystallizable phenols, cresols, tar-oils, and water, in preparations of carbolic acid; as also sulphurous acid, cupric sulphate, ferrous sulphate, and zinc chloride in preparations of these bodies respectively, with a view to ascertaining their values as disinfectants; but it cannot be too emphatically stated that all such tests are for the most part vain, and that direct appeal to bactericidal powers, as above described, alone avails.

Where, however, the quantitative analyses of such bodies are

insisted on, the following few methods may be found convenient :

Available Cl in Bleaching-powder.—Triturate 10 grammes of bleaching-powder in a mortar with successive small quantities of water, and transfer through a funnel to a stoppered litre flask. Make up to the mark with water. For a determination take 10 c.c. of the well-shaken turbid fluid (equal to a decigramme of the powder). Add from a burette $\frac{N}{10}$ arsenious acid in slight excess (until a drop ceases to produce a blue spot on KI- and-starch-paper). Then add fresh starch paste, and run in $\frac{N}{10}$ I solution from another burette until there is a slight permanent blue colour. The number of c.c. of I required gives the number of c.c. of arsenious solution that have been added in excess. Subtract this from the total added to obtain the number of c.c. of the standard arsenious solution, which are equivalent to a decigramme of the bleaching-powder. Each c.c. of the $\frac{N}{10}$ arsenious acid = .00354 gramme available chlorine.

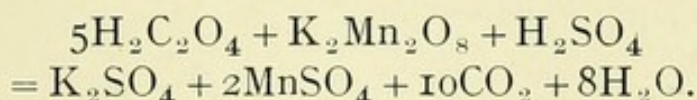
This method determines quantitatively chlorinated soda, Hermite solution, and chlorine, bromine, and iodine water.

Sulphites and Sulphurous Acid.—The presence of sulphites in food, etc., is determined thus : Strongly acidulate two portions in a suitable vessel with dilute pure H_2SO_4 , and over each place a piece of filter-paper moistened with lead acetate. To one portion add some pure granulated zinc, so as to obtain a slow evolution of hydrogen. Add water if much frothing occurs. Leave both for thirty minutes in a warm place. If the lead paper be blackened only over the vessel containing the zinc, it proves the presence of sulphites ; if both papers be blackened, other sulphur compounds are present, and the test is valueless.

Quantitative Estimation.—Iodine converts sulphurous acid into sulphuric. Dilute the solution to be estimated until it contains not more than .05 per cent. SO_2 . Run in $\frac{N}{10}$ I until, on the addition of starch paste, a permanent blue tint remains. One c.c. of the iodine solution = .0032 gramme SO_2 .

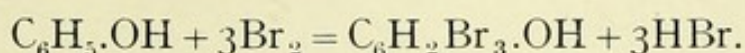
Permanganate—Condy's Fluid.—Render strongly acid with H_2SO_4 a decinormal solution of oxalic acid, and place a measured quantity in a porcelain dish. Run in the permanganate solution (properly diluted) from a burette until a permanent pink is produced. Five equivalents of oxalic acid require one equivalent of

permanganate for oxidation, and are thus equal to five atoms of available oxygen.



Carbolic Acid.—Water is estimated by slaking the carbolic acid with half its volume of a saturated solution of NaCl in a graduated tube. The diminution of the volume of the carbolic acid represents the amount of water present.

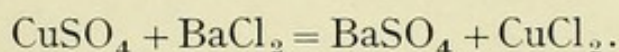
Determination of the Carbolic Acid.—The phenol equivalent of bromine water recently prepared is ascertained by titration against a known small quantity of pure phenol—say .25 gramme in 100 c.c. water. This standard bromine water is then run into a measured quantity of the solution to be estimated until excess of bromine appears. Tri-bromo-phenol is deposited in crystals. Half an hour is allowed to elapse, and if the excess of bromine has disappeared, more bromine is added, and the mixture shaken and allowed to stand. Excess of KI is now added, and the liberated I estimated by thiosulphate and starch. This liberated iodine corresponds to the bromine in excess. Subtract the latter from the total bromine added, and the remainder corresponds with the amount of phenol present.



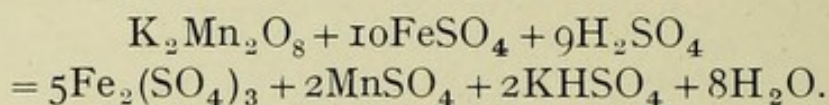
The specific gravity of crude carbolic acid should fall between 1.050 and 1.065. If it be less, it most likely contains light tar oil.

Phenol gives with ferric chloride a deep violet colour. Unfortunately this colour is produced by other bodies containing the benzene hydroxyl, such as salicylic acid, etc. Tri-bromo-phenol is a white crystalline body, very insoluble in water, and interesting as a delicate test for phenol, since tri-bromo-cresol is liquid. Coal-tar acids coagulate collodion; wood-tar does not. Further, wood-tar gives with ferric chloride a yellowish or greenish-brown tint, whilst phenol gives a deep violet.

Copper sulphate is estimated gravimetrically by precipitating its hot aqueous solution with barium chloride, drying and weighing the insoluble barium sulphate.



Ferrous sulphate is estimated by oxidizing its solution with standard permanganate.



Sixteen parts of O oxidize 112 parts Fe.

Mercuric chloride is estimated by dissolving it in HCl, and precipitating the sulphide by passing H_2S to saturation. The precipitate is allowed to stand for a time, then thrown on a filter and washed, until the washings leave no residue on evaporation. It is then dried at 100°C . and weighed. Hg is calculated from the weight of the HgS. The precipitate may contain free S, in which case it is washed with recently distilled CS_2 .

Zinc chloride and other zinc salts may be estimated by precipitating the carbonate, and afterwards converting this by ignition into ZnO. Weigh the oxide, and from the weight obtained calculate the amount of Zn.

CHAPTER XXIII

CEREALS

THE composition of a few common cereals is given in the following table :

		Proteid.	Fat.	Carbo- hydrates.	Cellulose.	Water.	Ash.
Wheat	11.0	1.7	71.2	2.2	12.0	1.9
Barley	10.1	1.9	69.5	3.8	12.3	2.4
Rye	10.2	2.3	72.3	2.1	11.0	2.1
Oats	11.0	5.2	57.3	12.0	11.8	2.7
Maise	9.9	5.4	68.9	2.2	12.3	1.3
Millet	10.4	3.9	68.3	2.9	12.3	2.2
Rice	6.8	1.6	68.1	9.0	10.5	4.0

It will be seen that the proteids vary somewhat in the different cereals. The fat appears in increased quantities in those cereals which grow in high latitudes. The chief carbohydrate is starch : it forms 65 to 70 per cent. of the whole grain. The ash averages about 2 per cent., and is composed principally of lime and phosphoric acid, thus resembling the ash of animal food-stuffs much more than that of vegetables. The high percentage of carbohydrates is an indication that cereals should be mixed with other foods richer in proteids and fat ; this physiological requirement we find almost universally complied with : butter is spread upon bread, and the mixture eaten with cheese. On the whole, cooked cereals are easily digested and absorbed.

Wheat-flour.—Wheat is the most important cereal used in this country. It is consumed to the extent of six bushels per head per annum. The grain of wheat consists of three portions : (1) the bran or outer envelope of cellulose, containing mineral matter, and forming 13.5 per cent. of the grain ; (2) the endosperm, constituting 85 per cent. of the whole, and consisting of nutritive material for the growth of the embryo ; (3) the embryo or young

plant, forming 1·5 per cent. of the grain. The bran consists of an outer layer of fibres of cellulose impregnated with salts, a middle layer of pigment cells, and an inner layer of aleurone grains. The endosperm consists of a delicate reticulum of cellulose, in whose meshes are found numerous starch granules. The embryo is composed of small cells rich in proteid and fat.

The milled grain known as flour differs in composition, according to whether the bran or embryo, or both, have been largely removed or retained. The reduction of bran to a powder by grinding is a difficult and expensive matter, and as a rule the miller removes it altogether. In roller-milling, the germ is also removed, in order to prevent the fat which it contains becoming rancid. Enzymes present in the germ act upon the starch, converting it into dextrin and sugar, which darken the colour of the bread; so the germ is got rid of also. This rejection of the bran and germ means the loss of some of the most useful constituents of the wheat; and the recognition of this loss has led to a number of patent processes for treating the bran and germ so as to prevent the production of a dark loaf. In the 'Hovis' process, the fat of the germ is treated with steam, with the object of preventing its becoming rancid. In the 'Frame Food' process, the bran is boiled with water under pressure, with the object of breaking down the cellulose, and extracting the bulk of the nitrogenous and mineral constituents. In Smith's patent the germ is partially cooked by superheated steam, whereby the ferment is killed which transformed the starch of the flour. According to the method adopted in milling, some flours contain more bran than others, and some more starches and gluten.

Wheat from different countries varies in chemical composition. Ordinary bread is made from a mixture of flours derived from different wheats, and sometimes such a mixture includes different types of milling.

The average composition of wheat-flour is :

Water	13·0
Sugar	·7
Ash	·8
Fat	1·5
Proteid	11·0
Starch, dextrin, and cellulose	73·0

Physical Characters of Flour.—Flour should be free from acidity, white in colour, and smooth when rubbed between the fingers. It should be entirely free from fungi and all other parasites. A yellow colour denotes age or fermentation. If flour be kept in a damp place, an odour is generated by the growth of moulds and various micro-organisms.

Gluten.—The crude proteid of flour known as gluten possesses a constituent, gliadin, which confers upon dough its characteristic adhesiveness. When dough is thoroughly washed so as to get rid of starch and all other soluble bodies, such as salts, albumin, sugar, etc., gluten remains as a somewhat tough and sticky mass; when this is blown up with a gas, it coheres sufficiently to remain in the form of a sponge. Barley, rice, and oatmeal do not contain gluten, but other forms of proteid, which are destitute of this viscid character; hence they cannot be made into bread unless mixed with a sufficient quantity of wheat-flour.

Estimation of Gluten.—Place 20 grammes of flour in a basin and stir it into a stiff dough with warm water; next thoroughly work the dough with the fingers in a fine muslin bag in a stream of running water, until all the starch and other soluble materials have been washed away. The absence of starch may be proved by the iodine test. Generally a small quantity of fats and salts (1 per cent.) remains. Now spread out the gluten in a weighed dish in a water oven; dry until a constant weight is obtained. This weight, minus the weight of the dish, represents the gluten.

A much more delicate and reliable method is the estimation of total nitrogen by Kjeldahl's process, as described in the section on milk. The total $N \times 6.3$ gives approximately the gluten. In carrying out the process, great care should be taken that no ammonia and no nitrates exist in the reagents used. If the gluten fall below 8 per cent., the flour may be regarded as not pure wheat-flour.

Ash.—The ash of wheat-flour consists principally of phosphates of potassium, magnesium, and calcium, together with mixed salts of sodium and iron, and lastly silica. The total quantity should not much exceed 1 per cent. The estimation should be done in a platinum basin, and a wholly white ash obtained. Ash amounting to 2 per cent. shows the addition of mineral adulterants.

Water.—This constituent should not exceed 16 per cent. The adulteration of wheat-flour at present consists essentially in the addition of other flours, as those of rice, maize, pea, and bean. The microscopic appearances of the different starch granules will assist in the detection of such adulterations.

Starch Granules.—To estimate the amount of starch in a substance, weigh out a gramme of the dried powdered material, and mix it with 50 c.c. of a 5 per cent. HCl solution in a flask, to which a reflex condenser is attached; boil for several hours under a hood: the starch is converted into sugar (dextrose). Make the solution slightly alkaline with NaOH solution, and estimate the dextrose by Fehling's method. The result, multiplied by .9, gives the quantity of starch in a gramme. Where cellulose is present, the small amount converted into sugar may be ignored. The microscopic appearances of many starch granules are such as to afford an easy means of recognition. If a mere speck of a particular flour or powdered starch be placed on a microscopic slide, a drop of water added, and a cover-slip applied, the starch granules can be thoroughly studied by low and high powers of the microscope. As in mounting specimens of bacteria, it should be noted that it is almost impossible to apply too little of the material to the slide. The student should observe that in most cases characteristic cells appear, but that many cells may be unrecognisable, as belonging to any particular kind of starch. Where starch granules of different food-stuffs closely resemble each other, it may be quite impossible to decide whether or not slight admixture has been effected. On the other hand, when the granules are dissimilar the slightest admixture is easily detected.

If an estimation of the amount of the adulteration be required, a rough average percentage of the foreign granules may be obtained by counting a number of fields, and this estimation may be checked by making a mixture containing the true and foreign ingredients in the proportions observed; such mixture should present the same microscopic appearances as the original. Several trials may be made in this way before the required match is obtained. The student should carefully study the microscopic characters of all starch granules occurring in vegetable foods, and make drawings of them.

1. **Granules of Wheat, Barley, and Rye.**—*Wheat.*—These are (1) large, round, or oval, which do not exhibit concentric striæ; (2) small, ill-defined granules scattered irregularly throughout the field. Intermediate sizes are rare.

Barley.—These are (1) large, (2) small, (3) intermediate in size. In a very few are there any markings.

Rye.—These are very similar to those of barley, except that in the large granules some show a rayed hilum and cracked edges; the large granules are more generally circular and flattened than those of wheat and barley, and somewhat larger.

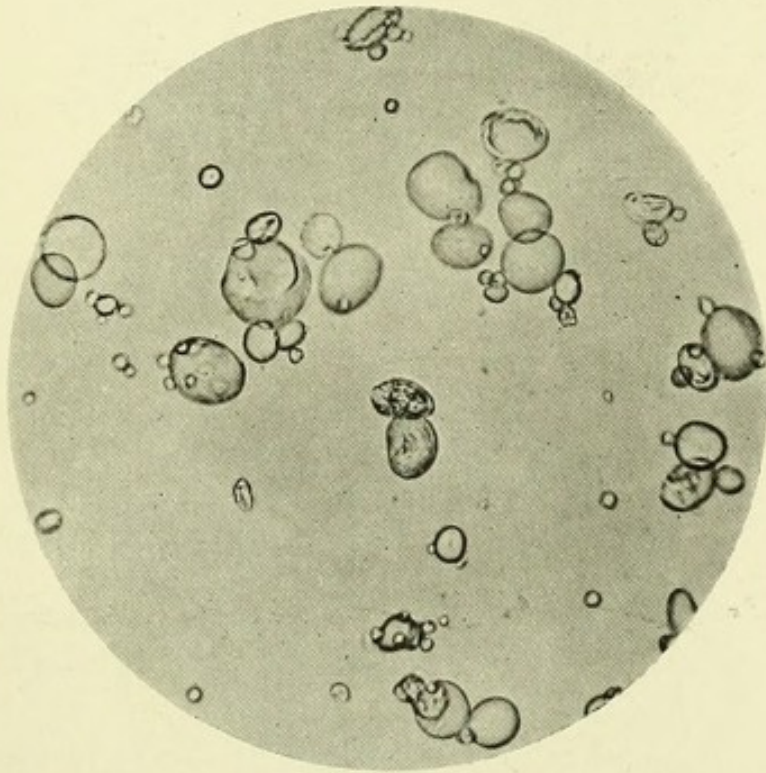
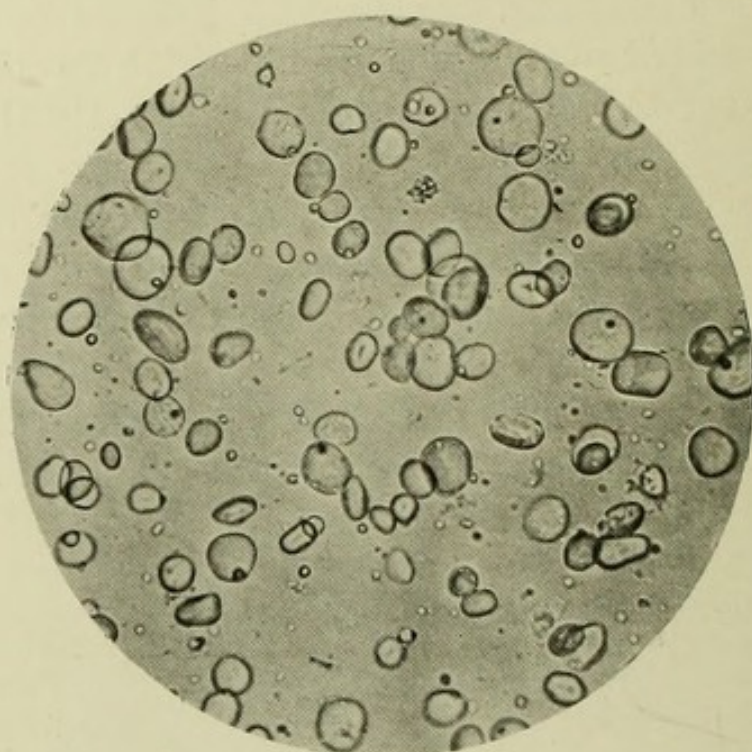
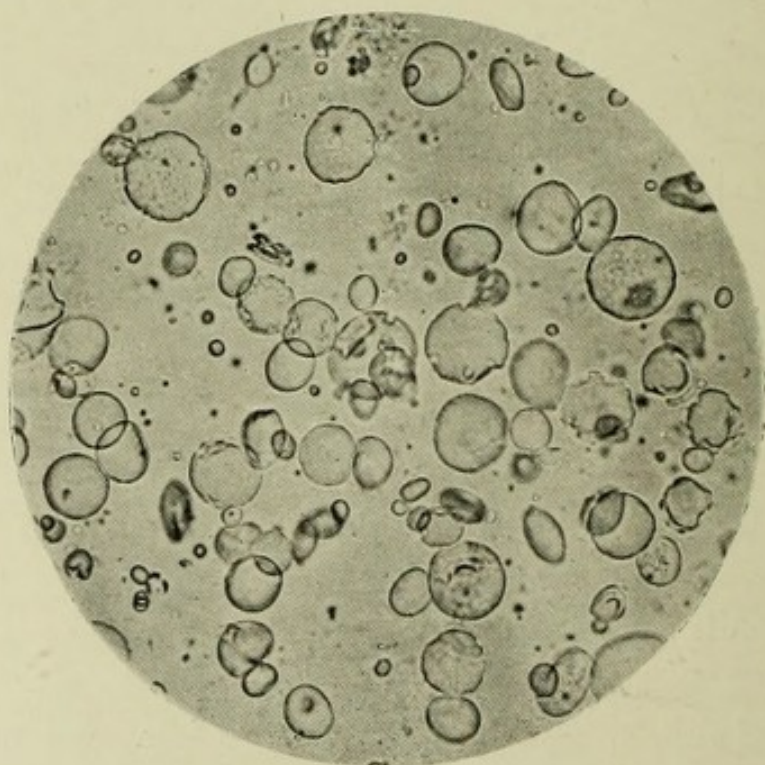


FIG. 32.—WHEAT. $\times 200$.

2. **Rice, Oatmeal, and Maize** exhibit small faceted and angular granules destitute of concentric markings. The granules of rice are small, and collect in part into angular masses. Those of oatmeal are slightly larger, and collect into rounded masses. Maize granules are much larger and more irregular in shape, and most of them possess a stellate hilum.

3. **Sago and Tapioca.**—These granules are irregular in outline, being angular and partially rounded; they are irregular in size, and mostly possess a central hilum; occasionally they exhibit

FIG. 33.—BARLEY. $\times 200$.FIG. 34.—RYE. $\times 200$.

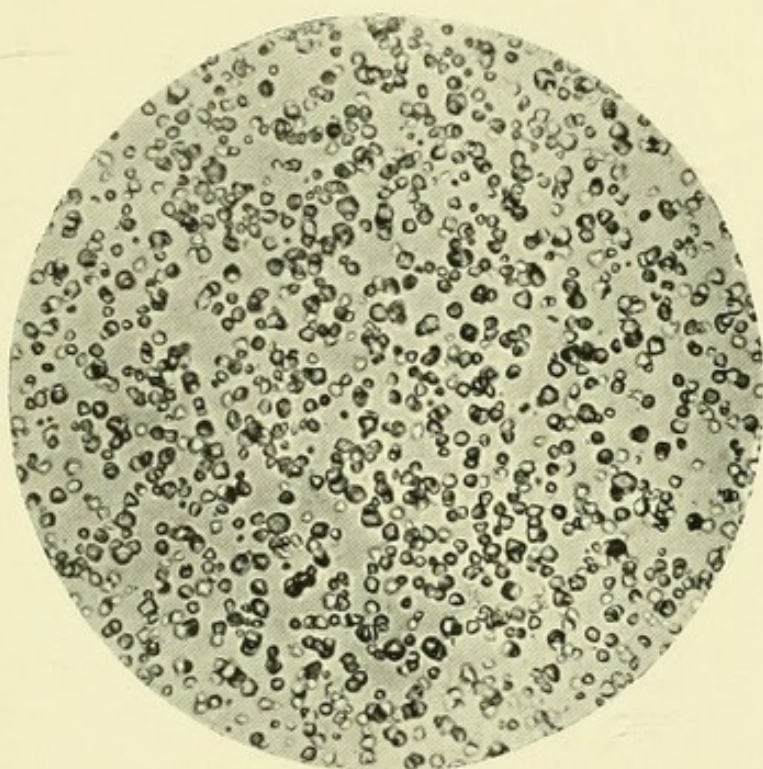


FIG. 35.—RICE. $\times 200$.

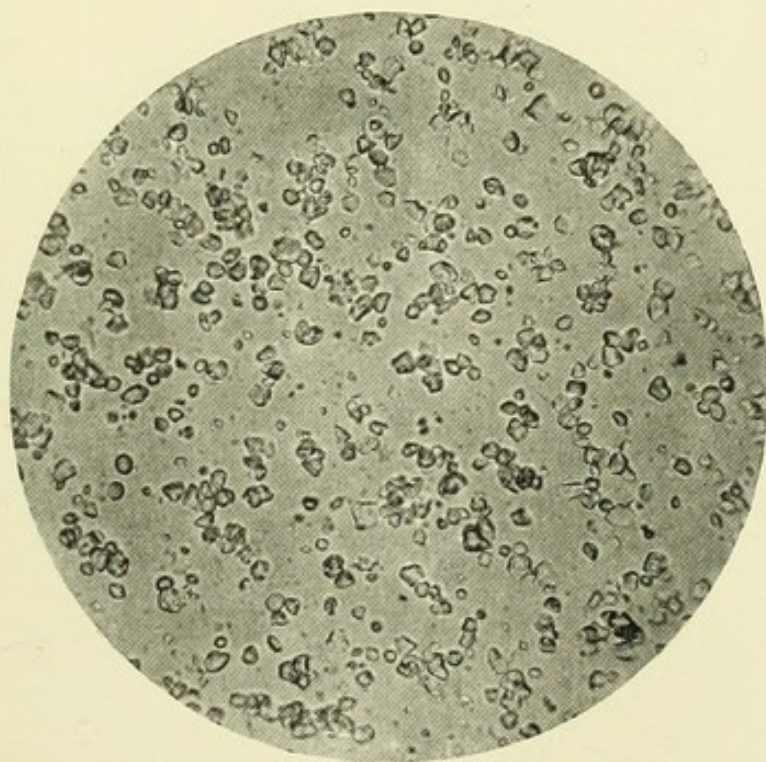
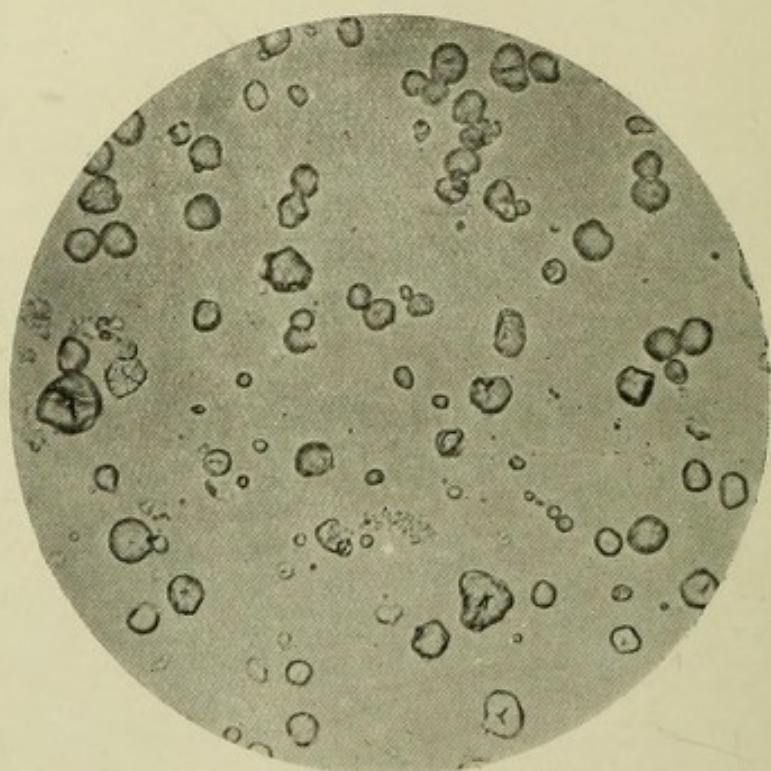
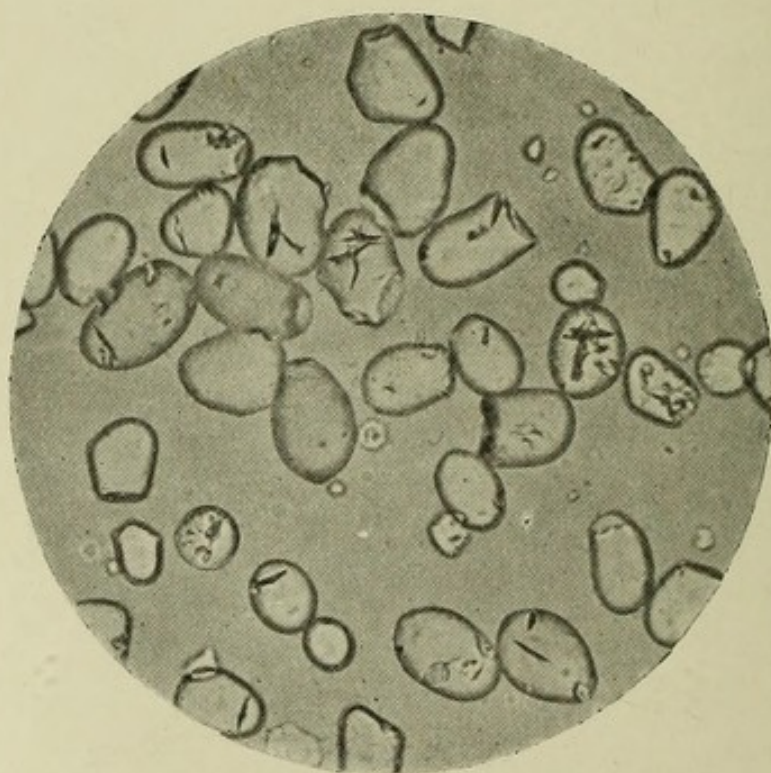


FIG. 36.—OAT. $\times 200$.

FIG. 37.—MAIZE. $\times 200$.FIG. 38.—SAGO. $\times 200$.

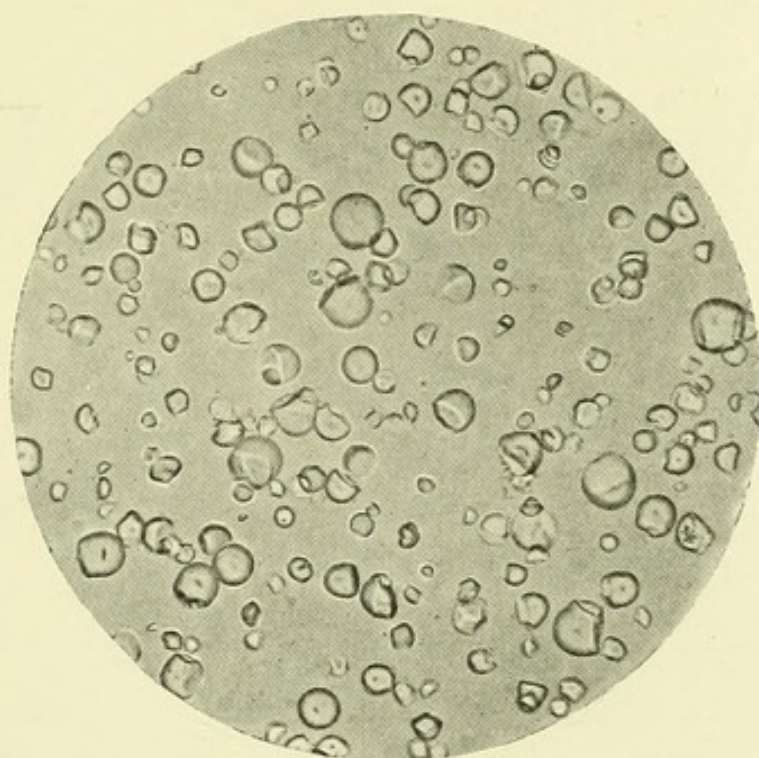


FIG. 39.—TAPIOCA. $\times 200$.

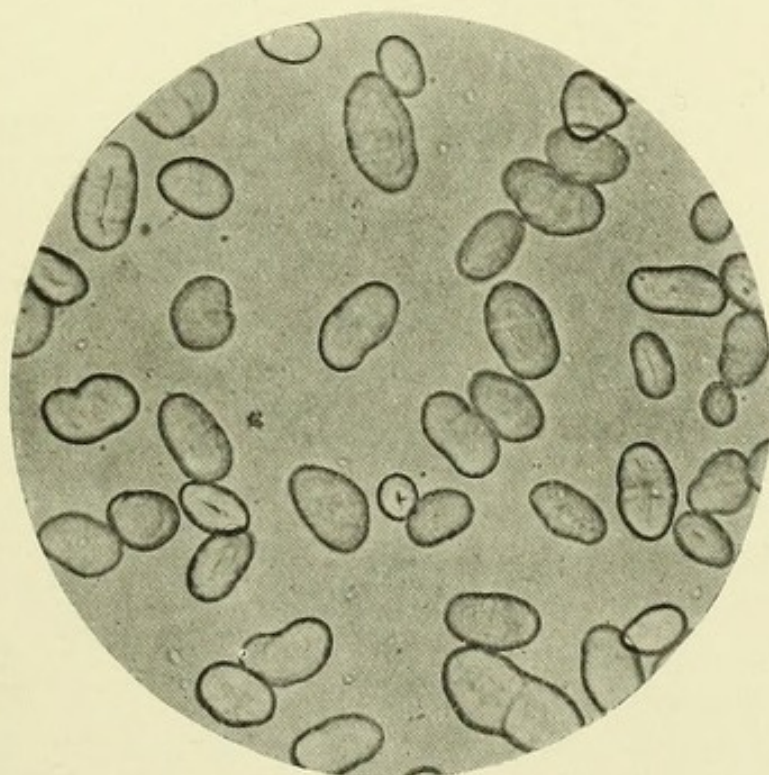


FIG. 40.—PEA. $\times 200$.

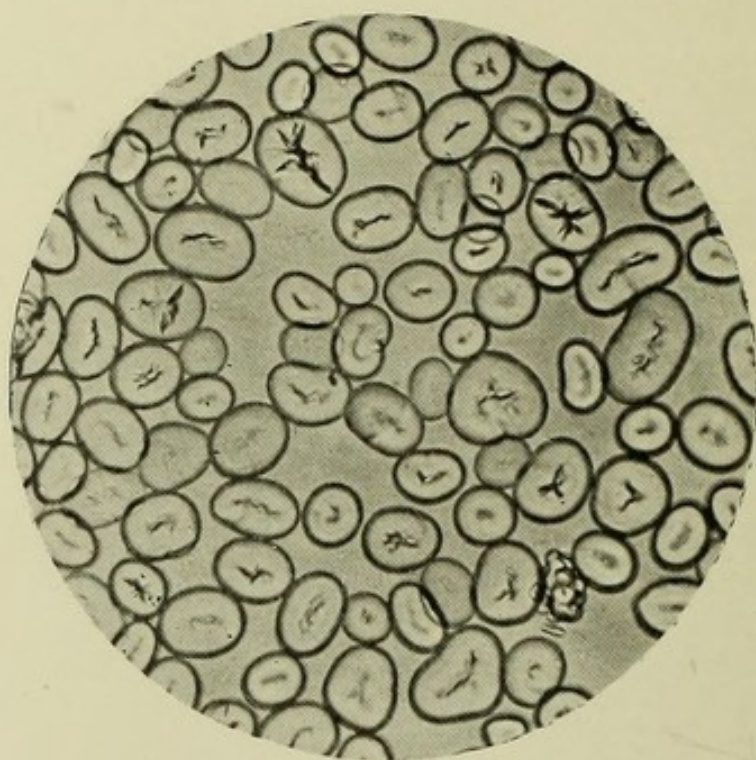


FIG. 41.—HARICOT BEAN. $\times 200$.

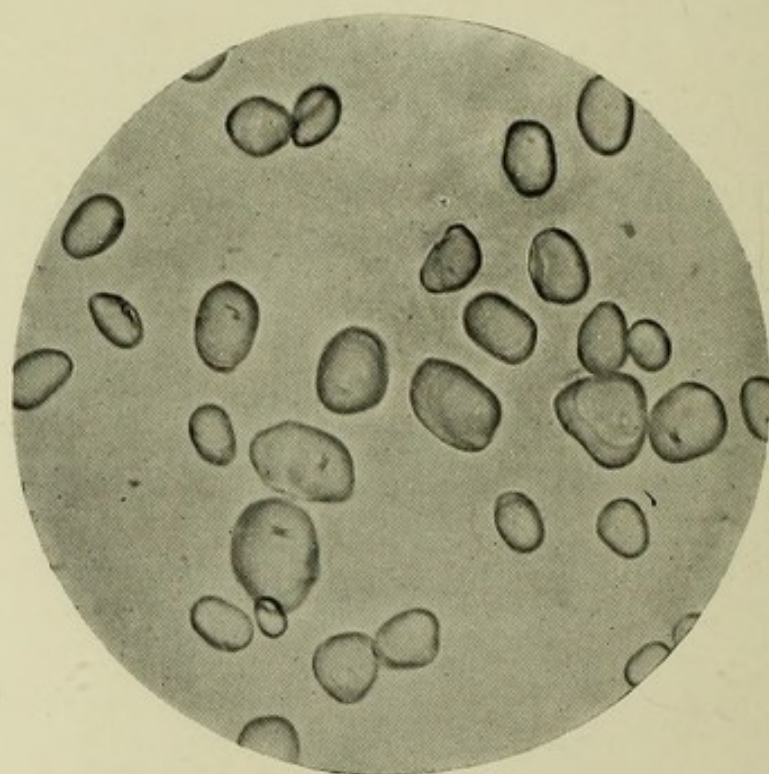


FIG. 42.—ARROWROOT. $\times 200$.

concentric striæ. Sago granules are large and very irregular in shape—for the most part somewhat rounded at one side and truncated at the opposite; the hilum is either stellate or linear. Tapioca granules are much smaller, and the hilum is generally placed towards the rounded extremity.

4. **Pea and Bean.**—These granules are oval in form, fairly uniform in size, and possess a central linear hilum and faint concentric striæ. Those of the pea present a central longitudinal hilum, sometimes exhibiting cross-striation. The granules of the

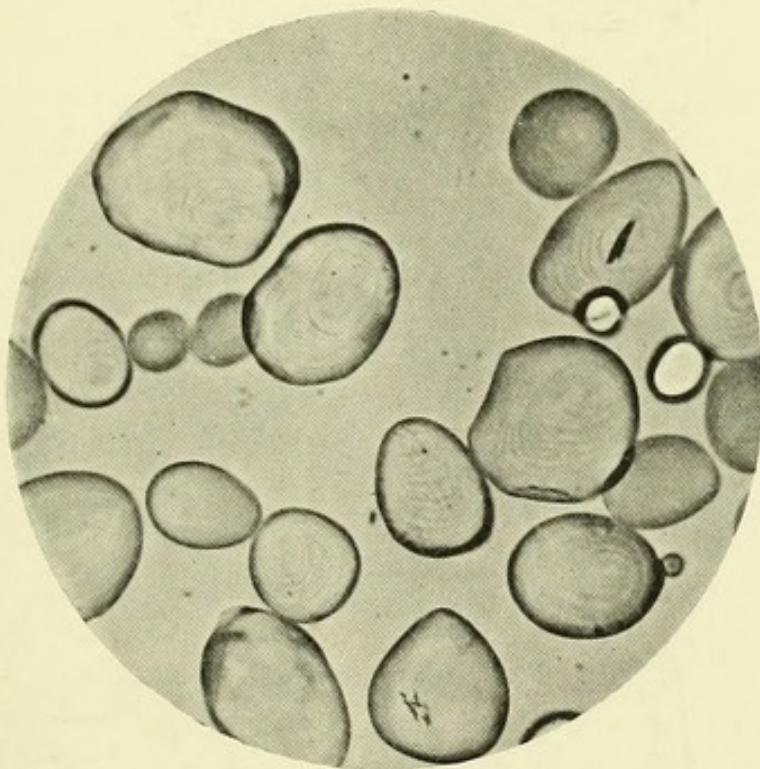


FIG. 43.—POTATO. $\times 200$.

bean are somewhat larger and broader, and the cross-striation of the central hilum is more marked.

5. **Arrowroot and Potato.**—The granules of these starches are large, pyriform, and marked distinctly with concentric striæ. A circular hilum is found in both, placed at the large extremity in arrowroot, and at the small in potato. The granules of arrowroot do not swell in a solution of KOH, as do those of the potato.

Parasites found in Wheat and Flour.—*Animal: Tylenchus tritici* (ear cockle).—In the infected ears of grain are to be seen the larvæ of a nematode worm, occurring as a white powder in dark misshapen grains. Specimens may be mounted directly in

Farrant's solution, or dehydrated and cleared in the ordinary manner, and mounted in Canada balsam.

Bruchus pisi and *Calandra granaria* are beetles (Coleoptera) which infest grain and pulses. The first attacks the pea, an allied species the bean, whilst *Calandra* is found in grain. The female

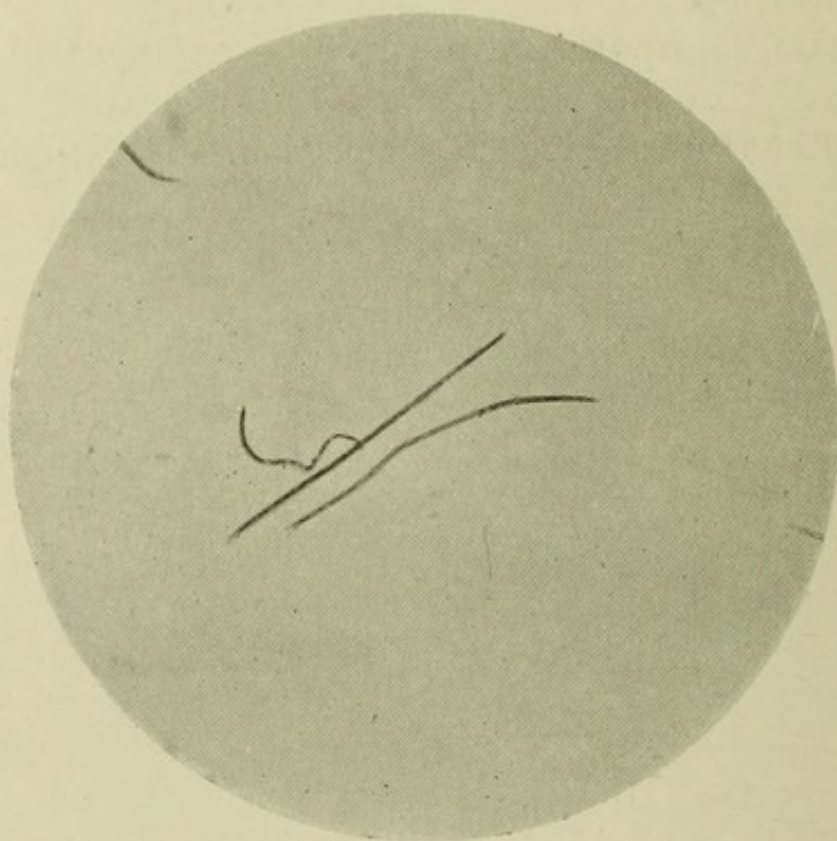


FIG. 44.—VIBRIO TRITICI. $\times 30$.



FIG. 45.—BRUCHUS PISI.



FIG. 46.—ACARUS FARINÆ.

lays her eggs in the young fruit, and the larvæ destroy the internal parts. The *C. granaria* perforates the husk of the grain and abstracts the contents.

Acarus Farinæ.—This parasite [is found in inferior] and damp flour. It may be distinguished from the *A. scabei* by its legs

remaining thick up to their extremities, whilst in the itch parasite the distal ends of the legs are quite thin.

Vegetable Parasites found in Wheat, Flour, Bread, etc.

— **Moulds** : *Penicillium glaucum*, *Aspergillus glaucus*, *Mucor mucedo*, and *Peronospora*.—These moulds are easily distinguished

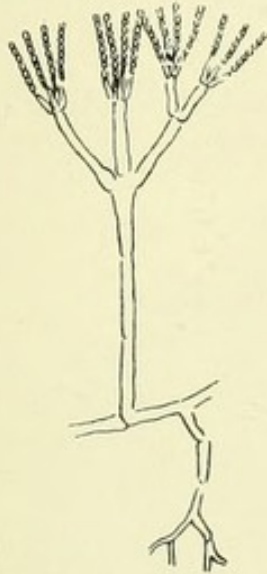


FIG. 47.—PENICILLIUM
GLAUCUM.



FIG. 48.—ASPERGILLUS
GLAUCUS.

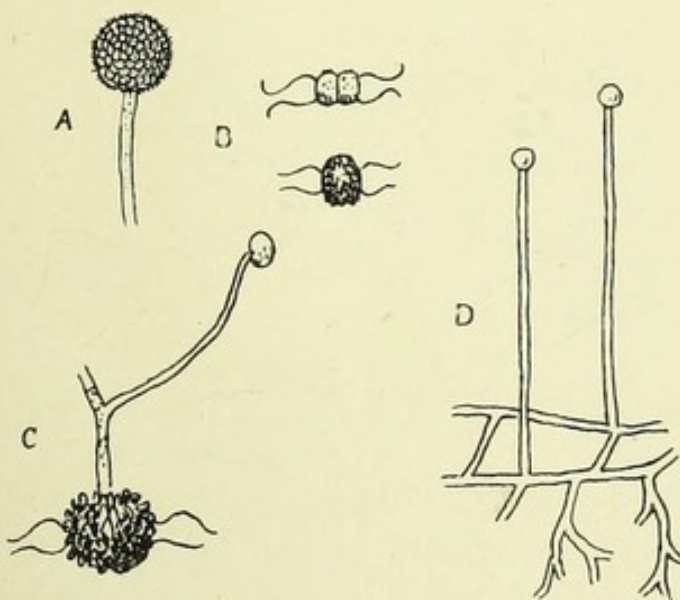


FIG. 49.—MUCOR MUCEDO.

A, Head ; B and C, conjugation ;
D, spore-bearing hyphæ.

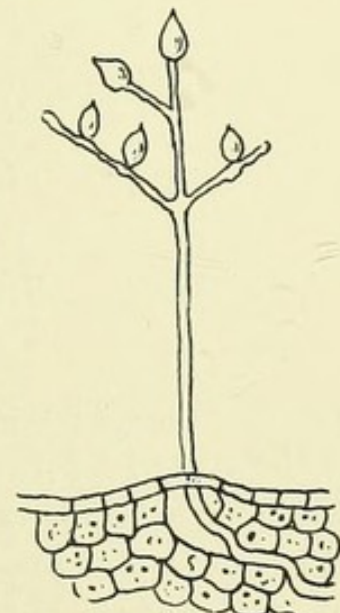


FIG. 50.—PERONOSPORA.

by the characters of the ends of the spore-bearing hyphæ. In penicillium the last hypha branches into three or four terminal filaments, which develop round or oval spores in rows in their

long axes. In aspergillus the end of the spore-bearing hypha enlarges, and from this pedicle-bearing spores grow out and form a more or less dense head. In mucor the end of the spore-bearing hypha enlarges greatly, and the spores, instead of growing out from the enlargement, as in aspergillus, grow inside a membrane which surrounds the head. When the spores have matured, the membrane ruptures and sets them free.

Peronospora, which caused the Irish potato famine of 1847, first affects the leaves, then travels down the stem, and finally attacks

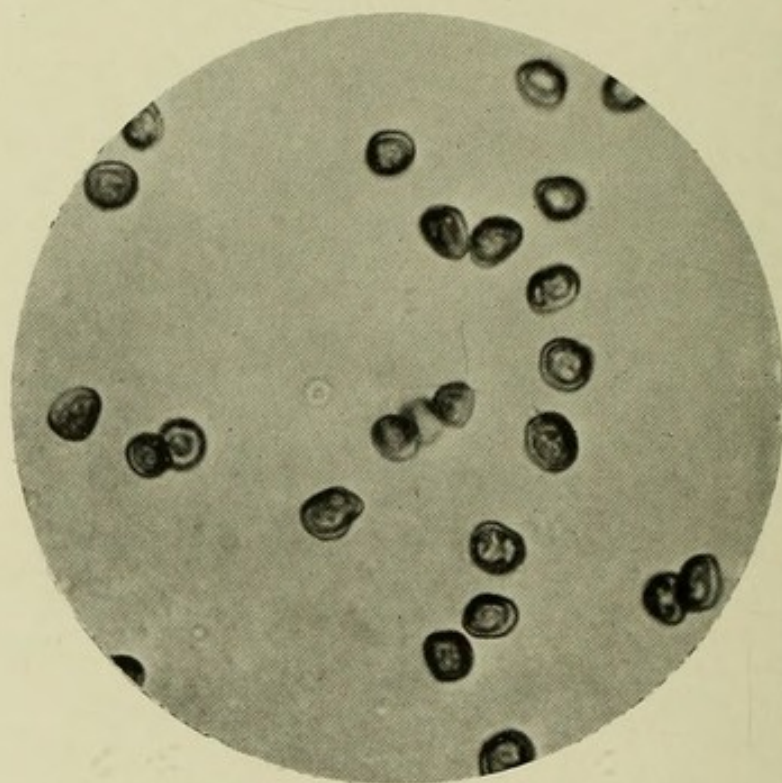


FIG. 51.—USTILAGO SEGETUM. $\times 250$.

the tubers. The spore-bearing hyphæ branch and rebranch, and at the end of a terminal branch a single spore is developed.

Ustilago Segetum (smut).—The spores of this parasite are found as a black powder infesting ill-developed ears of corn, and fall off when the ear is rubbed. Examined microscopically, they are seen to be brown, spherical, free spores.

Tilletia caries (bunt) is another member of the ustilaginæ, and is found in the interior of the grain; it may escape detection until the process of milling takes place. The spores are brown, spherical bodies, generally free, and give to the interior of the affected grain a sooty appearance and foetid odour. These spores germinate in

the spring, forming a hypha called the promycelium, which bears promycelial thread-like spores. The next stage in the life-history of this organism is the conjugation of contiguous spores. Two such conjugated spores bud and form an elongated secondary promycelial spore, which, if it find a suitable host, sends out hyphæ and enters the interior of the grain, where a mycelium is developed. After a time the hyphæ swell, become dark in colour, and a differentiation into spores takes place. As these ripen, the mycelial

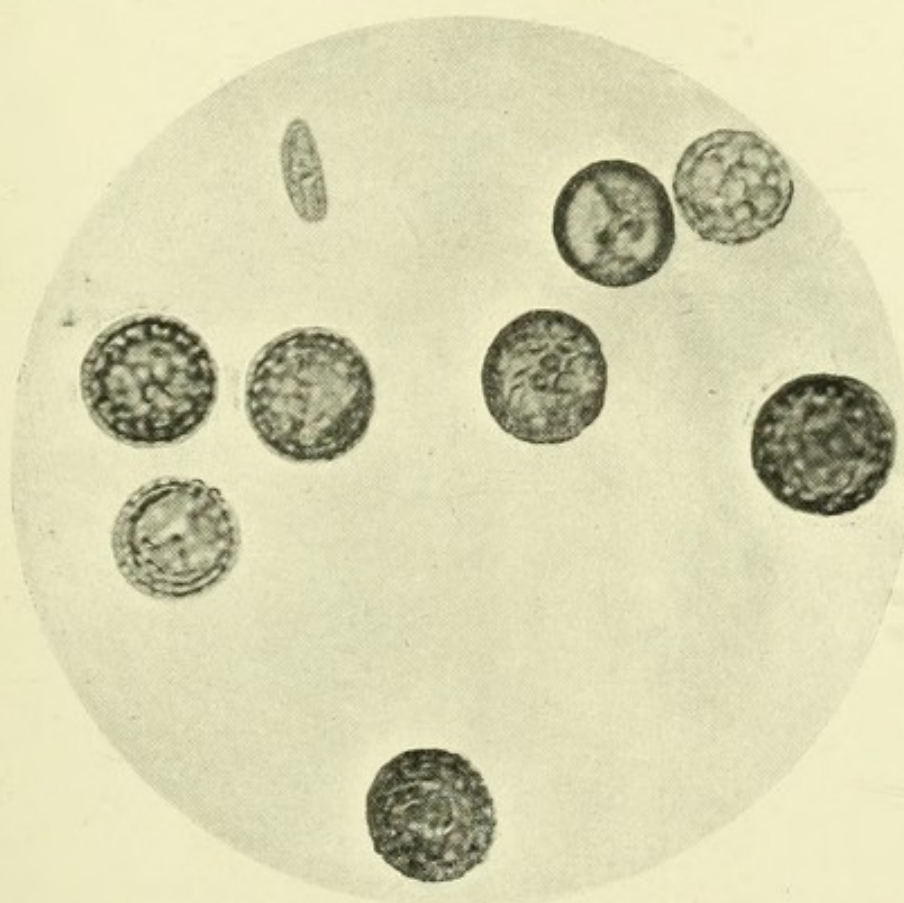


FIG. 52.—TILLETIA CARIES (UREDIO FÆTIDA). $\times 250$.

structure disappears, and leaves the resting spores in the condition from which the cycle commenced.

Puccinia graminis is one of a large number of parasitic species affecting corn in the manner above described. A spore attaches itself to a grain or stem, and sends hyphæ into its substance, from which a mycelium and spores are formed within; as a result, the grain ruptures, and the spores appear on the surface as rust. A distinctive feature of puccinia is the double spore attached to a peduncle. It is this form which is found attached to grain or grass

in the autumn, as rust, and which, known by the name teleutospore, remains quiescent during winter. In spring it germinates, and produces a non-parasitic mycelium. The individual cells of this mycelium produce filaments, known as gonidiophores, which in turn produce spores at their free ends. Distributed by the wind, these latter fall on the leaves of the barberry, where they germinate and form a dense mycelium in the substance of the leaf, giving rise to swellings which project on its under surface. Spherical structures, termed *æcidia*, form on the surface of a swelling, and

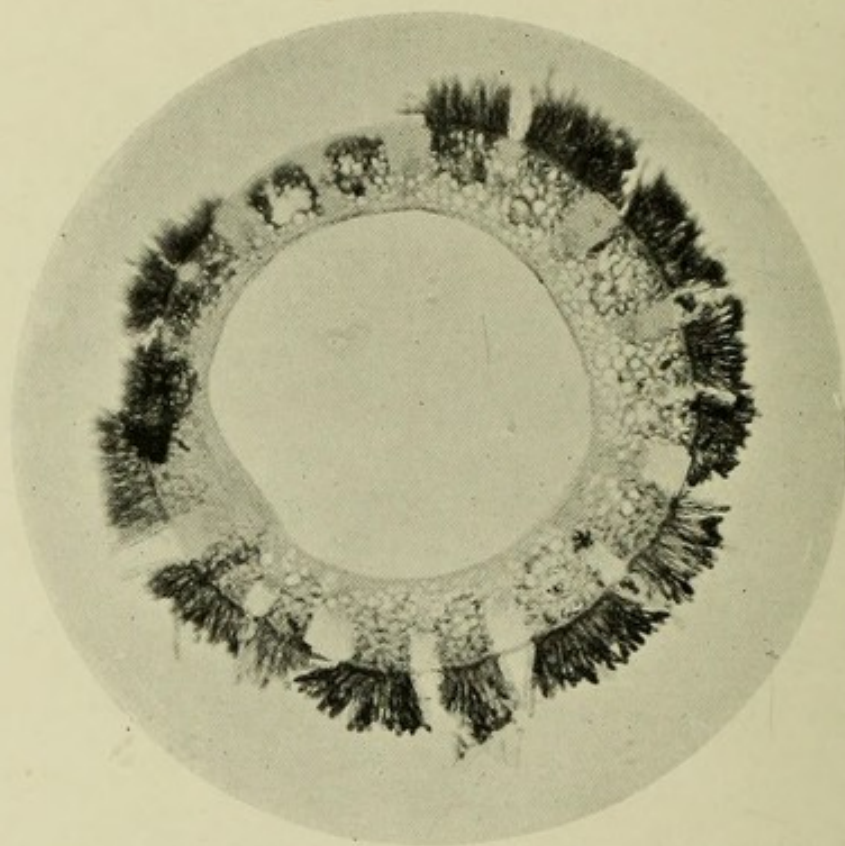


FIG. 53.—WHEAT STEM INFECTED WITH PUCCINIA.

develop within themselves spores which are set free on rupture of the wall of the *æcidium*. These spores are carried by the wind to grass plants, to which they attach themselves and develop a mycelium from which grow certain hyphæ, bearing single spores (*uredogonidia*). On rupture of the leaf of the host, the spores are to be seen as a yellow dust. Again the wind carries the gonidium to another grass, where it germinates, produces hyphæ, and repeats the previous process (*uredo* form). As the autumn approaches, special hyphæ produce gonidia, which have a septum perpendicular to the long axis, dividing the spore into two cells—the teleuto-

spore—which rests through the winter, and commences the cycle once more in the following spring.

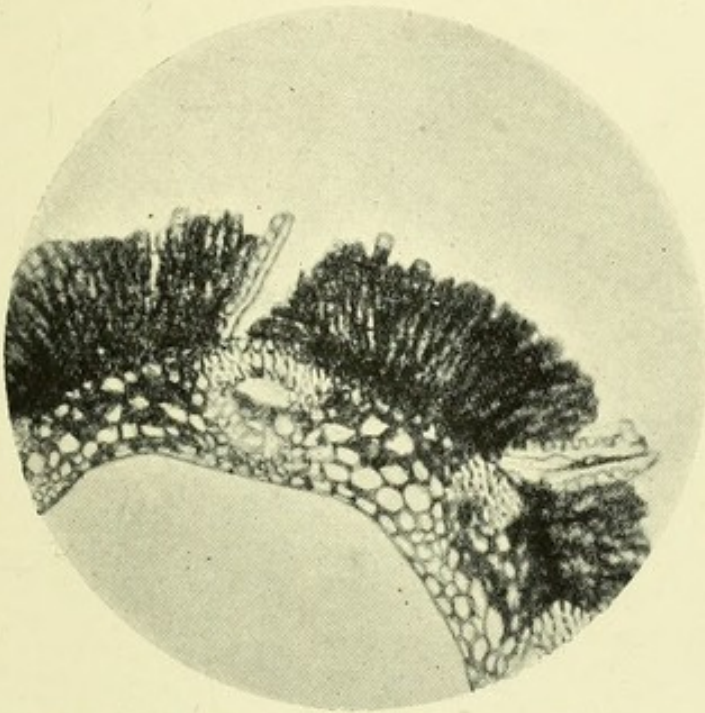


FIG. 54.—PORTION OF FIG. 48 SLIGHTLY MORE HIGHLY MAGNIFIED.

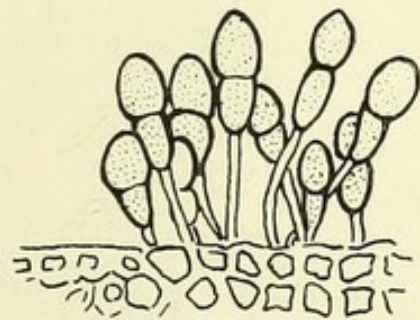


FIG. 55.—TELEUTOSPORES.

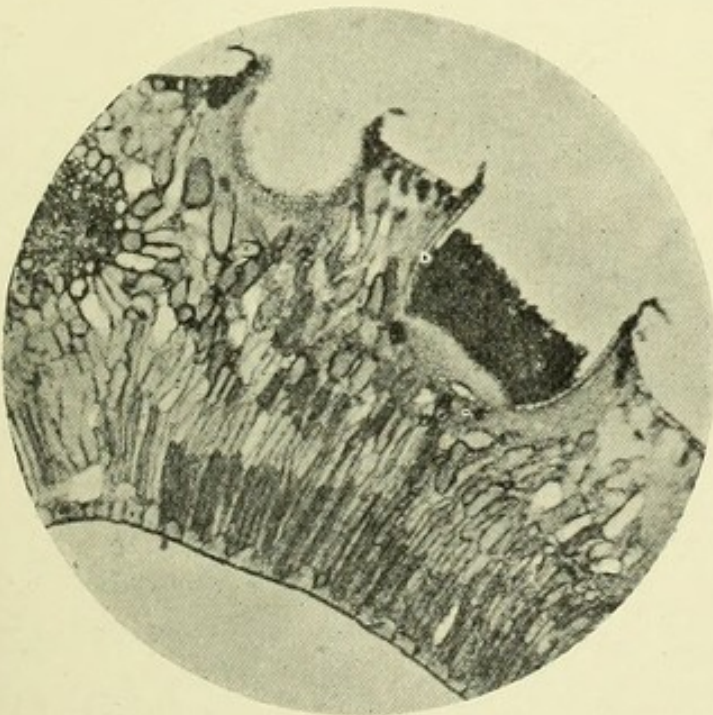


FIG. 56.—ÆCIDIUM BERBERIDIS.

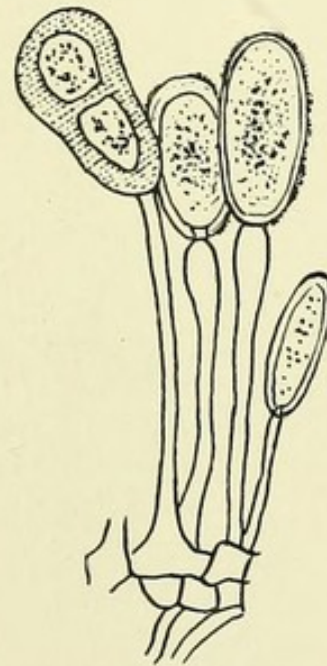


FIG. 57.—GONIDIOSPORES (UREDOPHORIA) AND TELEUTOSPORE.

Claviceps purpurea (ergot) grows in rye, and the mycelial growth (sclerotium) replaces the grain. The ergot masses (or grains) are

larger than the rye-grains, and of a deep purple colour. In the spring the sclerotium, which has rested through the winter, ger-

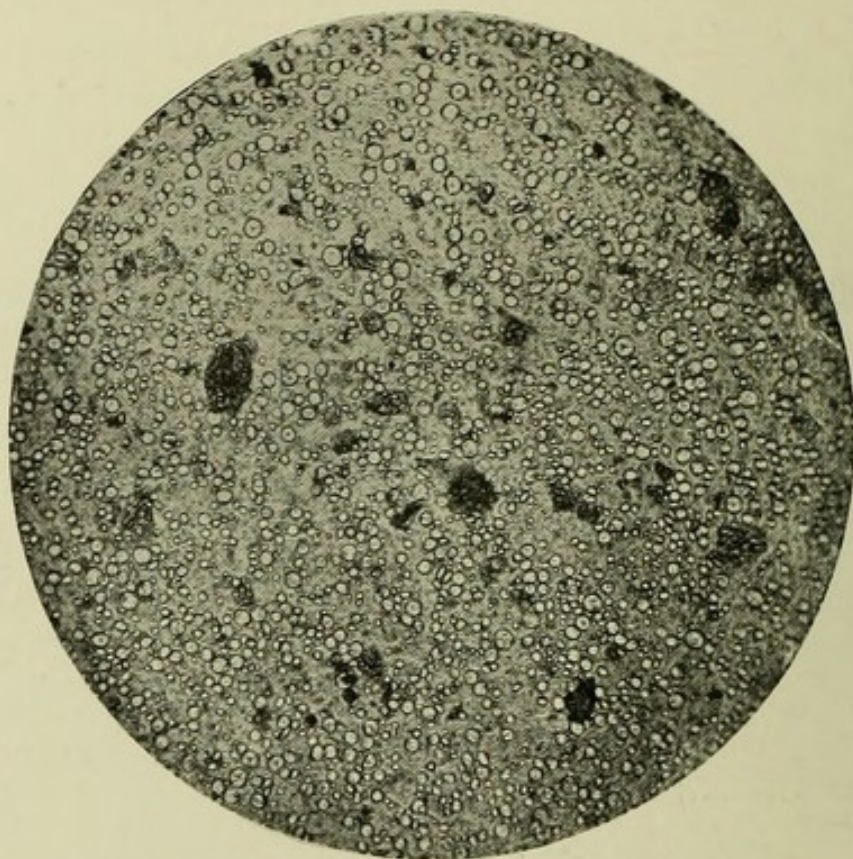


FIG. 58.—ERGOT IN RYE. $\times 30$.

minates, and produces long hyphæ (stromata), which develop a swelling at the distal end, which latter contains oval receptacles



FIG. 59.—SCLEROTIUM BEARING STROMATA. $\times 1$.

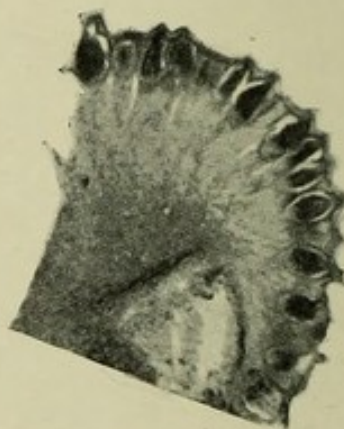


FIG. 60.—STROMA CONTAINING ASCOCARPS. $\times 75$.

(ascocarps). Attached to the inner end of the ascocarps are asci, containing eight filiform spores (ascospores). The asci rupture

and the spores escape. Carried by the wind, the spores alight on the ovary of the rye flower and form a mycelium. On the surface of this mycelium free spores (gonidia) develop, and are surrounded by a viscid substance, known as honey-dew, which attracts insects, by which the spores are carried to other flowers, where the process is repeated. This stage is known as the sphacelia form.

As the rye is developed, the mycelial growth increases to such an extent that the young grain is wholly absorbed, the pericarp is no longer able to contain it, and it projects like a spur from the

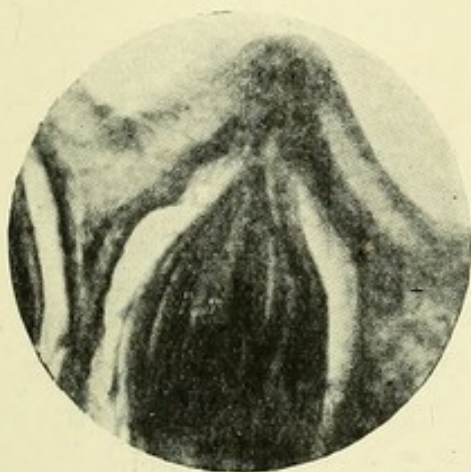


FIG. 61.—ASCOCARP CONTAINING
ASCI. $\times 350$.



FIG. 62.—ASCUS CONTAINING
ASCOSPORES.

spike. Ultimately it falls to the ground. The cycle is repeated in the following spring.

The seeds of *Lolium temulentum*, possessing narcotic properties, may gain access to flour, but rarely produce poisoning.

Bread.

Bread is chiefly made from wheat-flour. A dough is first formed by mixing the flour with water or other fluid, and a gas, generally CO_2 , is passed through it. Carbon dioxide is obtained either by the action of yeast or sugar, when this gas and alcohol are formed, or through the liberation of the gas from an alkaline bicarbonate by the action of an organic acid. The dough is sometimes aerated by charging water with air and mixing this with flour under pressure

in air-tight chambers ; afterwards the pressure is lowered by opening a trap, when the dough is blown up by the expanding gas, forming 'aerated' bread. The dough is then cooked in an oven at a temperature of about 400° F.

Composition of White Bread :

Water	40·0
Proteids	6·5
Fat	1·0
Starch, sugar, dextrin	51·2
Cellulose	·3
Ash	1·0

Composition of Whole Meal :

Water	45·0
Proteids	6·3
Fat	1·2
Starch, sugar, dextrin	44·8
Cellulose	1·5
Ash	1·2

During the cooking a crust is formed, which should neither be very light nor very dark in colour, and which should crack readily on breaking. The shining appearance of crust is due to the formation of dextrin, and its flavour and dark colour to the production of caramel. Two-thirds of the volume of a good loaf is gas. Great whiteness in a loaf, although much desired by the public, is by no means essential from a nutritive point of view, as a very white loaf possesses a maximum of starch and a minimum of proteid.

Comparative Composition of Crust and Crumb :

					Crust.	Crumb.
Water	17·15	44·45
Insoluble proteid	7·30	5·92
Soluble proteid	5·70	·75
Dextrin and sugar	4·88	3·79
Starch	62·58	43·55
Fat	1·18	·70
Ash	1·21	·84

By these figures it is seen that there is a much larger proportion of solids, and also more soluble proteids and carbohydrates, in the

crust than in the crumb. The crumb should be elastic in consistence, should have a sweet, nutty flavour, and be of a uniform whiteness throughout. As bread grows old, it becomes hard, and it has long been known that reheating softens it. The real explanation of the staling of bread does not seem to be known. Bibra holds that in fresh bread there is free water present, which, as staleness supervenes, unites with starch or gluten, and that reheating sets this water free. He states that the freshness will not return if the bread has lost 30 per cent. of its water. Others hold that the stale condition is produced by the shrinkage which takes place in the fibres forming the walls of the pores. The water vapour formed by the second heating drives these fibres apart again. It should be noted that during the baking of bread a large proportion of the fat is lost, amounting to as much as 7 per cent. in some instances, that the proteids are diminished from 1 to 2 per cent., and the carbohydrates from 3 to 4 per cent. Some of the starch is converted into soluble starch and dextrin to the extent of 8 per cent.

The estimation of water and mineral matter in bread is performed as in the case of flour. Twenty grammes of the crumb make a convenient quantity with which to work.

The ash is generally greater in weight than that of the flour used, owing to the sodium chloride, baking-powder, etc., added. Any excess of ash above 3 per cent. is generally regarded as due to salts added in order to improve the colour.

Silica is estimated by treating the ash with strong HCl and hot distilled water in a platinum dish, then filtering through a Swedish filter-paper, and carefully washing the platinum dish with further boiling distilled water, transferring the washings to the filter-paper. When the residue on the filter has been several times washed with boiling distilled water so that all soluble substances have passed through, it is dried in a water oven, transferred to a porcelain crucible, ignited, and weighed as silica. It should not exceed 2 per cent.

Acidity.—Soak 5 grammes of bread in 50 c.c. of water for an hour. Filter and titrate the filtrate with $\frac{N}{10}$ NaOH, using phenol phthalein as indicator. The number of c.c. of decinormal soda used multiplied by 6 equals milligrammes of glacial acetic acid

in 5 grammes of bread. The acidity should not exceed .11 per cent.

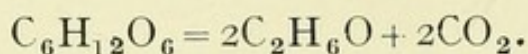
Adulteration.—Formerly alum was used to whiten inferior flours, but at present it is practically never found. The detection of alum in bread is carried out as follows : Dissolve a small quantity of hæmatoxylin in alcohol, and to this add a little freshly-prepared solution of ammonium carbonate in distilled water. Cubes of crumb are cut from the centre of a loaf, and small quantities of the solution poured upon them, after which they are removed to a water oven and dried at a low temperature. The production of a permanent lavender colour denotes the presence of alum. To a small degree magnesium salts simulate alum in this reaction, but the colour on drying is not so permanent. Silicate of alumina exists normally in flour, but in such small quantities that a 4-pound loaf will not contain more than 6 or 7 grains. The part played by alum when added to inferior flours is its checking fermentation, which otherwise would lead to the production of glucose, and consequently a discoloured bread. It is stated that alum increases the porosity of bread. This adulterant has been found in quantities ranging from 20 grains to 100 grains per 4-pound loaf.

Quantitative Estimation.—Reduce $\frac{1}{4}$ pound of the bread to ash, and separate off the silica on a filter by treatment with strong HCl and boiling water in the usual manner. The filtrate contains phosphates of lime and magnesia, iron, and aluminium. To this solution add 5 c.c. of $(\text{NH}_4)\text{HO}$, which will precipitate all the phosphates, and 20 c.c. of strong acetic acid, which redissolves the phosphates of lime and magnesia. Filter and wash the residue of phosphates of iron and aluminium with boiling water. Dry, ignite, and weigh. The residue is now dissolved in strong HCl, and diluted to 200 c.c., and the iron estimated colorimetrically. Convert the iron thus found into ferric phosphate by multiplying by 2.7, and subtract this from the weight of phosphates of iron and aluminium previously obtained ; deduct also the weight of the filter ash, and the difference is aluminium phosphate, which may be returned as commercial alum (crystallized ammonium alum) by multiplying by 3.7.

CHAPTER XXIV

ALCOHOL, ETC.

ETHYL alcohol is produced in all the beverages in which it is found from the fermentation of sugar by yeast.



Although alcohol is the principal constituent by which such beverages affect the nutrition of the body, it must not be forgotten that in many cases ethers, aldehydes, and other by-products of fermentation, are likewise found. Alcohol to the extent of 1 per cent. seems to be favourable to a digesting mixture in the stomach; 10 per cent. slightly retards gastric digestion, and 20 per cent. arrests it. Pancreatic digestion is much more sensitive to alcohol; but as digestion is not only a chemical process, but greatly influenced by the movements of the stomach and various other factors differing widely in different individuals, it is not surprising to find that alcohol has very different effects in its relation to individual cases. It is admitted on all hands that it quickens the activity of stomach movements and secretions. If the retarding influence of alcohol on the chemical part of digestion be weighed against its quickening influence on the flow of gastric juice and on gastric peristalsis, the balance is in favour of its use as a digestive stimulant. In certain conditions of disease these properties are greatly enhanced. Alcohol, unlike water, is freely absorbed by the mucous membrane of the stomach, and requires no digestion. It passes into the blood at once. Not only is it rapidly absorbed itself, but it assists the absorption of other bodies. Whilst it passes from the stomach into the blood, water passes from the blood into the stomach; the endosmotic equivalent of alcohol is 4.2, which means that for

every gramme of alcohol passing through an animal membrane in one direction, 4.2 grammes of water pass in the opposite.

Estimation of Alcohol in Brandy, Whisky, Beer, etc.—Place 300 c.c. of the beverage in a distillation flask and distil over two-thirds of this volume. Make up the distillate to the original 300 c.c. with distilled water, and determine the specific gravity of the mixture. From a table of specific gravities of different

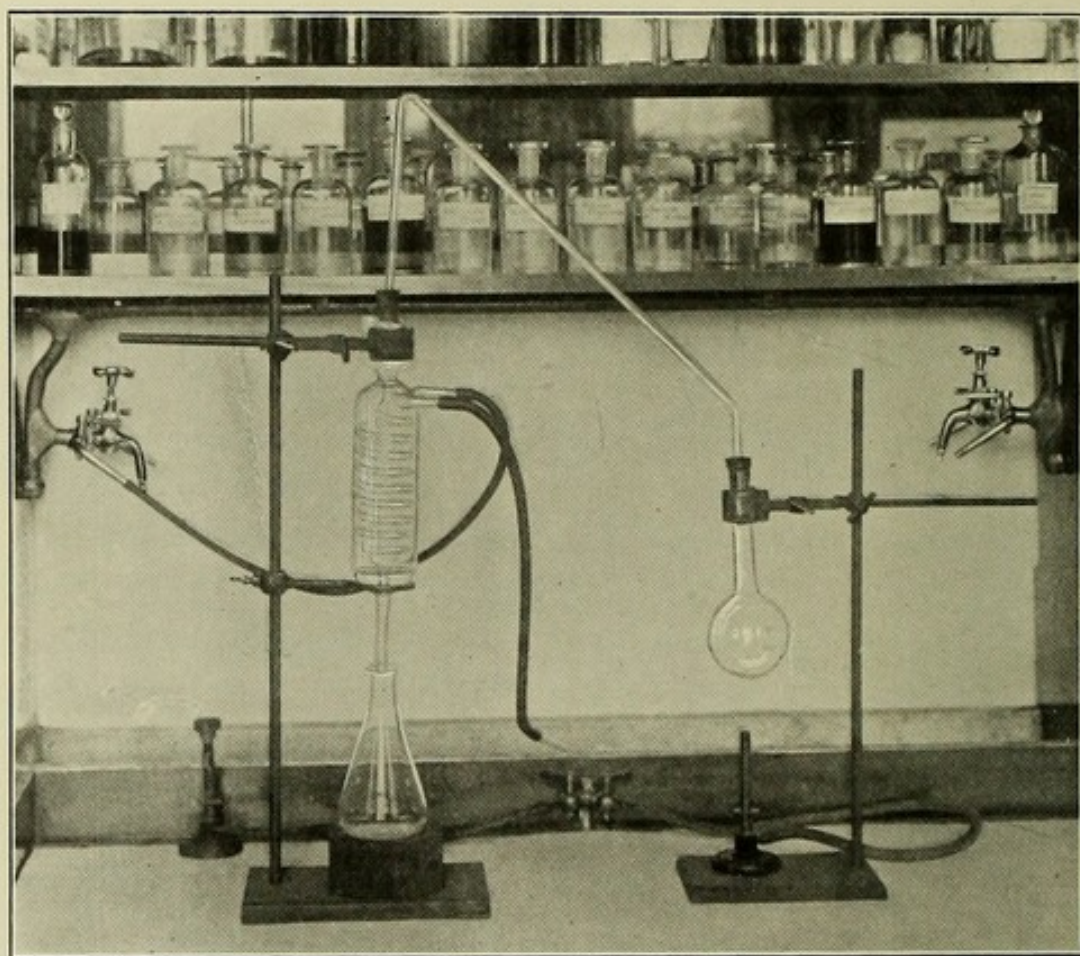


FIG. 63.—ESTIMATION OF ALCOHOL.

dilutions of alcohol in water read off the volume of alcohol corresponding with the figure obtained.

Spirits.—Whisky is made from malt, or malt and grain, and distilled in pot-stills. It is important to distinguish between genuine malt whisky, which is made in pot-stills, and grain whisky, which is prepared in patent stills. Malt whisky is made from malted barley, which is first dried and then made into a mash; subsequently the mash is fermented and afterwards distilled through a worm-still, heated over an open flame. This method of heating

produces a slight charring in some of the sugars, whereby furfural and other bodies characteristic of pot-still whisky are produced. The by-products, including fusel oil, are not separated from the spirit; hence this kind of whisky when young has a harsh and disagreeable taste, which mellows, however, when matured in casks. It is doubtful whether such maturation decreases to any degree the fusel oil. Grain whisky is made from a mixture of barley, rye, and maize, with just sufficient malt to convert their starch into sugar, and distilled by steam in a patent still, so that fusel oil and other by-products are largely separated from the alcohol. It is generally stored in old sherry casks, whereby a yellow colour is imparted to it. When taken from the still, it is about 60 degrees over proof, but its strength is generally diminished to 11 or 12 degrees before bonding. The strength of malt whisky when taken from the still is very variable, ranging from 10 to 50 degrees over proof, which likewise is reduced to 11 or 12 degrees over proof before bonding. It will thus be seen that patent still whisky is much purer than pot-still, containing, as it does, less by-products of fermentation. It should be further noted that, in consequence, patent still whisky does not improve so much on keeping as does pot-still whisky.

Brandy.—True brandy is distilled wine, and was originally procured from a rich cognac district in France. Its quality varies with the character of the grapes used, the best grapes yielding grande champagne, a genuine liqueur brandy. It is to be feared that little of the brandy sold in this country is so derived. Brandy contains, besides ethyl alcohol, volatile ethers in large amount, an important distinction from whisky. Its percentage of alcohol is about the same as that of whisky.

Rum is prepared from molasses, a by-product in the manufacture of sugar, but the best varieties are obtained by fermenting the juice of the sugar-cane. One by-product—ethyl butyrate—confers upon it its characteristic flavour. Like brandy, however, much of the rum sold in this country is made from silent spirit, flavoured with characteristic by-products.

Gin is prepared by distilling and redistilling a mixture of rye and malt. In the last distillation, juniper berries, salt, and hops are added, and the product is run off into cisterns lined with white

tiles, whereby colouring matters are prevented entering the spirit. The best gins are distilled in Holland; but much of the gin of commerce is concocted from silent spirit, resins, and juniper berries.

The term proof-spirit is applied to a mixture of 57.06 per cent. by volume of absolute alcohol in water. It has a specific gravity of 919.8 at 15° C.

Brandy, whisky, and rum may be 25 degrees under proof—that is, may contain 75 per cent. of the alcohol found in proof-spirit. Gin may be 35 degrees under proof—that is, may contain 65 per cent. of the alcohol found in proof-spirit.

Spirits generally contain 40 to 60 per cent. of alcohol; wines 8 to 16; and beers 5 to 7.

Fusel oil, or amylic alcohol, is the most important impurity of spirit. It is more injurious than ordinary alcohol, and should not be permitted to exceed .2 per cent.

Estimation of Fusel Oil: Rose's Method.—Chloroform quickly removes fusel oil from dilute spirit, and the presence of fusel oil in chloroform increases the capacity of the latter for dissolving ethylic alcohol. So, therefore, if chloroform be shaken with dilute ethyl alcohol containing fusel oil, its volume will be considerably greater than when shaken with the same volume of pure ethyl alcohol.

Into a Rose's tube of capacity 180 c.c. (graduated portion containing 50 c.c.) measure 20 c.c. chloroform. Dilute the spirit to be tested until it has the specific gravity of 934.6 at 15° C. (corresponding to 50 per cent. alcohol by volume). If the sample is weaker than 50 per cent., it must be fortified with absolute alcohol. Now run in upon the chloroform 100 c.c. of this prepared spirit; stopper the tube, and immerse in water for a short period, in order that the chloroform may settle, which operation may be hastened by occasionally tapping the tube. At the end of an hour read off the volume of the bottom layer. If the sample of spirit be pure, this volume will be 37.1 c.c. But if it contain 1 per cent. by volume of fusel oil, the bottom layer will read 39.1 c.c., thus giving 1 per cent. by volume fusel oil for 2 c.c. increase in the volume of the chloroform.

The following simple tests detect the presence of fusel oil:
(1) Distil off four-fifths of the sample, and extract the residue with

ether; allow the extract to evaporate spontaneously, and treat what is left with H_2SO_4 and sodium acetate: the odour of pear is emitted. (2) Evaporate 50 c.c. slowly over a steam bath; carefully smell the remainder for traces of fusel oil. (3) Decolourize a portion of the sample with animal charcoal, and add a few drops each of hydrochloric acid and colourless aniline oil. In the presence of fusel oil a rose tint is produced in the aniline oil.

Tests for Methylated Spirit.—(1) Odour; (2) a weak solution of sodium nitro-prusside (1 per cent.) and ammonia, added to a mixture containing methylated spirit, give a red colour within ten or fifteen minutes.

Wines.—Wines are produced by fermenting the juice of the grape. The juice is obtained by crushing the grapes, and in order to avoid squeezing the stalks and stones too much, which would give rise to undesirable constituents, treading is the method generally adopted. Grape-juice consists of proteids, sugars, and acids. The relative proportions of proteid and sugar influence the character of the wine, as the yeast plant which furnishes the ferment lives upon the proteid, and splits the sugar, forming alcohol and other products. If yeast grow in little sugar and much proteid, it can maintain its existence until all the sugar is changed; such a wine is said to be dry and acid, like hock. Conversely, if there be much sugar and little proteid, the growth of yeast comes to an end before all the sugar is used, and that left behind produces a sweet taste in the wine. Intermediate proportions of sugar and proteids produce corresponding results. It may be noted, though, that no matter what the proportions of proteid and sugar, fermentation cannot proceed after 16 volumes per cent. of alcohol have appeared in the liquid; this is why a natural wine can never contain more than this proportion of alcohol. Sherry and port are fortified wines—that is, containing, as they do, more than 16 per cent. of alcohol, they have the difference added to them. Claret and hock are natural wines. The quality of wine depends on the species of yeast used, the variety of grape, the soil and climatic conditions of growth of the grape, and the mode of its cultivation. The colour of red wines is produced by a pigment residing in the skins of the grapes, which is turned red by the acids present. As alcohol is produced, it dissolves out this pigment, and so colours

the distillate. Wine, when placed in casks, undergoes important changes: water evaporates more quickly through the wood-work than does the alcohol, and so the alcohol becomes concentrated. Further, some oxidation of the tannic acid takes place; this causes white wines to be somewhat darker in colour, and red wines lighter, through the carrying down of some of their pigments by oxidized tannic acid. Frequently a small amount of yeast enters the cask, and continues the fermentation, thereby increasing the quantity of alcohol. With the lapse of time, some of the alcohol is oxidized into acetic acid, and certain compound ethers are formed. Wine in bottles adds to its contained ethers, although its alcoholic strength rarely, if ever, increases. It is an error to suppose that very old wine contains most alcohol: slow oxidation in the case of wines, as in all other organic compounds, produces degeneration. It is more than probable that no wine improves in quality after a period of ten to fifteen years.

Constituents of Wine.—Wines contain various alcohols, the chief of which is ethyl alcohol, and alcohol in varying quantities. Most of the stronger wines are fortified, so that they may keep better.

The estimation of alcohol is carried out in the same manner as that described under spirits.

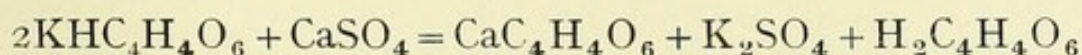
Acids of Wines.—The acids found in wines are chiefly tartaric, malic, and tannic, and certain acids of the fatty series, such as acetic, formic, etc., are produced during fermentation. Of these, tartaric and tannic acids are most important. Tartaric acid forms with potassium a bi-tartrate. As alcohol increases in wine, this salt becomes less soluble, and finally falls out in the form of a crust, so that the acidity of wines diminishes on keeping. Tannic acid is obtained from the skins and stalks of the grapes used; it diminishes by oxidation on keeping, and in old wines is small in amount. In a good wine the total acidity is not more than .5 per cent. of crystallized tartaric acid. It is estimated by first getting rid of the CO_2 by shaking, and then titrating the sample with $\frac{N}{10}$ NaOH, using phenolphthalein as indicator. Each c.c. of $\frac{N}{10}$ NaOH corresponds with 7.5 milligrammes of crystallized tartaric acid.

Ethers of Wines.—Ethers are produced by the chemical action which takes place between the acids and alcohols contained in the

wine. Their variety is very great. Volatile ethers are obtained from volatile acids, such as acetic, and these, especially acetic ether, predominate in natural wines. Fixed ethers are derived from fixed acids, such as tartaric, and are found in fortified wines. Ethers impart to wine its so-called bouquet. *Ænanthic* ether, although existing to the extent of 1 in 50,000 of wine, imparts the peculiar vinous smell and taste to all wines in common.

Sugars in Wines.—The chief sugar of wine is *lævulose*, of which a natural wine should not contain more than .5 per cent. Fortified wines may contain from 2 to 25 per cent. Extractives found in wine consist of gums and carbohydrates of several kinds, and contribute to the taste and so-called body of the wine.

The plastering of wine consists in the addition of calcium sulphate, whereby the bi-tartrate of potassium is decomposed and an insoluble tartrate of lime formed—



—together with a deposit of certain phosphates. In France the addition of this salt is not allowed in greater quantity than .2 per cent.

Port wine is rich in tannin, and to certain inferior wines this astringent, together with alum and catechu, is added. Port contains a large amount of extracts, which give it a full body, and old port a large proportion of ethers, of which (unlike to sherry) the fixed ethers predominate over the volatile.

Sherries, as imported into this country, are all fortified and plastered, and contain from 15 to 25 per cent. of alcohol by weight. Old sherry contains a large proportion of volatile ethers, and to this property much of its value as a stimulant must be attributed.

Champagne is produced from black grapes, and depends for its character very largely upon the quality of the grapes of a particular vintage. The expressed juice, after sedimentation for twelve hours, is drawn off and fermented; it is then bottled and allowed to undergo secondary fermentation for a couple of years, during which time much CO_2 is produced, and a deposit. To the wine, which is up till now sour, cane-sugar, which has been dissolved in old champagne, is added in varying quantities. Dry champagnes which find their way to England contain little sugar—not more than

2 or 3 per cent. of this liqueur—whilst sweet champagnes exported to other countries may contain 15 to 20 per cent. of the same liqueur. With regard to the action of wines on digestion, it may be stated in a word that these beverages have a much more inhibitory effect upon salivary, gastric, and pancreatic digestions than spirits or a mixture of alcohol and water of the same alcoholic strength.

Adulterants.—The common adulterants of wine are water, ethers, alum, tannin, and sugar. Salicylic and boric acids occur naturally in very small quantities in grapes, as also a great variety of colouring matters. As might be expected, many colouring agents are added to wines, such as magenta, cochineal, indigo, aniline colours, and vegetable infusions, like logwood, blackberry, and elderberry, the detection and separation of which are matters for chemical analyses too fine for the scope of this work.

Alcohol Table.

Sp. Gr. at 15° C.	Per Cent. Alcohol (Vol.).	Per Cent. under Proof.	Sp. Gr. at 15° C.	Per Cent. Alcohol (Vol.).	Per Cent. under Proof.
1·000	0·00	100·00	·973	23·10	59·52
·999	0·66	98·84	·972	24·08	57·80
·998	1·34	97·66	·971	25·07	56·06
·997	2·12	96·29	·970	26·04	54·37
·996	2·86	95·00	·969	26·95	52·77
·995	3·55	93·78	·968	27·86	51·18
·994	4·27	92·50	·967	28·77	49·60
·993	5·00	91·23	·966	29·67	48·00
·992	5·78	89·87	·965	30·57	46·44
·991	6·55	88·50	·964	31·40	44·97
·990	7·32	87·16	·963	32·19	43·60
·989	8·18	85·65	·962	32·98	42·20
·988	9·04	84·15	·961	33·81	40·74
·987	9·86	82·70	·960	34·54	39·47
·986	10·73	81·20	·959	35·28	38·18
·985	11·61	79·65	·958	36·04	36·83
·984	12·49	78·10	·957	36·70	35·68
·983	13·43	76·46	·956	37·34	34·57
·982	14·37	74·82	·955	38·04	33·32
·981	15·30	73·18	·954	38·75	32·08
·980	16·24	71·54	·953	39·47	30·84
·979	17·17	69·90	·952	40·14	29·66
·978	18·25	68·00	·951	40·79	28·52
·977	19·28	66·20	·950	41·32	27·60
·976	20·24	64·53	·949	41·84	26·67
·975	21·19	62·87	·948	42·40	25·70
·974	22·18	61·13	·947	42·95	24·74

Alcohol Table—continued.

Sp. Gr. at 15° C.	Per Cent. Alcohol (Vol.).	Per Cent. under Proof.	Sp. Gr. at 15° C.	Per Cent. Alcohol (Vol.).	Per Cent. over Proof.
·946	43·56	23·66	·899	66·25	16·11
·945	44·18	22·58	·898	66·69	16·88
·944	44·79	21·50	·897	67·11	17·61
·943	45·41	20·43	·896	67·53	18·34
·942	46·02	19·36	·895	67·93	19·05
·941	46·59	18·36	·894	68·33	19·74
·940	47·13	17·40	·893	68·72	20·42
·939	47·67	16·46	·892	69·11	21·11
·938	48·21	15·50	·891	69·50	21·79
·937	48·75	14·57	·890	69·92	22·53
·936	49·29	13·63	·889	70·35	23·29
·935	49·81	12·70	·888	70·77	24·02
·934	50·31	11·82	·887	71·17	24·73
·933	50·82	10·94	·886	71·58	25·44
·932	51·32	10·05	·885	71·98	26·15
·931	51·82	9·20	·884	72·38	26·85
·930	52·29	8·36	·883	72·77	27·52
·929	52·77	7·52	·882	73·15	28·19
·928	52·24	6·70	·881	73·54	28·87
·927	53·72	5·86	·880	73·93	29·57
·926	54·19	5·03	·879	74·33	30·26
·925	54·66	4·20	·878	74·70	30·92
·924	55·13	3·38	·877	75·08	31·58
·923	55·60	2·56	·876	75·45	32·23
·922	56·07	1·74	·875	75·83	32·89
·921	56·54	0·92	·874	76·20	33·54
·920	56·98	0·14	·873	76·57	34·19
·9198	57·06	Proof	·872	76·94	34·84
		Per Cent. over Proof.	·871	77·29	34·45
·919	57·45	·68	·870	77·64	36·07
·918	57·92	1·51	·869	78·00	36·69
·917	58·36	2·28	·868	78·36	37·33
·916	58·80	3·05	·867	78·73	37·98
·915	59·22	3·78	·866	79·12	38·65
·914	59·63	4·50	·865	79·50	39·32
·913	60·07	5·27	·864	79·86	39·96
·912	60·52	6·07	·863	80·22	40·60
·911	60·97	6·86	·862	80·60	41·26
·910	61·40	7·61	·861	81·00	41·96
·909	61·84	8·37	·860	81·40	42·66
·908	62·31	9·20	·859	81·80	43·35
·907	62·79	10·03	·858	82·19	44·04
·906	63·24	10·84	·857	82·54	44·66
·905	63·69	11·64	·856	82·90	45·28
·904	64·14	12·41	·855	83·25	45·90
·903	64·58	13·18	·854	83·60	46·51
·902	65·01	13·92	·853	83·94	47·11
·901	65·41	14·62	·852	84·27	47·70
·900	65·81	15·33	·851	84·60	48·27
			·850	84·93	48·84

Alcohol Table—*continued.*

Sp. Gr. at 15° C.	Per Cent. Alcohol (Vol.).	Per Cent. over Proof.	Sp. Gr. at 15° C.	Per Cent. Alcohol (Vol.).	Per Cent. over Proof.
·849	85·26	49·38	·820	94·00	64·74
·848	85·59	50·00	·819	94·26	65·18
·847	85·94	50·61	·818	94·51	65·62
·846	86·28	51·21	·817	94·76	66·07
·845	86·61	51·78	·816	95·03	66·53
·844	86·93	52·34	·815	95·29	67·00
·843	87·24	52·90	·814	95·55	67·46
·842	87·55	53·43	·813	95·82	67·92
·841	87·85	53·96	·812	96·08	68·38
·840	88·16	54·50	·811	96·32	68·80
·839	88·46	55·02	·810	96·55	69·20
·838	88·76	55·55	·809	96·78	69·61
·837	89·08	56·10	·808	97·02	70·03
·836	89·39	56·66	·807	97·27	70·46
·835	89·70	57·20	·806	97·51	70·88
·834	89·99	57·71	·805	97·73	71·26
·833	90·29	58·23	·804	97·94	71·64
·832	90·58	58·74	·803	98·16	72·02
·831	90·88	59·26	·802	98·37	72·40
·830	91·17	59·77	·801	98·59	72·77
·829	91·46	60·28	·800	98·80	73·14
·828	91·75	60·79	·799	98·98	73·47
·827	92·05	61·32	·798	99·16	73·81
·826	92·36	61·86	·797	99·35	74·14
·825	92·66	62·38	·796	99·55	74·50
·824	92·94	62·88	·795	99·75	74·83
·823	93·23	63·38	·794	99·96	75·18
·822	93·49	63·84	·7938	100·00	75·25
·821	93·75	64·30			

Beer.—Beer is said to be produced by the fermentation of malt and hops, although many beers contain little of either.

Porter or stout is made in the same manner as beer, but the malt is first roasted, with the result that caramel is produced, which imparts the dark colour to the beverage. Malt liquors have little retarding influence on salivary digestion, but have some inhibitory action on gastric digestion. Various sugars have recently been substituted for malt, and the commercial sulphuric acid employed to convert them is liable to contain arsenic. In Lancashire in 1900 an outbreak of arsenical poisoning occurred, in which arsenic amounting to $\frac{1}{10}$ grain per gallon was frequently found, and it was stated in some cases that 1 grain in a gallon was found. Beer has suffered from the addition of the following adulterants :

sulphurous acid, sulphuric acid, ferrous sulphate, various sulphides, tartaric acid, salicylic acid, boracic acid, alum, and common salt.

In testing the acidity of beer, it should first be decolourized by admixture with a solution of basic lead acetate and filtration.

Where common salt has been added, an allowance not exceeding 50 grains per gallon must be made for the amount of this compound present in the water, malt, and hops used.

Sulphurous acid is added to regulate the fermentation and to produce a flavour of age.

Salicylic Acid.—Distil a convenient quantity of the beer until only a small fraction remains, and treat this with ferric chloride to obtain the characteristic red colour.

Boric acid may be recovered from the ash of beer.

An abnormally high acid figure denotes commencing deterioration, or the addition of a mineral acid to clarify and give the beer a hard taste.

The normal acidity of beer is produced by CO_2 , acetic acid, lactic acid, malic, and other organic acids, and may be estimated in terms of glacial acetic acid by titration against $\frac{N}{10}$ NaOH (1 c.c. = 6 milligrammes glacial acetic acid).

The acidity of beer should not exceed 30 c.c. $\frac{N}{10}$ NaOH per 100 c.c. of the beverage. Before distillation for the determination of alcohol in beer, the fluid should be well shaken, to dispel as much CO_2 as possible, rendered slightly alkaline with caustic soda, and slightly diluted with water. The addition of a little tannin will prevent frothing.

Lime and Lemon Juices.—The Board of Trade requires that these juices shall have a specific gravity of 1.030, and shall have acidity of 6.8 per cent. citric acid. The specific gravity is determined in the usual manner; and the acidity by titration with $\frac{N}{10}$ soda (1 c.c. = .006 gramme citric acid). Where sulphuric or other mineral acid is added as an adulterant, it is estimated in the usual way. These juices are generally fortified with 3 to 4 per cent. of alcohol.

Vinegar.—Vinegar should contain at least 3 per cent. of acetic acid, and not more than the merest traces of any free mineral acid.

Estimation of Acetic Acid.—Dilute the vinegar with an equal quantity of distilled water, and titrate with $\frac{N}{10}$ NaOH, using phenolphthalein as indicator (1 c.c. $\frac{N}{10}$ NaOH = 0.006 gramme acetic acid).

Detection and Estimation of Free Mineral Acid.—Sulphuric acid is that most commonly found. Place a few drops of vinegar on a white porcelain slab, and near by place a few drops of a solution of methyl violet in water. With a glass rod bring the vinegar and methyl violet together. If a trace of free acid be present, the violet changes to blue, and if more than a trace be present, to green. In the absence of a mineral acid, the violet remains unchanged.

Mustard.—Mustard is derived from the seeds of the black and white mustard plants (*Brassica nigra* and *alba*). A little turmeric and coal-tar colours are usually added to the ground seeds, and sometimes foreign starches and ground chillies (small pods of Cayenne pepper). These adulterants are all harmless. Starch is readily detected by the iodine test. Turmeric becomes brownish-red under the action of ammonia. White mustard is recognised under the microscope by the hexagonal or 'infundibuliform' cells of the cuticle, possessing a central ostium occupied by the so-called 'mucilage' cells.

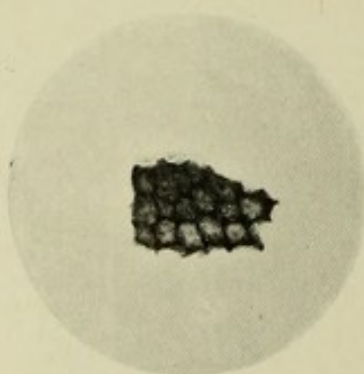


FIG. 64.—CELLS OF CUTICLE OF MUSTARD.

Pepper.—Black pepper is derived from the unripe berries of *Piper nigrum*, and white pepper from the ripe fruit. A transverse section of a black pepper berry presents an external layer of cells somewhat resembling bean starch granules, within these a layer of elongated cells arranged transversely to the foregoing, next a reticulum containing oil globules, more internally still a layer of flask-shaped cells, and finally a central mass of angular cells containing starch.

Pepper is largely adulterated, but with substances which are harmless. These are various foreign starches, palm-nut powder, ground stones of olives, ground shells of walnuts, and occasionally chalk, clay, and brick-dust.

The ash of black pepper should not exceed 6.5 per cent.,

and that of white pepper should not exceed 3.5 per cent. In microscopically examining pepper, it must be remembered that, unlike mustard, pepper naturally contains starch.

Sugar.—The sugar of commerce is largely derived from the sugar-cane, but a portion is obtained from beet and the maple.

The preparation of cane-sugar is roughly the following: The initial steps consist in crushing the canes, bleaching the expressed juice with sulphurous acid, neutralizing with lime, and coagulating all albuminous matters by boiling. Later, this boiled mass is

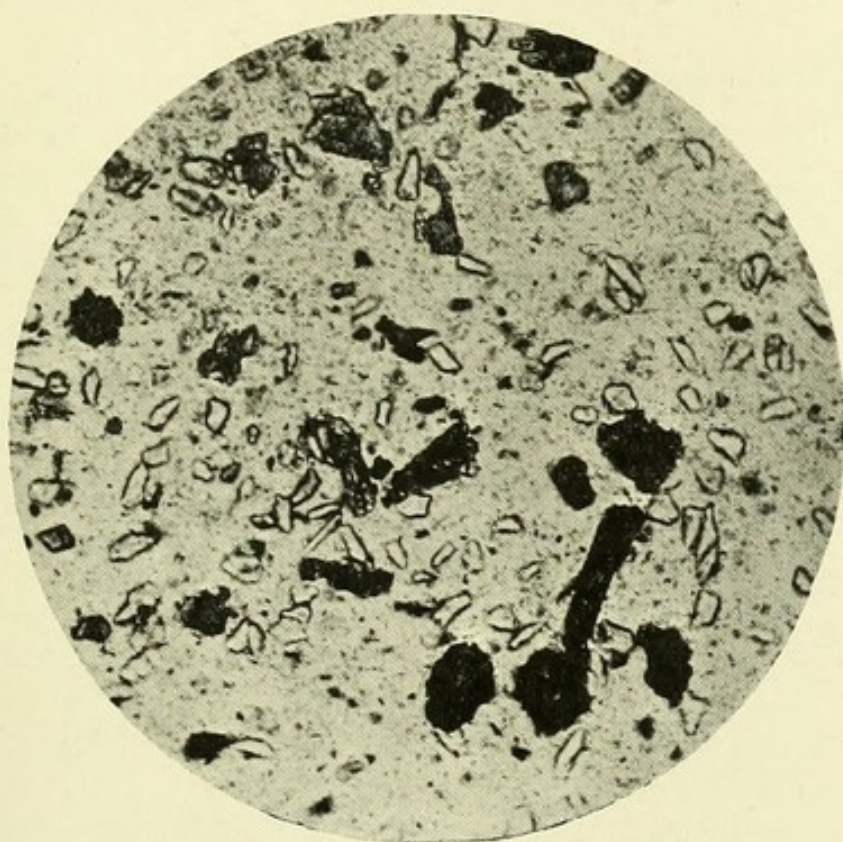


FIG. 65.—BLACK PEPPER. $\times 30$.

filtered, the filtrate evaporated down, and the uncrystallizable sugar (glucose) separated by a centrifuge. The raw sugar is thus obtained in crystalline form, mixed with impurities. The residue is sold as molasses. The refining of sugar consists in remelting it, filtering, and clarifying with charcoal, after which it is evaporated *in vacuo*, and if loaf-sugar be required, run into moulds.

Ultramarine blue and other colouring matters are sometimes added to loaf-sugars to improve their colour. To detect ultramarine blue, dissolve the sample in water, allow the colouring

matter to settle, collect and wash it with water. Hydrochloric acid will discharge the colour, and liberate H_2S .

Colouring matters foreign to sugar may generally be discovered by washing about 100 grammes of the sugar in 90 per cent. alcohol in a flask. When the dye is removed, the solution is filtered, evaporated to dryness, and again dissolved in a little alcohol. Some threads of wool, slightly mordanted with aluminium acetate, are placed in the solution, which is warmed on a water-bath; the wool is removed after a time, washed with water, and dried, when it retains a permanent yellow dye. The natural colouring matters of sugar will not thus permanently dye wool.

The ash of genuine sugar does not exceed 2 per cent.

The amount of cane-sugar in a sample may be determined by transforming it to grape-sugar, and estimating the amount of the latter by Fehling's method. The inversion is performed by heating a quantity of the sugar with about a tenth of its bulk of strong hydrochloric acid for ten to fifteen minutes on a water bath. The inverted fluid before titration is neutralized with sodium carbonate.

If a solution of KOH and $CuSO_4$ be heated with some grape-sugar, reddish-brown suboxide of copper is formed, and a definite relation exists between the quantity of copper sulphate thus changed and the amount of sugar present. This test is somewhat modified in Fehling's method.

Fehling's solution consists of a mixture of equal parts of the following two solutions: (1) 34.64 grammes $CuSO_4$ dissolved in 500 c.c. water; (2) 173 grammes of sodio-potassic tartrate dissolved in water, to which are added 100 c.c. of sodic hydrate solution of a specific gravity of 1.34, and the mixture made up to 500 c.c. The union of (1) and (2) produces a litre of Fehling's solution. They should be kept separate in well-stoppered bottles, in a dark and cool cupboard, and mixed only just before use.

A dilute solution (as near as possible to 1 per cent.) of the sugar is next made in water, and with this a burette is charged. Fifty c.c. of Fehling's solution are boiled in a porcelain dish, and into the boiling fluid is run that amount of the dilute sugar, which, when boiled for two minutes, just decolourizes the Fehling's solution. To determine when sufficient sugar has been added, rapidly filter

the hot solution into another white dish, and observe whether or not a faint tint of blue or bluish-green remains in the filtrate. If so, too little sugar has been used, and another trial must be made. It may be difficult to detect this faint tint of blue, especially as the filtrate may be somewhat yellow. Acidify a small quantity of the filtrate with acetic acid, and add a drop or two of potassium ferrocyanide: a bronze coloration indicates that some copper salt remains unchanged. By a series of trials in this manner, the precise amount of sugar required to reduce 50 c.c. of Fehling's solution is obtained. In solutions of 1 per cent. of sugar, 50 c.c. of Fehling's solution are reduced by .2375 gramme of grape-sugar, .2470 gramme of invert sugar, .2572 gramme of lævulose, .3380 gramme of lactose, and .3890 gramme of maltose.

Tea.—Tea consists of the dried leaves of several varieties of *Camellia thea*. The leaves are prepared for microscopical examination by soaking in water until they assume their original shape, when

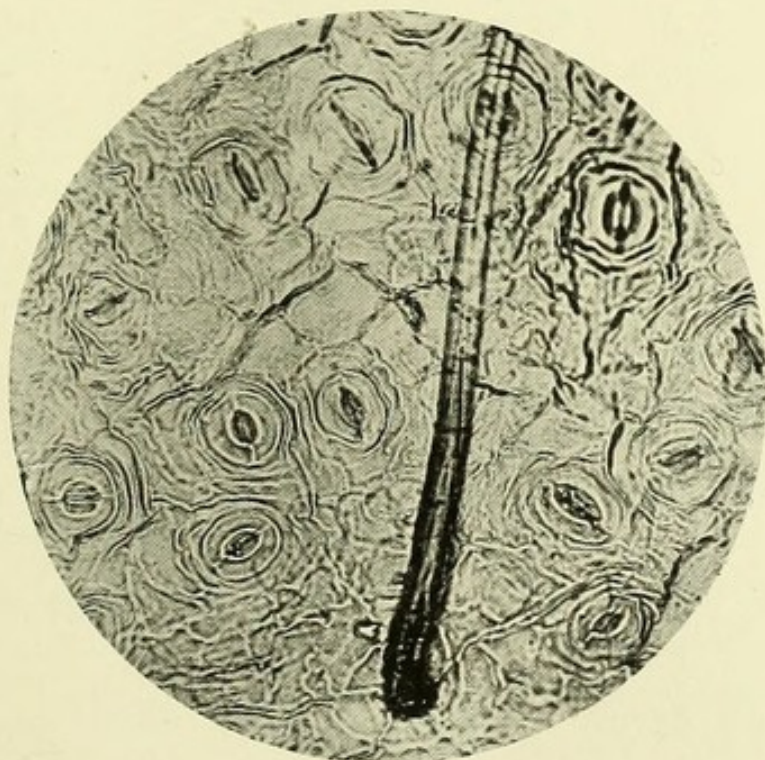


FIG. 66.—CUTICLE OF TEA-LEAF. $\times 200$.

they are carefully dried between layers of blotting-paper and mounted on large microscopic slides in Farrant's solution. The leaf is elliptical, and possesses an emarginate apex. The ribs form a looped network, arranged symmetrically on either side of the mid-

rib, and approaching, but not quite reaching, the edge of the leaf, thereby leaving a clear marginal space. The margin is serrated from a point near to the apex to another point some little distance from its attachment to the stalk; the point of each serration is surmounted by a small spine.

When a leaf is immersed in a warm 20 per cent. solution of NaOH, mounted on a slide, and the cover-slip pressed down, long tenacious, branched cells, termed idioblasts, are to be seen. These



FIG. 67.—IDIOBLASTS IN SECTION OF
TEA-LEAF. $\times 160$.

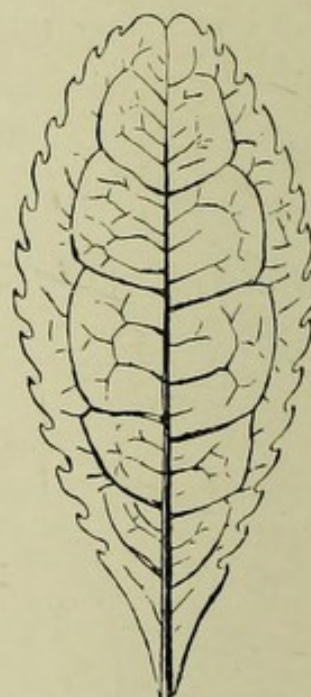


FIG. 68.—TEA-LEAF.

cells do not occur in any other leaves likely to be mistaken for tea.

Black and green teas differ only in their mode of preparation.

Composition of an Average Sample of Black Tea:

Water	8.2
Thein	3.2
Tannic acid	16.4
Pectin, cellulose, chlorophyll	40.6
Proteids	18.0
Alcoholic extract	7.3
Ash	6.3

Of these constituents the most important are the alkaloid thein and tannic acid, for these, with .5 per cent. of volatile oil, produce the characteristic effects of tea.

Indian and Ceylon teas are richer in all three constituents (thein, tannin, volatile oil) than China teas ; and green tea is richer in tannic acid than black ; but the amount of thein is about the same in both.

If tea be infused for five minutes in the usual manner, about one-fourth of the weight of the leaf goes into solution. The thein is so soluble that it passes into solution almost immediately, but the tannic acid requires some time to dissolve. There is less tannic acid after three minutes' solution than after five, and less after five than after ten ; after a longer interval there is not very much change, as practically all the soluble materials have been extracted in ten minutes ; therefore the less tannic acid desired, the shorter should be the time of infusion. The method of infusion is, from a health point of view, more important than the character of leaf used. First, the water should be of medium hardness, well aerated, and just brought to the boiling-point, when tea is infused. If the water be too hard, the lime and other salts present interfere with the extraction of some of the constituents of the leaf ; if, on the other hand, it be too soft, an unpleasant, bitter material is extracted. Infusion should last for about three minutes, as not only does prolonged infusion extract too much tannic acid, but it also dissipates the volatile oil to which the fragrance of tea is largely due. A further point of import is that too much leaf should not be infused ; considerably less than the proverbial tea-spoonful per head, when properly infused, is sufficient to produce the most fragrant and pleasant beverage. The addition of milk to tea, through the proteids that it contains, tends to precipitate some of the tannic acid. Sugar adds considerably to its nutritive value. The average proportions of the three active ingredients in ordinary teas in use at the present day are roughly as follows :

Thein	2 to 4 per cent.
Tannin	10 to 12 „
Volatile oil5 „

Adulteration.—Admixture with foreign leaves, such as elder-leaf, sloe-leaf, and the leaf of the willow, has been effected. A

low-power microscope readily detects any of these (the leaves most commonly employed) from the tea-leaf, as none of them possess

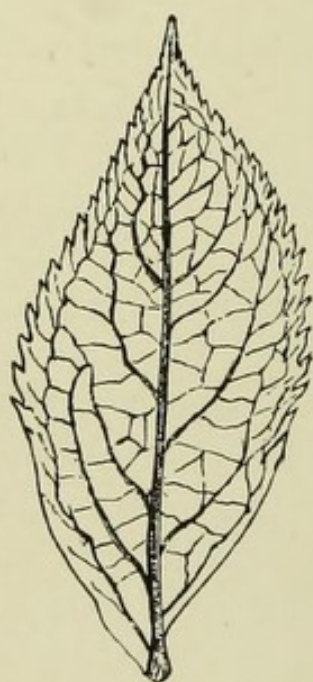


FIG. 69.—ELDER-LEAF.

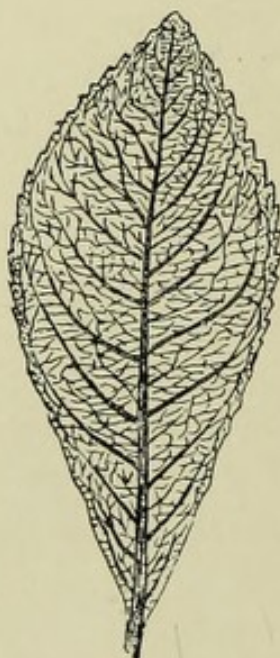
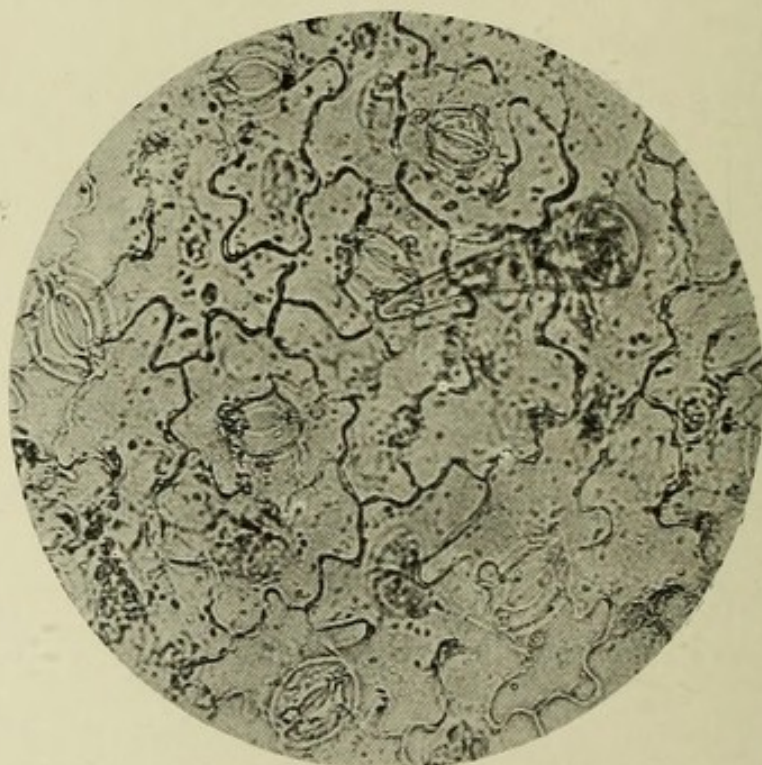


FIG. 70.—WILLOW-LEAF.



FIG. 71.—SLOE-LEAF.

FIG. 72.—CUTICLE OF TOBACCO-LEAF, $\times 200$.

an emarginate apex, nor do their systems of venation leave a clear space within the margin. The employment of infused

leaves has been practised, and it may be sometimes difficult to distinguish certain prepared leaves from the genuine leaf. Various chemicals have been used to colour and 'face' previously infused leaves, such as turmeric, sulphate of lime, Prussian blue, and black-lead. Old leaves have been worked up with sand and gum, and re-rolled. It may be quite impossible to detect small quantities of such leaves in adulterated samples, since genuine teas vary much in the relative amounts of their constituents. The ash of tea should fall between 4.7 and 6.2 per cent., and the ash soluble in water should not fall below 30 per cent. of the total ash. Reference to these figures will often assist in arriving at a conclusion as to whether or not used leaves have been added. In faced teas the ash is sometimes 10 per cent., whilst in exhausted teas it is rarely more than .8 per cent. The weight of the ash is determined by carefully incinerating a convenient quantity of tea—say 5 grammes—in a platinum dish, and weighing the greenish-gray mineral residue. This is the total ash. The contents of the dish are next treated with boiling water and thrown on a Swedish filter-paper. The insoluble portion is thoroughly washed on the filter with water, reignited, and weighed. The difference between this and the previous weight represents the soluble ash.

Estimation of Thein.—This estimation is also of value where the presence of exhausted leaves is suspected. Extract 5 grammes of finely powdered tea with 300 c.c. of boiling water, in a flask fitted to a reflex condenser, for two hours. Repeat the extraction a second and third time, allowing two hours in each case. Collect the three extracts in a beaker; add neutral lead acetate, and boil for ten minutes. Filter. Free the filtrate from lead by passing through it H_2S . Evaporate to dryness on a water bath with some freshly ignited magnesia and clean sand, and when thoroughly dry, powder, and carefully extract with chloroform in a Soxhlet apparatus. Evaporate the chloroform extract and boil the residue with water. Filter. Evaporate the filtrate to dryness; continue the drying at a temperature under $100^\circ C$. Weigh, to obtain the amount of thein in 5 grammes of tea. Thein under the microscope appears as long, white, silky needles. If the preliminary extractions are not thoroughly performed, some of the thein will remain in the tissues of the leaf.

A short and rapid method of detecting them in tea-leaves is the following : Take two watch-glasses of the same size and place in one a small quantity of tea, and cover with the other. Mount the pair on a wire gauze over a small Bunsen flame. In five minutes the upper glass will exhibit numerous drops of moisture ; in ten minutes some fine needles of them will be seen ; and in fifteen minutes a thick crop of fully formed needles will have condensed on the watch-glass. Exhausted leaves produce no such crystals. If the watch-glass be floated on cold water, crystallization is hastened.

Catechu is added to tea to produce a semblance of richness to the infusion. When present in quantity, it may be detected by precipitating an infusion of tea with neutral lead acetate and filtering. Five c.c. of the filtrate, when mixed with 2 drops of dilute ferric chloride solution, assume a green colour, which ultimately settles as a darker precipitate.

Estimation of Tannin : Proctor's Modification of Lowenthal's Method.—Ascertain how much permanganate of potassium is reduced by tannic acid, and other readily oxidizable substances in the infusion. Precipitate the tannin by gelatin, and once more determine the amount of permanganate reduced. The difference represents the quantity of permanganate decomposed by tannin.

Coffee.—Coffee is derived from *Coffea arabica*. The bean is enclosed in an outer layer of fruit like the stone in a cherry, and consists of two symmetrical halves faced together, and covered by a husk. The external pulp is removed by fermentation, and the beans are dried in the air ; later, the husk is separated by rolling. Many varieties of bean are to be found, the finest of which is Mocha. The beans must be roasted in order to prepare the beverage. The composition of raw and roasted Mocha coffee-beans is as follows :

	Raw.	Roasted.
Caffein	1.08	.82
Caffeic acids	8.46	4.74
Sugar	9.55	.43
Alcoholic extract	6.90	14.14
Fats	12.60	13.59
Legumin, dextrin, cellulose ..	48.69	61.09
Moisture	8.98	.63
Ash	3.74	4.56

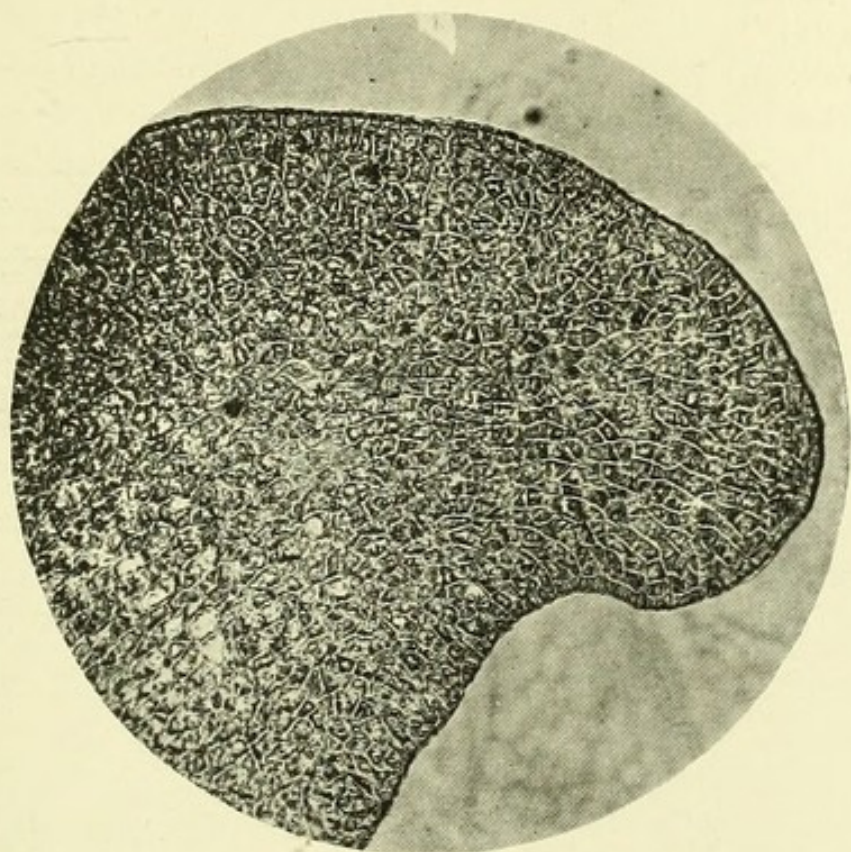


FIG. 73.—COFFEE BERRY. $\times 30$.

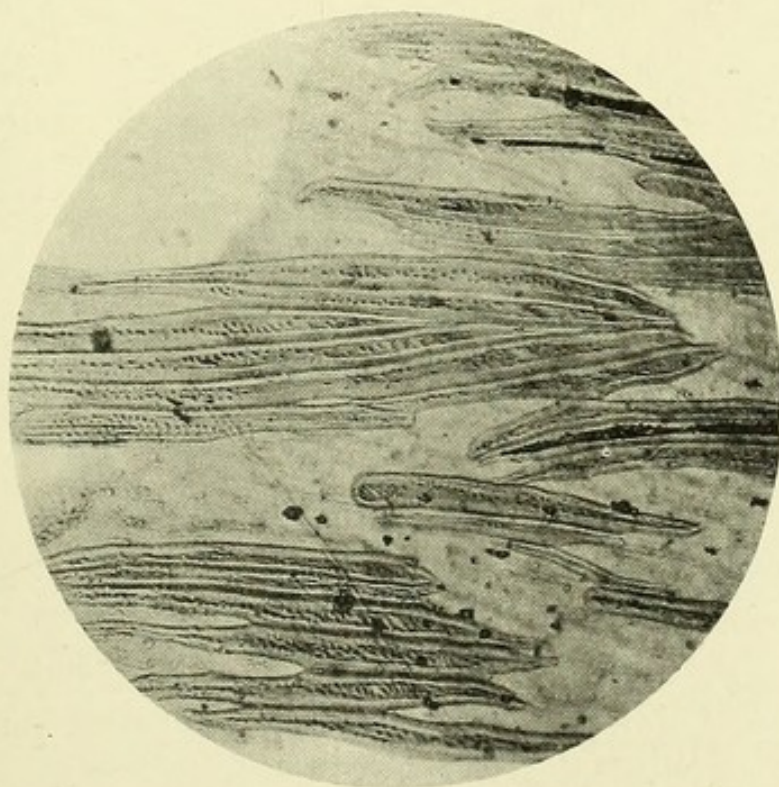


FIG. 74.—GROUND COFFEE, SHOWING CELLS OF TESTA. $\times 100$.

The roasting of coffee dissipates about 21 per cent. of the total caffein and about 10 per cent. of fat, and produces an oil—caffeoil—to which the aroma of roasted coffee is due.

Adulteration of Coffee.—The principal foreign substance found in coffee is chicory, a preparation of the root of the wild endive. Although the sale of chicory is allowed, and its admixture with coffee is very general, it is fraudulent to add it to samples sold as pure coffee. The quantity of chicory added to coffee varies very much, reaching sometimes 90 per cent. of the whole. It imparts a slightly bitter flavour to coffee, but is used principally to blacken and thicken it. Chicory is easily distinguished by the following characters: (1) Its odour is very different to that of coffee. (2) Roasted chicory sinks in water rapidly, whilst roasted coffee



FIG. 75.—LACTEAL VESSELS
OF CHICORY. $\times 100$.



FIG. 76.—DOTTED VESSELS
OF CHICORY. $\times 100$.

floats for some time, and sinks slowly, owing to the oil in the coffee preventing the particles being readily moistened. Moreover, the sediment of the coffee remains hard, whilst that of chicory is soft. (3) The specific gravity of a 10 per cent. infusion of dried chicory in water, raised to the boiling-point, maintained thereat for thirty seconds and filtered, is rarely below 1,018, and averages about 1,022. The specific gravity of a coffee infusion prepared in the same manner is never higher than 1,010, and averages 1,008. Other and rarer adulterants, such as ground carrots, turnips, etc., will give infusions of specific gravities of 1,015 and over. (4) Microscopic examination of the powder will demonstrate the characteristic dotted and lacteal ducts of chicory, whereas in coffee portions of the membrane or testa lining the berry, and containing the characteristic spindle cells, will appear,

as also endosperm cells. (5) All foreign bodies added to coffee are devoid of caffein. (6) If to a 5 per cent. infusion of pure coffee is added a slight excess of basic lead acetate, a precipitate falls, leaving a colourless supernatant fluid: the corresponding supernatant fluid in chicory is coloured.

When acorns, potatoes, sago, etc., are mixed with coffee, microscopic examination will detect their starch granules. Infusions of coffee and pure chicory are not blued by iodine. Caramel may be detected by its shining particles when viewed with a hand lens, as they stand out in contrast with the dull particles of coffee; also by its ready solubility in water.

Various artificial coffee-beans containing little or no real coffee have been found at times upon the market. Coffee extracts are deficient in caffein.

Cocoa.—Cocoa is prepared from the seeds of a cucumber-like fruit—*Theobroma cacao*. The seeds are separated from the fruit, heaped together for some days, and allowed to ferment, which modifies their bitterness and darkens their colour. They are next roasted, when the symmetrical halves of the seed separate as cocoa-nibs on being submitted to pressure in a machine. The nibs may be sold in this form, or they may be ground between hot rollers. In the latter case the fat is melted, and the products of grinding are consequently reduced to a fluid. A considerable portion of the fat is removed by pressure, and the remainder, having been run into moulds, and thus converted into solid slabs, is once more ground and sold as a powder. Strictly speaking, cocoa is not soluble in water; the Dutch manufacturers add alkalies to it, which saponify the fat and somewhat soften the fibres of the cocoa.

Composition of Cocoa as Raw Nibs:

Fat	50.44
Starch	4.26
Proteids	13.20
Various astringents	6.71
Gum and cellulose	8.57
Other non-nitrogenous bodies	5.80
Colouring matter	2.20
Alkaloid84
Water	5.23
Ash	2.75

The chief alkaloid of cocoa is theobromine (dimethyl-xanthin), a body closely related to caffein. In the commercial powder the 50 per cent. of fat is reduced to 30, or under.

Adulterants.—Foreign starches, which can be more or less easily detected by the microscope. Alkalies are frequently added in considerable quantities for the purpose of increasing the solubility of the cocoa. A determination of the ash, which in unadulterated varieties rarely exceeds 4 per cent., will assist in detecting such additions.

Chocolate is ground cocoa from which the fat has, or has not, been removed. Sugar, starch, and various flavouring materials are added, and the whole melted and thrown into moulds, or prepared for distribution in other ways.

Theobromine may be estimated thus: Remove the fat and caffein by petroleum spirit, and dry the extract on the water bath. Boil this extract in water for a considerable time. Next extract the residue not affected by petroleum with chloroform for several hours in a Soxhlet apparatus. Drive off the chloroform on a water bath, and boil the extract several times with water. Mix the two extracts in water, and evaporate to dryness in a platinum dish. Weigh the residue as theobromine.

Arsenic in Food, Beverages, Etc.

The most convenient test for arsenic is Reinsch's. A small quantity of the material to be tested is placed in a beaker and rendered acid with dilute HCl. A piece of clean copper-foil is placed in the mixture, and the whole is boiled for half an hour, and allowed to cool. If on removal the copper be unaffected, arsenic is absent; if on the copper there be deposited a grayish film, arsenic is probably present. The copper-foil is washed in distilled water, dried, and placed in a test-tube, which is heated over a Bunsen burner. The arsenic is oxidized and sublimes, condensing on a cool part of the tube. The deposit is examined with a microscope to detect the octahedral crystals of arsenic trioxide.

The following method for examining beer for arsenic was recommended a few years ago by a committee of chemists. Two hundred c.c. of the beer are heated to boiling in a porcelain dish;

30 c.c. of pure HCl and a piece of clean, bright copper-foil, $\frac{1}{4}$ by $\frac{1}{2}$ inch, added; the boiling is continued for three-quarters of an hour, care being taken to replace the water lost by evaporation. If at the end of that period the copper remain bright, no arsenic is present; if a deposit appear, the foil is washed with water, alcohol, and ether, dried at 100° C., and heated in a 2-inch reduction-tube. Any sublimate that is obtained must be examined under a magnifying power of 200 diameters. An arsenical deposit is characterized by octahedral or tetrahedral crystals.

Sulphites are frequently added to beer, and when present will produce black copper sulphide; but this stain remains unchanged when the copper is heated, and of course gives no sublimate. It is recommended that sulphites be got rid of by boiling the solution for a few minutes with HCl and bromine water. It is frequently necessary to get rid of the organic material in food by heating with oxidizing agents, such as a mixture of chlorate of potassium and HCl; or by heating with melted potassium nitrate previous to testing for arsenic.

As arsenic acid only responds to Reinsch's test after prolonged boiling, and in the presence of much acid, it is advantageous to reduce the arsenic to the arsenious condition by the addition of a solution of cuprous chloride in HCl. The most reliable test for the detection of arsenic is Marsh's. Fit a flask with a cork carrying two glass tubes, a funnel tube, and a bent tube fitted to a horizontal drying-tube containing a roll of blotting-paper soaked in lead acetate solution and dried, a plug of cotton-wool, granulated calcium chloride, and a second thick plug of cotton-wool. This tube is narrowed to a stem, which is continued into a hard-glass tube, which is also continued into a finer glass tube drawn out to a point. A Bunsen burner carrying a hood is arranged under the hard-glass segment. Place 20 grammes of pure zinc in the flask, and run in sufficient HCl from the funnel to produce an evolution of hydrogen. When the hydrogen flame burns with a round tip, all air has been removed from the apparatus. Now place the Bunsen under the hard-glass tube, and run in 20 c.c. of the acid. In the absence of arsenic in the materials, no trace of a mirror is observed in the contracted portion of the tube just beyond the flame in half an hour. Air must not be admitted to the zinc during

the addition of acid, lest the mirror become black and unevenly distributed, instead of brown and compactly placed. Should this blank experiment be unsatisfactory, it must be ascertained where the fault lies by changing the materials methodically; and when it has been discovered that the acid, or the zinc, or the apparatus is at fault, the necessary correction must be made. When, then, with satisfactory reagents and apparatus, no trace of a deposit is obtained, 10 c.c. of the liquid to be tested and 10 c.c. HCl are slowly introduced into the flask through the funnel without air-bubbles. Slow introduction is important when, in such cases as beer, the liquid tends to froth. If in ten minutes no mirror appear, another 10 c.c. of the liquid, with 10 c.c. HCl, are added, and the experiment is continued for twenty minutes, acid being added from time to time as necessary.

Preparation of a Series of Standard Mirrors.—A blank experiment is performed, and when it is evident that arsenic is wholly absent, a new tube is joined to the drying-tube. A solution of HCl and arsenious oxide (1 c.c. = .001 milligramme arsenious oxide) is prepared, and 2 c.c. of this solution are introduced into the apparatus. If the zinc be sensitive, a distinct brown mirror is obtained in twenty minutes. It should be noted that some forms of pure zinc, from an unknown cause, are not sufficiently sensitive to produce a mirror with minute quantities of arsenic. That portion of the tube containing the mirror is now sealed off, while the hydrogen still passes, as contact with the air causes the mirror gradually to fade. Further mirrors are similarly made containing double, treble, quadruple, and quintuple proportions of arsenic. A little practice will enable the performer to obtain deposits of arsenic neatly and equally distributed. It is to be remembered that the first portion of every test must be a blank experiment of at least twenty minutes; a fresh tube should always be substituted for that containing the mirror, and the experiment continued for a further fifteen minutes. Should a second mirror form, the quantity of arsenic with which it corresponds must be added to that obtained by the first. These tests are only approximate, and mirrors corresponding with less than .003 milligramme of arsenious oxide cannot be safely relied on. It is well in all cases where a mirror has been obtained to perform

a duplicate test, in order to exclude accidental contamination. The narrow portion of the tube containing the mirror, which should not be denser than that produced by .01 milligramme arsenious oxide, is cut off, the hydrogen replaced by air and the end sealed up. The tube, held in the tongs, is then drawn several times through the flame of a Bunsen, until the mirror has disappeared; when cold, minute crystals of arsenious oxide can be identified by the microscope, or recognised by the naked eye through their sparkling appearance when placed before a luminous flame.

The HCl must be purified from arsenic by the addition of bromine and excess of sulphurous acid, followed by distillation, when the middle portion of the distillate alone is collected.

(See Appendix for description of modification of this method.)

Arsenic is frequently dissociated in volatile form from arsenical wall-papers. Small grains of arsenious acid, and sometimes metallic arsenic, may enter the atmospheres of factories. Arsenic has, further, been found in curtains, carpets, artificial flowers, and colouring matters introduced into cookery. Abel has shown that the gaseous form is due to the action of moulds, which live upon the paste on wall-papers. *Aspergillus*, *mucor*, and *penicillium* can produce this change. The exact nature of the gaseous compound is not known, but it possesses the garlic smell of arseniuretted hydrogen.

Objects from Various Sources.

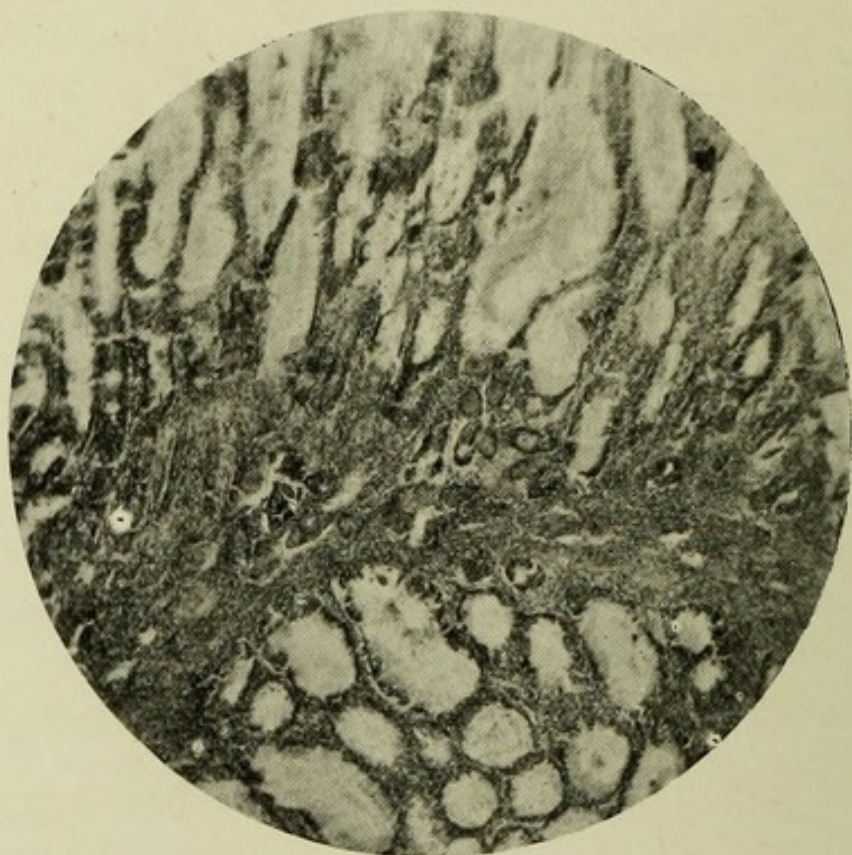


FIG. 77.—OVA OF *BILHARZIA HÆMATOBIA*, FROM WALL OF THE BLADDER. $\times 38$.

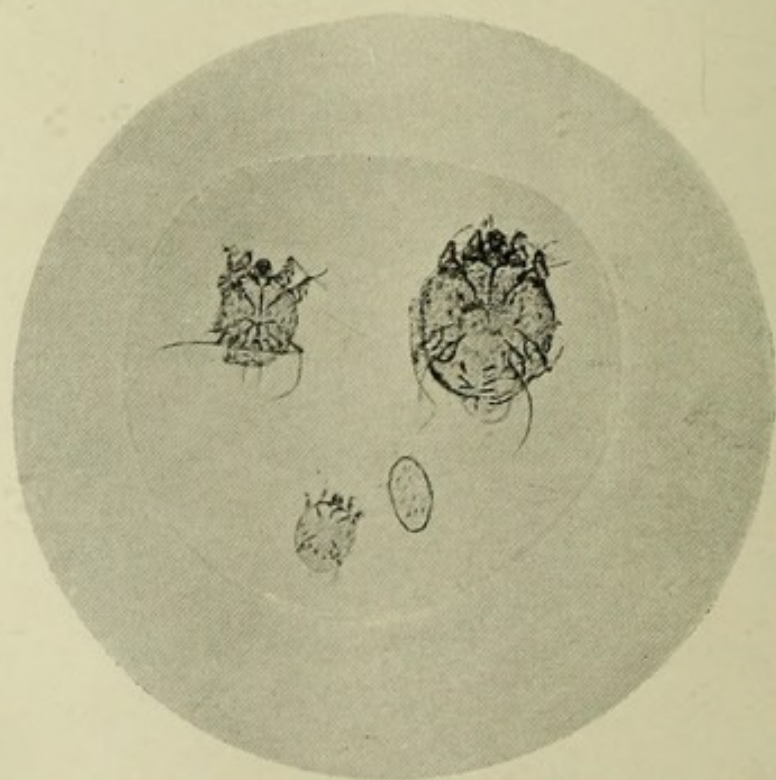


FIG. 78.—*SARCOPTES SCABEI* AND OVUM. $\times 30$.

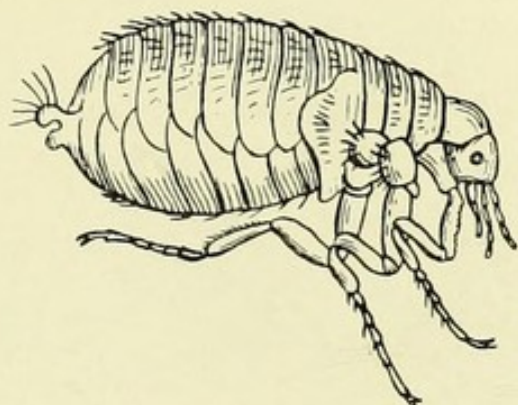


FIG. 79 —PULEX IRRITANS. $\times 10$.

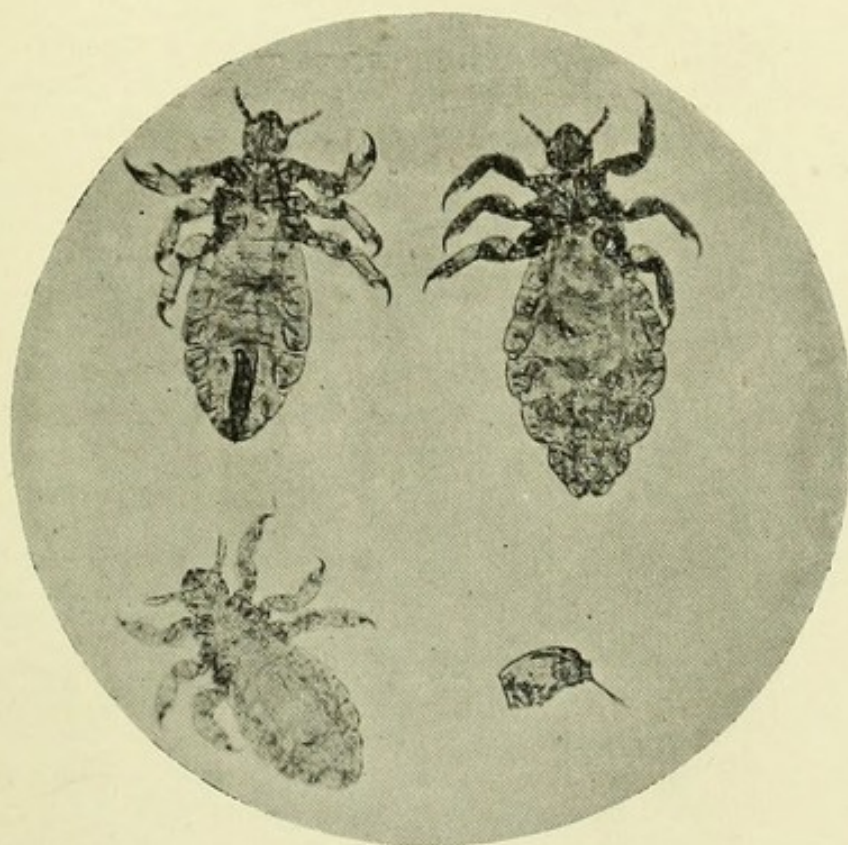


FIG. 80.—PEDICULUS VESTIMENTI. $\times 6$.

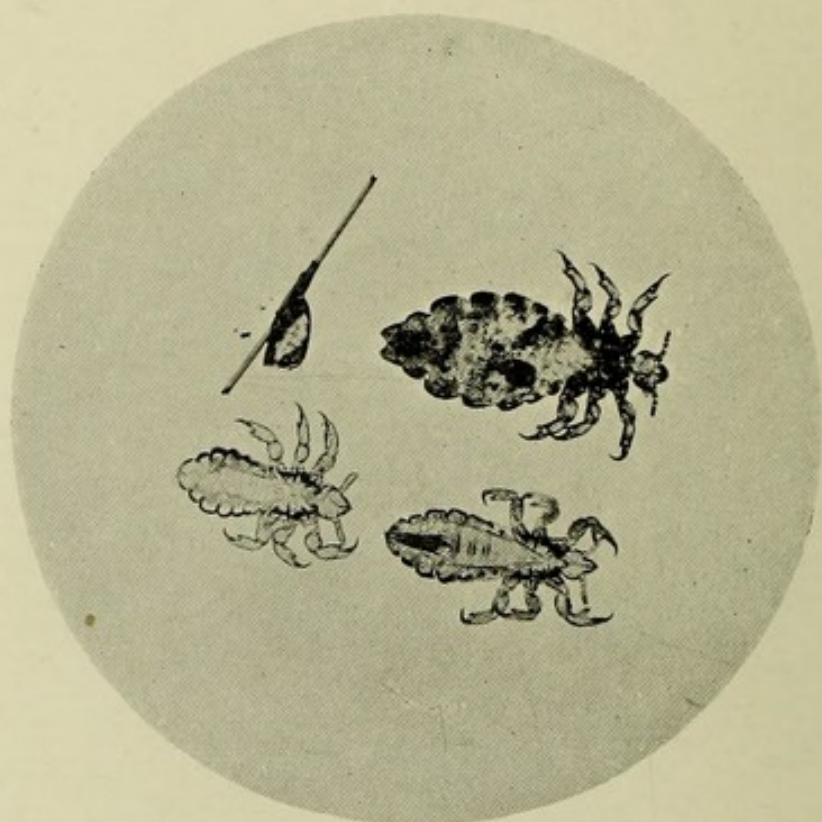


FIG. 81.—*PEDICULUS CAPITIS*. $\times 6$.

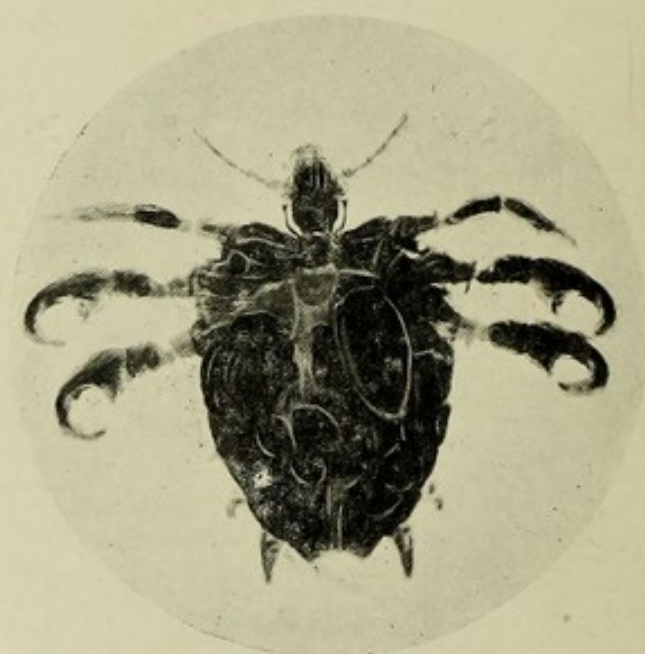


FIG. 82.—*PEDICULUS PUBIS*. $\times 20$.

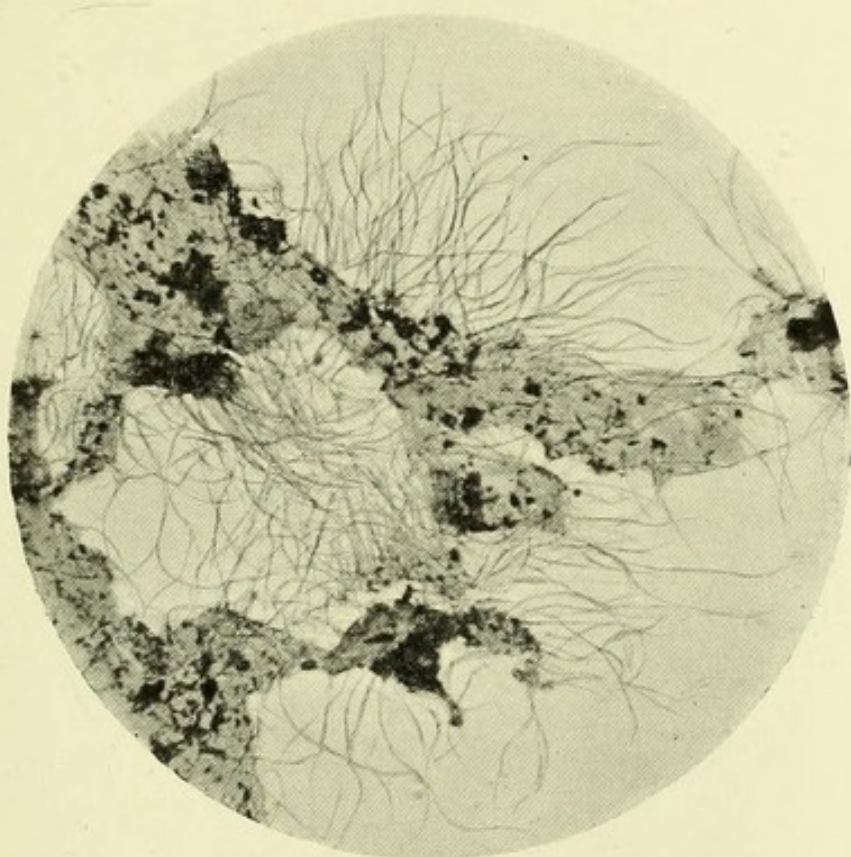


FIG. 83.—*BEGGIATOA ALBA*. $\times 34$.

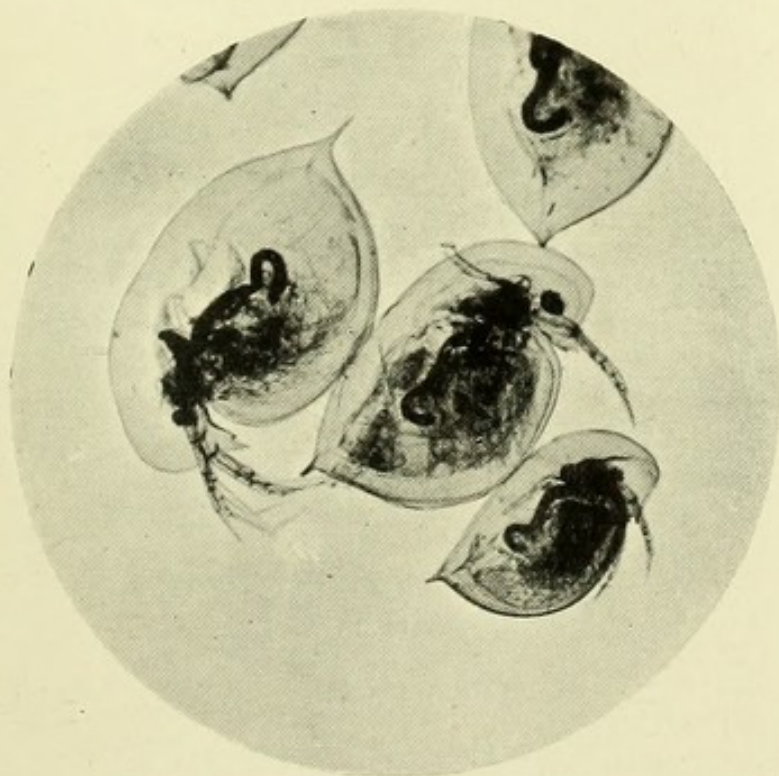
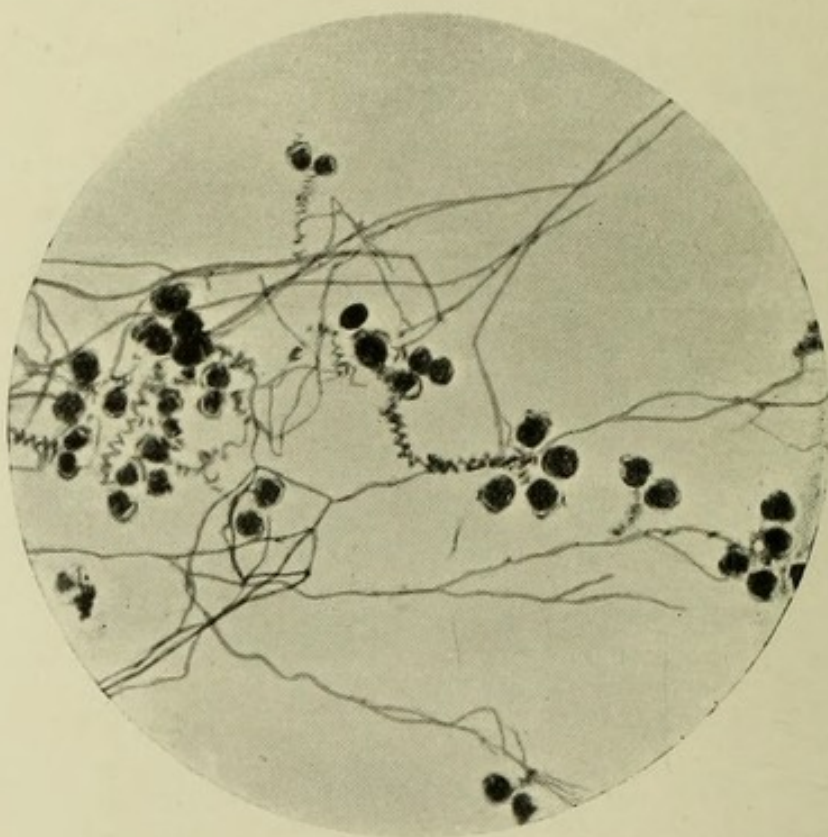
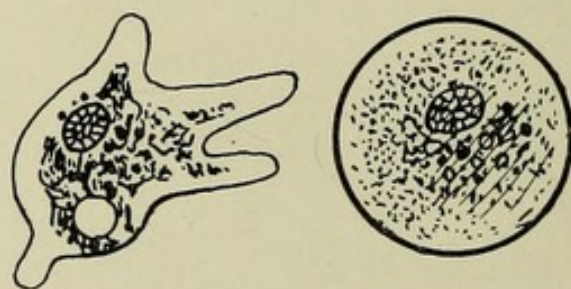


FIG. 84.—*DAPHNIA PULEX*. $\times 13$.

FIG. 85.—VORTICELLA. $\times 132$.

Motile.

Resting.

FIG. 86.—AMŒBA COLI.

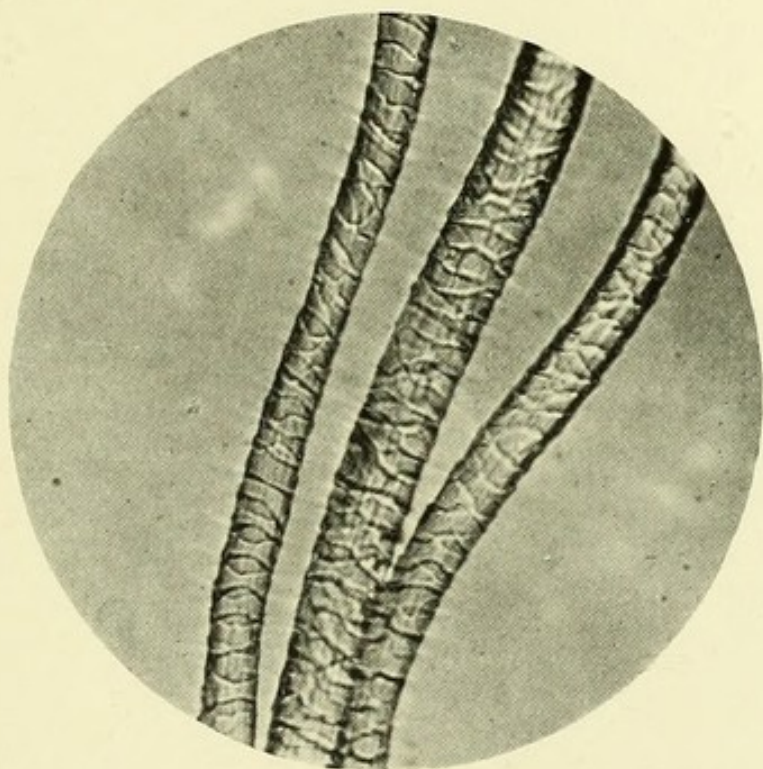


FIG. 87.—LEICESTERSHIRE WOOL. $\times 200$.

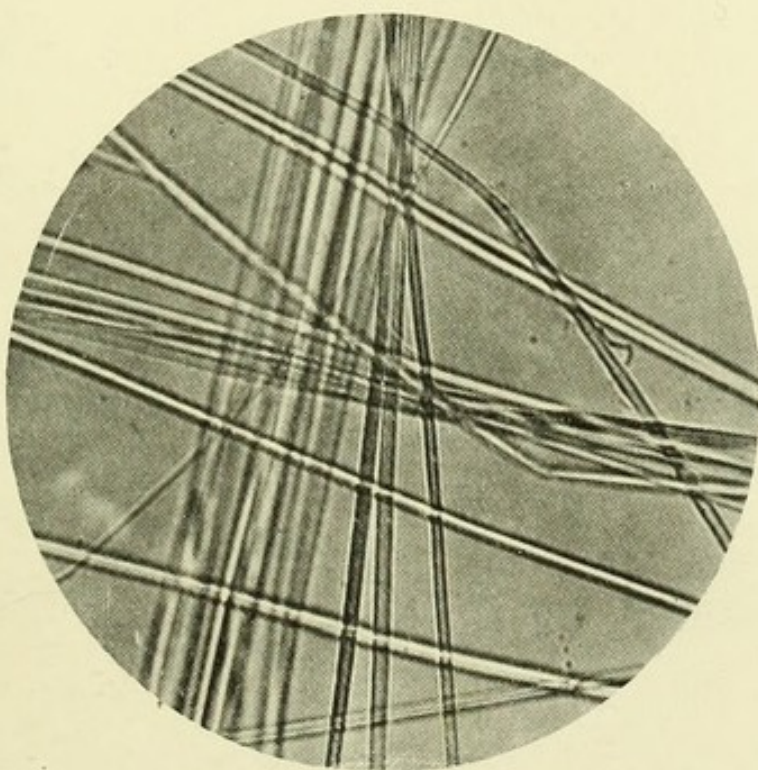


FIG. 88.—CHINESE SILK. $\times 200$.

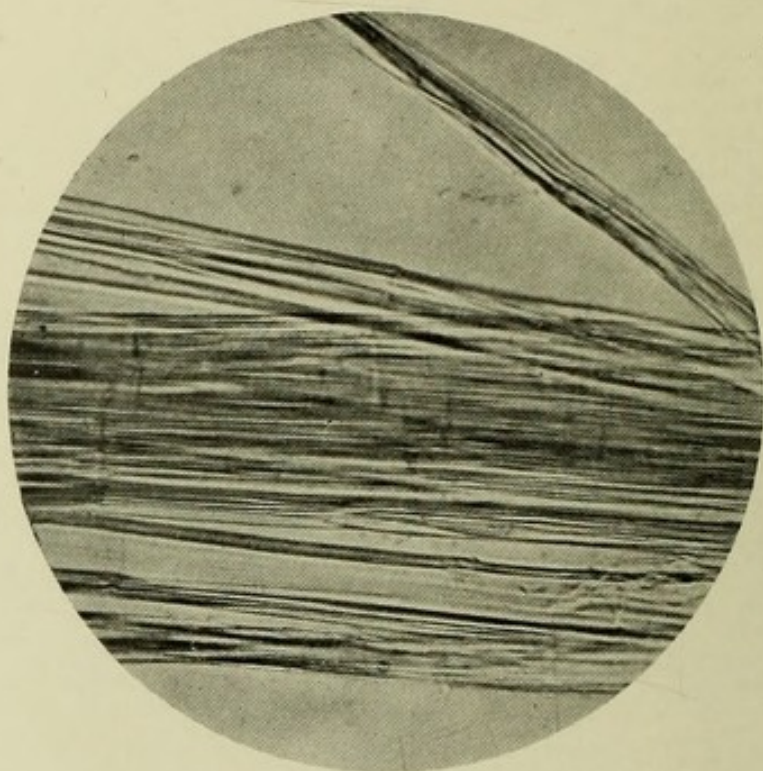


FIG. 89.—JUTE FIBRES. $\times 200$.

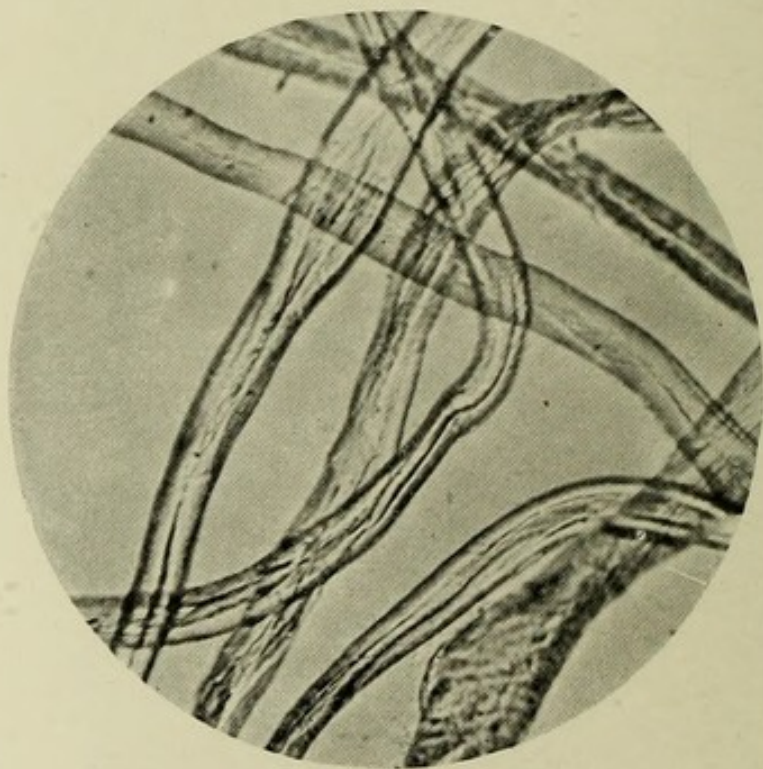


FIG. 90.—COTTON FIBRES. $\times 200$.



FIG. 91.—FLAX FIBRES. $\times 200$.

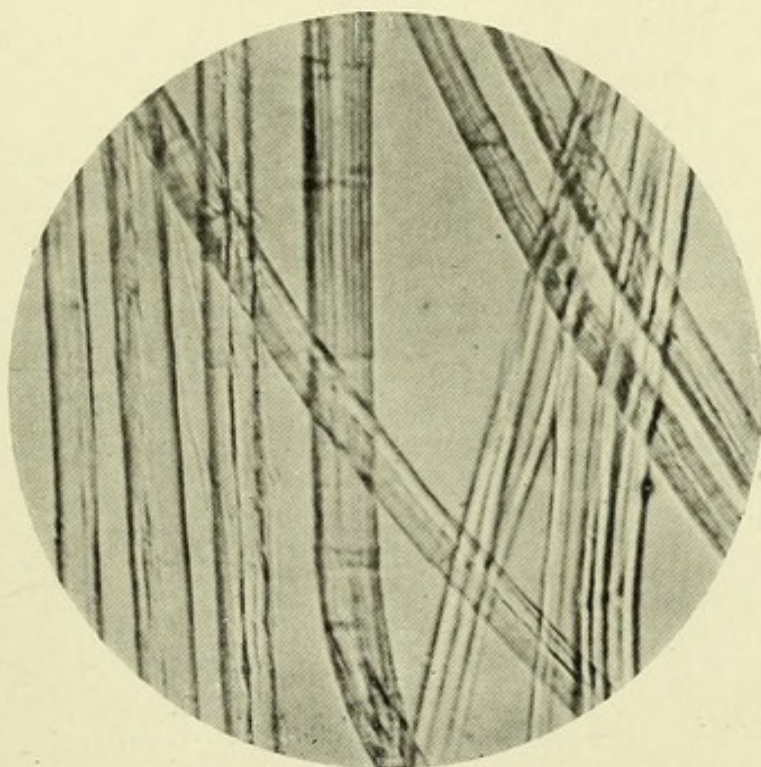


FIG. 92.—HEMP FIBRES. $\times 200$.

CHAPTER XXV

PRESERVED FOODS

MANY methods have been adopted for preserving foods, such as, (1) Cooking in vessels that are afterwards sealed from the air; (2) adding to the foods antiseptics, like boric acid and borax, sodium benzoate, salicylic acid, sodium fluoride, etc.; (3) salting; (4) smoking and drying; and (5) refrigeration. Most tinned foods are exposed to dangers arising from chemical changes which take place in the food through inefficient preservation. Some are damaged by the preservatives used, and others by colouring agents employed. Vegetables and fruits are especially liable to impregnation with the metallic impurities contributed by the tin and solder. The tinning may be carried out in the best possible manner, and still the foods contain toxic compounds. Tin, copper, and lead have produced evil in this way. Tinfoil round sweets furnishes lead. A sulphide of tin is frequently formed by the action of albuminous bodies upon containing vessels made of this metal. Varnished tins are equally bad, as most of the varnishes contain lead. Potted articles, such as fish, pickles, etc., that have been prepared with vinegar, should not be stored in metallic receptacles, as the acetic acid of the vinegar will inevitably dissolve the metals. In imperfectly preserved milks lactic acid may produce correspondingly evil results. Tinned vegetables have been frequently coloured by copper. Copper sulphate is known to impart a bright green colour to inferior peas; and whilst small quantities of this salt have not been proved harmful, larger quantities, such as 3 grains or more to the pound of peas, cannot be regarded as harmless, as it is now generally admitted that the albuminate of copper formed is rendered soluble by the processes of digestion. Of chemical disinfectants added to foods, boric and benzoic acids, and

their sodium salts, are perhaps the least harmful. Salicylates and formalin should not, under any circumstances, be employed.

The Report, issued in 1901, of a Departmental Committee, appointed to consider the use of antiseptics and colouring agents in food, recommended that formalin be absolutely prohibited; that salicylic acid be not used in greater proportion than 1 grain to the pound of solid food; that no preservative or colouring matter be used in milk; that boric acid, or mixtures of boric acid and borax, be alone allowed in cream and butter, in amounts not exceeding .25 per cent. in the former and .5 per cent. in the latter; that in infants' foods chemical preservatives of all kinds be prohibited; and that copper salts, used for 'greening' preserved foods, be prohibited.

The least objectionable method of preservation is refrigeration. This inhibits the action of organisms which produce decomposition, without adding anything harmful to the food or depriving it of any useful constituent. Drying is also, in some instances, a valuable method for food preservation.

The addition of quantities of salt, vinegar, and sugar to certain articles of food prevents decomposition, but in many cases detracts from their digestibility. The use of oils, as in the preservation of sardines, excludes air, and so retards the growth of putrefactive organisms. Although plausible excuses have been made for the use of various antiseptics in food-stuffs, there is no doubt that frequently very considerable deterioration of the food is produced, and also that the antiseptics themselves create disturbance in susceptible individuals. There are no valid arguments to justify the use of antiseptics in milk and butter, as these foods can be distributed to the consumer in a perfectly fresh condition without their aid. In permitting their use a premium is put upon the sale of inferior products.

The many condensed milks and infants' foods on the market profess to be sterile, and perfect substitutes for human milk. Careful bacteriological and chemical examinations do not always justify these claims. Several condensed milks are largely deficient in fat, whilst others are rich in starch and cane-sugar, and consequently impossible of complete digestion by infants of tender age. The unsweetened and condensed whole milks are perhaps

the best ; but the sweetened and condensed skim-milks are utterly worthless. The enormous number of proprietary foods for infants in existence to-day, each claiming to be a perfect substitute for mother's milk, and calling attention to the advantages it possesses over all its competitors, is a demonstration that the entire class is an imposition upon a credulous public.

APPENDIX

1 metre = 39.37 inches.

1 litre = 35.3 fluid ounces = 1.76 pints.

1 gramme = 15.432 grains.

28.35 grammes = 1 ounce.

1 litre of H at 0° C. and 760 milligrammes = .0896 gramme.

1 gallon of water = 10 pounds.

1 cubic foot of water = 6.228 gallons.

Approximate Atomic Weights in Round Numbers.

Al	27	Cu	63	O	16
As	75	H	1	K	39
Ba	137	I	127	Ag	108
Br	80	Fe	56	Na	23
Ca	40	Pb	206	S	32
C	12	Mg	24	Sn	118
Cl	35.5	N	14	Zn	65

Ammonia-Free Water.

Distil from a copper retort ordinary distilled water which has been rendered slightly alkaline by Na_2CO_3 . Reject the first portions, and stop the collection when the volume of water in the retort is reduced to 2 litres. Test the distillate from time to time with Nessler's solution.

Organically Pure Ammonia-Free Water.

To distilled water add 1 gramme KOH and .2 gramme potassium permanganate per litre; boil gently for twelve hours under a reflux condenser. Distil as in preparing ammonia-free water.

Baryta-water.

To a litre of freshly boiled distilled water, in a stoppered flask, add about 65 grammes of $\text{Ba}(\text{OH})_2$, and shake up from time to

time for two or three days. Allow the precipitate to settle, and pipette off the clear baryta-water. A saturated solution contains about 5 per cent. $\text{Ba}(\text{OH})_2$.

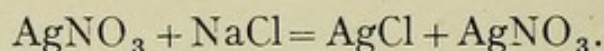
Sulphuretted Hydrogen Water.

Pour dilute HCl on FeS , and pass the gas through a small quantity of water into distilled water, until saturated. The solution should be kept in a well-stoppered bottle in a dark cupboard.

Potassium Chromate Solution.

Dissolve some crystals of pure K_2CrO_4 in pure distilled water, and add a drop or two of the standard solution of AgNO_3 , until a permanent red precipitate of silver chromate is formed. The appearance of this permanent precipitate insures the absence of chlorine in the reagent.

Standard Silver Nitrate Solution.



108 + 14 + 48 grammes AgNO_3 precipitate 35.5 grammes Cl .
 4.78 " " " 1 gramme "

Dissolve 4.78 grammes AgNO_3 in a litre of pure distilled water free from organic matter. One c.c. of this solution is equivalent to 1 milligramme Cl .

Standard Soap Solution.

Weigh out 12 grammes Castille soap, and dissolve in a litre of equal parts of methylated spirit and water. Carefully weigh .2 gramme dry CaCl_2 , and dissolve in a little pure HCl . Evaporate to dryness. Add a little distilled water, and again evaporate to dryness. Repeat the solution in water and evaporation until the last trace of acid has disappeared. Now dissolve the CaCl_2 in a litre of distilled water. One c.c. = the equivalent of .2 milligramme CaCO_3 . In other words, this solution possesses hardness = 20 parts per 100,000.

The soap solution is then titrated against 100 c.c. of the CaCl_2 solution, and diluted with the weak spirit, or fortified with more soap, until it registers a hardness of 20 parts per 100,000.

Standard Ammonium Chloride Solution.

53.5 grammes $(\text{NH}_4)\text{Cl}$ contain 17 grammes NH_3 .

3.14 „ „ „ 1 gramme „

Solution 1.—Dissolve 3.14 grammes dry anhydrous $(\text{NH}_4)\text{Cl}$ in a litre of ammonia-free distilled water. One c.c. of this solution = 1 milligramme NH_3 .

Solution 2.—Dilute 10 c.c. to 1,000 water to obtain a solution, 1 c.c. of which = .01 milligramme NH_3 .

Nessler's Solution.

Weigh out 35 grammes KI and 13 grammes HgCl_2 . Heat to boiling in 800 c.c. pure water. Stir until the salts are dissolved. Add cold saturated solution of HgCl_2 , until a permanent red precipitate appears. Add 120 grammes NaOH , and make up to a litre with water. In order to render the solution sensitive, add a little more HgCl_2 solution. When sensitive, the Nessler reagent has a slight yellow colour. A colourless solution is not sensitive. The clear solution should be syphoned off for use without interfering with any sediment that may form.

Alkaline Potassium Permanganate Solution.

Dissolve 8 grammes KMnO_4 and 200 grammes NaOH in a litre of distilled water. The solution should be boiled before use, so as to drive off any ammonia that may have existed as such, or as organic matter, in the water used for its preparation.

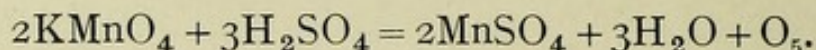
Starch Solution.

Place a platinum loopful of starch in 15 c.c. water in a test-tube, and boil till the liquid is quite clear. Cool, and the solution is ready for use. This reagent should be freshly prepared each time it is required.

Potassium Iodide Solution.

Dissolve a crystal of KI in water in a test-tube, and test a little of the fluid with starch solution to insure the absence of free iodine. Zinc iodide is preferable to potassium iodide, as it does not liberate free iodine on standing.

Standard Solution of Permanganate of Potassium.



316 grammes permanganate of potassium yield 80 grammes oxygen.

The solution has been found convenient for work when 10 c.c. yield 1 milligramme oxygen. A litre of this solution contains .1 gramme available O, and the amount of permanganate contained in this volume will be :

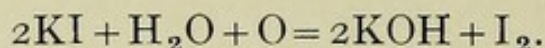
$$.1 \text{ gramme} \times \frac{316}{80} = .395 \text{ gramme.}$$

Thiosulphate Solution for Tidy's Process.

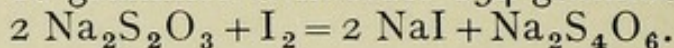
Dissolve 1 gramme of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in a litre of pure distilled water.

Standard Thiosulphate Solution for Thresh's Method.

This solution is of such strength that 1 c.c. = .25 milligramme O.



16 grammes O liberate 254 grammes I.



316 grammes thiosulphate combine with 254 grammes I ;

\therefore 16 grammes O are equivalent to 316 grammes $\text{Na}_2\text{S}_2\text{O}_3$, or to 496 grammes $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. (Sodium thiosulphate has 5 molecules of water of crystallization.)

$$\therefore 1 \text{ gramme O} = 31 \text{ grammes } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O},$$

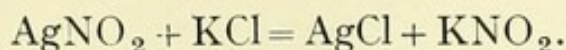
$$\text{and } .25 \text{ ,, } = 7.75 \text{ ,, }$$

Weigh out therefore 7.75 grammes crystalline sodium thiosulphate and dissolve in a litre of water. One c.c. = .25 milligramme O.

Solutions of thiosulphates must be made frequently, as they do not long retain their strength.

Standard Nitrite-Iodide Solution.

Dissolve .5 gramme NaNO_2 and 20 grammes KI in 100 c.c. of pure distilled water.

Standard Nitrite Solution.

154 grammes ,, correspond with 14 grammes N,
 11 ,, ,, ,, ,, 1 gramme N.

Weigh out 11 grammes pure AgNO_2 , and dissolve in boiling distilled H_2O . Add sufficient KCl to precipitate the whole of the silver. Make up the solution to 1 litre, and allow the AgCl to settle. Remove 100 c.c. of the clear supernatant fluid, and dilute to 1 litre with distilled water.

One c.c. of this solution = 0.1 milligramme N.

Standard Nitrate Solution.

101 grammes KNO_3 contain 14 grammes N.

7.21 ,, ,, ,, 1 gramme ,,

7.21 gramme ,, contains .1 ,, ,,

Weigh 7.21 gramme dry KNO_3 , and dissolve in 1 litre pure distilled water. One c.c. = .1 milligramme N.

Meta-Phenylene-Diamine.

One gramme of the base is dissolved in 250 c.c. distilled water, slightly acidulated with H_2SO_4 . When it turns dark in colour, it is clarified by admixture with animal charcoal and filtering.

Phenol-Sulphonic Acid.

Mix 12 grammes pure phenol with 6 c.c. distilled water and 74 c.c. of pure H_2SO_4 , and digest for two hours at 100°C .

Phenolphthalein.

Dissolve 1 gramme of the powder in 50 c.c. methylated spirit, and make up to 100 c.c.

Methyl Orange.

Dissolve .1 gramme of the powder in 100 c.c. distilled water. As a rule, this indicator is not affected by CO_2 .

Standard Solution of Lead.

1.83 grammes crystallized lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, contain 1 gramme Pb.

Dissolve with the aid of acetic acid, so as to procure a clear solution, 1.83 grammes $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ in a litre of distilled water. One c.c. = 1 milligramme Pb. When using, dilute ten times.

Standard Copper Solution.

Dissolve 3.95 grammes $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in a litre of distilled water. One c.c. = 1 milligramme Cu. When using, dilute ten times.

Standard Iron Solution.

1. Dissolve 1.004 grammes iron wire in nitro-hydrochloric acid. Precipitate with ammonia solution, wash and redissolve the ferric oxide in a little pure HCl. Dilute to 1 litre. One c.c. = 1 milligramme Fe.

2. Dissolve 4.96 grammes $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in a litre of distilled water. One c.c. = 1 milligramme Fe.

3. Owing to the impurities of FeSO_4 , it is more advantageous to prepare a standard solution of ammonium-iron-alum.

Dissolve 5.714 grammes $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_4 \cdot 6\text{H}_2\text{O}$ in a litre of distilled water. One c.c. = 1 milligramme Fe.

Standard Solution of Zinc.

Dissolve 4.4 grammes $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in a litre of pure distilled water. One c.c. = 1 milligramme Zn.

Normal Sodium Carbonate Solution.

Dissolve 53 grammes recently calcined Na_2CO_3 in a litre of distilled water.

$\frac{N}{10}$ Na_2CO_3 and $\frac{N}{50}$ Na_2CO_3 are obtained from the normal solution by diluting 10 and 50 times respectively.

Normal NaOH consists of 40 grammes pure NaOH in a litre of distilled water.

Decinormal ($\frac{N}{10}$) caustic soda is prepared by diluting the normal solution 10 times.

Normal Sulphuric Acid Solution.

Mix slowly about 30 c.c. of pure H_2SO_4 , specific gravity 1.84, with about 100 c.c. distilled water, and allow to cool. Transfer the mixture to a litre measure, and make up to the mark with distilled water. Run 25 c.c. of normal sodium carbonate solution into a beaker, and add a few drops of methyl orange. Now run the acid from a burette into the alkali until the neutral point is reached, and carefully read the amount. A simple calculation gives the amount of water to be added to make the acid of the normal strength—viz., 49 grammes H_2SO_4 per litre. Suppose 23 c.c. were required to neutralize the alkali, it is plain that 2 c.c. of water must be added to every 23 c.c. of the acid solution. It is necessary to do a fresh titration with normal alkali after adding the calculated amount of water.

$\frac{N}{10} \text{H}_2\text{SO}_4$ and $\frac{N}{50} \text{H}_2\text{SO}_4$ are prepared by diluting the normal ten and fifty times respectively.

Twenty-five per Cent. H_2SO_4 for the Estimation of O absorbed by Water.

Pour 250 c.c. redistilled H_2SO_4 into 750 c.c. of pure distilled water, and whilst the mixture is hot a few drops of the standard $\text{K}_2\text{Mn}_2\text{O}_8$ solution are added until a faint pink tinge is permanent. This insures that the acid will absorb no O.

Standard Oxalic Acid Solution for Use in the Estimation of CO_2 .

It is convenient to prepare this solution of such strength that 1 c.c. neutralizes as much $\text{Ba}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$ as .5 c.c. CO_2 at standard temperature and pressure. Oxalic acid $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]$ has a molecular weight of 126, and CO_2 of 44. A molecule of oxalic acid is equivalent to a molecule of carbon dioxide, since each unites with one molecule of BaO , to form barium oxalate and barium carbonate respectively.

\therefore 126 grammes oxalic acid are equivalent to 44 grammes carbon dioxide.

Since the weight of a litre of $\text{CO}_2 = 22 \times .0896$ gramme, the weight of .5 c.c. = $\frac{22 \times .0896 \times .5}{1000} = .0009856$ gramme.

\therefore the weight of oxalic acid in 1 c.c. of the required standard solution = $\frac{126}{44} \times .0009856$ gramme = .00282 gramme. This is 2.82 grammes per litre.

As a stronger solution of oxalic acid keeps better, a stock preparation of ten times this strength—viz., 28.19 grammes per litre—is made, and diluted to one-tenth strength when required.

Normal HCl.

Normal HCl is prepared by making an approximate solution, and titrating it against normal alkali, as in the case of normal H_2SO_4 . Normal HCl contains 36.5 grammes HCl per litre.

$\frac{N}{10}$ HCl is prepared from normal by diluting with water to one-tenth strength.

A Few Brief Notes on the General Chemical Reactions of the more commonly occurring Metals and Acids.

Oxidation.—A compound is oxidized when its oxygen or acid-forming part is increased. If ferrous oxide be heated in the air it becomes ferric oxide: $2\text{FeO} + \text{O} = \text{Fe}_2\text{O}_3$. Also ferrous chloride (FeCl_2) can be 'oxidized' to ferric chloride (FeCl_3), although no O is incorporated.

The following are oxidizing agents: The halogens, HNO_3 , H_2O_2 , $\text{K}_2\text{Mn}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$. The halogens effect oxidation through their direct addition— $\text{FeCl}_2 + \text{Cl} = \text{FeCl}_3$. Nitric acid splits into water and the anhydride— $2\text{HNO}_3 = \text{H}_2\text{O} + \text{N}_2\text{O}_5$; and the anhydride further splits into nitric oxide and oxygen— $\text{N}_2\text{O}_5 = 2\text{NO} + 3\text{O}$. Hydrogen peroxide splits into oxygen and water— $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$.

The free oxygen then liberates a halogen or performs some other type of oxidation: $2\text{FeCl}_2 + \text{H}_2\text{O}_2 + 2\text{HCl} = 2\text{FeCl}_3 + 2\text{H}_2\text{O}$.

Permanganic acid first splits into water and the anhydride; afterwards the anhydride splits into oxygen and manganous oxide: $\text{H}_2\text{Mn}_2\text{O}_8 = \text{H}_2\text{O} + \text{Mn}_2\text{O}_7$; and $\text{Mn}_2\text{O}_7 = 2\text{MnO} + 5\text{O}$.

The oxidizing action of permanganate in acid solution where sufficient acid is present to dissolve oxides is somewhat different from the corresponding action in alkaline solutions.

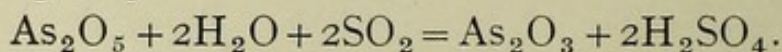
$\text{H}_2\text{Mn}_2\text{O}_8$ in acid solution gives up 5O.

$\text{H}_2\text{Mn}_2\text{O}_8$ in alkaline solution gives up 3O.

The oxidation of chromic acid depends similarly on the splitting of chromic anhydride into oxygen and chromic oxide.

Reduction.—A compound is reduced when its oxygen or acid-forming part is diminished. The following are reducing agents: nascent H, sulphurous acid, H_2S , SnCl_2 , HI.

Hydrogen will reduce compounds in acid, alkaline, or neutral solution. Sulphurous acid reduces compounds through SO_2 readily becoming SO_3 :

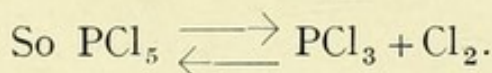


Hydrogen sulphide is not much used as a reducing agent, on account of the deposit of S, which is difficult of filtration.

Stannous chloride reduces bodies by its ready conversion into stannic chloride in acid solution.

Hydriodic acid is a strong reducing agent through its decomposition into H and I.

Chemical Mass Action.—If chlorine be allowed to act on PCl_3 in the cold, PCl_5 is formed: $\text{PCl}_3 + \text{Cl}_2 = \text{PCl}_5$. If the latter be heated it is decomposed into chlorine and phosphorus trichloride: $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$.

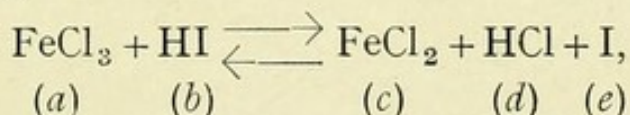


Ammonium chloride on heating is dissociated into NH_3 and HCl , and the dissociation increases with the rise of temperature; further, for every temperature the ratio of the dissociated to the undissociated portion is a constant. If whilst volatilizing NH_4Cl we desire the least dissociation, we must proceed as follows: If a represent the number of undecomposed molecules of NH_4Cl in a given quantity, and b and c the number of molecules of NH_3 and HCl respectively, then $\frac{a}{b \cdot c}$ is a constant for any definite temperature.

If b or c is increased, a must become larger, because $\frac{a}{b \cdot c}$ is a constant—*i.e.*, we must volatilize NH_4Cl in an atmosphere of NH_3 or HCl .

Dissociation may be effected by solution, and in this case the dissociation increases with the dilution.

In the equation



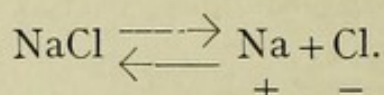
for every degree of concentration the relation holds,

$$\frac{a \cdot b}{c \cdot d \cdot e} \text{ is a constant.}$$

If we wish the reaction to take place from left to right (ferric chloride to be reduced to ferrous chloride), b must be increased, whereby a becomes smaller. By employing a large excess of HI the ferric salt may be quantitatively reduced to ferrous salt, as occurs in the quantitative determination of iron. It is important that the student should perform all reactions as nearly as possible quantitatively. If we desire to oxidize all the HI , then a must be as large as possible, whereby b practically tends to become zero.

Ion Hypothesis of Arrhenius.—Solid NaCl and distilled water are both non-conductors of electricity—*i.e.*, non-electrolytes. If

the NaCl be dissolved in the distilled water the solution becomes a good conductor of electricity. This observation applies to all acids, bases, and salts. In anhydrous condition they are non-electrolytes; in aqueous solution they are electrolytes. Arrhenius proposed the view that the NaCl on dissolving in the water dissociated into positively charged Na ions and negatively charged Cl ions:



If the poles of an electric battery be inserted in such a solution the positive pole or anode repels the positive ions (cations), and attracts the negative ions (anions), and the latter as soon as they come into contact with the anode give up their negative electricity, become neutral, and separate out. At the cathode the cations are discharged. The ions alone, and not the undissociated molecules, cause the conduction of the current. Since equivalent ions carry equal amounts of electricity (Faraday), the more ions there are present in unit volume of a solution the better is its conductivity. Thus by determining the conductivity of a solution of an electrolyte, the degree of dissociation can be ascertained. In this manner it has been found that strong acids and bases, being good conductors, are largely dissociated, whilst weak acids (H_2CO_3 , HCN) and weak bases (NH_4HO) are slightly dissociated; these are bad conductors.

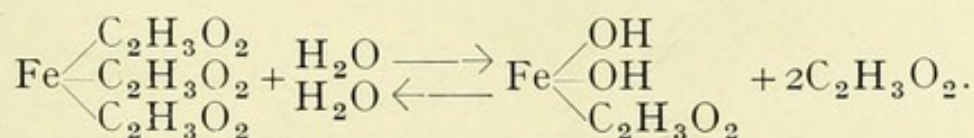
In the well-known interaction between NaCl and AgNO_3 there are present in the solution dissociated and undissociated salts. Positive Ag ions unite with negative Cl ions and form neutral AgCl, which is insoluble and therefore separates out, whereby equilibrium in the solution is upset. Equilibrium is re-established by further dissociation of NaCl and AgNO_3 , with the result that more AgCl is formed, and this action goes on until all the Cl separates out as AgCl. Silver ions form a reagent for Cl ions. *The work of qualitative analysis is to find out tests for all ions and methods for their separation.*

Reverting to the formula $\frac{a}{b \cdot c} = \text{a constant}$, we see that if we wish to decrease the solubility of a salt it is only necessary to increase the concentration of one of the ions into which it dissociates—i.e., to add an excess of the precipitant. The amount of this excess depends on the solubility of the salt. In the case of such an insoluble salt as BaSO_4 , a very slight excess of Ba or SO_4 is sufficient, whereas in the case of the more soluble PbSO_4 , a greater excess of Pb or SO_4 ions is required.

In the separation of precipitates by filtration, the size of the

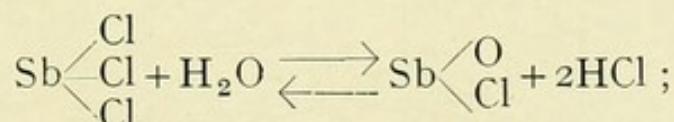
filter should be regulated by the amount of the precipitate, and not by the volume of the liquid. The washing of a precipitate should be continued until the wash-water fails to give evidence of foreign substances.

Hydrolysis.—Although pure water is a bad conductor of electricity, it is still electrically dissociated to a small extent, and this is sufficient to bring about decompositions known as hydrolysis, which are reversible. Neutral ferric and aluminium salts present an acid reaction in solution. Neutral ferric acetate when boiled is converted into insoluble basic acetate and free acetic acid, and the decomposition is more easily effected the more dilute and the hotter the solution. When the solution cools, the insoluble basic salt goes back into solution :



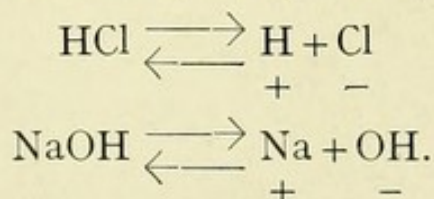
Increased temperature and dilution favour hydrolysis, and by reason of this hydrolytic action it is frequently impossible to procure anhydrous salts by evaporating their aqueous solutions.

To further illustrate the hydrolytic action of water, and at the same time the influence of mass action, take a solution of antimony chloride in concentrated HCl, and add a small quantity of H₂O, when a heavy precipitate of antimony oxychloride falls. The addition of a little concentrated HCl causes this to dissolve. Further addition of water precipitates the salt, and further acid dissolves it :



accordingly, by increasing the mass action of the water the reaction takes place from left to right, whilst by increasing the HCl the reaction is reversed.

Acidity and Alkalinity.—An acid reaction depends on the presence of free H ions ; an alkaline on hydroxyl ions :

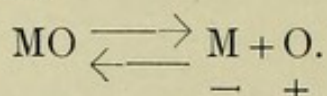


Certain substances which change colour on coming in contact with one or other of these compounds are used as indicators.

As an indicator for free H ions, methyl orange (which acts as a weak acid) is often used. The undissociated molecule of methyl

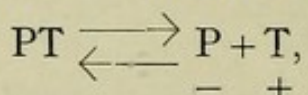
orange, which may be represented by MO, is pink, whilst its anion M is deep yellow.

When dissolved in water—



If there be an accumulation of hydrogen ions, as when a small amount of strong acid is present, the dissociation is diminished, and the pink colour of the undissociated MO appears. Weak acids also lessen the dissociation, but a much larger excess is necessary, hence methyl orange is a more sensitive indicator for strong than for weak acids.

Phenolphthalein, which may be represented by PT, also a weak acid, has a colourless undissociated molecule, whilst its anion P is intensely red. In aqueous solution it is decomposed slightly,



and the solution is colourless, because there are not enough anions present to colour it red. If a strong base be added, the HO ions of the base unite with the free H ions to form water, more PT is dissociated, and the H and HO unite as fast as they are set free, forming more water. Thus P ions accumulate, and the solution becomes red.

Dry-way Reactions.—In investigating precipitates and minerals we make use of (1) fusibility, (2) volatility, (3) ability to colour a non-luminous flame, (4) behaviour towards oxidizing and reducing agents.

The base of the flame where the temperature is low serves to test volatile substances for colour.

The fusing zone lies a little more than a third from the base, and about midway between the outside and inside of the mantle, which is broadest at this part. This is the hottest portion (over 2,000° C.), and serves to test fusibility and volatility.

The outer border of the fusing zone, known as the lower oxidizing flame, serves for testing the oxidation of substances in vitreous fluxes.

The upper oxidizing zone, at the non-luminous tip, is used for oxidations where the very highest temperature is not required.

The lower reducing zone lies about one-fifth from the base, on the inner border of the fusing zone, next to the dark cone. Reducing gases are here mixed with oxygen, so that many substances reducible by the upper reducing flame are unaffected. This part serves for reduction on charcoal and in vitreous fluxes.

The upper reducing flame is at the luminous tip of the dark inner

cone, which may be produced by gradually diminishing the supply of air. It should be reduced to such size that a porcelain dish placed over it will not be blackened. It contains no free oxygen, but much separated incandescent carbon, and has consequently a much stronger reducing action than the lower reducing zone. It is used for the reduction of metals collected in incrustations.

Test of Fusibility.

The following degrees of heat are recognised in flame work :

1.	525° C.	-	-	-	a faint red glow.
2.	700° C.	-	-	-	dark red glow.
3.	950° C.	-	-	-	bright red glow.
4.	1,100° C.	-	-	-	yellow glow.
5.	1,300° C.	-	-	-	faint white glow.
6.	1,500° C.	-	-	-	full white glow.

Tin	melts at	232° C.
Lead	„ „	327° C.
Zinc	„ „	420° C.
Antimony	„ „	630° C.
Aluminium	„ „	658° C.
Silver	„ „	960° C.
Copper	„ „	1,080° C.
Platinum	„ „	1,780° C.

Oxidation and Reduction in Vitreous Beads.

Mount a fine piece of platinum wire in a glass rod, and make a borax bead thus : Heat the wire to redness, and quickly dip it into borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), then heat until a portion of the salt fuses to the wire. Repeat the dipping into the salt and heating until a bead 1.5 millimetres is obtained. It is better not to make a loop on the end of the wire. In order to attach the substance to be tested moisten the bead with pure water, and dip it into the finely powdered substance. Hold the bead horizontally in the flame to prevent it falling off. Introduce too little of the substance into the bead rather than too much. Oxidize in the lower oxidizing flame, and reduce in the lower reducing zone. Cool in the dark inner cone to prevent oxidation taking place by cooling in the air.

Reduction on Charcoal.

Melt a crystal of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) in the flame, and mix a small quantity with an equal quantity of the substance to be tested. Place on charcoal, and remove first to the

lower oxidizing flame until the paste has melted, then move it into the lower reducing flame. The melt swells up through evolution of CO_2 , and when this has ceased, and the mass melts quietly, the reduction is complete. Cool in the dark zone. Remove the mass to a little water in an agate mortar; triturate, when the sodium carbonate goes into solution, charcoal floats on the surface, and the metal sinks to the bottom. Pour away the fluid, wash, and proceed to test the metal with acids, salts, etc.

1. The metal is white—Ag, Pb, Sn, Pt.

Warm with a few drops of HNO_3 : Ag and Pb dissolve readily. Silver will be detected by the addition of a drop of HCl , whereby AgCl is formed. Lead is recognised by the white PbSO_4 formed on the addition of a drop of H_2SO_4 .

If the metal is unchanged by treatment with HNO_3 it is probably platinum. Dissolve in aqua regia, evaporate to dryness, dissolve in a little water, add potassium chloride, and a yellow crystalline precipitate will separate out confirmatory of Pt.

If on treatment with HNO_3 the metal changes into a white insoluble oxide, it is tin. Dissolve another fragment of the metal in concentrated HCl , and test for tin with solution of HgCl_2 .

2. The metal is yellow to red: Cu.

Copper readily dissolves in HNO_3 . A drop of potassium ferrocyanide produces a brown precipitate.

Reduction in the Upper Reducing Flame.

This method detects volatile elements such as arsenic, antimony, bismuth, and cadmium, which are reducible by H or charcoal.

Hold in one hand a small portion of the substance on a thin asbestos thread in the upper reducing zone. In the other hand, closely over the substance to be tested, hold a white porcelain dish filled with water, when a metallic mirror is formed on the dish, which can duly be examined.

Reduction on Charcoal by the Blowpipe.

Mix the substance with double its amount of anhydrous sodium carbonate; fix the mixture in a hollow in the charcoal, and apply the flame.

CuO , PbO , Bi_2O_3 , SnO_2 , Sb_2O_3 , Fe_2O_3 , NiO , and CoO are reduced to a fused metallic globule (Pb, Bi, Sb, Sn), to a sintered mass (Cu), or to a glistening metallic particle (Fe, Ni, Co).

The oxides of zinc, cadmium, and arsenic are easily reduced to metal. They are so volatile that they pass as vapours from the reducing zone to the oxidizing zone, where they are deposited as coloured oxides outside the hollow in the charcoal.

The incrustation of Zn is yellow whilst hot, and white when cold. The oxide of cadmium is brown, and the oxide of arsenic white. Volatilization of arsenic gives rise to the characteristic garlic odour.

Chlorates, nitrates, and nitrites cause a very rapid combustion of the glowing charcoal, known as deflagration.

Wet-way Reactions.

A reaction is indicated by (1) formation of a precipitate ; (2) change of colour ; (3) evolution of a gas.

In order to carry out analysis definitely, we must know the sensitiveness of each reaction. The student should work with reagents of known strengths, and for ordinary qualitative work it is recommended that solutions of the reagents be used, as Blochmann suggested, of double-normal, normal, half-normal, fifth-normal, and tenth-normal strengths. In this way he will be able to draw a conclusion, by the size of the precipitate formed, as to the approximate amount of the substance present.

Reactions of the more commonly occurring Metals (Cations).

It is convenient to divide the metals into five groups :

1. Metals whose chlorides are insoluble, or difficultly soluble, and whose sulphides are insoluble in dilute acids. They may accordingly be precipitated from their solutions by means of either HCl or H_2S .

2. Metals whose chlorides are soluble, but whose sulphides are insoluble in dilute acids. They may therefore be precipitated from their solutions by means of either HCl or H_2S .

3. Metals whose sulphides are soluble in dilute acids, but insoluble in water and alkalies. They are precipitated by H_2S only from alkaline solutions.

4. Metals whose sulphides are soluble in water, but whose carbonates are insoluble in the presence of ammonium chloride. They are precipitated by $(NH_4)_2CO_3$ in presence of NH_4Cl , but not by any of the above reagents.

5. The alkalies and magnesium. They are not precipitated by any of the above reagents.

GROUP I.

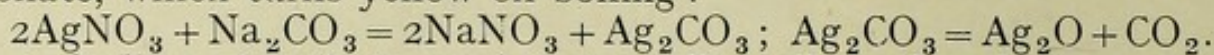
Silver.—Ag, Pb, mercurous Hg. [Thallium and tungsten also.]

Wet Reactions.—1. Potassium and sodium hydroxides precipitate brown silver oxide, $2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O$,

insoluble in excess of precipitant, but soluble in HNO_3 , and $(\text{NH}_4)\text{OH}$. On standing, the solution in $(\text{NH}_4)\text{OH}_2$ deposits black $(\text{AgNH}_3)_2\text{O}$.

2. Ammonia: If ammonia be cautiously added, the first drops produce a white precipitate, which changes quickly to the brown oxide, Ag_2O , soluble in excess of $(\text{NH}_4)\text{OH}$.

3. Sodium carbonate produces a precipitate of white silver carbonate, which turns yellow on boiling:



4. Sodium phosphate precipitates yellow silver phosphate.

$3\text{AgNO}_3 + 2\text{Na}_2\text{HPO}_4 = 3\text{NaNO}_3 + \text{NaH}_2\text{PO}_4 + \text{Ag}_3\text{PO}_4$. Silver phosphate is soluble in HNO_3 and NH_4OH .

5. HCl and soluble chlorides throw down from neutral and acid solutions white curdy AgCl , soluble in NH_4OH , insoluble in HNO_3 .

6. H_2S precipitates from neutral, alkaline, and acid solutions black Ag_2S , insoluble in NH_4OH and dilute KCN .

Dry-way Reactions.—Fused with soda on charcoal, silver compounds yield a white metallic button without incrustation (difference from lead and tin), readily soluble in HNO_3 (difference from tin).

The solution is not precipitated by very dilute H_2SO_4 , but is immediately precipitated by HCl (difference from lead).

Lead.—1. KOH and NaOH precipitate white lead hydroxide, soluble in excess of the precipitant: $\text{Pb}(\text{NO}_3)_2 + 2\text{KOH} = 2\text{KNO}_3 + \text{Pb}(\text{OH})_2$.

2. Ammonia precipitates the white hydroxide, insoluble in excess of the reagent.

3. Alkali carbonates precipitate white basic lead carbonate.

4. KCN precipitates white lead cyanide, insoluble in an excess.

5. HCl and soluble chlorides precipitate white lead chloride, difficultly soluble in cold water, more soluble in hot water.

6. KI precipitates yellow lead iodide, PbI_2 , more insoluble in water than the chloride.

7. K_2CrO_4 precipitates yellow lead chromate, PbCrO_4 , insoluble in acetic acid, but soluble in HNO_3 , and in caustic alkali.

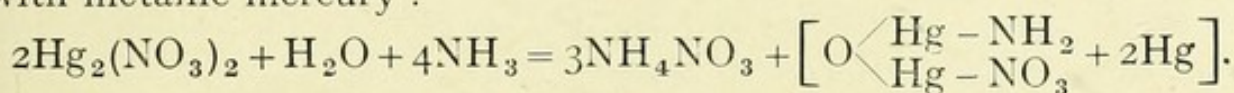
8. H_2S produces in the most dilute lead solutions a black precipitate of PbS .

9. H_2SO_4 produces white, difficultly soluble PbSO_4 (soluble in 22,800 parts of water, less soluble in water containing a little H_2SO_4 , and quite insoluble in alcohol).

Dry-way Reactions.—Heated on charcoal with sodium carbonate, lead compounds yield a malleable button, surrounded by an incrustation of yellow oxide. The bead is turned black in the reducing flame owing to the separation of lead.

Mercurous Mercury.—1. KOH precipitates black Hg_2O .

2. Ammonia precipitates a black amido-mercuric compound with metallic mercury :



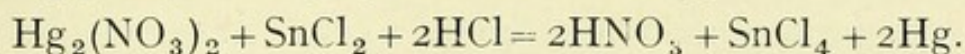
3. Alkali carbonates precipitate a yellow carbonate, Hg_2CO_3 , which rapidly becomes gray.

4. KCN precipitates metallic Hg and $\text{Hg}(\text{CN})_2$.

5. K_2CrO_4 precipitates red Hg_2CrO_4 on boiling.

6. KI precipitates green Hg_2I_2 soluble in excess of the precipitant.

7. SnCl_2 precipitates gray metallic mercury :



Dry-way Reactions.—Mercury compounds sublime on heating in the closed tube. Mercuric chloride first melts, then vaporizes, forming a crystalline deposit on the cold sides of the tube. Mercurous chloride sublimes; the sublimate, for the most part white, contains a slight grayish tint, due to the decomposition of a small part of the substance into mercuric chloride and mercury. These tests are of some value in differentiating between corrosive sublimate and calomel.

Mercuric iodide gives a yellow sublimate, which becomes red on being rubbed with a glass rod.

Sulphide of mercury gives a black sublimate.

All mercury compounds, when mixed with sodium carbonate and heated in a closed tube, yield a mirror, consisting of small globules of mercury. Rub the mirror with a little blotting-paper rolled on a glass rod, when the small drops will run together into larger ones, so that they can be removed.

GROUP II.

Mercuric Mercury.—1. KOH precipitates yellow HgO , readily soluble in acids.

2. Ammonia precipitates white mercuric amido-chloride, 'infusible precipitate,' which volatilizes before it melts. It is soluble in hot ammonium chloride and acids, forming 'fusible precipitate.'

3. Alkali carbonates precipitate from both the chloride and the nitrate a brownish basic carbonate in the cold, which, on boiling, loses CO_2 and is changed into HgO .

4. KCN produces no precipitate in solutions of HgCl_2 . In a concentrated solution of nitrate it produces $\text{Hg}(\text{CN})_2$, soluble in excess of the cyanide. This is the only cyanide of the heavy metals soluble in water.

5. H_2S throws down a precipitate, first white, later yellow and brown, and finally black. Further, H_2S produces a black precipitate composed wholly of HgS , which is insoluble in dilute boiling acids, in caustic potash and soda, and in $(\text{NH}_4)_2\text{S}$, but soluble in sodium or potassium sulphide.

6. Ferrous sulphate reduces mercurous nitrate to metallic Hg . Mercuric chloride and cyanide are not reduced by ferrous sulphate.

7. SnCl_2 reduces mercuric salts, first to calomel (Hg_2Cl_2), and then to metal.

8. Cu , Zn , and Fe precipitate Hg from solutions of its salts. On placing a drop of a solution of a mercurous or mercuric salt on a bright piece of copper-foil a gray spot is formed, which can be made as bright as silver when dried and rubbed.

Dry-way Reactions.—See Mercurous Mercury, p. 267.

Lead.—1. KOH precipitates white lead hydroxide, $\text{Pb}(\text{OH})_2$, soluble in excess of the precipitant.

2. Ammonia precipitates the white hydroxide, insoluble in excess of the precipitant.

3. Alkali carbonates precipitate white basic lead carbonate. Alkali bicarbonates precipitate normal carbonate.

4. KCN precipitates white lead cyanide, insoluble in excess of reagent.

5. HCl precipitates white lead chloride, PbCl_2 , difficultly soluble in cold water.

6. KI precipitates yellow lead iodide PbI_2 , more insoluble in water than the chloride.

7. K_2CrO_4 precipitates yellow PbCrO_4 , insoluble in acetic acid, but soluble in HNO_3 and KOH .

8. H_2S precipitates from the most dilute alkaline, neutral, or acid solutions a black lead sulphide, PbS . From hydrochloric acid solutions an orange-red precipitate of lead sulpho-chloride, $(\text{PbCl})_2\text{S}$, is at first obtained, which is decomposed immediately by more H_2S , forming (in the same manner as mercuric salts) black lead sulphide, soluble in dilute boiling HNO_3 and in strong cold HCl .

9. H_2SO_4 precipitates the difficultly soluble white PbSO_4 .

(These reactions are described under Group I., but for convenience they are repeated here.)

Copper.—Cuprous compounds are rapidly oxidized to cupric.

1. KOH precipitates in the cold yellow $\text{Cu}_2(\text{OH})_2$, which loses water on boiling, becoming red Cu_2O .

2. KCN precipitates white cuprous cyanide: $\text{Cu}_2\text{Cl}_2 + 2\text{KCN} = 2\text{KCl} + \text{Cu}_2(\text{CN})_2$, soluble in excess, forming colourless cuprous potassium cyanide: $\text{Cu}_2(\text{CN})_2 + 6\text{KCN} \rightleftharpoons \{\text{Cu}_2(\text{CN})_8\} \text{K}_6$.

This solution contains no cuprous ions, but ions of potassium and cuprous cyanide $\{Cu_2(Cn)_8\}$. It gives no precipitate with KOH or H_2S ; this property is utilized in the separation of Cu from Cd. If $Cu_2(CN)_8$ be diluted with much water the following compounds are successively formed (all of which are readily decomposed by H_2S , with deposition of black Cu_2S): $\{Cu_2(CN)_4\} K_2$, $\{Cu_2(CN)_3\} K$, $Cu_2(CN)_2$.

Cupric salts in aqueous solution are blue or green; in anhydrous condition white or yellow.

The sulphate, acetate, chloride, and nitrate are soluble in water; most of the remaining salts are insoluble in water, but soluble in acids.

1. KOH produces in the cold a blue precipitate of cupric hydroxide: $CuSO_4 + 2KOH = Cu(OH)_2 + K_2SO_4$, which on boiling is changed to brownish-black cupric oxide.

2. Ammonia in small quantity precipitates a green powdery basic salt, extremely soluble in excess, forming an azure-blue solution.

3. KCN produces at first yellow cupric cyanide, which quickly loses $(CN)_2$ to become white cuprous cyanide, soluble in excess of KCN.

4. H_2S precipitates colloidal black CuS , which in neutral or slightly acid solutions tends to run through the filter. In order to prevent this and to precipitate Cu quantitatively from a solution, much dilute HCl is added, and H_2S passed through the solution. CuS is soluble in KCN and in hot dilute HNO_3 , but insoluble in boiling dilute H_2SO_4 (difference from cadmium). CuS is fairly soluble in $(NH_4)_2S$, but insoluble in potassium or sodium sulphide (difference from Hg).

5. Potassium ferrocyanide precipitates in neutral and acid solutions amorphous reddish-brown cupric ferrocyanide, insoluble in dilute acids, but soluble in ammonia, forming a blue solution.

Dry-way Reactions.—The borax bead when saturated with a copper salt is green in the oxidizing flame; if it contain little its colour is blue.

The blowpipe reaction on charcoal gives spongy metal but no globule.

Copper salts colour the flame blue or green.

Bismuth.—The proper solvent for bismuth, as for most metals, is HNO_3 . It forms two oxides—yellow Bi_2O_3 , and brown Bi_2O_5 . Bi is therefore either trivalent or pentavalent like As, Sb, P, and N.

Bi salts are all insoluble in much water because of being hydrolized into an insoluble basic salt.

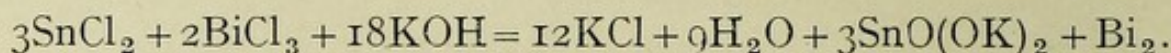
1. KOH precipitates the white hydroxide, $Bi(OH)_3$, which when boiled becomes $BiO.OH$, through losing one molecule of water.

2. Ammonia precipitates a white basic salt (not hydroxide) varying in composition with concentration and temperature.

3. Alkali carbonates precipitate, according to temperature and concentration, a number of basic carbonates.

H_2S precipitates brown Bi_2S_3 , insoluble in cold dilute mineral acids and alkaline sulphides, soluble in dilute hot nitric acid and in concentrated boiling HCl .

4. Stannous chloride in the presence of KOH reduces bismuth salts to metallic bismuth.



If too much KOH be used metallic Sn will separate out ; if too little, black stannous oxide will be deposited.

5. Metallic zinc precipitates metallic Bi : $2BiCl_3 + 3Zn = 3ZnCl_2 + Bi_2$.

Dry-way Reactions.— Bi salts colour the flame a pale greenish-white. Heated with soda on charcoal before the blowpipe, a button is obtained surrounded by a yellow incrustation of bismuth oxide. In the upper reducing flame Bi is reduced to metal, which is volatilized and burnt in the upper oxidizing flame. Cold porcelain held just above the oxidizing flame receives a fine deposit, barely visible, which on being treated with hydriodic acid turns to scarlet bismuth hydriodic acid : $Bi_2O_3 + 8HI = 3H_2O + BiI_4H$. Breathing on this deposit causes the colour to disappear, but as soon as the moisture has evaporated it reappears.

Cadmium.—Cadmium is generally associated with zinc in its ores—often as the crystalline oxide, CdO , mixed with calamine.

1. KOH precipitates white amorphous cadmium hydroxide, $Cd(OH)_2$, insoluble in excess of the reagent (difference from lead and zinc). The hydroxide is converted by gentle ignition into the brown oxide. Stronger ignition, especially of the nitrate, produces the black crystalline oxide.

2. Ammonia precipitates the white hydroxide, soluble in excess (difference from lead), forming complex cadmium ammonium compounds, as with zinc, nickel, etc.

3. Alkali carbonates precipitate white basic carbonate insoluble in excess.

4. KCN precipitates white amorphous $Cd(CN)_2$, readily soluble in excess, forming $Cd(CN)_4K_2$.

5. H_2S produces in sulphuric acid solutions of cadmium salts containing oxygen a pure yellow precipitate of cadmium sulphide, CdS , insoluble in alkaline sulphides (difference from As), soluble in boiling dilute (1 in 5) H_2SO_4 (difference from Cu).

The sulphide produced from halogen salts by H_2S is at first a deep orange-yellow, growing lighter under further action of the

reagent, but never reaching the sulphur yellow obtained from the oxygen salt.

6. $(\text{NH}_4)_2\text{S}$ produces in ammoniacal solutions yellow colloidal CdS , which has a tendency to pass through the filter. These hydrosal forms, common to zinc, aluminium, and other bodies, can be changed to the insoluble hydrogel forms by precipitation with concentrated salt solutions, or by boiling, or by addition of acids.

Dry-way Reactions.—On heating with soda on charcoal a brown incrustation of CdO is formed.

CdO in the upper reducing flame is changed to metal, which volatilizes, and in the upper oxidizing flame goes back to oxide. This oxide contains suboxide capable of reducing Ag_2O to metal. The film of cadmium oxide received on porcelain, when moistened with AgNO_3 , produces a black deposit of metallic silver. This reaction is very sensitive.

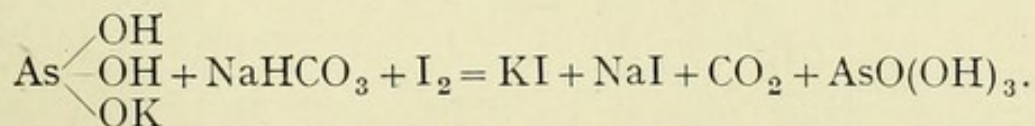
Arsenic.—Arsenic, like phosphorus and nitrogen, forms two oxides, the trioxide As_2O_3 , and the pentoxide As_2O_5 .

Arsenic trioxide is found as (1) isometric As_2O_3 , white arsenic; (2) monoclinic As_2O_3 ; (3) amorphous As_2O_3 . The monoclinic form dissolves in 80 parts of cold water; the amorphous variety in 25. If white arsenic be treated with water it is not wet, but assumes a characteristic appearance like meal. The trioxide dissolves readily in HCl , and as an acid anhydride in alkalis, forming in the latter soluble arsenites (salts of arsenious acid). Free arsenious acid has not been isolated.

1. H_2S precipitates yellow As_2S_3 insoluble in acids, but dissolved by alkalis and alkaline sulphides. The anhydride forms sulpho- as well as oxy-salts, and where sulpho-salts are formed H_2S produces no precipitation, or only a partial precipitation, from arsenites; hence to procure complete precipitation of As as As_2S_3 sufficient free acid should exist in the solution to prevent the formation of soluble sulpho-salts.

2. AgNO_3 precipitates from neutral solutions of arsenites yellow $\text{As}(\text{OAg})_3$, soluble in nitric acid and ammonia. AgNO_3 , when used quantitatively, should be preceded by a little HNO_3 in order that complete precipitation of arsenites may occur. Further, the silver nitrate should be previously treated with ammonia until the Ag_2O just dissolves.

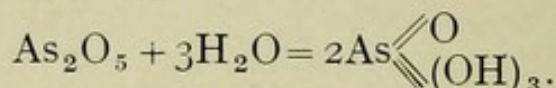
3. Iodine solution is decolourized by arsenious acid with the formation of arsenic acid. If the reaction be used quantitatively acid solutions must be neutralized with NaHCO_3 , and not with normal carbonate, which decolourizes I :



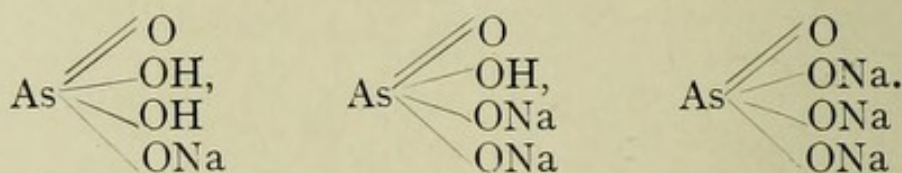
4. Stannous chloride in presence of concentrated HCl reduces an arsenite to metallic As.

5. Magnesium ammonium chloride produces no precipitation in dilute arsenite solutions in the presence of ammonia (difference from arsenic acid).

Arsenic pentoxide and its compounds, As_2O_5 , is a white fusible substance which may be obtained by heating arsenic acid. By strong ignition it is converted into As_2O_3 and O_2 . It is soluble in water forming arsenic acid :



Rhombic prisms of the formula $2\text{AsO}(\text{OH})_3, \text{H}_2\text{O}$ may be obtained, and when heated to 100°C . these lose their water to form a crystalline powder (ortho-arsenic acid, $\text{AsO}[\text{OH}]_3$). By gentle ignition more water is given off, and pyro-arsenic acid, $\text{As}_2\text{H}_4\text{O}_7$, is formed, which on further ignition is changed to metarsenic acid, AsHO_3 . In this respect arsenic acts like phosphoric acid. Like ortho-phosphoric acid, arseniates (salts of arsenic acid) form mono-, di-, and tri-metallic salts :



Alkaline arseniates are soluble in water ; other arseniates are soluble in acids, but insoluble in water.

1. AgNO_3 produces in neutral solutions brown silver arseniate (difference from arsenious and phosphoric acids), soluble in ammonia and acids.

2. H_2S passed into a moderately acid solution of arsenic acid gradually reduces the latter to arsenious acid with deposition of S ; the arsenious acid is then rapidly precipitated as As_2S_3 . This explains the liquid remaining clear for a time, after which it gradually becomes turbid. Nearly all the arsenic is precipitated as As_2S_5 if the gas be rapidly passed into a cold solution containing considerable HCl. If the gas be passed into a hot solution containing much concentrated HCl, a mixture of As_2S_3 and As_2S_5 is precipitated. In concentrated HCl solution the As exists as AsCl_5 , which is not readily reduced by H_2S , but is precipitated as As_2S_5 ; on addition of water the pentachloride is changed to arsenic acid, which is reduced by H_2S to arsenious acid before precipitation. To precipitate arsenic quickly from arseniates without much HCl, it is then only necessary to reduce the arsenic acid by boiling with sulphurous acid, and after boiling off the excess to lead the gas rapidly into the solution, when arsenious sulphide is precipitated.

As_2S_5 , like As_2S_3 , is insoluble in boiling concentrated HCl , but soluble in alkalis, alkaline sulphides, and ammonium carbonate.

3. MgCl_2 throws down in the presence of $(\text{NH}_4)\text{HO}$ and $(\text{NH}_4)\text{Cl}$ a white crystalline precipitate of magnesium ammonium arseniate :

$\text{As} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \\ \diagdown \text{O} \diagup \\ \diagdown \text{ONH}_4 \diagup \end{array} \text{Mg}$. This precipitate on ignition is changed into magnesium pyro-arsenate, and is used for the quantitative estimation of As.

4. Ammonium molybdate (150 grammes commercial ammonium molybdate $\{(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}, 4\text{H}_2\text{O}\}$ dissolved in a litre of water, to which is added a litre of HNO_3 of specific gravity 1.2) in excess precipitates in boiling HNO_3 solution yellow crystalline ammonium arseno-molybdate $(\text{NH}_4)_3\text{AsO}_4, 12\text{MoO}_3$).

Marsh's Test for As.

Arsenious or arsenic compounds are reduced to arsine, AsH_3 , by nascent H, produced by the action of H_2SO_4 on Zn. If zinc and HCl be used a high temperature is necessary. Oxides are quickly reduced, sulphides slowly. This test is extremely delicate, detecting as little as .0007 milligramme As. All reagents must be carefully freed from arsenic.

Arsine is an unpleasant-smelling poisonous gas, which, on being heated in the absence of O, is decomposed into As and H; heated in air it is oxidized to water and arsenic trioxide.

Chemically-pure zinc dissolves with difficulty in chemically-pure H_2SO_4 , so that a small piece of platinum is generally added to accelerate the reaction. The electric current formed through the contact of Zn and Pt causes a rapid evolution of H. But as arsine produced in this way always contains some solid arsine, it is necessary to use two flasks equipped for the generation of H; one of these, the larger, contains pure Zn, pure H_2SO_4 , and Pt; the other, in size about 100 c.c., contains not more than 3 grammes granulated zinc, and about 20 c.c. arsenic-free H_2SO_4 (1 volume H_2SO_4 , specific gravity 1.82, to 8 volumes H_2O); it is in this that the substance to be tested is placed. These flasks are joined, and the air in the second is displaced by H from the first, which can do no harm through connection with Pt, as no arsine is formed in the first flask. Attached to the second flask is the glass tube for the production and collection of the arsenical mirror, consisting of two segments, a proximal wide and a distal narrow segment turned up at the free end. The wide segment is supported by a roll of iron gauze to prevent bending of the glass whilst heating. A small furnace is adjusted under the wide segment. Hydrogen is briskly passed

through the apparatus, and after all air has been expelled it is lighted at the free end of the small tube. Care should be taken to ascertain that all air has been driven out, as a mixture of air and H is very explosive. The supply of H is regulated by a clip attached to a piece of rubber tubing on the arm connecting the flasks. A glass tube attached to the same arm, and dipping under mercury, allows H to escape in case it is evolved too rapidly. The H flame is reduced in height to 1 to 2 millimetres, and kept constant during the experiment. When H has passed through the heated tube for two hours and no trace of a mirror appears, it may be assumed that the reagents are free from As, and the substance to be tested, in solution, is introduced into the second flask by a tapped funnel, and attached stem which dips under the surface of the fluid.

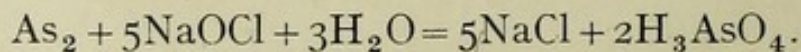
If arsenic be present a mirror will form in the narrow segment in a few minutes. When the mirror has cooled the section of tube containing it is carefully removed and weighed. It is again weighed empty, and from the difference in weight the amount of As is calculated. The method of comparison with standard mirrors is more accurate in those cases where only minute quantities of arsenic are present. If the section of tube containing the mirror be held obliquely in a small flame, As_2O_3 is formed, possessing the odour of garlic; when cold the characteristic octahedral crystals are found.

Further confirmation may be obtained by sealing the small tube, adding a drop of HCl, and passing a little H_2S into the solution, when yellow arsenious sulphide is formed.

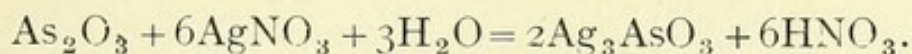
Reinsch's Test.

If a piece of copper foil, recently polished, be placed in a solution of arsenious acid a gray film of copper arsenide, As_2Cu_5 , is formed on the foil. In concentrated solutions this deposit takes place in the cold, but in dilute solutions only on warming. As antimony is also deposited on copper it is necessary to test the film in the dry way.

Dry-way Reactions.—Metallic As burns, giving off a garlic-like odour. Mixed with sodium carbonate and heated on charcoal all arsenic compounds give this odour. Oxygen compounds are readily reduced to metal in the upper reducing flame. A porcelain dish filled with water and held immediately over the sample collects the metallic vapours as a dark-brown film, which is soluble in sodium hypochlorite solution, forming arsenic acid :



If the dish be held in the upper oxidizing flame the vapours are burnt with a bluish flame to As_2O_3 , which, when moistened with AgNO_3 solution and vapour of ammonia blown on it, produces a yellow coloration due to Ag_3AsO_3 , disappearing on addition of more ammonia (difference from antimony) :



Antimony.—Antimony is a white, brittle metal which burns to form Sb_2O_3 , which on stronger ignition in the presence of air is transformed to Sb_2O_4 . The trioxide is dissolved by HCl into antimony trichloride, which by water is easily changed into a basic salt.

Like arsenic, Sb forms antimonous and antimonie compounds.

Antimonous Salts.—1. H_2O precipitates a basic salt, which by more water is changed into oxide.

2. NaOH , NH_4OH , Na_2CO_3 , etc., precipitate hydrated oxide.

3. H_2S precipitates from moderately acid solutions orange-red Sb_2S_3 , soluble in $(\text{NH}_4)_2\text{S}$, and KOH .

4. KI does not liberate I when treated with antimonous compounds in solution (difference from antimonie compounds).

5. Zinc precipitates metallic Sb from antimonous solutions.

If a strip of Pt and a piece of zinc-foil be immersed in an antimony solution acidified with HCl , so that the two metals touch, a black stain of Sb is deposited on the Pt , which does not disappear on the removal of the zinc (difference from tin).

Antimonie Compounds.—1. H_2S precipitates from moderately acid solutions orange-red Sb_2S_5 , soluble in HCl (concentrated), in $(\text{NH}_4)_2\text{S}$, and alkalis, but insoluble in $(\text{NH}_4)_2\text{CO}_3$.

2. Nascent H acting in any solution produces stibine SbH_3 . This gas passed through a red-hot glass tube in a Marsh apparatus forms a metallic mirror nearer to the hot zone than As . It burns with a pale greenish-white flame to water and Sb_2S_3 . A deposit on porcelain is insoluble in sodium hypochlorite (difference from arsenic).

3. HI reduces antimonie compounds in acid solutions with separation of I (difference from antimonous compounds).

Dry-way Reactions.—Antimony compounds impart a pale greenish white colour to the flame. Heated with Na_2CO_3 on charcoal a button of metal is obtained surrounded by a white incrustation. Oxygen compounds are reduced in the upper reducing flame to metal which is volatile, and burns in the upper oxidizing flame to trioxide, which can be deposited on porcelain. If the deposit be moistened with AgNO_3 solution and ammonia vapour blown upon it, it becomes black owing to the separation of metallic Ag .

Tin.—Tin mostly occurs in the form of the dioxide, SnO_2 , and never in the free state. It forms two classes of compound—stannous and stannic.

Stannous Compounds.—Tin dissolved in HCl produces stannous chloride with evolution of H . This salt with two molecules of water of crystallization ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) is the 'tin salt' of commerce. It dissolves clear in water, but on adding more water it becomes turbid owing to the separation out of a basic salt $\text{Sn} \begin{smallmatrix} \text{OH} \\ \text{Cl} \end{smallmatrix}$, which easily dissolves in HCl . The same turbidity is produced on standing in the air. Therefore to preserve a solution of SnCl_2 it is necessary to add HCl to prevent the formation of the basic salt, and metallic tin to maintain the stannous condition.

1. KOH precipitates white gelatinous $\text{Sn}(\text{OH})_2$, readily soluble in excess.

2. Alkali carbonates precipitate the white hydroxide, less soluble in excess of these precipitants than in KOH or NaOH .

3. H_2S precipitates brown SnS , soluble in strong HCl ; therefore no SnS is precipitated if the solution be very acid.

4. Metallic Zn precipitates tin as a spongy mass from both stannous and stannic compounds.

5. Mercuric chloride is reduced in stannous solutions to mercurous chloride. If stannous chloride be present in excess gray Hg is formed.

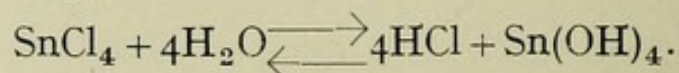
6. A trace of SnCl_2 added to a solution of chloride of gold, AuCl_3 , precipitates metallic gold, which appears bluish-green by reflected light, and brown by transmitted light.

Stannic Compounds.—Stannic compounds are not obtained from stannic oxide, which is difficultly soluble in acids; they are produced from stannous salts or metallic tin.

Stannic chloride is a colourless fuming liquid, which boils at 120°C .; on adding water it crystallizes out in two forms— $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$, and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. The latter is known in commerce as a dyeing mordant.

The addition of chlorine to stannous chloride produces SnCl_4 .

1. Hydrochloric and sulphuric acids produce in solutions of α -stannic compounds no precipitate (difference from β -stannic compounds). Very dilute H_2SO_4 sometimes produces a basic sulphate, and in very dilute HCl a slight turbidity occurs, which increases on boiling:



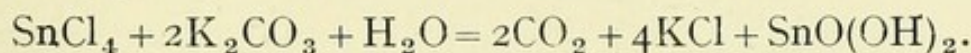
2. Potassium sulphate produces no precipitate in the cold (difference from stannyl chloride).

3. KOH precipitates gelatinous $\text{Sn}(\text{OH})_4$, which remains unchanged on drying in air, but becomes $\text{Sn}(\text{OH})_2$ when dried over H_2SO_4 .

This compound is soluble in excess of KOH. In solubility in alkali, stannic hydroxide behaves like carbonic acid, $\text{CO}(\text{OH})_2$, and silicic acid, $\text{SiO}(\text{OH})_2$.

4. Ammonia precipitates stannic acid from a solution of SnCl_4 ; tartaric acid prevents this precipitation (difference from β -stannic acid).

5. K_2CO_3 precipitates stannic acid soluble in excess :



β -Stannic Compounds.—The oxidation of the metal with hot HNO_3 results in the formation of $\text{Sn}(\text{OH})_4$, which when dried over H_2SO_4 becomes $\text{Sn}(\text{OH})_2$, a polymer of the α -body just considered in the α -stannic group. As no ortho-stannates are known it is customary to designate the two polymeric series as α -stannates, and β -stannates or metastannates.

Whilst α -stannic acid is soluble in dilute mineral acids β -stannic acid is almost insoluble.

1. If β -stannic acid be treated with concentrated HCl a chloride separates out, soluble in H_2O .

2. The solution contains β -stannic chloride (stannyl chloride), whose aqueous solution, when treated with HCl, gives a chloride of the form $\text{Sn}_5\text{O}_5\text{Cl}_4(\text{OH})_6, 4\text{H}_2\text{O}$.

3. The aqueous solution of stannyl chloride when boiled gives up β -stannic acid insoluble in dilute acids.

Stannic polymers seem to be analogous to the varied polymeric forms of silicic acid.

4. KOH precipitates from stannyl chloride β -stannic acid insoluble in excess.

5. H_2SO_4 precipitates from solutions of stannyl chloride white stannyl sulphate changed by the action of water to β -stannic acid (difference from α -stannic chloride).

6. Ammonia also precipitates β -stannic acid in presence of tartaric acid (difference from α -stannic chloride).

7. H_2S precipitates yellow stannic sulphide, SnS_2 , from both α - and β -compounds, soluble in HCl and $(\text{NH}_4)_2\text{S}$.

8. HgCl_2 produces no precipitate in solutions of stannic salts.

Dry-way Reactions.—Heated with soda on charcoal a small button of metal is obtained, which on removal of the flame exhibits a white coating of oxide. If a little tin be added to the copper borax bead (pale blue) it becomes in the reducing flame a transparent ruby red.

Gold and platinum reactions will not be discussed.

GROUP III.

Ammonium Sulphide Group.

Al, Cr, Fe, Zn, Mn, Ni, Co.

(Titanium, uranium, beryllium, thorium, zirconium, yttrium, cerium, erbium, lanthanum, neodymium, praseodymium, niobium, and tantalum will not be discussed.)

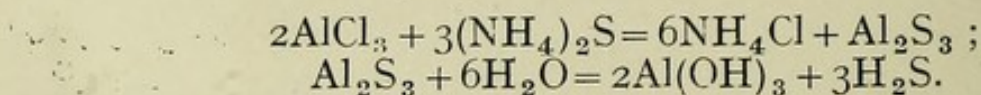
Aluminium—Aluminium is trivalent, and occurs for the most part in the form of silicates. Only one oxide is known, Al_2O_3 , and therefore only one series of salts is found. The salts as a rule are colourless, and being readily hydrolized their solutions in water are acid. This explains the fact that the insoluble oxide or hydroxide, and not aluminium chloride, is found on evaporating a solution of aluminium chloride in water. Aluminium hydroxide reacts as an acid towards strong bases, and as an alkali towards strong acids.

The formation of alums of the general formula, $\begin{matrix} \text{Al}=\text{SO}_4 \\ | \\ \text{SO}_4-\text{R} \end{matrix} \cdot 12\text{H}_2\text{O}$, is a characteristic feature of aluminium. These double salts are most readily produced by interaction with ammonium, potassium, caesium, and rubidium compounds; they crystallize usually in octahedra.

1. KOH produces a precipitate of the gelatinous hydroxide soluble in excess.

2. $(\text{NH}_4)\text{OH}$ produces a precipitate of the same body insoluble in excess. This hydroxide, in common with all colloidal bodies, exists in the insoluble *hydrogel* and soluble *hydrosol* forms. By boiling a solution of *hydrosol* it can be changed into *hydrogel*. The same change is effected by adding a salt to the solution. The hydrosol form of $\text{Al}(\text{OH})_3$ cannot, however, be changed to hydrogel by boiling, but by addition of salts ('salting out'), preferably NH_4Cl .

3. $(\text{NH}_4)_2\text{S}$ precipitates the hydroxide, for the reason that the sulphide is completely hydrolized by water :



4. Alkali and barium carbonates precipitate the hydroxide.

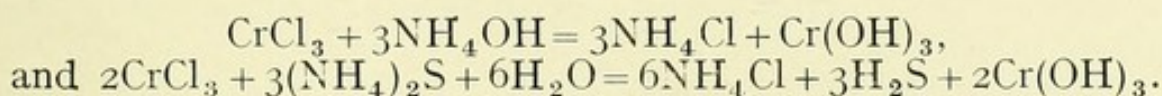
5. Alkali phosphates precipitate gelatinous AlPO_4 , soluble in mineral acids, insoluble in acetic acid (difference from Ca, Sr, Ba, Mg), but readily soluble in KOH or NaOH.

Dry-way Reactions.—Heated with sodium carbonate on charcoal before the blowpipe, aluminium compounds give a white infusible oxide, which when moistened with cobalt nitrate and reheated gives Thénard's blue.

Aluminium salts are not volatile, and do not colour the flame. All aluminium salts, save the phosphate and silicate, are converted by ignition in the air into the oxide Al_2O_3 .

Chromium.—Chromium forms chromous and chromic compounds. The chromous compounds are so unstable that they are practically seldom met with, so that chromic forms alone require consideration.

1. Ammonia and ammonium sulphide. (Cr_2S_3 can only be obtained by a dry method. When treated with H_2O it is decomposed into H_2S and $\text{Cr}(\text{OH})_3$.)



Chromic hydrate is somewhat soluble in excess of ammonia, forming a violet solution. To precipitate $\text{Cr}(\text{OH})_3$ then, boil the solution and use as little ammonia as possible. Ignition of the hydroxide forms the green oxide Cr_2O_3 .

2. KOH precipitates the hydroxide readily soluble in excess.

3. H_2S produces no precipitate in acid solutions of Cr salts.

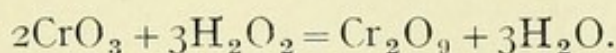
4. Alkali carbonates precipitate the hydroxide, as with Al .

5. Alkali phosphates precipitate CrPO_4 , a greenish amorphous compound, readily soluble in mineral acids and in cold acetic acid.

All chromium compounds may be readily oxidized to chromates.

Chromic acid and chromates are strong oxidizing agents in acid solution.

Chromic acid in neutral solution with H_2O_2 is converted into blue chromium peroxide soluble in ether :



1. AgNO_3 produces in neutral chromate solutions red silver chromate, soluble in mineral acids and ammonia, insoluble in acetic acid.

2. Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, produces in solutions of normal chromates and di-chromates yellow PbCrO_4 , soluble in HNO_3 , insoluble in acetic acid.

3. Barium chloride precipitates yellow BaCrO_4 , soluble in mineral acids, insoluble in acetic acid. The precipitation from solution of di-chromates is only complete on addition of an alkali acetate. Ignition of 2CrO_3 produces $\text{Cr}_2\text{O}_3 + \text{O}_3$.

Ignition of $2\text{K}_2\text{Cr}_2\text{O}_7$ produces $2\text{K}_2\text{CrO}_4 + \text{Cr}_2\text{O}_3 + \text{O}_3$.

Dry-way Reactions.—All chromium compounds colour the borax bead an emerald green in both the oxidizing and reducing flames.

The blowpipe reaction with Na_2CO_3 on charcoal results eventually in green infusible oxide.

Fusion with nitre and soda in a platinum wire loop yields a yellow

melt of alkali chromate, which, on solution in acetic acid water, gives, with AgNO_3 , red silver chromate. This is a delicate reaction.

Iron.—Two forms of iron, ferrous and ferric, are found.

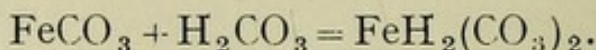
Ferrous Compounds.—1. $(\text{NH}_4)\text{HO}$ produces in neutral solutions an incomplete precipitate of white $\text{Fe}(\text{OH})_2$.

2. KOH produces in absence of air complete precipitation of ferrous hydroxide, $\text{Fe}(\text{OH})_2$, quickly oxidized by the air into ferric hydroxide.

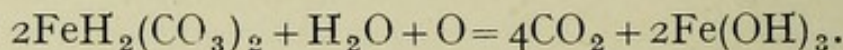
3. H_2S produces no precipitate in acid solutions. In neutral solutions a small amount of black sulphide is precipitated, and much more if an alkali acetate be added in considerable quantity (mass action).

4. $(\text{NH}_4)_2\text{S}$ precipitates black FeS completely, which is readily soluble in acids with evolution of H_2S .

5. Na_2CO_3 or K_2CO_3 precipitates the white carbonate, FeCO_3 , which in contact with air changes to brown $\text{Fe}(\text{OH})_3$. This ferrous carbonate is soluble in carbonic acid forming ferrous bicarbonate :

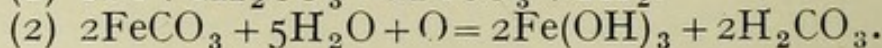
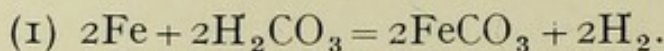


The latter compound, found in certain natural waters, is decomposed by atmospheric oxygen, with separation of ferric hydroxide :



A water containing ferrous bicarbonate on standing in contact with air will become turbid by the separation out of ferric hydroxide. To prevent this it is necessary to completely fill the bottle, and so tightly cork it that air is excluded.

Iron rusts thus : (1) an acid, even H_2CO_3 , forms a ferrous salt, with evolution of H ; (2) oxygen and water now act on the ferrous salt, turning out ferric hydroxide, and setting free the same amount of acid which was used in forming the ferrous salt :



The free acid once more initiates the cycle.

6. KCN precipitates yellowish-brown $\text{Fe}(\text{CN})_2$, soluble in excess, and forming $\text{K}_4[\text{Fe}(\text{CN})_6]$, a potassium salt, and not a ferrous salt. This salt is seen by its reactions to be composed of K and $\text{Fe}(\text{CN})_6$ ions.

There are two cyanogen compounds with iron—ferrocyanides and ferricyanides.

7. $\text{K}_4\text{Fe}(\text{CN})_6$ produces in solutions of ferrous salts, excluded from the air, a white precipitate, which on admission of air is oxidized to Prussian blue.

8. $K_3Fe(CN)_6$ precipitates from neutral or acid solutions dark Turnbull's blue.

9. KCNS gives no reaction with ferrous salts (difference from ferric salts).

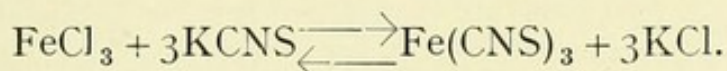
Ferric Compounds.—1. NH_4HO precipitates brown gelatinous ferric hydroxide, $Fe(OH)_3$, readily soluble in acids.

2. KOH throws down the same salt.

3. ZnO precipitates the hydroxide.

4. Sodium hydrogen phosphate, Na_2HPO_4 , in large excess, throws down yellowish-white $FePO_4$, insoluble in acetic acid, readily soluble in mineral acids.

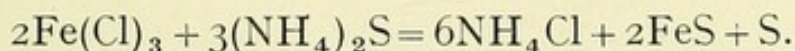
5. KCNS produces in solutions of ferric salts a blood-red colour :



6. $K_4Fe(CN)_6$ produces in neutral or acid solutions Prussian blue.

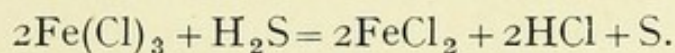
7. $K_3Fe(CN)_6$ gives with ferric salts no precipitate, only a brown coloration (difference from ferrous salts).

8. $(NH_4)_2S$ throws down black ferrous sulphide, with separation of S :



FeS is readily soluble in acetic acid.

9. H_2S , in common with many other bodies, reduces ferric to ferrous salts with separation of S :



Both ferrocyanides and ferricyanides on ignition leave KCN and FeC_2 (iron carbide).

Dry-way Reactions.—The borax bead containing little iron is yellow when hot, and colourless when cold in the oxidizing flame, faint green in the reducing flame. When strongly saturated with an iron salt, it is brown while hot and yellow when cold in the oxidizing flame ; in the reducing flame it is bottle-green. The blow-pipe with soda on charcoal gives a gray particle of metallic iron difficult of recognition.

Zinc.—Zinc is readily soluble in all acids, and in HCl , H_2SO_4 , and $C_2H_4O_2$, with evolution of H . Zinc is always bivalent, and produces but one series of salts.

1. KOH precipitates white $Zn(OH)_2$, easily soluble in excess.

2. $(NH_4)OH$ precipitates from neutral solutions, free from ammonium salts, $Zn(OH)_2$, readily soluble in ammonium salts.

3. Ammonium carbonate precipitates a white basic carbonate soluble in excess. The presence of ammonium salts prevents this precipitation.

4. Barium carbonate produces no precipitate in the cold, but on boiling the zinc is deposited as basic carbonate.

5. H_2S precipitates incompletely ZnS from neutral solutions of zinc salts of mineral acids.

6. $(\text{NH}_4)_2\text{S}$ precipitates from neutral or alkaline solutions all the Zn as amorphous sulphide, which tends to run through the filter, like other hydrosol compounds. Boiling, or the addition of acids, or precipitation with concentrated salt solutions, changes the hydrosol into insoluble hydrogel. To obtain ZnS , therefore, in a form that can be filtered, its solution is boiled, and is made to contain a considerable amount of an ammonium salt.

7. $\text{K}_4\text{Fe}(\text{CN})_6$ throws down white zinc ferrocyanide, which is changed by an excess of $\text{K}_4\text{Fe}(\text{CN})_6$ into insoluble zinc-potassium ferrocyanide. This reaction is used in the volumetric determination of Zn.

Dry-way Reactions.—The blowpipe reaction with soda on charcoal yields no metallic zinc, on account of its volatility; an incrustation of oxide, yellow while hot, white when cold, is obtained. ZnO moistened with cobalt nitrate gives a green infusible mass—Rinnmann's green.

Manganese.—*Manganous Compounds.*—1. KOH precipitates white $\text{Mn}(\text{OH})_2$, which rapidly becomes brown in the air.

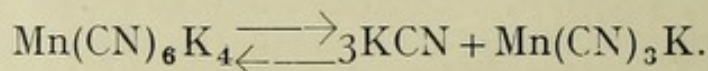
2. $(\text{NH}_4)\text{OH}$ precipitates from neutral solutions, free from ammonium salts, half of the Mn, as $\text{Mn}(\text{OH})_2$. In the presence of sufficient NH_4Cl none of the hydroxide comes down.

3. $(\text{NH}_4)_2\text{CO}_3$ throws down, even in the presence of ammonium salts, the white carbonate (difference from Mg).

4. *Volhard's Reaction.*—Lead peroxide and concentrated HNO_3 . If a solution containing only traces of Cl be boiled with peroxide of lead and concentrated HNO_3 diluted with water, and the residue allowed to settle, the clear fluid acquires a violet-red colour, due to permanganic acid. This delicate reaction is not possible in the presence of much HCl or chlorides, since permanganic acid would thereby be destroyed.

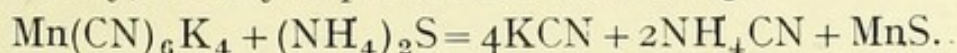
5. $(\text{NH}_4)_2\text{S}$ precipitates from manganous salts flesh-coloured hydrated manganous sulphide.

6. KCN throws down a brownish precipitate, soluble in excess, and forming a brown solution. On warming, a green precipitate separates out, soluble in more KCN , by which a yellow solution is formed. This salt is very unstable, and when the yellow solution is diluted with water the green salt again separates :



The manganous potassium cyanide is not precipitated by $(\text{NH}_4)_2\text{S}$

in the presence of considerable KCN ; but the dilute solution, on the contrary, readily deposits MnS on boiling :



By this means Mn is separated from Ni, as a dilute solution of nickel potassium cyanide is not precipitated by $(\text{NH}_4)_2\text{S}$.

Dry-way Reactions.—The borax bead is amethyst-red in the oxidizing flame with small amounts of Mn ; with larger amounts it is brown, and may be mistaken for nickel. In the reducing flame Mn is colourless, Ni gray. Fused with nitre and sodium carbonate on platinum foil, Mn salts produce a green melt.

Manganic and Permanganic Acids.—Free manganic acid, H_2MnO_3 , has not been isolated, and permanganic acid, HMnO_4 , is only known in aqueous solution. The anhydride of the latter, Mn_2O_7 , has been isolated, in the form of oily, reddish-brown drops, by the addition of concentrated H_2SO_4 to the cooled solution of a permanganate. On being warmed, it explodes with scintillation : $\text{Mn}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + 2\text{H}_2\text{O} + 5\text{O}$.

The salts of permanganic acid, the permanganates, are all soluble in water, with a violet colour, and are energetic oxidizers.

If the oxidation take place in acid solution, the permanganic acid is reduced to MnO ; if in alkaline solutions, to MnO_2 .

Thus, 2KMnO_4 (in acid solution) = $\text{K}_2\text{O} + 2\text{MnO} + 5\text{O}$; and 2KMnO_4 (in alkaline solution) = $\text{K}_2\text{O} + 2\text{MnO}_2 + 3\text{O}$.

Oxalic acid, tartaric acid, and hydrogen peroxide are all oxidized by permanganates.

Nickel.—Nickel forms two oxides—nickelous oxide, NiO , and nickelic oxide, Ni_2O_3 . The first behaves as an anhydride, the second as a peroxide. They dissolve in acids forming salts of bivalent Ni.

1. KOH throws down light green $\text{Ni}(\text{OH})_2$, insoluble in excess, soluble in acids.

2. $(\text{NH}_4)_2\text{HO}$ precipitates a green basic salt, soluble with a blue colour in excess.

3. $(\text{NH}_4)_2\text{CO}_3$ precipitates apple-green nickel carbonate, soluble in excess.

4. BaCO_3 produces no precipitate in the cold, but on prolonged boiling all the nickel is thrown down as a basic carbonate.

5. H_2S produces no precipitate from highly acid solutions, but from solutions containing a trace of free acetic acid and an alkali acetate all the metal is thrown down as black sulphide, NiS .

6. $(\text{NH}_4)_2\text{S}$ throws down from neutral solutions NiS , somewhat soluble in excess, readily so in presence of free ammonia. Nickel sulphide is best precipitated by adding considerable NH_4Cl , and saturating the solution with H_2S . Obtained thus, NiS can be easily filtered, and the filtrate is free from Ni.

7. KCN precipitates bright green $\text{Ni}(\text{CN})_2$, readily soluble in excess.

8. Na_2HPO_4 throws down green $\text{Ni}_3(\text{PO}_4)_2$, readily soluble in acids, even acetic acid.

9. KNO_2 gives no precipitate in dilute solutions (difference from Co).

In concentrated solutions a reddish-brown precipitate of $\text{Ni}(\text{NO}_2)_2 \cdot 4\text{KNO}_2$ is precipitated; and in the presence of alkaline earths a yellow crystalline precipitate is obtained, $\text{Ni}(\text{NO}_2)_2 \cdot \text{Ba}(\text{NO}_2)_2 \cdot 2\text{KNO}_2$, readily soluble in boiling water, with a green colour.

Dry-way Reactions.—The borax bead is brown in the oxidizing flame, resembling somewhat the strongly saturated manganese bead. In the reducing flame a gray bead is obtained. Treated with soda on charcoal, a greenish-coloured deposit is formed, bluish if cobalt be present.

Cobalt.—Cobalt forms, like Fe, three oxides— CoO , Co_3O_4 , Co_2O_3 . If these three oxides be dissolved in an acid cobaltous salts of bivalent Co are formed, corresponding with CoO . Simple cobaltic salts (corresponding with Co_2O_3) are unknown.

1. KOH precipitates in the cold, blue basic $\text{Co} \begin{smallmatrix} \text{OH} \\ \text{Cl} \end{smallmatrix}$, which on warming is further decomposed into pink cobaltous hydroxide, $\text{Co}(\text{OH})_2$. Cobaltous compounds in aqueous solution are pink, in the anhydrous condition yellow or green, and blue in aqueous solution containing HCl .

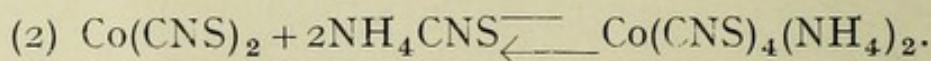
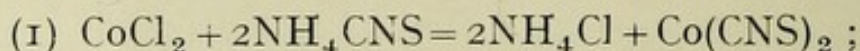
2. $(\text{NH}_4)\text{OH}$ precipitates, in the absence of ammonium salts, a blue basic salt, soluble in excess of ammonium chloride.

3. Alkali carbonates produce a precipitate of a reddish basic salt, that produced by ammonium carbonate being soluble in excess of the precipitant.

4. H_2S produces no precipitate in presence of mineral acids, but in neutral solutions containing an alkali acetate a black precipitate of CoS , insoluble in ammonium sulphide and acetic acid.

5. KNO_2 precipitates from concentrated solutions of cobalt salts containing acetic acid, yellow potassium cobaltic nitrite, $\text{Co}(\text{NO}_2)_6 \cdot \text{K}_3$ (difference from Ni).

6. Ammonium sulphocyanate when added to a cobaltous solution produces a fine blue, due to ammonium cobaltous sulphocyanate. The reaction takes place in two stages:



On adding water the blue disappears, and the pink of cobaltous salts takes its place. If amyl alcohol, or a mixture of equal parts

amyl alcohol and ether, be now added, the blue returns, and the upper layers of the mixture present an unmistakable blue, when only $\frac{1}{36}$ milligramme of Co is present. The blue possesses a characteristic spectrum. Nickel salts produce no coloration of amyl alcohol. Iron may interfere with the colour if present, so that it is well to throw out iron by precipitation with sodium carbonate.

Dry-way Reactions.—The borax bead is blue in both oxidizing and reducing flames. Held for a considerable time in the upper reducing flame, reduction to the gray metal takes place.

On charcoal, gray metallic cobalt is formed, which can be removed by a magnet, dissolved in HCl, and the characteristic blue obtained.

GROUP IV.

Alkaline Earths (Ca, Sr, Ba).

The carbonates of these metals are mostly colourless and insoluble in water. On ignition they yield white, luminous, infusible oxide. BaO is, however, not very luminous, and the carbonate loses its CO₂ only at a white heat. The sulphates and oxalates are very difficultly soluble: BaSO₄ is most insoluble, and CaSO₄ most soluble. Of the oxalates the calcium salt is most insoluble. The solubility of strontium salts lies midway between that of Ca and Ba salts, as the atomic weight (of which solubility is a function) of Sr lies between the atomic weights of Ca and Ba.

Calcium.—Calcium is very widely distributed in Nature, both as carbonate and sulphate.

1. (NH₄)OH in the pure condition produces no precipitate with Ca salts. On standing in the air, it absorbs CO₂, and causes a turbidity of CaCO₃.

2. (NH₄)₂CO₃, as found in commerce, is a mixture of ammonium bicarbonate, NH₄.HO.CO₂, and ammonium carbamate, NH₄.NH₂.CO₂. Ammonia is therefore added, whereby the bicarbonate is changed to the normal carbonate; the latter produces a precipitate of CaCO₃, which is at first flocculent, but after standing for a time becomes crystalline. This change takes place more quickly on heating. The reaction is reversible; hence an excess of the precipitant should be added, and the solution boiled only long enough to render the precipitate crystalline.

3. Ammonium oxalate in neutral or alkaline hot solutions deposits large crystals of calcium oxalate, insoluble in water and acetic acid, soluble in mineral acids.

4. H₂SO₄ produces a precipitate only in concentrated solutions. Alcohol brings down all the CaSO₄ from an aqueous solution. CaSO₄ dissolves in hot HCl, and in concentrated (NH₄)₂SO₄

solution, forming $(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2$, which is decomposed by water.

5. CaSO_4 produces no precipitate in solutions of calcium salts (difference from Sr and Ba).

6. Na_2HPO_4 throws down in neutral solutions CaHPO_4 ; if ammonia be added at the same time, tertiary calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is precipitated.

7. Absolute alcohol, or a mixture of equal parts absolute alcohol and ether, dissolves chloride and nitrate of Ca.

With the exception of potassium carbonate, all deliquescent salts dissolve in absolute alcohol, whilst all other salts, as a rule, are insoluble, or very difficultly soluble, in it.

Dry-way Reactions.—Calcium compounds heated with soda before the blow-pipe are changed to the infusible glowing oxide. Volatile Ca compounds colour the flame brick-red. Ca exhibits in its spectrum several lines in the orange and yellow, one in the green, and one in the ultra-violet.

Strontium.—Strontium occurs commonly with Ca.

1. $(\text{NH}_4)\text{OH}$. Same reaction as with Ca.

2. $(\text{NH}_4)_2\text{CO}_3$. Same reaction as with Ca.

3. $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Same reaction as with Ca, with the exception that strontium oxalate is somewhat soluble in acetic acid.

4. Dilute H_2SO_4 precipitates SrSO_4 , less soluble in water than CaSO_4 .

5. CaSO_4 produces in neutral or slightly acid solutions, after a time, a precipitate of SrSO_4 .

6. Alkali chromates produce in dilute solutions no precipitate (difference from Ba). From very concentrated solutions strontium chromate is precipitated.

Dry-way Reactions.—The blow-pipe reaction on charcoal is similar to that of Ca. Volatile salts of Sr colour the flame carmine-red. Spectrum: a number of red lines and a blue line.

Barium.—Like Sr, barium is almost always associated with Ca.

1. NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ give the same reactions as Ca and Sr.

2. Ammonium oxalate: same as with Ca and Sr, except that barium oxalate is much more soluble in water.

3. Alkali phosphates: same as with Ca.

4. Alkali chromates precipitate from neutral solutions BaCrO_4 (difference from Ca and Sr).

5. Absolute alcohol dissolves neither the nitrate nor the chloride; These salts are not deliquescent. SrCl_2 is deliquescent, and consequently soluble in absolute alcohol.

6. Dilute H_2SO_4 brings down BaSO_4 , even in most dilute solutions. This precipitate is practically insoluble in water (1 in 344,000).

Dry-way Reactions.—Heated with soda on charcoal before the blow-pipe, barium compounds, unlike Ca and Sr, fail to give a luminous mass, since the BaCO_3 formed does not decompose at this temperature into CO_2 and infusible oxide, but sinters together without perceptible change. Volatile salts colour the flame yellowish-green. As the sulphate is but very slightly volatile, it is necessary to change it into chloride before committing it to the flame reaction.

Spectrum.—A number of lines are seen, some in the orange, more in the green.

GROUP V.

Alkalies (K, Na, NH_4).

[Cæsium, rubidium, and lithium belong to this group, but will not be discussed.]

These metals decompose water with evolution of H and formation of strongly alkaline hydroxides, which do not lose their water, even on fusion. The salts of these metals are colourless, more or less volatile, and easily soluble in water. The carbonates, cyanides, borates, and secondary and tertiary phosphates exhibit an alkaline reaction in aqueous solution.

Potassium.—Potassium forms very few salts that are difficultly soluble in water. The chlorplatinate, acid tartrate, and perchlorate are the least soluble, and are therefore employed in detecting potassium.

1. Hydrochlorplatinic acid (prepared by dissolving platinum in aqua regia) precipitates yellow octahedral crystals of potassium chlorplatinate, K_2PtCl_6 .

K_2PtCl_6 on ignition decomposes into $2\text{KCl} + \text{Pt} + 2\text{Cl}_2$.

2. Tartaric acid precipitates from neutral solutions of potassium salts white crystalline precipitate of acid potassium tartrate, readily soluble in mineral acids, difficultly soluble in acetic acid.

3. Hydrofluosilicic acid, H_2SiF_6 , added in considerable excess to a solution of a potassium salt, precipitates potassium silicofluoride, K_2SiF_6 , difficultly soluble in water and dilute acids, but insoluble in alcohol.

Dry-way Reactions.—Potassium compounds colour the flame violet. Very small quantities of Na conceal the violet; if, therefore, the flame be viewed through a cobalt glass or indigo solution the yellow sodium rays are cut off.

The spectrum exhibits a very bright line in the red and two faint lines in the ultra-violet.

Sodium.—Sodium occurs very extensively in Nature.

1. Potassium pyroantimonate, $K_2H_2Sb_2O_7$, precipitates from neutral or slightly alkaline solutions of sodium salts white crystalline sodium pyroantimonate, which, like acid potassium tartrate, is more rapidly deposited by rubbing the sides of the vessel with a glass rod. The test, if made in an acid solution, results in an amorphous precipitate of pyroantimonic acid. All metals other than the alkalis must be absent.

2. Tartaric acid and hydrochlorplatinic acid do not precipitate sodium salts.

Sodium peroxide, a heavy yellow powder, parts with O on addition of a little water. More water transforms Na_2O_2 to H_2O_2 and caustic soda, but on account of the heat of the reaction the H_2O_2 is split into H_2O and O. This may be prevented by putting small quantities of Na_2O_2 into ice-water.

H_2O_2 in Acid Solution.—1. Titanium sulphate gives with H_2O_2 a distinct yellow colour. This is the most delicate test for H_2O_2 .

2. Chromic acid : If a trace of dichromate of potassium be added to an acid solution of H_2O_2 in ether, and the mixture shaken, the ether is coloured a beautiful blue (chromium peroxide).

3. Permanganic acid in acid solution is decolourized by H_2O_2 .

4. Starch paste + KI + H_2O_2 = immediate production of a blue colour.

5. H_2O_2 in alkaline solution reduces $AuCl_3$ to metal with evolution of O.

6. Salts of Mn, Ni, and Co bring down dark hydrates from alkaline solutions of H_2O_2 .

Dry-way Reactions.—Salts of Na colour the flame a monochromatic yellow. The spectrum possesses a yellow line coincident with the D line of the solar spectrum.

Ammonium.—Ammonium carbonate and nitrate occur in small quantities in the air. Various derivatives occur in connection with the decomposition of dead organic matter.

1. Hydrochlorplatinic acid precipitates from solutions of ammonium salts yellow crystalline $(NH_4)_2PtCl_6$, distinguished from the corresponding potassium salt by its leaving Pt only on ignition, and by emitting the smell of NH_3 on treatment with strong bases.

2. Tartaric acid precipitates white crystalline acid tartrate of ammonium, distinguished from the potassium salt by leaving carbon alone on ignition ; and by emitting the smell of NH_3 on heating with a base.

Dry-way Reactions.—All ammonium salts except those with non-volatile acids are completely volatilized on heating in a closed

tube. Ammonium salts do not impart a very characteristic colour to the flame : the border of the flame is tinged slightly greenish.

Magnesium.—Magnesium salts are very abundant in nature. They are nearly all colourless and soluble in water. The metal slowly decomposes water, forming an oxide, MgO . It reacts directly with N at 300°C ., forming magnesium nitride, Mg_3N_2 , which is readily decomposed by water into magnesium hydroxide and ammonia.

1. $(\text{NH}_4)\text{OH}$ produces, in the absence of ammonium salts, a precipitate of $\text{Mg}(\text{OH})_2$. But if NH_4Cl or other ammonium salt be present, the hydroxide will be dissolved owing to the formation of $(\text{NH}_4)_2\text{MgCl}_4$.

2. $(\text{NH}_4)_2\text{CO}_3$ precipitates, in the absence of other ammonium salts, a basic salt, varying in composition with the temperature and concentration of the solution.

3. Sodium phosphate (the characteristic reagent) produces, in solutions containing ammonium chloride and ammonia, a white crystalline precipitate of ammonium-magnesium phosphate ; the precipitation is hastened by rubbing the sides of the beaker with a glass rod. In very dilute solutions some considerable time is required for the formation of the precipitate.

Dry-way Reactions.—The blow-pipe reaction with soda on charcoal produces a strongly luminous white oxide. Ca, Sr, and Al compounds act in the same way. Magnesium salts are non-volatile, fail to colour the flame, and give no flame spectrum, but a characteristic spark spectrum.

Short Notes on the more commonly occurring Anions (Electro-negative).

The presence of hydrogen ions in aqueous solutions is characteristic of all acids. Bunsen's classification of the acids based upon the different solubilities of their barium and silver salts is as follows :

GROUP I.—Acids whose Ag salts are insoluble in water and in HNO_3 , but whose Ba salts are soluble in water.

GROUP II.—Acids whose Ag salts are soluble in HNO_3 , but difficultly soluble or insoluble in water, and whose Ba salts are soluble in water.

GROUP III.—Acids whose Ag salts are white and soluble in HNO_3 , but whose Ba salts are difficultly soluble or insoluble in water, but soluble in HNO_3 .

GROUP IV.—Acids whose Ag salts are coloured and soluble in HNO_3 , but whose Ba salts are insoluble in water and soluble in HNO_3 .

GROUP V.—Acids whose Ag and Ba salts are soluble in water.

GROUP VI.—Acids whose Ag salts are soluble in water, but whose Ba salts are insoluble in HNO_3 .

GROUP VII.—Non-volatile acids which form soluble salts with the alkalies alone.

GROUP I.

Ag salts insoluble in H_2O and in HNO_3 , Ba salts soluble in H_2O .

HCl.— AgNO_3 produces a precipitate insoluble in HNO_3 .

BaCl_2 produces no precipitate.

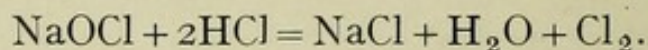
HCl is a colourless gas, readily soluble in water. Specific gravity of a saturated aqueous solution is 1.21. Commercial HCl has a specific gravity of 1.18, and contains about 37 per cent. of the gas.

Nearly all chlorides are soluble in water. The following are insoluble : Hg_2Cl_2 , AgCl , Cu_2Cl_2 , PbCl_2 , BiOCl , SbOCl , $\text{Hg}_2\text{Cl}_2\text{O}$.

When HCl is oxidized the H is burnt to water, and Cl is set free. Its oxidation may be effected by MnO_2 , by HNO_3 , etc.

Free Cl is a greenish yellow gas with suffocating odour ; is soluble in water, and is a strong oxidizing agent.

HOCl (hypochlorous acid), obtained by shaking chlorine-water with yellow mercuric oxide until the solution loses its smell of Cl, is a vigorous bleaching agent. It oxidizes HCl with evolution of Cl :



H_2SO_4 and H_2CO_3 set free HOCl from hypochlorites.

HOCl shaken with Hg forms brown, basic $\text{Hg}_2\text{Cl}_2\text{O}$, insoluble in water, soluble in HCl. Free Cl shaken with Hg forms white mercurous chloride, HgCl_2 , insoluble in HCl.

HBr (hydrobromic acid).—1. AgNO_3 produces a curdy, yellowish precipitate of AgBr , insoluble in HNO_3 , soluble in $(\text{NH}_4)\text{OH}$, KCN, and sodium thiosulphate.

2. Chlorine-water liberates Br from bromides, which is soluble in CHCl_3 or CS_2 , forming a brown solution. Excess of chlorine-water changes it into yellowish BrCl (difference from iodine).

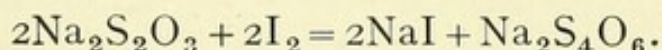
3. Nitrous acid does not separate Br from a dilute cold solution of bromide (difference from I).

HI (hydriodic acid).—1. AgNO_3 produces a yellow, curdy precipitate of AgI , insoluble in HNO_3 and slightly soluble in ammonia. Chlorine rapidly changes this into AgCl .

2. Salts of Pb precipitate yellow PbI_2 , soluble and colourless in much hot water, but precipitated again on cooling.

3. Nitrous acid liberates iodine from an iodide in dilute solution, forming a yellowish to brown colour (difference from chlorides and bromides).

Free I in solution is decolourized by sodium thiosulphate, with formation of sodium tetrathionate and sodium iodide :



Chlorine and bromine react differently with sodium thiosulphate. They oxidize it to sodium sulphate, with separation of sulphur. The liberated sulphur is then oxidized by the halogens to sulphuric acid. Weak oxidizing agents alone can transform sodium thiosulphate into sodium tetrathionate.

Free iodine colours starch-paste blue.

HCN (hydrocyanic acid).—1. AgNO_3 dropped slowly into a solution of an alkali cyanide forms a precipitate of AgCN on addition of each drop, which redissolves on stirring. Ignition of AgCN produces cyanogen gas and metallic silver: $2\text{AgCN} = \text{Ag}_2 + (\text{CN})_2$.

Silver nitrate gives no precipitate with mercuric cyanide, which is a non-electrolyte, but combines with it, forming $\text{Hg}(\text{CN})_2$, AgNO_3 , $2\text{H}_2\text{O}$.

2. Prussian blue. This reaction may be applied to KCN by converting it into potassium ferrocyanide by the addition of a ferrous salt, and adding a little HCl and a small quantity of ferric chloride.

3. The cyanide is changed to sulphocyanate by treatment with $(\text{NH}_4)_2\text{S}_2$ in a porcelain or other dish, and evaporating to dryness. To the residue is added some HCl and a drop of ferric chloride, whereby the blood-red colour is produced.

4. Mercurous nitrate added to a solution of alkali cyanide produces a gray precipitate of metallic Hg (difference from chloride, bromide, or iodide).

$\text{Fe}''(\text{CN})_6\text{H}_4$ (hydroferrocyanic acid).—1. Concentrated H_2SO_4 decomposes all cyanides. In the case of ferrocyanides, on warming complete decomposition takes place, with evolution of CO , which burns with a blue flame.

2. The silver salt is white, insoluble in dilute HNO_3 and $(\text{NH}_4)\text{HO}$, but soluble in KCN . Treated with concentrated HNO_3 , it is changed to orange silver ferricyanide, which is soluble in ammonia.

3. BaCl_2 gives no precipitate.

4. Ferric salts produce Prussian blue.

5. Cupric salts produce a brown precipitate.

$\text{Fe}'''(\text{CN}_6)\text{H}_3$ (hydroferricyanic acid).—1. AgNO_3 precipitates orange silver ferricyanide, insoluble in HNO_3 , soluble in $(\text{NH}_4)\text{HO}$.

2. BaCl_2 gives no precipitate.

3. Ferrous salts precipitate Turnbull's blue.

4. Ferric salts give no precipitate, but a brown coloration.

5. Ferricyanides are reduced by ammonia, with formation of N .

6. Dilute H_2SO_4 produces no HCN in the cold (difference from cyanides), but does so on warming.

7. Concentrated H_2SO_4 decomposes all ferricyanides on warming, with production of CO and sulphates.

HCNS (sulphocyanic acid).—1. Concentrated H_2SO_4 decomposes thiocyanates with deposition of S and evolution of COS, SO_2 , CO_2 , HCOOH .

2. AgNO_3 precipitates white AgCNS , insoluble in dilute HNO_3 , soluble in ammonia.

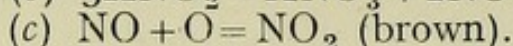
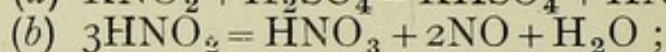
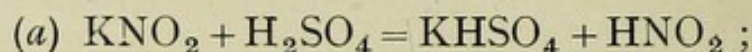
3. Ferric salts produce a blood-red coloration, $\text{Fe}(\text{CNS})_3$, soluble in ether.

4. $\text{Hg}(\text{NO}_3)_2$ precipitates white mercuric thiocyanate, very difficultly soluble in water, but readily soluble in excess of KCNS . The dry powder expands greatly on application of heat (Pharaoh's serpents).

GROUP II.

AgNO_3 produces a precipitate soluble in HNO_3 . BaCl_2 produces no precipitate.

HNO_2 (nitrous acid).—1. Dilute H_2SO_4 decomposes all nitrites, with evolution of brown vapours :

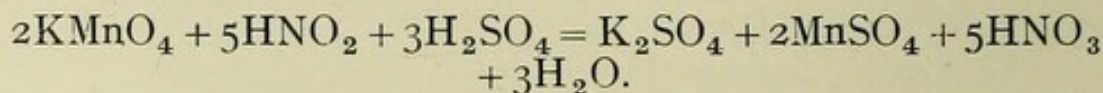


2. Concentrated H_2SO_4 acts in the same way, but much more energetically.

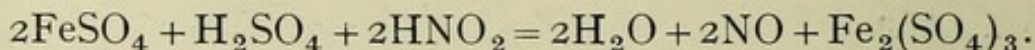
3. AgNO_3 produces a precipitate of needles of AgNO_2 difficultly soluble in cold water.

4. HI is oxidized by nitrous acid with separation of I . A nitrite + $\text{KI} + \text{H}_2\text{SO}_4$ + starch paste gives a blue colour. Many oxidizing agents produce the same reaction.

5. Warm potassium permanganate is reduced and rendered colourless by nitrous acid :



6. Ferrous salts are oxidized to ferric salts with evolution of NO :



7. A solution of a nitrate, to which a little H_2SO_4 is added, produces, with phenylene diamine, Bismark brown.

H_2S (hydrogen sulphide, hydrosulphuric acid).—1. Concentrated H_2SO_4 decomposes all sulphides on warming, with evolution of SO_2 , and deposition of S, and after heating for some time the S is oxidized by the H_2SO_4 to SO_2 .

2. AgNO_3 precipitates black Ag_2S , insoluble in cold nitric acid, but soluble in hot HNO_3 .

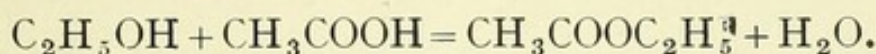
3. Lead salts, especially in solution containing excess of alkali, precipitate black lead sulphide. All sulphides which are decomposed by HCl evolve H_2S , which colours filter-paper, moistened with an alkaline lead solution, black.

4. Sodium nitroprusside, $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$, is coloured reddish-violet by S ions, but not by SH ions. Accordingly, H_2S does not give this reaction, except in the presence of alkali.

5. Methylene-blue test. To the solution to be tested for H_2S a tenth volume of strong HCl is added, and a knife-bladeful of para-amido-dimethyl-aniline sulphate. The mixture is stirred until solution is complete, when one or two drops of dilute FeCl_3 solution is added. If $\cdot 018$ milligramme H_2S per litre be present the blue colour is distinct after half an hour's standing.

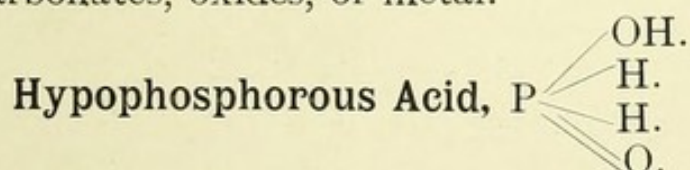
CH_3COOH (acetic acid).—1. Dilute H_2SO_4 sets acetic acid free from its salts.

2. Concentrated H_2SO_4 has the same action. Acetic acid is volatile, and has a characteristic odour. Warmed with ethyl alcohol in the presence of H_2SO_4 , acetic acid forms ethyl acetate, recognised by its fruity odour.

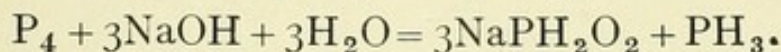


3. FeCl_3 produces a dark-brown colour in solutions of acetic acid or acetates. When the mixture is boiled the iron is precipitated as basic acetate.

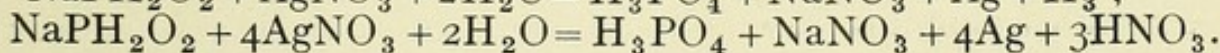
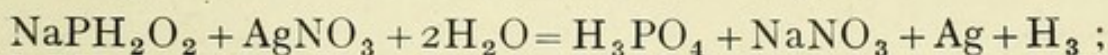
Dry-way Reactions.—Acetates when ignited, are transformed to carbonates, oxides, or metal.



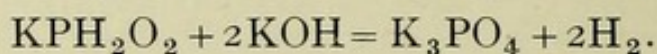
If phosphorus be boiled with dilute alkali, hypophosphites are formed, with evolution of phosphine (PH_3) :



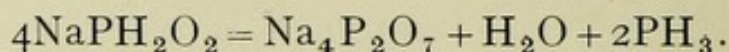
1. Dilute H_2SO_4 produces no reaction with hypophosphites.
2. Concentrated H_2SO_4 when warmed with hypophosphites is reduced to SO_2 , recognised by its smell.
3. BaCl_2 produces no reaction.
4. Cu , Hg , and Au salts are reduced to metal.
5. AgNO_3 is reduced to metal, with or without evolution of H , according to the relative amounts of the reagents :



6. Strong caustic potash when boiled with hypophosphites converts them into phosphates, with evolution of H :



7. Nascent hydrogen reduces hypophosphorous acid to phosphine.
Dry-way Reactions.—On ignition hypophosphites are converted into phosphates and phosphine.

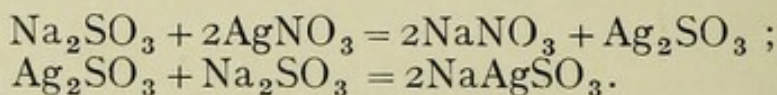


GROUP III.

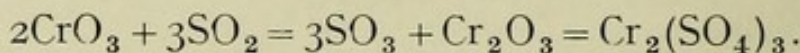
AgNO_3 produces a white precipitate soluble in HNO_3 . BaCl_2 has the same action.

Sulphurous Acid, H_2SO_3 , $\text{SO} \begin{smallmatrix} \text{OH.} \\ \text{OH.} \end{smallmatrix}$

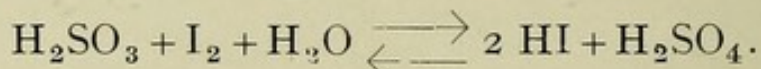
1. Dilute H_2SO_4 separates SO_2 from sulphides in the cold.
2. Concentrated H_2SO_4 has a more energetic action of like nature.
3. AgNO_3 precipitates from solutions of sulphites white crystalline silver sulphite, soluble in excess :



4. Chromic acid is reduced to green chromic salt :



5. Sulphurous acid decomposes iodine solutions :



6. Sodium nitroprusside and zinc sulphate produce a red colour (difference from thiosulphates).

Carbonic Acid, $\text{C} \begin{smallmatrix} \text{OH.} \\ \text{OH.} \\ \text{O.} \end{smallmatrix}$

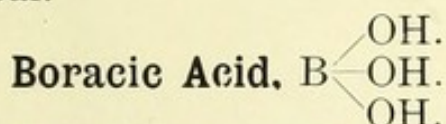
CO_2 is formed by the combustion of C, and dissolves in H_2O to form carbonic acid, which breaks up again on heating.

1. Dilute H_2SO_4 decomposes most carbonates with effervescence.
2. Strong H_2SO_4 produces more vigorously the same action.
3. BaCl_2 precipitates white crystalline BaCO_3 .
4. AgNO_3 precipitates white Ag_2CO_3 , soluble in ammonia and nitric acid.

Several carbonates dissolve in an excess of carbonic acid, forming

bicarbonates, which on boiling with water lose CO_2 and are reprecipitated as carbonates.

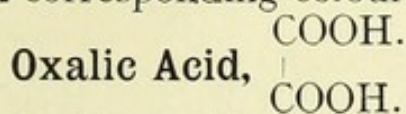
Dry-way Reactions.—On ignition carbonates are reduced to oxides, and in the cases of the noble metals to the metallic state. The alkali carbonates melt without apparent decomposition. BaCO_3 does not melt, and is not decomposed by the blow-pipe on charcoal.



Boracic (boric) acid crystallizes in plates, which when heated to 100°C. lose water and become metaboric acid, HBO_2 , which, heated to 160°C. , becomes pyroboric acid, $\text{H}_2\text{B}_4\text{O}_7$, which latter on ignition loses all its water, and becomes BO_3 . Borates are derived from meta- and pyro-boric acids.

1. Dilute H_2SO_4 gives no reaction with borates.
2. Strong H_2SO_4 gives no visible reaction. Boric acid is liberated from most borates, and may be recognised by its green colour in the Bunsen flame.
3. BaCl_2 precipitates white $\text{Ba}(\text{BO}_2)_2$, soluble in excess and in NH_4Cl .
4. If turmeric paper be saturated with free boric acid, and carefully dried, it becomes reddish-brown; if moistened with KOH it turns bluish-black; or if little boric acid be present, grayish-blue. Borates treated with HCl give the same reaction. It should be noted that molybdic, titanous, and a few other acids turn turmeric paper brown.

Dry-way Reactions.—Alkali borates melt on ignition, forming a colourless glass, which can dissolve many metallic oxides and take on corresponding colours.



Oxalic acid crystallizes in colourless monoclinic prisms, $\begin{matrix} \text{COOH} \\ \text{COOH} \end{matrix} \cdot 2\text{H}_2\text{O}$, which loses its water of crystallization when placed over H_2SO_4 . When heated it decomposes into H_2O , CO_2 , and CO .

1. Dilute H_2SO_4 produces no reaction.
2. Concentrated H_2SO_4 separates off water, forming CO_2 and CO .
3. BaCl_2 precipitates barium oxalate soluble in oxalic and acetic acids.
4. CaCl_2 precipitates white calcium oxalate, insoluble in oxalic acid, ammonium oxalate, and acetic acid, but readily soluble in HCl . It is the most insoluble oxalate.

Alkali oxalates and barium oxalate, on ignition, become carbonates, with evolution of CO. The oxalates of the noble metals and of iron, copper, nickel, etc., leave the metal.

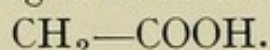
Tartaric Acid $(\text{CHOH})_2(\text{COOH})_2$.—1. Dilute H_2SO_4 produces no reaction.

2. Strong H_2SO_4 carbonizes the acid, with evolution of SO_2 .

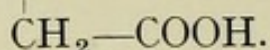
3. AgNO_3 in free tartaric acid produces no reaction. In solution of a neutral tartrate white silver tartrate is thrown down, soluble in HNO_3 and NH_4OH . The solution in ammonia, when warmed, deposits metallic silver. This reaction is not certain in the presence of other acids. The tartaric acid should first be precipitated as acid potassium tartrate by rendering the solution alkaline with solid K_2CO_3 , whereby soluble potassium tartrate is formed, and then carefully acidifying the solution with glacial acetic acid. Acid tartrate separates out, and when filtered off and washed with cold water is dissolved in the least possible quantity of caustic soda. AgNO_3 is now added, and the precipitate formed dissolved in ammonia without excess. The resulting solution is then warmed to 65° to 70° C. On standing twenty minutes Ag is deposited as a mirror on the sides of the tube.

Dry-way Reactions.—On ignition tartaric acid first fuses and then chars with a smell of burnt sugar.

Alkali tartrates leave a residue of carbon and alkali carbonate. In the case of ammonium tartrate the carbonate escapes. The tartrates of the alkaline earths leave carbonates, which on stronger ignition are changed to oxides.



Citric Acid, $\text{C}(\text{OH})\text{—COOH.}$



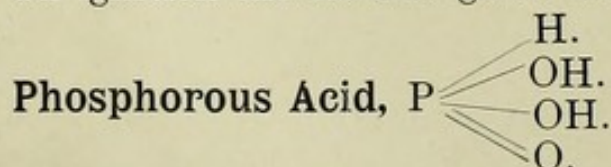
1. Dilute H_2SO_4 . No reaction.

2. Strong H_2SO_4 . Carbonization and evolution of SO_2 on warming.

3. BaCl_2 and CaCl_2 give no precipitate in neutral solutions (difference from tartaric acid).

4. AgNO_3 precipitates from neutral solution $\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$, soluble in HNO_3 and NH_4OH . On heating the ammoniacal solution to 65° C. no silver mirror is formed, but on heating to boiling the Ag is gradually deposited.

On ignition the citrates gives the same reactions as the tartrates.

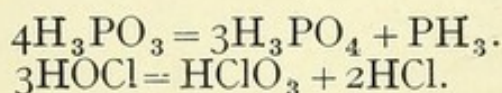


When P is burnt slowly in the air P_2O_3 is formed, which, when

treated with water, becomes phosphorous acid. This acid is more readily formed by the action of water on PCl_3 .

1. Dilute H_2SO_4 . No reaction.
2. Concentrated H_2SO_4 . No reaction until warmed, when it is reduced to SO_3 .
3. Nascent H reduces phosphorous acid to phosphine, PH_3 . Silver nitrate is coloured yellow with phosphine, as with arsine. The mixture of H and PH_3 burns with an emerald-green flame.
4. AgNO_3 produces at first a white precipitate of silver phosphite, which on warming becomes metallic silver.
5. Strong KOH solution changes phosphite to phosphate, with evolution of H.

On ignition phosphorous acid, like hypochlorous acid, is changed to phosphoric acid. This is accomplished at the cost of its own oxygen, whilst the oxidizing portion of the acid is reduced to the hydrogen compound.



Metaphosphoric Acid, $\text{P} \begin{array}{l} \text{OH.} \\ \diagup \\ \text{O.} \\ \diagdown \\ \text{O.} \end{array}$

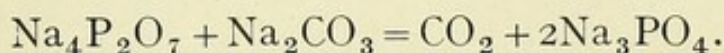
This is obtained by dissolving P_2O_5 in cold water.

1. H_2SO_4 produces no visible reaction.
2. AgNO_3 throws down white AgPO_3 , soluble in ammonia and nitric acid.
3. Ammonium molybdate produces no precipitate in the cold, but on boiling the acid solution metaphosphoric acid is changed to orthophosphoric acid, and yellow ammonium phosphomolybdate is formed.
4. Solution of albumin is coagulated by an aqueous solution of the free acid (difference from ortho- and pyro-acids).
5. Nascent H does not reduce this acid (difference from phosphorous acid).

Pyrophosphoric Acid ($\text{H}_4\text{P}_2\text{O}_7$) is formed by heating the ortho-acid to 213°C .

1. Dilute H_2SO_4 . No reaction.
2. AgNO_3 produces a white precipitate, soluble in ammonia and in nitric acid.
3. Ammonium molybdate produces no precipitate in the cold, but yellow ammonium phosphomolybdate on warming.

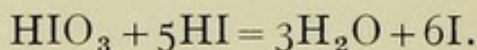
Pyrophosphates when fused with sodium carbonate become orthophosphates :



Iodic Acid (HIO_3).—1. Neither dilute H_2SO_4 nor strong H_2SO_4 decompose HIO_3 , but if reducing substances are present it is reduced with separation of I.

2. AgNO_3 precipitates white AgIO_3 , soluble in ammonia, difficultly soluble in HNO_3 .

3. HI reduces iodic acid, with separation of I.

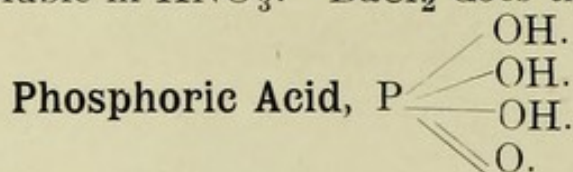


SO_2 in moderate quantities causes separation of I. Zn dust reduces neutral iodates to iodides.

Dry-way Reactions.—Heated on charcoal, iodates deflagrate, and some yield free I.

GROUP IV.

AgNO_3 produces a coloured precipitate in neutral solutions soluble in HNO_3 . BaCl_2 does the same.



Orthophosphoric acid is produced by oxidizing P with HNO_3 , or by boiling meta- and pyro-acids with water. It is tribasic, and forms salts by the replacement of one, two, or three of its H atoms by metals.

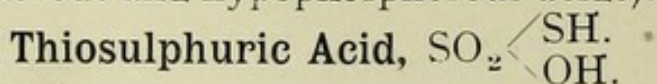
1. Dilute and concentrated H_2SO_4 produce no visible reaction.

2. AgNO_3 precipitates yellow Ag_3PO_4 (difference from meta- and pyro-), soluble in HNO_3 and NH_4OH .

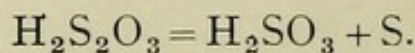
3. Magnesia mixture (NH_4Cl , NH_4OH , MgCl_2) precipitates crystalline ammonium-magnesium phosphate, soluble in all acids, insoluble in 2.5 per cent. ammonia.

4. Ammonium molybdate in excess precipitates from HNO_3 solutions in the cold yellow crystalline ammonium phosphomolybdate, readily soluble in alkalies and in ammonia.

5. Nascent H does not reduce H_3PO_4 (difference from phosphorous and hypophosphorous acids).



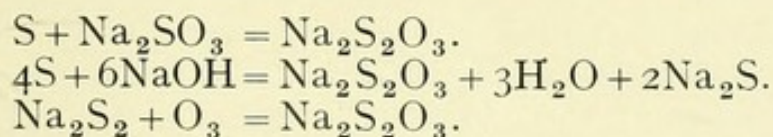
This acid is very unstable. In aqueous solution it rapidly decomposes into S and H_2SO_3 .



The salts are more stable than the acid.

Thiosulphates may be formed by boiling sulphur with sulphites,

by boiling sulphur with hydroxide of an alkali or alkaline earth, and by the oxidation of polysulphides.

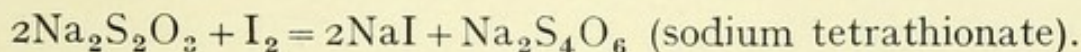


1. H_2SO_4 (concentrated and dilute) decomposes thiosulphates, with separation of yellow S.

2. AgNO_3 produces a precipitate which rapidly becomes yellow, brown, and black (Ag_2S).

3. BaCl_2 in excess precipitates white crystalline barium thiosulphate difficultly soluble in cold water, readily soluble in hot water.

4. Iodine is decolourized by thiosulphates :



5. FeCl_3 produces in solutions of thiosulphates a dark violet colour, which disappears after a time, leaving a colourless solution of FeCl_2 and $\text{Na}_2\text{S}_4\text{O}_6$.

6. Zinc salts and sodium nitroprusside produce no red colour (difference from sulphides).

Dry-way Reactions.—Alkaline thiosulphates heated out of contact with the air are transformed into sulphate and polysulphide. The polysulphide is further changed into sulphide and sulphur.

GROUP V.

AgNO_3 produces no precipitate in acid or neutral solutions. BaCl_2 produces no precipitate.

Nitric Acid (HNO_3).—1. Dilute H_2SO_4 gives no reaction (difference from nitrous acid).

2. Concentrated H_2SO_4 mixed with a nitrate evolves NO_2 (brown vapours with characteristic odour).

3. Ferrous salts are oxidized by nitric acid, with reduction of the latter to NO. In the cold the NO combines with the excess of ferrous salt, forming a dark-brown unstable compound.

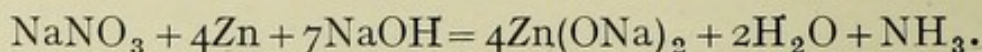
4. A solution of indigo is decolourized by warming with nitric acid (oxidation).

5. KI is not decomposed by pure dilute HNO_3 (difference from nitrous acid).

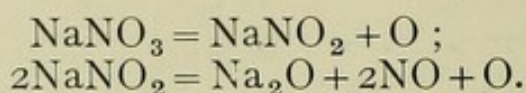
6. A few c.c. of diphenylamine solution (Lunge's reaction) are placed in a test-tube and covered by the solution to be tested for nitric acid. A blue ring at the zone of contact indicates its presence.

7. **Brucine reaction.** Mix the solution to be tested with three times its volume of pure concentrated H_2SO_4 and 1 c.c. of brucine solution (.2 gramme brucine in 100 c.c. concentrated H_2SO_4). If HNO_3 be present a red colour rapidly appears, changing to orange, yellow, and finally greenish-yellow. Nitrous acid does not give this reaction if it be present in the 'nitrose' condition—i.e., dissolved in concentrated H_2SO_4 . Watery solutions of nitrites always yield a small amount of HNO_3 when treated with H_2SO_4 , and therefore give the brucine reaction.

8. Zinc in alkaline solution reduces HNO_3 to NH_3 :



Dry-way Reactions.—Nitrates deflagrate on being heated on charcoal. The charcoal burns at the expense of the oxygen of the nitric acid, with scintillation. On ignition nitrates are changed into nitrites, with loss of O, and on stronger ignition into oxide :

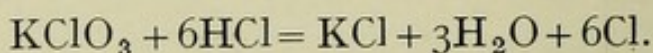


Chloric Acid (HClO_3).—1. Dilute H_2SO_4 sets free chloric acid from chlorates, which is gradually changed, with loss of chlorine and oxygen, into perchloric acid.

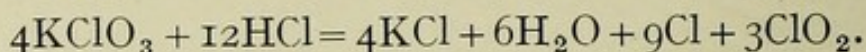
2. Concentrated H_2SO_4 decomposes all chlorates with liberation of greenish-yellow chlorine dioxide gas (explosive if warmed).

3. Nascent H reduces chlorates to chlorides in alkaline, neutral, and acid solutions.

4. Concentrated HCl decomposes all chlorates with evolution of Cl.



Or more exactly :



Perchloric Acid (HClO_4).—Free perchloric acid is very explosive. It is obtained by distilling potassium perchlorate with strong H_2SO_4 . The salts are very stable, and soluble in water.

1. Perchloric acid is not attacked by H_2SO_4 , nor reduced to chloride by zinc-dust.

2. Potassium salts precipitate the white crystalline KClO_4 , relatively insoluble in water.

Dry-way Reactions.—Perchlorates deflagrate on being heated on charcoal. On fusing they lose O, leaving chlorides behind.

Persulphuric Acid ($\text{H}_2\text{S}_2\text{O}_8$).—1. Persulphates are decomposed in aqueous solution, forming sulphate, oxygen, and free sulphuric acid. Much of the oxygen escapes as ozone.

2. Dilute H_2SO_4 acts in the same way.
3. Strong H_2SO_4 converts a persulphate into a strongly oxidizing liquid (Caro's acid).
4. AgNO_3 precipitates black silver peroxide (Ag_2O_2).
5. Manganese, cobalt, nickel, and lead salts are oxidized in the presence of alkali to black peroxides.

GROUP VI.

AgNO_3 produces no precipitate. BaCl_2 produces a white precipitate almost insoluble in acids.

Sulphuric Acid (H_2SO_4).—1. H_2SO_4 gives no reaction.

2. AgNO_3 gives no precipitate in dilute solutions, but forms a white crystalline precipitate of Ag_2SO_4 in concentrated solutions, difficultly soluble in water (1 in 200).

3. BaCl_2 throws down in the most dilute solutions white BaSO_4 insoluble in acids.

4. Nascent H (zinc and acid) does not reduce sulphates.

Dry-way Reactions.—Neutral alkaline sulphates melt after a time without decomposition. Acid salts of the alkalies give off H_2O and SO_3 .

Sulphates heated on charcoal with sodium carbonate are reduced to sodium sulphide, which, when placed on a bright silver surface, produces a black stain of Ag_2S .

Hydrofluoric Acid (HF).—1. Dilute H_2SO_4 causes a very slight reaction.

2. Concentrated H_2SO_4 , when warmed with a fluoride, sets free HF , which attacks glass.

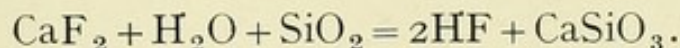
3. The etching test. The substance to be tested for fluoride is placed in a small platinum basin. A watch-glass, whose convex surface is covered with beeswax, has some letters written on it, and is placed over the basin. On warming the basin the letters are etched by the gas as it escapes. The wax can be prevented from melting by placing some cold water in the concavity of the watch-glass.

4. BaCl_2 produces in alkaline solutions of fluorides a thick precipitate of barium fluoride soluble in much mineral acid, soluble in much ammonia.

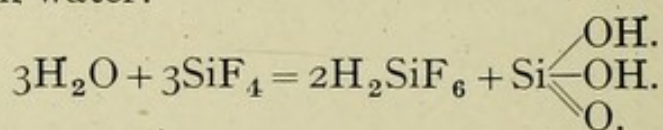
5. AgNO_3 causes no precipitate in solution of soluble fluorides.

All fluorides are decomposed by heating with concentrated H_2SO_4 , forming sulphates.

Most fluorides are unchanged by ignition. They are more or less decomposed by heating with silica in moist air.



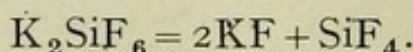
Hydrofluosilicic Acid (H_2SiF_6) is formed by the action of silicon fluoride on water.



When the silicic acid is filtered off, H_2SiF_6 remains in solution.

1. Dilute H_2SO_4 causes but a very slight decomposition.
2. Concentrated H_2SO_4 forms silicon fluoride with evolution of HF, which etches glass and causes a drop of water to become turbid.
3. KCl brings down from solutions which are not too dilute potassium silicofluoride, a gelatinous mass difficultly soluble in water, soluble in NH_4Cl .
4. Ammonia decomposes all soluble silicofluorides, with separation of H_2SiO_3 .

On heating, silicofluorides are changed into fluoride of the metal and silicon fluoride :



GROUP VII.

Non-Volatile Acids which form Soluble Salts with the Alkalies.

Silicic Acid, $\text{Si}(\text{OH})_4$ and $\text{Si} \begin{array}{l} \text{OH.} \\ \text{OH.} \\ \text{O.} \end{array}$

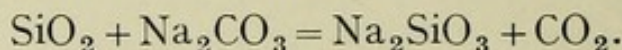
[Titanic, tungstic, niobic, tantalic, and zirconic acids belong to this group, but will not be discussed.]

Free silicic acid occurs in amorphous minerals containing water. Various opals contain from 3 to 36 per cent. of H_2O .

The anhydride SiO_2 occurs as rhombohedra in quartz and other minerals, and mixed with the amorphous acid it is found in agate, jasper, flint, etc.

There are two classes of silicates—water-soluble and water-insoluble.

Water-soluble silicates ('water-glasses') are obtained by fusing silica or silicates with caustic alkali or alkali carbonate :



1. HCl added to a solution of Na_2SiO_3 throws out silicic acid.
2. Ammonium salts added to solutions of 'water-glasses' throw out silicic acid as hydroxide.

Water-insoluble silicates :

1. *Decomposable by Acids.*—A large number of silicates are decomposed by evaporation with HCl, whereby the silica is deposited as a jelly or as a powdery mass.

2. *Undecomposable by Acids.*—*Examples.*—Micas, glasses, porcelains, feldspars, etc.

To extract silicic acid from these bodies it is necessary to (1) fuse with alkali carbonate, lead oxide or boron trioxide; or (2) to heat with H_2SO_4 and HF, whereby silicates soluble in acid are formed.

Carbolic Acid ($\text{C}_6\text{H}_5\text{OH}$).—1. In aqueous solutions bromine-water precipitates white tri-bromo-phenol in dilutions as slight as 1 in 44,000; on standing twenty-four hours, 1 in 60,000. (Bromine-water gives a similar precipitate with thymol.) The precipitate, when washed with sodium-amalgam and acidified with HCl, is reconverted into phenol.

2. Gently heated with NH_4OH , and a drop of sodium hypochlorite added, a blue colour is produced (green if the solution be dilute), which changes to red in acids.

3. FeCl_3 produces a violet colour, perceptible in dilutions of 1 in 3,000.

4. KNO_2 and concentrated H_2SO_4 produce a brown colour, changing to green, and finally to blue.

5. The most sensitive reaction is that with Millon's reagent: To 20 c.c. of the solution to be tested add 5 to 10 drops of Millon's reagent, and boil to obtain a beautiful red coloration of the mixture, which becomes deeper on standing. The limit of sensibility is 1 in 200,000. Salicylic acid gives the same reaction.

Salicylic Acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$.

1. When heated with CaO it yields phenol.

2. FeCl_3 produces a violet colour perceptible in dilutions of 1 in 100,000. As this colour depends on the presence of the phenol-hydroxyl it does not differentiate salicylic from carbolic acid.

3. Bromine-water has the same action as on phenol.

Benzoic Acid ($\text{C}_6\text{H}_5\text{COOH}$).—1. HCl precipitates benzoic acid from concentrated solutions of its salts, in white feathery crystals, sparingly soluble in cold water, easily soluble in boiling water, alcohol, ether, CHCl_3 . On heating it emits a characteristic odour.

2. When heated with lime, benzene is evolved, which may be distilled off and identified.

3. Heated alone at 120°C ., it melts, and afterwards sublimes, producing an irritating vapour which readily condenses to white crystals.

4. FeCl_3 in neutral solutions gives a reddish-white precipitate of basic ferric benzoate ($\text{Fe}_2(\text{C}_6\text{H}_5\text{CO}_2)_6$, Fe_2O_3).

5. Ammoniacal BaCl_2 in presence of alcohol gives no precipitate.

For the separation of the groups, and the individual members of a group, a systematic work on qualitative chemical analysis, such as that of Fresenius, must be consulted.

Water saturated with air at 10° C. dissolves 8.68 c.c. O at N.T.P.

"	"	"	15° C.	"	6.96 c.c.	"
"	"	"	20° C.	"	6.28 c.c.	"

The following salts contain the numbers of molecules of water of crystallization indicated: $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$; $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; $\text{Pb}_2(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 3\text{H}_2\text{O}$; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

At 15° C. 100 grammes of water will dissolve the following amounts, expressed in grammes, of the salts indicated :

BaSO_4	0.006	KBr	38.500
CaSO_4	0.208	CaCl_2	40.800
$\text{Ba}(\text{NO}_3)_2$	7.800	NH_4Br	44.900
NaHCO_3	8.800	NaBr	46.500
K_2SO_4	9.600	SrBr_2	50.300
Na_2SO_4	11.900	$\text{Mg}(\text{NO}_3)_2$	50.500
KHCO_3	18.300	BaBr_2	51.000
KNO_3	21.200	$\text{Ca}(\text{NO}_3)_2$	53.800
Na_2CO_3	22.000	NH_4NO_3	55.300
KCl	25.000	KI	58.500
NH_4Cl	26.500	NaI	63.500
$(\text{NH}_4)_2\text{SO}_4$	33.200	BaI_2	66.900
MgSO_4	34.000	MgCl_2	66.900
NaNO_3	34.200	CaI_2	67.000
NaCl	36.100	K_2CO_3	100.000

INDEX

- ACARUS domesticus, 173
 farinae, 202
- Acid, acetic, 223, 293
 estimation in vinegar, 223
 benzoic, 147, 303
 boracic, 145, 155, 182, 223, 295
 carbolic, 183, 189, 303
 carbonic, 295
 chloric, 300
 citric, 141, 296
 hydriodic, 290
 hydrobromic, 290
 hydrochloric, 290
 hydrocyanic, 291
 hydroferricyanic, 291
 hydroferrocyanic, 291
 hydrofluoric, 301
 hydrofluosilicic, 302
 hydrosulphuric, 292
 hypochlorous, 290
 hypophosphorous, 293
 iodic, 298
 manganic, 283
 metaphosphoric, 297
 nitric, 299
 nitrous, 292
 oxalic, 295
 perchloric, 300
 persulphuric, 300
 phosphoric, 298
 phosphorous, 296
 pyrophosphoric, 297
 salicylic, 147, 223, 303
 silicic, 302
 sulphocyanic, 292
 sulphuric, 301
 sulphurous, 188, 223, 294
 tartaric, 296
 thiosulphuric, 298
- Acidity, 261
 of beer, 223
- Acidity of bread, 211
 of milk, 132
 of water, 17, 21, 88
 of wines, 218
- Actinomyces, 169
- Adams's process, 134
- Adulteration of beer, 222
 of bread, 212
 of butter, 153
 of cheese, 173
 of cocoa, 236
 of coffee, 234
 of milk, 143
 of tea, 229
 of wines, 220
- Air, ammonia in, 116
 analysis of, 97
 bacteria in, 122
 carbon dioxide in, 108
 monoxide in, 112
 composition of, 105
 humidity of, 105
 noxious gases in, 120
 ozone in, 118
 Pouchet's aeroscope, 119
 sulphur dioxide in, 117
 suspended matter in, 119
- Alcohol, 213
 estimation of, 214
 table, 220
- Alkaline permanganate, 44, 253
- Alkalinity, 261
- Alluvium, 3
- Alum, 212
- Aluminium, 278
- Ammonia-free water, 251
- Ammonium, 288
- Amœba, 68, 70
 coli, 244
- Anguillulæ, 70
- Anions, 289

- Annato, 148, 162
 Antimonic compounds, 275
 Antimonous compounds, 275
 Antimony, 275
 Apjohn's formula, 101
 Arrowroot, 200, 201
 Arsenic, 271
 in beer, 222
 in food, 236
 Arsine, 273
 Ascarus lumbricoides, 170, 171
 Aspergillus glaucus, 173, 203

 Bacillus coli communis, 77, 78, 151
 cyanogenus, 150
 enteritidis sporogenes, 77, 78, 151
 prodigiosus, 5, 150
 subtilis, 149
 synxanthus, 150
 tuberculosis, 150
 typhosus, 1, 78, 151, 186, 187
 Bacteria in milk, 149
 Bagshot sands, 3, 4, 88
 Barium, 286
 Barley, 195, 196
 Barometers, 98
 Fortin, 98
 Kew, 98
 Baryta-water, 251
 Bean, 200, 201
 Bechi's test, 162
 Beer, 222
 acidity of, 223
 arsenic in, 222
 boric acid in, 223
 salicylic acid in, 223
 sulphurous acid in, 223
 Beggiatoa alba, 67, 72, 243
 Birotation ratio, 142
 Bismark brown, 53
 Bismuth, 269
 Bleaching-powder, 188
 Bothriocephalus latus, 167
 Boulder clay, 3
 Boyle's law, 97
 Brandy, 214, 215, 216
 Bread, 209, 210
 Bromine, 180
 Bruchus pisi, 202
 Brucine test, 54
 Bursaria, 66, 74
 Butter, 152
 adulteration of, 153
 colouring matters in, 162
 composition of, 152
 cotton-seed oil in, 162

 Butter, curd and salt in, 154, 155
 fat, 155, 156
 density of, 157
 melting-point of, 156
 iodine absorption, 158
 microscopic examination of, 157
 preservatives in, 155
 refractive index of, 157
 Reichert-Wollny process, 159
 Valenta's test, 159
 water in, 153

 Cadmium, 270
 Cælosphærium, 66
 Calandra granaria, 202
 Calcium, 285
 Carbon (organic), 39
 Carchesium Lachmanni, 67, 74
 Casein, 126
 Catchment area, 3
 Catechu, 232
 Cereals, 191
 Chalk, 3, 4, 80, 85
 Champagne, 219
 Chara fragalis, 70
 Charles's law, 97
 Cheese, 172
 adulteration of, 173
 composition of, 173
 moulds in, 173
 mucor in, 173
 Penicillium in, 173
 Piophila casei in, 173
 Tyrothrix in, 173
 Chemical mass action, 259
 Chicory, 234
 Chloride of lime, 178
 Chlorine, 180, 290
 Chocolate, 236
 Chromium, 279
 Clark's process, 28
 Claviceps purpurea, 207
 Coal, 3
 Coal-tar, 183
 Cobalt, 284
 Cocoa, 235
 Coffee, 232
 Condyl's fluid, 188
 Conferva bombycina, 74
 Conradi's medium, 78
 Copper, 268
 sulphate, 189
 zinc couple method, 55
 Cosmarium, 70
 Cotton, 68, 74, 246
 Cream, 139

- Crenothrix, 67, 72
 Crum's method, 55, 91
 Cryptomonas, 70
 Crystalline rocks, 3
 Cuprous chloride method, 116
 Cyllin, 184, 187
 Cysticercus bovis, 167
 cellulosæ, 165, 169

 Daphnia pulex, 72, 243
 Decinormal solutions, 14, 15
 Density of butter-fat, 157
 relative, 102
 Dew-point, 104
 Diatoms, 68, 70, 72
 Diphenylamine test, 54
 Disinfectants, 175
 Dissociation, 259
 Distoma hepaticum, 168, 169
 Dried milk, 148
 Dry-way reactions, 262

 Egg, *Ascarus lumbricoides*, 68
 Tænia solium, 68
 Trichocephalus dispar, 68
 Elder-leaf, 230
 Endorina, 66
 Ethers of wines, 218
 Euplotes Charon, 68
 Eustrongylus gigas, 171

 Fat (butter), 155
 (milk), 128, 134
 Fault, 4
 Fehling's method, 226
 solution, 226
 Ferric compounds, 281
 Ferrous compounds, 280
 sulphate, 190
 Filaria medinensis, 171
 Flax, 247
 Formalin, 146, 187
 Frankland's method, 123
 Fuelling's method, 94
 Fungi, 65
 Fusel oil, 216
 Fusibility, 262, 263

 Gin, 215, 216
 Glaisher's formula, 104
 Gluten, 193
 Greensands, 3, 4, 80
 Griess's test, 53, 91
 Ground water curve, 5

 Haldane's method, 113
 Hardness in water, 24, 25, 80

 Hehner's test, 146
 Hemp, 68, 247
 Hempel's gas burette, 107
 Hermite solution, 179
 Hesse's apparatus, 119
 method, 122
 Houzeau's test, 118
 Human milk, 130, 131
 Hydra, 68
 Hydrodictyon, 74
 Hydrogel forms, 278
 Hydrogen peroxide, 288
 Hydrolysis, 261
 Hydrosol forms, 278

 Igneous rocks, 6
 Infusoria, 65
 Iodine, 180
 Ion hypothesis, 259
 Iron, 280
 in water, 25, 33, 80, 88
 Ironstones, 3
 Isochlors, 19
 Izal, 184, 187

 Jute, 246

 Kimmeridge clay, 3
 Kjeldahl's method, 91, 140

 Lactalbumin, 127
 Lactoglobulin, 127
 Lactose, 128
 Laplace's formula, 101
 Lead, 266, 268
 in water, 34, 35
 Leffmann-Beam process, 139
 Lemon-juice, 223
 Leptomitius lacteus, 74
 Lias, 3
 Lime-juice, 223
 Limestone, 3, 80
 Linen, 68
 Liquor carbonis detergens, 187
 Lolium temulentum, 209
 London clay, 3, 4
 Lunge and Zeckendorf's method, 111
 Lysol, 184

 Magnesium, 289
 in water, 24, 25, 29, 31, 79, 80
 Maize, 195, 198
 Manganese, 282
 Manganic acid, 283
 Marsh's method, 237, 273
 Meat, 164

- Melosira, 72
 Mercuric chloride, 190
 Mercury, 267
 salts, 178, 267
 Meridion, 66
 Metals, 265
 Metaphenylene-diamine, 53, 255
 Methylated spirit, 217
 Methyl orange, 255
 Milk, 125
 acidity of, 132
 adulteration of, 143
 annato in, 148
 ash of, 129, 140
 Bacillus coli communis in, 151
 cyanogenus in, 150
 enteritidis sporogenes, 151
 potato in, 149
 prodigiosus in, 150
 subtilis in, 149
 synxanthus in, 150
 tuberculosis in, 150
 typhosus in, 150, 151
 boracic acid in, 145
 composition of cow's, 125
 cream of, 139
 fat of, 128, 134
 human, 130, 131
 Micrococcus rosaceus in, 150
 muco-proteid in, 127
 Oidium lactis in, 150
 pasteurization of, 149
 Penicillium glaucum in, 150
 reaction of, 132
 Saccharomyces cerivisiæ in, 149
 Sarcina rosea in, 150
 saffron in, 148
 salicylic acid in, 147
 skimmed, 148
 solids of, 139
 not fat, 140
 specific gravity of, 132
 staphylococci in, 151
 sterilization of, 149
 streptococci in, 151
 sugar of, 142
 turmeric in, 148
 Mucor mucedo, 203
 Mustard, 224
 Navicula, 74
 Nessler's reagent, 42, 253
 New red sandstones, 3
 Nickel, 283
 Nitrates in water, 32, 41, 51, 52, 80, 82
 Nitric ferment in water, 39
 Nitrites in water, 32, 41, 51, 52, 53, 80, 82
 Nitrobacter, 51
 Nitrogen (organic), 39
 Nitrosomonas, 51
 Normal solution, 14, 15
 Nostoc, 72
 Oat, 195, 197
 Odour of water, 7, 13
Oidium lactis, 150
 Old red sandstones, 3
 Oolite, 3, 4, 79, 80
 Ordnance survey, 3
 Oscillatoria, 74
 Ova, *Ascarus lumbricoides*, 68
 Bilharzia hæmatobia, 240
 Tænia solium, 68
 Trichocephalus dispar, 68
 Oxidation, 258, 263
 Oxygen, 181
 dissolved in water, 59
 Oxyuris vermicularis, 170, 171
 Ozone, 118
 Pandorina, 66
 Paramœcium, 68, 72
 Parasites, various, 165, 201
 Pasteurization of milk, 149
 Pea, 199, 201
Pediculus capitis, 242
 pubis, 242
 Vestimenti, 241
Penicillium glaucum, 150, 173, 203
 Pepper, 224
 Permanganic acid, 283
 Peronospora, 203, 204
 Pettenkofer's method, 109
 Phenol, 183, 189, 303
 Phenolphthalein, 255
 Phenolsulphonic acid, 57, 255
 Phosphates in water, 29, 31
 Picric acid, 57
Piophila casei, 173
 Pleurococcus, 70
 Plumbo-solvency, 17, 79, 88
 Porosity of soil, 95
 Post-tertiary deposits, 3
 Potassium, 287
 chromate, 252
 iodide, 253
 Potato, 201
 Pouchet's aeroscope, 119
 Preserved foods, 248
 Primary deposits, 3
 Psorosperms in meat, 169

- Puccinia graminis*, 205
Pulex irritans, 241
 Purbeck marble, 3

 Qualitative analysis, 260

 Reduction, 258
 on charcoal, etc., 263, 264
 Reinsch's test, 274
 Rideal-Walker method, 185
Rivularia, 66
 Rose's tube, 216
 Rum, 215, 216

Sarcoptes scabiei, 240
Schlerostomum duodenale, 171
 Sea-water, 88
 Sedgwick and Tucker's method, 123
 Sesame oil in butter, 162
 Sewage effluents, 90
 Shales, 3
 Shallow wells, 3
 Silk, 245
 Sloe-leaf, 230
 Silver, 265
 Sodium, 288
 Soils, 94
 specific gravity of, 95
 apparent of, 95
 heat of, 95
 Soxhlet's apparatus, 135, 136
Sphærotilus natans, 72
Spirogeira, 72
 Sprengel's method, 56
 Standard ammonium chloride, 253
 arsenical mirrors, 238
 copper, 256
 iron, 256
 lead, 256
 nitrate, 255
 nitrite, 255
 nitrite-iodide, 254
 normal HCl, 258
 H₂SO₄, 257
 Na₂CO₃, 256
 oxalic acid, 257
 permanganate, 254
 silver, 252
 soap, 252
 thiosulphate, 254
 zinc, 256
 Starch solution, 253
 granules, 194
 arrowroot, 200, 201
 barley, 195, 196
 bean, 200, 201
 Starch granules:
 maize, 195, 198
 oat, 195, 197
 potato, 201
 rice, 195, 197
 rye, 195, 196
 sago, 195, 198
 tapioca, 195, 199
 wheat, 195
 Stokes tube, 135, 138
 Streptococci in water, 77, 78
 Strontium, 286
 Sugar, 225
 Sulphites, 188
 in butter, 155
 Sulphuretted hydrogen water, 252
 Sulphurous acid, 188, 223, 294
 Synura uvella, 74

 Tabellaria, 66, 72
Tænia echinococcus, 167, 169
 mediocanellata, 167
 solium, 165, 166, 167, 169
 Tea, 227
 composition of black, 228
 leaf, 227, 228
 tannin in, 229, 232
 thein in, 229, 231
 volatile oil in, 229
 Tertiary deposits, 3
 Theobromine, 236
 Thermometers, 97
 Thiosulphate solution, 254
 Thresh's method, 59
 Tidy's process, 48, 81, 91
Tilletia caries, 204, 205
 Tin, 276
 stannous and stannic compounds
 of, 276, 277
 Tobacco-leaf, 230
Trichina spiralis, 167, 168, 171
Trichocephalus dispar, 171
 Trinitro-phenol, 57
Tylenchus tritici, 201

Ulothrix, 70
Uroglena, 66, 70
Ustilago segetum, 204

 Vernier, 99
Vibrio cholerae asiaticæ, 1, 187
 Vinegar, 223
 acetic acid in, 223
 mineral acids in, 224
 Volatility, 262

Volvox, 66, 72

Vorticella, 72, 74, 244

Wanklyn's process, 42, 47

Water, 1

acidity of, 17, 21, 88

albuminoid ammonia in, 40, 46, 47, 81, 90

algæ in, 65

aluminium in, 25

anabena in, 66, 70

Bacillus coli in, 77, 78

enteritidis sporogenes in, 77, 78

typhosus in, 1, 78

bacteriological examination of, 1, 76

bear, 74

biological examination of, 2, 65

calcium in, 25, 29, 30, 79, 80

carbon dioxide in, 63

chalk in, 80, 85

chemical examination of, 2, 14

chlorides in, 18, 20, 21, 22, 25, 80

chromium in, 37

colour of, 7, 11

copper in, 34, 36

enzymes in, 38

erosive action of, 18

free and saline ammonia in, 40, 44, 45, 46, 47, 81

hardness in, 24, 25, 80

iron in, 25, 33, 80, 88

lead in, 34, 35

magnesium in, 24, 25, 29, 31, 79, 80

nitrites in, 32, 41, 51, 52, 80, 82

nitric ferment in, 39

nitrites in, 32, 41, 51, 52, 53, 80, 82

odour of, 7, 13

organic matter in, 38

Water, oxidizable organic matter in, 48

oxygen dissolved in, 59

peaty, 6, 87, 88

phosphates in, 29, 31

physical examination of, 2, 7

plumbo-solvency in, 17, 79, 88

poisonous metals in, 33

pure, 84

rain, 85

reaction of, 17

sediment, 65

silica in, 25, 31

solid residue in, 29

sulphates in, 29, 32

taste of, 10, 13

tin in, 37

turbidity of, 7, 11

zinc in, 36

Weald clay, 3

Werner-Schmidt method, 137

Westphal's balance, 133, 135

Wet-way reactions, 265

Wheat, 191, 195

flour, ash, 193

composition, 192

Whisky, 214, 215, 216

Willow-leaf, 230

Wines, 217

acids of, 218

adulteration of, 220

constituents of, 218

ethers of, 218

sugars in, 219

Winkler's method, 62

Wood cells, 68

Wool, 68, 70, 245

Zinc, 281

in water, 36

salts, 190

THE END

815

