Course of practical chemistry : as adopted at University College, Toronto / by Henry Croft.

Contributors

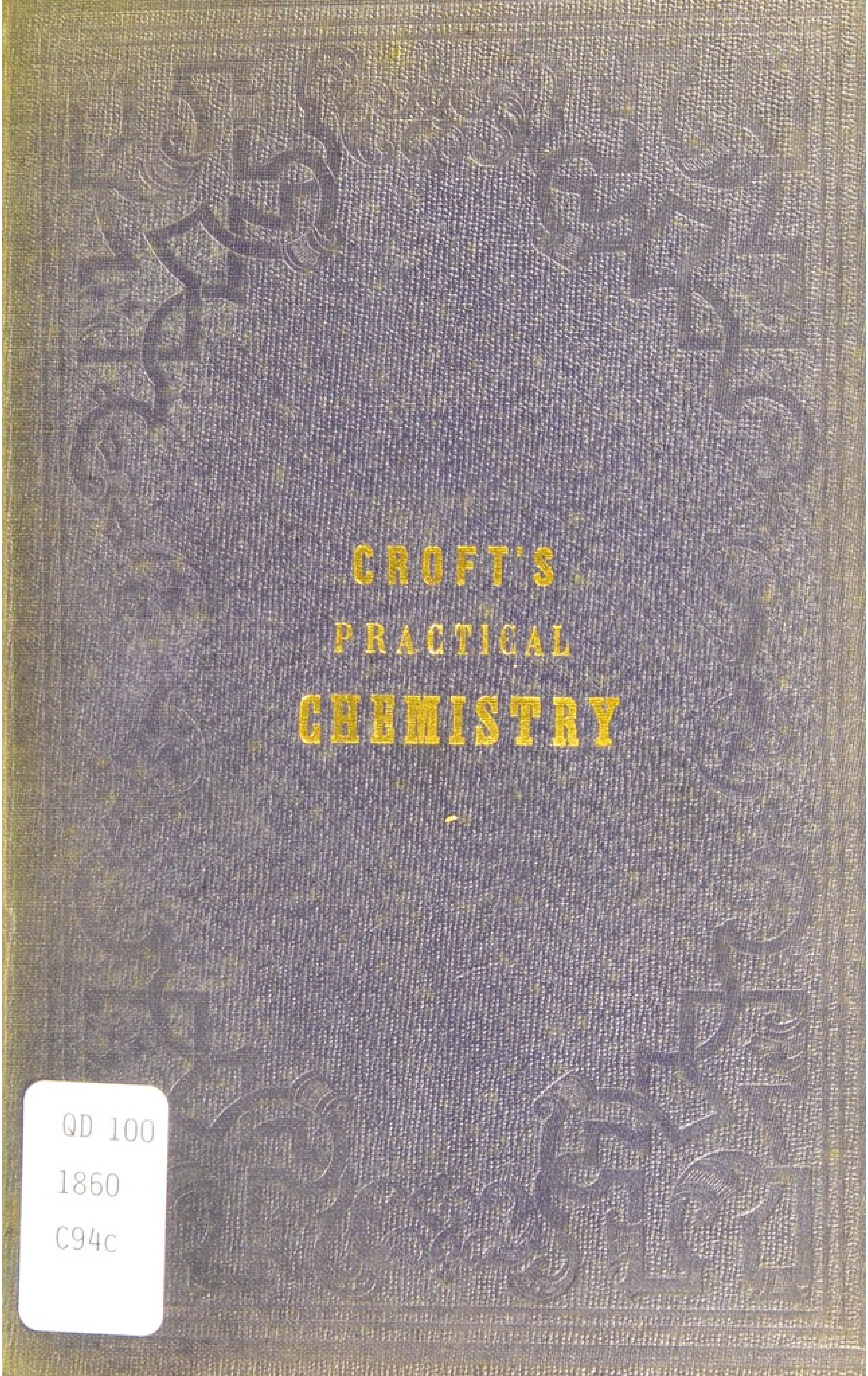
Croft, Henry.

Publication/Creation

Toronto : MacLear, 1860.

Persistent URL

https://wellcomecollection.org/works/sffthgnu



CROFT'S
PRACTICAL
CHEMISTRY

William Francis
from his old chum,
H. C.

PREFACE.

The following pages contain an outline of the course of practical chemistry adopted by the writer in University College, and will be found to correspond very closely with a similar work by Dr. Odling; differing however in some respects, to meet the requirements of Canadian students, and being in accordance with the plan of instruction, which after many years' experience the writer has found best adapted to the wants of his pupils.

Unnecessary matter has been as far as possible excluded, only the most reliable and easily applicable tests being mentioned, and as the work makes no claim to originality, it has not been thought necessary to refer to authorities, except in a few instances.

Being intended merely as a guide and assistance to the writer's pupils, it by no means aims at taking the place of those more complete and valuable works on analytical chemistry which should be in the hands of every student wishing to perfect himself in the science. The following list comprises those which the writer would especially recommend, and which have been freely used in the compilation of the present work.

Odling's Course of Practical Chemistry.
Fresenius' Analytical Chemistry.
Rammelsberg's Anleitung.
Rose's Analytische Chemie.
Otto's Lehrbuch der Chemie.
Graham's Elements.
Otto's Detection of Poisons.
Abel and Bloxam's Handbook.
Northcote & Church's Manual.
Williams' Chemical Manipulation.

Old habits and predilictions, which are difficult to eradicate even by the aid of conviction, must serve as an excuse for the employment of symbols such as NO^5, SO^3 and PO^5, instead of HNO^3, H^2SO^4 and H^3PO^4.

The want of tables for the examination of the smaller divisions, may excite surprise; the omission has been intentional, as the writer is of opinion that the constant reference to tables materially interferes with the use of the pupils' memory and reasoning faculties.

The following pages having been written under an overwhelming press of other business, many errors and omissions have doubtless crept in. The writer will feel obliged to his fellow chemists on this continent for any corrections or emendations.

UNIVERSITY COLLEGE,
JANUARY, 1860.

TABLE OF CONTENTS.

CHAPTER I.

PAGE.
Reagents :

Dry Reagents :

CHAPTER II.

ANALYSIS. DETECTION OF BASES.

DETECTION OF ACIDS.

CHAPTER III.

POISONS.

CHAPTER IV.

MISCELLANEOUS.

SYMBOLS AND EQUIVALENTS OF THE COMMONER ELEMENTS.

Oxygen	O	8
Chlorine	Cl	35.5
Bromine	B	80.
Iodine	I	126
Fluorine	F	19
Sulphur	S	16
Phosphorus	P	31
Carbon	C	6
Boron	Bo	11
Silicon	Si	22
Nitrogen	N	14
Hydrogen	H	1
Potassium	K	39
Sodium	Na	23
Barium	Ba	68
Strontium	Sr	44
Calcium	Ca	20
Magnesium	Mg	12
Aluminum	Al	13.7
Manganese	Mn	27.5
Iron	Fe	28
Chromium	Cr	26.7
Nickel	Ni	29.6
Cobalt	Co	29.5
Zinc	Zn	32.6
Cadmium	Cd	56
Bismuth	Bi	208
Copper	Cu	32
Lead	Pb	103
Tin	Sn	58
Antimony	Sb	120.3
Arsenic	As	75
Silver	Ag	108
Mercury	Hg	100
Gold	Au	197
Platinum	Pt	98.7

CHAPTER I.

APPARATUS.

The apparatus required for the performance of the experiments to be detailed in the present work is of an exceedingly simple character and can be obtained at a comparatively trifling cost. The following may be mentioned as the most essential.

As in this country chemical apparatus is not as yet a very common article of commerce, and as it is possible that some readers may be placed in positions where they cannot readily procure it, a few directions are given for making substitutes for some of the rare or more costly pieces of apparatus, such make-shifts being of course unnecessary in the larger towns, or where the student is willing to incur some expense in procuring suitable working materials. The reader is referred for much valuable information on this head to "Faraday's Chemical Manipulation" and G. Williams' more recent work.

Some dozens of test tubes.

A test tube stand.

A few small retorts.

A spirit lamp, which in lack of a better can be made from a common medicine bottle, with a tin tube passing through the cork to hold the wick. This tube can be covered when not in use by another tin or glass tube, closed at one end.

A double spirit lamp is very necessary in many cases.

A few porcelain dishes and capsules; the latter can be replaced to a great extent by watch glasses or glass plates placed on white paper, or by small dishes or flat boxes made out of paper itself, as recommended by Faraday.

A retort stand, which, if not obtainable in its ordinary form, can be made by fixing a round rod of wood into a flat board of eight or nine inches square, and making the rings of rather stout iron wire; the shank is then twisted into a coil about two inches long, of such a diameter as to slide easily over the wooden rod. Such a ring will be quite secure when supporting a dish.

Triangles, to support crucibles on these rings, can easily be constructed from three pieces of iron wire.

Filter stands. These can be constructed in the same way as the retort stands, or by fixing a piece of thin board on two uprights, the board having various apertures in it for the reception of the funnels.

Glass funnels, in diameter from one to three inches, together with a few much larger ones.

Filtering paper of two kinds, the coarse brown for larger operations, the white for more delicate experiments. For very accurate investigations, the filters, after having been cut, should be soaked for some hours in diluted hydrochloric acid, and then thoroughly washed and dried.

Glass plates.

Glass rods.

Glass tubes, of small bore and thick in the glass for experiments with gases, and thin in the glass for reduction tests.

The reduction tubes are made by cutting a piece of tubing to double the length of the required tube, by means of a triangular file, heating the centre portion over the flame of a spirit lamp, keeping it constantly turning, drawing out when soft, and fusing up at each shoulder.

Thin glass tubes closed at both ends may be used instead of rods.

A mouth-blowpipe, with a few pieces of platinum foil and wire. The flame used for blowpipe experiments may be that of a wax candle or a camphene lamp.

Some porcelain and Hessian crucibles.

A small platinum crucible or capsule.

Vulcanized tubing or sheet caoutchouc.

A few beaker glasses of different sizes. In default of them, ordinary glasses may be used, and very good precipitating glasses for qualitative experiments may be made from common phials, cutting off the top by means of a filed scratch and a hot wire.

Glass flasks. The common Florence oil flasks may be used, although inconveniently large for many operations.

Narrow and wide-mouthed phials, for preparing gases.

A spirting bottle or edulcorator is made by fixing a short tube, drawn out at one end to a rather fine point, but thick in the glass, into the cork of an eight ounce phial. When half filled with water, if air be blown in and the bottle suddenly inverted, a stream of water will be driven out with considerable force, which is useful for washing precipitates.

REAGENTS.

The following reagents will be required. The formulæ are appended, as in the following pages they will frequently be used for the sake of shortness. It must be remembered that in these formulæ the water is not shown.

Sulphuric Acid	$S\ O^3$
Nitric	$N\ O^5$
Hydrochloric	$H\ Cl$
Hydrosulphuric	$H\ S$
Hydrofluosilicic	$Si\ F^3,\ H^3\ F^3$
Tartaric	$\overline{Tar}$
Oxalic	$C^2\ O^3$
Acetic	$\overline{Ac}$
Iodic	$I\ O^5$
Cyanide of Potassium	$K\ Cy$
Ferrocyanide of “	$K^2\ Cfy$
Ferricyanide of “	$K^3\ Cfdy$
Sulphocyanide of “	$K\ Csy$
Borax	$Na\ O,\ 2\ B\ O^3$
Potassa	$K\ O$
Ammonia	$N\ H^3$
Baryta	$Ba\ O$
Lime	$Ca\ O$
Carbonate of Potassa	$K\ O,\ C\ O^2$
“ Soda	$Na\ O,\ C\ O^2$
“ Ammonia	$2\ N\ H^4O,\ 3\ C\ O^2$
Chloride of Ammonium	$N\ H^4,\ Cl$
“ Barium	$Ba\ Cl$
“ Calcium	$Ca\ Cl$
“ Magnesium	$Mg\ Cl$
Sesquichloride of Iron	$Fe^2\ Cl^3$
Bichloride of Platinum	$Pt\ Cl^2$
Sulphide of Ammonium	$N\ H^4,\ S$
Phosphate of Soda	$Na^2O^2,\ HO,\ PO^5$
Nitrate of Baryta	$Ba\ O,\ N\ O_5$
Sulphate of Lime	$Ca\ O,\ S\ O^3$
Protochloride of Tin	$Sn\ Cl$
Acetate of Lead	$Pb\ O,\ \overline{Ac}$
Sulphate of Copper	$Cu\ O,\ S\ O^3$
Chloride of Mercury	$Hg\ Cl$
Nitrate of Silver	$Ag\ O,\ N\ O^5$
Chromate of Potassa	$K\ O,\ Cr\ O^3$
Iodide of Potassium	$K\ I$
Acetate of Potassa or Soda	$K\ O,\ \overline{Ac}$
Molybdate of Ammonia	$NH^4O,\ MoO^3$
Oxalate of Ammonia	$N\ H^4O,\ C^2O^3$
Sulphate of Potassa	$K\ O,\ S\ O^3$
Solution of Indigo	
“ Litmus	
Test Papers	
Nitrate of Potassa	$K\ O,\ N\ O^5$
Oxide of Bismuth	$Bi\ O^3$
“ Copper	$Cu\ O$
Microcosmic Salt	$N\ H^4O,\ Na\ O,\ H\ O,\ P\ O^5$
Chlorate of Potassa	$K\ O,\ Cl\ O^5$
Sulphate of Iron	$Fe\ O,\ S\ O^3$

In the following paragraphs, the impurities usually occurring in these reagents will be mentioned, the tests by which they can be discovered, and the means by which they may be removed, or pure reagents prepared. (For fuller details consult Fresenius.)

SULPHURIC ACID.

This acid not unfrequently contains lead, arsenic and nitric acid. The two former may be detected by diluting with water and passing hydrosulphuric acid through the mixture, when a black or yellow precipitate will be formed, or the arsenic may be detected by other processes (see Chap. III). The nitric acid may be detected by the decolorizing action of the sulphuric acid on a solution of indigo. If the acid be mixed with a drop or two of indigo solution, so as to give it a faint blue colour, and the whole be then boiled, the disappearance of the colour will indicate the presence of nitric acid. It may also be detected by diluting with an equal bulk of water, allowing the mixture to cool and introducing a crystal of green vitriol, a brown coloration round the salt will be produced if nitric acid is present.

These impurities are of little consequence in ordinary analytical investigations, and the preparation of pure sulphuric acid for toxicological purposes will be mentioned under the head of arsenic.

The nitric acid may be removed by boiling for a short time.

The specific gravity of pure sulphuric acid is 1.845, but it is seldom that we meet with a specimen which comes up to this density.

The dilute acid, obtained by mixing the concentrated acid with six parts of water, is free from lead, as the sulphate (if present) is deposited on dilution and can be allowed to subside.

NITRIC ACID.

The commercial acid usually met with is so impure as to be unfit for all analytical investigations. It generally contains traces of sulphuric and large quantities of hydrochloric acid, the latter detected by diluting the concentrated acid with twice its weight of water, and adding a solution of nitrate of silver, a white curdy precipitate of chloride of silver being produced; the former impurity is detected by diluting the concentrated acid with several times its weight of water and adding chloride of barium, a white precipitate of sulphate of baryta is formed. If the acid be not sufficiently diluted, a granular precipitate of nitrate of baryta will be formed, which will dissolve in excess of water.

The commercial acid frequently contains earthy or alkaline salts, which remain behind after evaporation.

The hydrochloric acid may be removed by adding nitrate of silver as long as any turbidity is produced, allowing the chloride to settle, decanting off and distilling from a retort till only a small quantity is left. It may also be purified without the use of silver, by distilling and from time to time examining the acid which passes over, until it is found to be free from hydrochloric acid; what passes over after that is pure. Owing to the violence with which the acid boils, it may be better not to distil but to use the residual liquid. In this case, however, earthy matters may be present.

Fuming nitric acid (s. g.=1.48 to 1.50) is sometimes required. This may be obtained by distilling at a moderate temperature equal parts of powdered nitre and sulphuric acid. If the nitre has not previously been purified, the first portions passing over must be rejected as containing hydrochloric acid, the presence or absence of which is proved as described above. The nitre may be purified by moistening the powder with nitric acid, and heating until quite dry; all the chlorine will thus be expelled.

HYDROCHLORIC ACID.

The acid of commerce is often very impure, containing sulphuric and sulphurous acids, arsenic, iron and chlorine. The sulphuric acid is detected by chloride of barium; the sulphurous either by the same reagent applied after boiling the acid with a little nitric, or, better, by heating the acid with a little protochloride of tin, and putting into the mouth of the tube a paper covered with carbonate of lead. If sulphurous acid is present, the lead will be blackened by the evolution of sulphuretted hydrogen. A few drops of sulphate of copper may be added to the heated mixture, when black sulphide of copper will be precipitated if sulphurous acid is present. The arsenic can be detected by means to be described hereafter; and the iron by neutralizing with ammonia, either adding acetic acid until the ammonia is supersaturated, and then testing with ferrocyanide of potassium, or by adding sulphide of ammonium, when a greenish black colour or precipitate will be produced if iron is present. If the strong or even diluted acid were used at once with the ferrocyanide, a blue coloration would be produced either immediately or after a time. The chlorine can be detected by heating the acid with solution of indigo; loss of colour is the result if chlorine is present.

It is best to prepare a pure acid, as follows: 13½ parts of sulphuric acid freed from nitric by boiling, are mixed with 4 parts of water and the mixture cooled, this is poured over 8 parts of common salt contained in a flask or retort, and gently heated in a sandbath. The gas evolved is conducted by a bent tube into 12 parts of water contained in a bottle, which must be kept cool by water or ice. The tube must dip only just beneath the surface of the water, and the flask or retort must be provided with a safety tube. When all the gas has been evolved, the acid in the receiver will have a specific gravity of from 1.11 to 1.12.

HYDROSULPHURIC ACID.

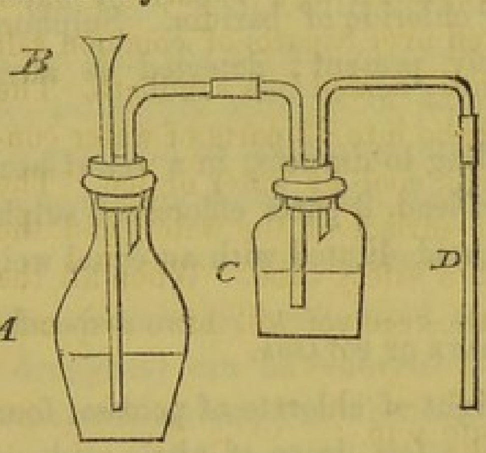
Sulphuretted hydrogen is best prepared from the protosulphide of iron. This is obtained by throwing a mixture of 30 parts iron filings and 20 parts of powdered sulphur into a red hot crucible, from time to time, and waiting after the addition of each portion until incandescence has ceased. It is better prepared by boring a hole in the bottom of a large crucible, filling it with iron nails, and placing it on the grate of a strong furnace (most of our anthracite stoves will give sufficient heat), so that the hole remains free; lumps of sulphur are then thrown in from time to time. If the crucible has been raised to a bright red heat, the sulphide flows out through the hole and can be collected in a shovel placed to receive it.

The gas is obtained from the sulphide by acting on it with sulphuric acid mixed with three parts of water, or by introducing the sulphide and water into a bottle furnished with a gas delivery tube and a long funnel reaching below the surface of the water. Sulphuric acid is then poured in until effervescence ensues. A wide tube with a small funnel fitting loosely into it may take the place of the long funnel.*

---

* The solution remaining should be filtered and evaporated. Very pure sulphate of the protoxide of iron crystallizes out, which can be recrystallized, or precipitated from its solution by alcohol, and the granular salt dried. In this form it keeps long without oxidizing.

If the end of the gas delivery tube be ground off obliquely, which can be done either on a file moistened with oil of turpentine, or on a whetstone kept constantly moist, and the evolution of gas be moderate, there will be little danger of any of the liquor being carried over. For very accurate experiments, however, it is better to send the gas through a washing bottle, before it passes into the water intended to dissolve it. The tubes can be connected by vulcanized caoutchouc joints.



The water is known to be saturated when, on closing the aperture of the bottle with the thumb and strongly agitating, the thumb is no longer pressed in but rather pushed off. The solution cannot well be kept for any length of time, especially if the bottle containing it be frequently opened.

The solution should not become black on the addition of ammonia, as that shows the presence of iron.

HYDROFLUOSILICIC ACID.

This reagent is of little use, being employed solely in the detection of baryta.

Equal parts of sand and powdered fluor spar are mixed with 6 parts of sulphuric acid in a flask, and heated in a sand bath. The gas is conducted by a bent tube into a little mercury placed in a jar or glass, water is poured on to the mercury. The fluoride of silicon evolved is decomposed by the water, gelatinous silica is separated and hydrofluosilicic acid dissolved. The liquid must be kept stirred, and when evolution of gas ceases the whole is thrown on to linen and the filtrate collected.

Hyposulphite of soda may replace this acid as a test for baryta in neutral solutions.

TARTARIC ACID.

The pharmaceutical acid is sufficiently pure. Dissolve 1 part in 8 parts of water. The solution will not keep very long. As a test for potassa, a solution of bitartrate of soda is preferable to tartaric acid (see post. p. 31).

OXALIC ACID.

The commercial acid is sufficiently pure, but can readily be further purified by recrystallization. Dissolve 1 part in 8 or 10 of water. The solution is not liable to change.

ACETIC ACID.

The *acidum aceticum fortissimum* of the shops is sufficiently strong. It is in general tolerably pure, but sometimes contains sulphuric acid, which may be detected by chloride of barium. Sulphurous and hydrochloric acids are rarely present; detected as already described.

Pure acid is obtained by distilling to dryness, in a retort heated on a sand bath, 10 parts acetate of lead, 3 parts effloresced sulphate of soda, with 2½ parts sulphuric acid diluted with an equal weight of water.

IODIC ACID. IODATE OF POTASSA.

Digest iodine with an equal weight of chlorate of potassa, four or five times its weight of water, and a few drops of nitric acid, until the iodine disappears. The solution on cooling will deposit iodate of potassa, which can be purified by resolution and crystallization. If iodic acid is required, the hot solution is mixed with chloride of barium as long as a precipitate is formed; this is collected on a filter, washed, and then digested for some hours with sulphuric acid (5 parts of the dry iodate of baryta require about 1 of common acid), filtered off, washed, and the filtrate evaporated at a moderate heat. On standing some days, or by resolution, &c., the iodic acid crystallizes.

CYANIDE OF POTASSIUM.

Can be obtained sufficiently pure from the dealers in photographic chemicals.

FERROCYANIDE OF POTASSIUM.

The commercial salt is quite pure.

FERRICYANIDE OF POTASSIUM.

Can often be obtained pure from the druggists, or may be prepared by passing chlorine into a concentrated solution of the yellow ferrocyanide until it no longer produces a blue precipitate with perchloride of iron. The solution is then boiled violently and filtered whilst boiling. Fine red crystals separate out, which may be slightly washed with water before being dried.

SULPHOCYANIDE OF POTASSSIUM.

46 parts of dry ferrocyanide of potassium, 17 parts carbonate of potassa and 32 of sulphur, are heated in a covered iron pan to fusion at a gentle heat. The heat is continued till the mass fuses quietly, then raised to faint redness. The fused mass is removed from the pan, powdered, boiled with alcohol, and filtered; the crystals which separate from the alcohol on cooling are the pure salt.

An extempore solution of sulphocyanide of ammonium can be easily prepared by adding excess of hydrocyanic acid to sulphide of ammonium, and heating till the solution is inodorous.

CARBONATE OF SODA.

The commercial crystallized carbonate of soda (subcarbonate of the druggists) can be rendered sufficiently pure for most purposes by recrystallization; but when an absolutely pure salt is required, as in toxicological investigations, the following process must be adopted. A quantity of bicarbonate of soda (carbonate of the druggists) is put into a filter, or into an old retort neck, or a phial with the bottom cut off, the mouth in the two latter cases being closed by a piece of linen; water is then poured on and allowed to run through until the washings give no trace of precipitate or even opacity, either with chloride of barium or nitrate of silver, the liquid having been previously neutralized with *pure* nitric acid. The residue on the filter is dried, heated to expel the second equivalent of carbonic acid, and the residue dissolved in water. This should again be tested for sulphuric and hydrochloric acids.

DRY CARBONATE OF SODA.

For blowpipe experiments and analysis of minerals is prepared as above.

CARBONATE OF POTASSA.

The commercial salt of tartar (subcarbonate of the druggists) is exceedingly impure, containing generally sulphuric, hydrochloric and silicic acids; the two former detected, after supersaturation with *pure* nitric acid, as already described, and the latter by supersaturation with pure hydrochloric acid, evaporation to dryness, and treatment of the residual mass with water. An insoluble residue indicates silicic acid.

The bicarbonate (carbonate of the druggists) is much purer, and by heating this, to expel the second equivalent of carbonic acid, a salt is obtained sufficiently pure for most purposes. When, however, a perfectly pure carbonate is required, it must be prepared from the bitartrate of potassa previously well washed with water, calcined in an iron pan, lixiviated with water; the solution filtered and boiled down to dryness in a clean iron or silver vessel.

For the analysis of silicates and insoluble sulphates by fusion with alkaline carbonates, a mixture of about equal parts of the above mentioned dry salts of soda and potassa is very useful, as it fuses at a moderate temperature. This mixture may be readily obtained by incinerating Rochelle salt in a platinum or iron vessel until all the carbon has been burnt off.

CARBONATE OF AMMONIA.

The sesquicarbonate of the shops is generally pure; any dark coloured portions must be scraped off. The salt is dissolved (in the cold) in 4 parts of water and mixed with 1 part of liquid ammonia, to neutralize the excess of carbonic acid.

Hydrochloric and sulphuric acids may be detected by the tests already mentioned, and metallic impurities by the addition of sulphide of ammonium to the solution of the salt. No precipitate or coloration should be produced.

POTASSA.

The commercial *potassa fusa* is generally very impure; even that said to be purified by means of alcohol often contains many impurities. These are carbonic, silicic, sulphuric and hydrochloric acids, alumina, and oxide of lead.

The carbonic acid is detected by effervescence on addition of nitric acid to the solution; the other three acids in the manner already described (ante p. 17-18); the alumina by the production of a precipitate on the addition of a solution of sal ammoniac; and the lead by hydrosulphuric acid.

Ordinary potassa may be used for most experiments, but for delicate investigations the solution must be prepared by boiling 1 part of pure carbonate (see above) in 10 parts of water in a clean iron or silver pan, adding about 2 parts of slacked lime in small portions, boiling for a few minutes after each addition, and replacing the water lost by evaporation, until a portion of the clear liquid drawn off by a siphon does not effervesce on addition of excess of hydrochloric acid. The liquid is obtained clear by allowing it to settle, or by filtering through linen. When pure, the whole is allowed to stand until clear and the liquid drawn off and kept in well stoppered bottles.

SODA.

As carbonate of soda is more readily obtained pure than the corresponding salt of potassa, it is better to prepare caustic soda than to attempt the preparation of absolutely pure potassa. The solution of soda may almost universally be employed instead of that of potassa, and is prepared in precisely the same manner.

AMMONIA.

The commercial solution is generally pure, and may be diluted with an equal bulk of water. It may be tested for hydrochloric acid as already described, for carbonic acid by a solution of chloride of calcium, and for lime by a solution of oxalate of ammonia. A precipitate will indicate the presence of the impurity.

CHLORIDE OF AMMONIUM.

The commercial salt often contains iron, detected by a greenish tint produced on the addition of sulphide of ammonium. To obtain it pure a few drops of the sulphide are added to the solution of the chloride, the mixture boiled until all smell has disappeared, and the solution filtered from the sulphide of iron. When heated on platinum foil it should leave no residue.

SULPHIDE OF AMMONIUM.

Obtained by passing hydrosulphuric acid into solution of ammonia until the liquid produces no precipitate in sulphate of magnesia. Even if this point be not reached the solution is still available. The solution may be considered either as sulphide ($N\,H^4, S$) or as hydrosulphide (hydrosulphate) $N\,H^4, S + H\,S$. By keeping it becomes yellow, and then contains bisulphide $N\,H^4, S^2$. This old solution is useful in certain cases.

PHOSPHATE OF SODA.

The commercial salt is sufficiently pure for most purposes, but it frequently contains small traces of sulphates, from which it is difficult to free it by mere crystallization. If required of absolute purity it must be prepared by digesting phosphorus with 10 times its weight of pure nitric acid of s. g. 1, 2, until dissolved, evaporating to a syrup and heating until no fumes of nitric acid are given out, neutralizing with pure carbonate of soda, and crystallizing.

The sulphuric acid may be detected by the production of a precipitate on the addition of chloride of barium, which precipitate remains undissolved on the addition of pure nitric or hydrochloric acid.

CHLORIDE OF BARIUM.

The commercial salt is tolerably pure. It may be prepared either by dissolving the native carbonate in hydrochloric acid, and repeated crystallization, or from the native sulphate, by strongly heating a mixture of 6 parts of the finely pounded mineral with 1 of charcoal and 1½ of flour in a Hessian crucible for about half an hour. The mass is extracted with water, supersaturated with hydrochloric acid, the solution evaporated to crystallization, and the salt which separates purified by recrystallization. The solution must be perfectly neutral and not changed by sulphide of ammonium.

NITRATE OF BARYTA.

Can be obtained pure either by recrystallization of the commercial salt (used for pyrotechnic purposes), or by employing dilute nitric instead of hydrochloric acid, as described in the preceding paragraph.

BARYTA WATER.

Sulphide of barium, prepared as described in preceding paragraph from the sulphate, is boiled with oxide of copper until a portion of the filtered liquid gives a white and not a dark precipitate with acetate of lead. The solution is filtered rapidly, and preserved in well stoppered bottles. If the solution is concentrated, the crystallized hydrate will separate on cooling; which can be preserved for use.

LIME WATER.

Freshly slacked lime is mixed with distilled water and well stirred for some time, the liquid is thrown away, and a fresh portion of water poured on. After standing some time, being frequently stirred, the solution is filtered. The first portions of water used often contain alkali.

CHLORIDE OF CALCIUM.

Marble or chalk is dissolved in hydrochloric acid, filtered, the solution supersaturated with ammonia, again filtered from the precipitate, the filtrate boiled and precipitated with solution of carbonate of ammonia, and the precipitate well washed. This is perfectly pure carbonate of lime, and is used in mineral analyses where the alkali is to be determined. This pure carbonate is then introduced into heated dilute hydrochloric acid, until neutralized, and the solution filtered.

The chloride must be neutral and free from iron and ammonia. The former is detected by sulphide of ammonium, the latter by boiling with excess of caustic potassa.

SULPHATE OF LIME.

Pure chloride of calcium is precipitated with sulphuric acid, the precipitate well washed out until the filtrate is no longer acid, the residue on the filter boiled with a large quantity of water, and the solution filtered.

CHLORIDE OF MAGNESIUM.

May be obtained like the foregoing salt, using the commercial carbonate; it may however be conveniently replaced by the sulphate of magnesia, which, as sold by the druggists, is sufficiently pure for analytical purposes.

SESQUICHLORIDE OF IRON.

Tinctura ferri muriatici will answer for most purposes. The pure salt is obtained by dissolving hydrated sesquioxide of iron in heated dilute hydrochloric acid to saturation, and filtering.

The hydrated oxide of iron is obtained by dissolving green vitriol (ante p. 14) in water, boiling, adding nitric acid as long as effervescence is produced, precipitating with ammonia, filtering and washing.

PROTOCHLORIDE OF TIN.

Digest excess of granulated tin with strong hydrochloric acid, dilute with water and filter into a bottle containing some pieces of metallic tin. The diluting water may be slightly acidulated with hydrochloric acid.

BICHLORIDE OF PLATINUM.

Platinum is dissolved in a mixture of nitric and hydrochloric acids, evaporated to dryness at a gentle heat, and the residue dissolved in a small quantity of water.

ACETATE OF LEAD.

Commercial sugar of lead may be purified by recrystallization.

SULPHATE OF COPPER.

The same applies to blue vitriol.

CHLORIDE OF MERCURY.

Corrosive sublimate is quite pure; it requires 16 or 20 parts of water for solution.

NITRATE OF SILVER.

The officinal preparation is generally pure, but when not fused often contains a trace of free acid.

CHROMATE AND BICHROMATE OF POTASSA.

The commercial bichromate is pure; the neutral chromate may be obtained from it by carefully neutralizing the solution with pure carbonate of potassa, evaporating and crystallizing.

IODIDE OF POTASSIUM.

The officinal preparation is generally pure. For adulterations see Chap. IV.

ACETATE OF POTASSA.

The officinal preparation must be kept in a solid form, and when required for use may be dissolved in 2 or 3 parts of water.

SOLUTION OF INDIGO.

Powdered indigo is digested for some days with the strongest sulphuric acid, the solution mixed with water, allowed to settle and decanted from the precipitate and undissolved pigment.

SOLUTION OF LITMUS.

A few lumps of litmus are boiled for some time with water, the solution filtered and preserved in a bottle which is *not corked*. A piece of thin linen tied over the mouth will prevent the entrance of dust; if the bottle be closed the solution is apt to decompose.

MOLYBDATE OF AMMONIA.

May be obtained by gently roasting the native sulphide of molybdenum, mixed with an equal weight of pounded quartz, or by digesting it with aqua regia and evaporating to dryness. The residue in either case is digested in solution of ammonia, the solution filtered and evaporated to crystallization. When required in testing for phosphoric acid, a few grains of the salt are dissolved in water (see Addenda).

OXALATE OF AMMONIA.

By neutralizing carbonate of ammonia with oxalic acid, crystallizing and redissolving. This reagent may generally be dispensed with.

SOLUTION OF SULPHUROUS ACID.

By heating sulphuric acid with either charcoal or sulphur, and passing the evolved gas through water.

SOLUTION OF CHLORINE.

By gently heating binoxide of manganese with hydrochloric acid and proceeding as above.

These two solutions, as well as that of starch, must be prepared when required, as they will not keep for any length of time.

SULPHATE OF POTASSA.

A solution of this salt is sometimes required. The officinal preparation is pure, and difficultly soluble in water.

The above mentioned solutions of salts should usually consist of 1 part of salt to about 10 of water, unless in some few cases, where more of the solvent is required. In these as in all other experiments, distilled water only should be employed.

DRY REAGENTS.

BORAX.

Is used only in blowpipe experiments, and is in general sufficiently pure for this purpose. It is heated in a crucible until it ceases to swell, and pulverized when cold.

NITRATE OF POTASSA.

Common nitre may be recrystallized two or three times, or the powdered salt may be moistened with a little nitric acid, and heated to dryness, being frequently stirred, redissolved and crystallized.

OXIDE OF BISMUTH.

Is not absolutely essential, but is of use in converting sulphide into oxide of arsenic. Prepared by dissolving either the metal or the basic nitrate in as little nitric acid as possible, adding excess of water, pouring off the liquid, and digesting the residual precipitate with excess of ammonia, filtering, washing and drying.

OXIDE OF COPPER.

Employed for the same purpose; is obtained by dissolving pure copper in nitric acid, evaporating to dryness and heating until all the acid is expelled and the residue is pure black.

ZINC. IRON. COPPER.

Either in strips or bars.

TEST PAPERS.

Red and blue litmus and yellow turmeric papers may generally be obtained of the druggists. They may be prepared by digesting litmus in water and turmeric in spirits of wine, filtering, adding a few drops of weak acid for the red paper, passing through the solutions strips of unsized paper, and drying. The papers must be kept in a closely corked bottle. An infusion of the purple dahlia may be substituted. Papers coloured with this are turned red by acids and green by alkalies.

FLUORIDE OF CALCIUM.

The mineral fluor spar is sometimes required in form of powder.

AMMONIA-PHOSPHATE OF SODA.

6 parts of phosphate of soda are dissolved with 1 part of sal ammoniac in 2 parts of boiling water and allowed to cool. The crystals are freed from adhering chloride of sodium by repeated crystallization.

CHAPTER II.

ANALYSIS. DETECTION OF BASES.

PRELIMINARY EXAMINATION.

When the substance under examination is a simple base, acid or salt, its nature may frequently be ascertained by a few preliminary experiments, and even when it is a mixture much valuable information may be thus obtained.

In case of a simple salt the colour is to be observed.

Salts of copper are green or blue.
Salts of nickel and chromium are generally green.
Salts of cobalt are red or blue.
Salts of manganese are often pink.
Salts of chromic acid are generally red or yellow.
Protosalts of iron are pale green, &c. &c.

A portion of the substance in powder is heated either on platinum foil or in a tube held obliquely.

It volatizes completely or partially—Salts of ammonia, mercury, arsenic, some salts of cadmium and antimony.
A yellow sublimate is formed and the odour of sulphurous acid is observed—Sulphur or a sulphide.
A white crystalline sublimate is formed—Probably arsenic is present.
An amorphous sublimate may be caused by salts of ammonia and mercury.

A portion of the substance is heated on charcoal by means of the blowpipe flame.

Deflagration takes place—Nitrate, chlorate, bromate, or iodate.
Oxide of lead also produces slight deflagration.
The substance blackens—Organic matter.

A portion of the substance is fused with carbonate of soda and cyanide of potassium.

A metallic globule is obtained—Lead, tin, bismuth, antimony.
Red metallic spangles are found in the fused mass—Copper.
Incrustations are formed on the charcoal—Lead, antimony, zinc, cadmium.
(See the blowpipe tests for these metals.)

The substance heated with caustic potassa evolves pungent vapours of ammonia—Salt of ammonia.

The salt fuses without change—Probably a salt of an alkali.

The salt becomes white but does not fuse—Probable presence of an earth or alkaline earth.

TABLE FOR THE DETECTION OF BASES.

I. Precip'd by HCl, insoluble in excess.	II. Precip'd by H_2S, from acid solution.	III. Precip'd from the preceding filtrate by $NH^4.S$, after addition of $NH^4.Cl$ and NH^3.	IV. Precip'd from preceding filtrate by NH^4O, CO^2 after gentle boiling.	V. Precip'd from preceding filtrate by phosphate of soda.	VI. Not precip'd by either of the preceding reagents.
$AgCl$ $PbCl$ Hg^2Cl	Soluble in NH^4S. PtS—black AuS^3—black SnS—brown SnS^2—yellow AsS^3—yellow AsS^5—yellow SbS^3—orange SbS^5—orange Insoluble in NH^4S. PbS—black CuS—black HgS—black BiS^3—black CdS—yellow	FeS—black CoS—black NiS—black MnS—buff ZnS—white Al^2O^3—white Earthy phosphate—white Earthy oxalate—white Cr^2O^3—greenish	BaO, CO^2 SrO, CO^2 CaO, CO^2	Mg^2O^2, NH^4O, PO^5	KO NaO NH^3
	NOTE.—A white precipitate or opalescence, caused by precipitation of S, indicates Fe^2O^3, or CrO^3; in the latter case, the original solution was red or yellow, and changes to green (see 'Chromium').	$NH^4.S$ acts upon solutions of Al^2O^3 and Cr^2O^3 in the same manner as NH^3, and precipitates the oxides; the sulphides cannot be formed in the wet way. The earthy phosphates and oxalates are precipitated when the original salt has been dissolved in an acid.			
	If a precipitate is formed, the whole is thrown on to a filter and well washed.	If a precipitate is formed, the whole is thrown on to a filter and well washed.	If a precipitate is formed, the whole is thrown into a filter, washed out, and the filtrate if necessary is concentrated by evaporation.		

GENERAL DIRECTIONS.

The bases (metallic oxides) are divided into four classes or groups by their behaviour to the following reagents, viz., hydrosulphuric acid, sulphide of ammonium, and carbonate of soda, which may be termed the group tests.

Class I.—Metals which are precipitated from acid solutions by hydrosulphuric acid, the sulphides formed being insoluble in dilute acids.

$$Cu\,O.\,S\,O^3 + H\,Cl + H\,S = Cu\,S + S\,O^3 + H\,Cl + H\,O$$

These metals are to be found in the first and second columns of the preceding table.

Class II.—Metals which are precipitated from neutral and alkaline solutions by sulphide of ammonium, but not from acid solutions by hydrosulphuric acid, the sulphides if formed being soluble in dilute acid.

$$Fe\,O,\,S\,O^3 + Am\,S = Fe\,S + Am\,O,\,S\,O^3$$

$$Fe\,O,\,S\,O^3 + H\,Cl + H\,S = Fe\,S + S\,O^3 + H\,Cl + H\,O$$

The decomposition in this second equation cannot take place, as the $Fe\,S$ if formed would be dissolved either by the $H\,Cl$ which has been added or by the $S\,O^3$ which has been set free.

Some metals are precipitated by sulphide of ammonium as oxides and not as sulphides, but it does not appear desirable to make a separate class of them. See third column of table.

Class III.—Metals which are precipitated as carbonates from neutral and alkaline solutions by carbonate of soda, but neither by hydrosulphuric acid nor by sulphide of ammonium, the sulphides if formed being soluble in water.

$$Ba\,O.\,N\,O^5 + Na\,O.\,C\,O^2 = Ba\,O,\,C\,O^2 + Na\,O.\,N\,O^5$$

See columns four and five.

Class IV.—Metals which are not precipitated by either of the above reagents, their sulphides and carbonates being soluble in water.

These classes may be still further subdivided by the following reactions.

Class I. *a.*—Metals which are precipitated by hydrochloric acid, the precipitate being insoluble in excess of the precipitant. See first column of table.

I. *b.*—Metals which are not precipitated by hydrochloric acid, or, if so, the precipitate is soluble in excess of the precipitant.

bb.—Metals which form sulphides soluble in sulphide of ammonium.

bbb.—Metals which form sulphides insoluble in sulphide of ammonium.

Class II. *a.*—Metals which form sulphides (or oxides, see above) soluble in dilute hydrochloric acid.

b.—Metals which form sulphides insoluble or nearly so in dilute hydrochloric acid.

Class III. *a.*—Metals which are precipitated as carbonates by carbonate of ammonia, from solutions to which sal ammoniac has been added.

b.—Metals which are not so precipitated, but are thrown down on the addition of phosphate of soda.

Class I. *a.*—Lead, silver, dinoxide of mercury.

b. bb.—Arsenic, antimony, tin, platinum, gold.

bbb.—Mercury, lead, copper, bismuth, cadmium.

Class II. *a.*—Iron, zinc, manganese, aluminum, chromium (the two latter as oxides).

b.—Cobalt, nickel.

Class III. *a.*—Barium, strontium, calcium.

b.—Magnesium.

Class IV.—Potassium, sodium, ammonium.

SPECIAL DIRECTIONS.

The process of analysis will then be as follows. Supposing, for the sake of simplicity, that a soluble salt or a mixture of soluble salts is under examination. If the salt itself or the solution is clear and colourless, but on mixing with water becomes white and opaque, and a portion remains insoluble even on boiling, we may suspect the presence of bismuth or antimony. In that case a little hydrochloric or nitric acid is added, until the solution is clear. Some salts of protoxides of tin and of dinoxide of mercury are also decomposed by water.

I. *a.*—The addition of $\mathrm{H\,Cl}$ produces a white precipitate.

$\mathrm{H\,Cl}$ produces no precipitate, add $\mathrm{H\,S}$ in excess, filter the precipitate (A), wash with water, digest with $\mathrm{Am\,S}$, filter. If nothing remains, *i. e.* if the whole is dissolved, the metals must belong solely to I. *bb*, if a residue remains it must consist of the metals of I. *bbb*, the solution in $\mathrm{Am\,S}$ is supersaturated with $\mathrm{H\,Cl}$, a white opacity or precipitate, without any tinge of colour, shows that none of the metals of I. *bb* were present.

II.—If $\mathrm{H\,S}$ produces no precipitate, we proceed to look for the metals of the second class in the same solution; or if a precipitate has been formed, we use the filtrate A. Ammonia is added, together with a little $\mathrm{Am\,Cl}$, and then $\mathrm{Am\,S}$. The precipitate, if any, is thrown on to a filter, washed with water (B) heated with dilute $\mathrm{H\,Cl}$, a black residue indicates II. *b*, the solution contains the metals of II. *a*.

III.—If no precipitate is produced by either of the above reagents, we proceed to test the solution with $\mathrm{Na\,O,\,C\,O^2}$ or $\mathrm{Am\,O,\,C\,O^2}$, in many cases it is better to use the latter; if a precipitate has been formed by $\mathrm{Am\,S}$, we use the filtrate B, carbonate of ammonia is added, and the solution boiled for a few minutes, the precipitate if any thrown on to a filter and washed (C), the residue contains metals of III. *a*. A portion of the filtrate C is mixed with $\left.\begin{matrix}\mathrm{Na^2\,O^2}\\ \mathrm{H\,O}\end{matrix}\right\}\mathrm{P\,O^5}$, a precipitate shows III. *b*.

IV.—If no precipitate has been formed either by Am O, C O^2 or by $\left.\begin{matrix}\text{Na}^2\,\text{O}^2\\ \text{HO}\end{matrix}\right\}\text{P O}^5$, or if a precipitate has been formed by the former (Am O, C O^2), but none by the latter, then the remainder of the filtrate C is evaporoted to dryness, heated strongly until all ammoniacal fumes have disappeared, the residue if any contains the metals of Class IV.

If however a precipitate has been formed in a portion of filtrate C by the phosphate, then the residual portion is evaporated as above, heated strongly, dissolved in a little water, and mixed with solution of baryta until it reacts strongly alkaline, the mixture gently warmed, filtered and washed, the solution treated with Am O, C O^2 as long as a precipitate is formed, filtered, washed, the solution evaporated to dryness. The residue if any contains the metals of Class IV., free from magnesium, which is the only metal belonging to Sub-Class III. *b*.

In proceeding to the consideration of the several classes, it will be found more convenient to commence with the last. As we are at present treating only of substances soluble in water, and the metals are all insoluble, we have to deal solely with oxides (and analogous compounds) when soluble, or their combination with acids.

Class IV.—(Filtrate C.)—Potassa, soda, ammonia, and their salts.

POTASSA.

In a free state, is characterized—

1. By its caustic and persistent alkaline reaction on test paper.
2. By its easy solubility in water.
3. By giving with excess of tartaric acid a crystalline precipitate, which is more readily formed by violent agitation; the solution must be rather concentrated.
4. By giving with bichloride of platinum, after supersaturation with hydrochloric acid, a yellow crystalline precipitate, difficultly soluble in water and insoluble in alcohol.

Salts of potassa are characterized—

1. By their solubility (excepting those formed in 3 and 4).
2. By test No. 3; if the solution is not alkaline, bitartrate of soda

may with advantage be substituted for the tartaric acid, the test becomes thereby infinitely more delicate.*

3. By test No. 4. The solution should not be too weak, and should be slightly acidulated with hydrochloric acid. When very small quantities are present, it is better to add the acid and chloride, evaporate to dryness and treat with alcohol, a yellow residue shows salt of potassa.

4. By tinging the flame of alcohol or of the blowpipe of a faint violet tint. To make this experiment it is necessary to use a *perfectly* clean platinum wire, as the slightest trace of soda interferes with the reaction, a portion of the salt is attached to the wire and heated in the point of the blowpipe flame.

SODA.

In a free state, is characterized—

1. By its caustic and persistent alkaline reaction on test paper.
2. By its easy solubility in water.
3. By giving no precipitate with $\overline{\text{Tar}}$.
4. By giving no precipitate with Pt. Cl^2.

Salts of soda are characterized by tests 2, 3 and 4, and

5. By communicating to the flame of the blowpipe or of alcohol a yellow tinge. This is the test by which salts of soda are usually detected.

AMMONIA.

In a free state, is characterized—

1. By its alkaline and evanescent action on test paper.
2. By its pungent odour.
3. By giving a precipitate with excess of $\overline{\text{Tar}}$ only in very concentrated solutions (see note).
4. By the same behaviour to Pt Cl^2 as K O.

Salts of ammonia are characterized by tests 3 and 4, 3 being of little value.

---

* This excellent modification of the potassa test is due to Mr. Plunkett, Ch. G. 1858. Even salts of ammonia when not very dilute are precipitated by this reagent, but the presence of these salts is easily detected and they may be readily removed (see "Ammonia").

5. By being entirely vaporized by heat.

6. By evolving a pungent and alkaline gas when treated with a solution of caustic potassa. This is the best test for salts of ammonia, if its quantity is so small as to be imperceptible by the organ of smell, a rod moistened with $H\,Cl$, held over the dish or watch glass in which the experiment is made, will produce dense white fumes of sal ammoniac.

In examining a complicated mixture it is necessary to test for $N\,H^3$ by the above reaction, with some of the original compound, as from the addition of ammonical salts it cannot be detected afterwards. But if none of the metals belonging to Classes I. II. and III. are present, then we examine the original substance for $N\,H^3$ by test 6. Another portion is examined for soda by test 5; after heating the mixture to drive off salts of $N\,H^3$, and for potassa by tests 3 and 4, after similar treatment.

CLASS III.—(Filtrate B.)—Baryta, strontia, lime and magnesia.

Of these the first two are readily soluble in water, the third is very difficultly soluble (1 to 1000), and the last almost insoluble (1 to 5000). They all exhibit alkaline reaction, but with the last it is feeble on account of its insolubility.

BARYTA.

Soluble salts of baryta are characterized by the following reactions:

1. Solution of sulphate of lime, or dilute sulphuric acid causes an immediate precipitate of sulphate of baryta, which is insoluble in all acids.

2 They are entirely precipitated by sulphates.

3. They communicate to the flame of alcohol a faint greenish yellow colour, especially evident with the chloride.

4. They are precipitated by hydrofluosilicic acid; the precipitate is quite insoluble in alcohol. Hyposulphite of soda also causes a precipitate.

STRONTIA.

Soluble salts of strontia are characterized by the following reactions:

1. They are precipitated only after a time by sulphate of lime, or by sulphuric acid (in very dilute solutions).

2. They are entirely precipitated by sulphate of potassa.

3. They communicate a crimson red colour to the flame of alcohol.

4. They are not precipitated by hydrofluosilicic acid or hyposulphite of soda.

When chlorides of barium and strontium are mixed together, they can be separated by means of absolute alcohol, which dissolves the latter.

LIME.

Salts of lime are characterized by the following reactions :

1. They are not precipitated by sulphate of lime in concentrated or by dilute sulphuric acid in moderately strong solutions ; addition of alcohol causes a precipitate.

2. They are only partially precipitated by sulphate of potassa, a portion of sulphate of lime remaining dissolved.

3. They communicate a yellowish red colour to the flame of alcohol, easily distinguishable from that of strontia.

4. They are not precipitated by hydrofluosilicic acid or hyposulphite of soda.

5. They are precipitated by oxalic acid, and better, by oxalate of ammonia ; the precipitated salt is insoluble in acetic acid, but soluble in hydrochloric.

MAGNESIA.

Salts of magnesia are characterized by the following reactions :

1, 2, 3, 4, give negative results.

5. Oxalate of ammonia produces a white precipitate, soluble in salts of ammonia.

6. They give a precipitate with phosphate of soda $\left.\begin{matrix}Na^2\,O^2\\ H\,O\end{matrix}\right\}P\,O^5$ when in concentrated solution, but none when dilute ; in that case the addition of any salt of ammonia causes a crystalline granular precipitate $\left.\begin{matrix}Mg^2\,O^2\\ Am\,O\end{matrix}\right\}P\,O^5$, especially on agitation, or after standing, even in very dilute solutions. This precipitate is soluble in acetic acid.

7. Neutral salts are partly precipitated by ammonia and its carbonate, especially on warming. The precipitate is dissolved by sal ammoniac, and consequently is not produced when this salt is present.

8. They are completely precipitated by solutions of baryta and potassa, especially after warming.

When sal ammoniac is added to a solution of the salts of the preceding oxides, carbonate of ammonia produces a precipitate with the first three, but not with magnesia (7), most of its salts being soluble in sal ammoniac. They are all precipitated by carbonate of soda. In examining a mixture of the salts, or the filtrate B., we add sal ammoniac if not already present, then carbonate of ammonia, and heat the liquid gently for a few minutes; the whole is thrown on to a filter and washed (B. *a*). The residue on the filter is drenched with dilute hydrochloric acid, the solution which runs through thrown back on to the filter if it does not pass clear at once.

This solution is then divided into three portions.

Portion I. is tested with sulphate of lime. The immediate formation of a precipitate indicates baryta, but strontia and lime may be present; a precipitate only after a time excludes baryta, indicates strontia, but lime may also be present; the total absence of precipitate indicates lime.

Portion II. is treated with a saturated solution of sulphate of potassa (2), and allowed to stand an hour or more before filtering. The precipitate may contain all three bases, but the filtrate can only contain lime, which is detected by oxalic acid.

Dilute sulphuric acid may be used instead of the sulphate, in which case a portion of strontia will remain in solution, and the filtrate must be neutralized with ammonia.

Portion III. is evaporated to dryness and examined for strontia by burning alcohol.

Baryta can also be distinguished and separated from strontia and lime by the addition of hydrofluosilicic acid and alcohol, in which the salt of barium is quite insoluble; the solution can then be tested for strontia and lime. Hyposulphite of soda precipitates neutral solutions of baryta, but not of strontia.

The filtrate B. *a*. is tested for magnesia by the addition of phosplate of soda, test 6.

Class II. (Filtrate A.)—Oxides of aluminum, chromium, zinc, manganese, iron, nickel, and cobalt.

These oxides are all insoluble in water, and are characterized in their hydrated state by the following colours:

Aluminum—white.
Chromium—blueish, or dirty green.
Zinc—white.
Manganese—white, becoming brown.
Iron protoxide—white, becoming greenish, and lastly brown.
Iron sesquioxide—brownish red.
Nickel—pale green.
Cobalt—blue, becoming reddish.

The neutral and alkaline solutions are precipitated by Am S, with the following colours:

Aluminum } white.
Zinc }
Chromium—greenish.
Manganese—salmon or buff colour.
Iron }
Nickel } black.
Cobalt }

All these precipitates, with the exception of the last two, are readily soluble in hydrochloric acid.

The class may also be divided into two groups, dependant on the behaviour of the oxides to solutions of caustic potassa.

Oxides of zinc, chromium and aluminum, are soluble, the rest are insoluble; but this reaction, although applicable in analyses of simple salts, cannot be used in all cases of complex mixtures (see post pp. 41-42).

ZINC.

Salts of the oxide of zinc are characterized as follows:

1. Ammonia produces a white precipitate, readily soluble in excess.

2. Potassa produces a white precipitate, readily soluble in excess.

3. This alkaline solution is precipitated white by sulphide of ammonium, but not by the chloride. No other metal forms a white sulphide.

4. Heated on charcoal with carbonate of soda, the oxide is reduced; zinc volatilizes and produces an incrustation on the charcoal, which is yellowish when hot, but white when cold. Oxide of zinc heated with nitrate of cobalt becomes green.

ALUMINUM.

Salts of the oxide of aluminum (alumina) are characterized by the following reactions :

1. Ammonia produces (except when certain organic bodies are present, see p. 40) a white precipitate, insoluble or nearly so in excess of the precipitant.

2. Potassa produces a white precipitate, readily soluble in excess. The solution is not altered by boiling.

3. This strongly alkaline solution is precipitated by solution of sal ammoniac, but not by sulphide of ammonium.

4. When heated they become white, and when previously moistened with nitrate of cobalt they exhibit a blue colour; this test is not always very satisfactory.

CHROMIUM.

Salts of the sesquioxide of chromium are characterized by the following reactions :

1. Ammonia produces a greenish precipitate very slightly soluble in excess, especially after standing, forming a pink solution which yields a precipitate on boiling.

2. Potassa produces a greenish precipitate, easily soluble in excess, forming a bright green solution, which, if not very strongly alkaline, is readily precipitated by boiling.

3. As with alumina, but the precipitate is greenish.

4. When fused with nitre and a little carbonate of soda, they dissolve after a time and form a yellow salt, readily soluble in water, and which after acidulation with acetic acid yields a yellow precipitate with acetate of lead. The yellow solution, when boiled with hydrochloric acid and a little alcohol, becomes of a bright green colour.

5. Oxide of chro~~n~~ium communicates to a bead of borax a yellowish green colour in the inner and an emerald green tint in the outer flame. m

Chromium may be present in the form of chromic acid ($Cr O^3$) ; in that case the solution will probably be red or yellow. For the detection of the chromic acid see "Chro~~n~~ic Acid." m

If all three oxides are present, that of chromium is detected by the green colour of the potassa solution, from which on diluting and boiling the oxide is precipitated; the filtrate is divided into two parts, and tested for zinc and alumina by sulphide and chloride of ammonia. It must be borne in mind that oxide of chromium, if in excess, often carries down with it the oxide of zinc. Fusion with nitre and carbonate of soda would then effect the separation, the mass being extracted with water, and the residual oxides of zinc and alumina dissolved in acid.

MANGANESE.

The only oxide likely to occur in a soluble salt is the protoxide, the higher oxides are converted into protochloride by boiling with hydrochloric acid under evolution of chlorine.

Salts of the protoxide are characterized as follows:

1. Ammonia produces a white precipitate, insoluble in excess, gradually turning brown. If the solution contains an excess of sal ammoniac or other ammoniacal salts, no precipitate is formed at first, but a brown deposit after a time by oxidation. The hydrated protoxide is converted into a higher oxide,

2. Potassa acts in the same way; in presence of ammoniacal salts only a portion of the oxide is precipitated.

3. Hydrosulphuric acid produces no precipitate in acid solutions. Sulphide of ammonium produces a flesh or buff coloured precipitate of sulphide of manganese, insoluble in excess of the precipitant, easily soluble in acids, and turning brown by exposure to the air. The colour of this precipitate is very apt to be changed by the presence of slight impurities.

4. Salts of manganese fused with carbonate of soda on platinum foil in the outer flame of the blowpipe, produces a green colour. The addition of a trace of nitre increases the delicacy of the test, and a little borax added to the carbonate is recommended for the detection of very minute quantities.

5. Beads of borax and of double phosphate dissolve salts of manganese, and are of a violet colour in the outer but colourless in the inner flame of the blowpipe. The addition of a particle of tin foil assists the reduction in the inner flame.

6. If binoxide of lead is boiled with water and a little nitric acid, and a salt of manganese added, a beautiful deep pink or purplish solution is produced, owing to the formation of sesquioxide of the metal.

IRON.

Salts of the protoxide are characterized as follows:

1 & 2. Potassa and ammonia produce a white precipitate, which rapidly becomes dirty white, greenish, and lastly reddish brown. The presence of ammoniacal salts acts in the same way as upon salts of manganese.

3. Sulphide of ammonium produces a black precipitate easily soluble in acids. If the quantity of iron is very small, a greenish tint only is produced.

4. Ferrocyanide of potassium produces a blueish white precipitate, $Cfy^2 + \left.\begin{matrix}K\\Fe^3\end{matrix}\right\}$ which rapidly becomes darker, forming Prussian blue $Cfy^3 + Fe^4$.

5. Ferricyanide of potassium forms a dark blue precipitate, $Cfdy^2 + Fe^3$.

6. Sulphocyanide of potassium produces no alteration if the salt is pure; the least trace of peroxide causes a reddish colour.

7. A bead of borax is coloured dark red by a salt of iron in the oxidizing flame, and becomes bottle green in the reducing flame. These colours disappear almost totally on cooling.

Salts of the per (sesqui) oxide are characterized as follows:

1 & 2. Potassa and ammonia produce a reddish brown precipitate of hydrated sesquioxide. Ammoniacal salts do not prevent its formation.

3. Hydrosulphuric acid produces a turbid or milky appearance, owing to separation of sulphur; sulphide of ammonium produces a black precipitate which is protosulphide, the peroxide being reduced

4. Ferrocyanide of potassium produces a dark blue precipitate.

5. Ferricyanide changes the colour of the solution to brown, but forms no precipitate.

6. Sulphocyanide produces an intense blood red colour, which disappears on the addition of corrosive sublimate.

The presence of tartaric acid and of various other organic matters prevents the precipitation of peroxide of iron by ammonia. They have the same action on the salts of chromium and aluminum.

NICKEL.

1. Ammonia produces a pale green precipitate of hydrated oxide, readily soluble in excess of the precipitant, forming a blue solution. The presence of ammoniacal salts prevents the precipitation totally.

2. Potassa produces a pale green precipitate of the hydrate, insoluble in excess.

3. Sulphide of ammonium produces a black precipitate very difficultly soluble in hydrochloric acid. The supernatant liquid is often of a brownish colour.

4. Ferrocyanide of potassium produces a pale green precipitate.

5. Cyanide of potassium produces a yellowish green precipitate, soluble in excess, forming a brownish yellow solution readily decomposed by sulphuric or hydrochloric acid, when the cyanide of nickel is reprecipitated.

6. A bead of borax acquires a reddish yellow colour from oxide of nickel in the outer flame of the blowpipe; the addition of nitre changes the colour to purple.

COBALT.

1. Ammonia produces a blue precipitate, soluble in excess, forming a reddish brown solution from which potassa precipitates little or nothing. Ammoniacal salts act as with nickel.

2. Potassa forms a blue precipitate, which turns green on exposure and pale red on boiling.

3. Sulphide of ammonium produces a black precipitate very difficultly soluble in hydrochloric acid.

4. Cyanide of potassium produces a brownish white precipitate ($Co\,Cy$) readily soluble in excess of the precipitant, especially when heated and in presence of free hydrocyanic acid. The solution then contains $Ccoy + K^3$ (cobalticyanide of potassium), which is not decomposed by the addition of sulphuric or hydrochloric acid.

5. Borax dissolves compounds of cobalt and produces both in the inner and outer flame beads of a splendid blue colour.

When a mixture of all these oxides is to be examined, the following processes may be adopted.

If the filtrate from the precipitate formed by hydrosulphuric acid in the acid solution is colourless, the absence of chromium, nickel, and probably of cobalt, is indicated. If after addition of sal ammoniac, neutralization by ammonia and addition of sulphide of ammonium (whether a precipitate has been produced by ammonia or not), the precipitate formed is white, the absence of iron, nickel and cobalt is indicated; small quantities of chromium and manganese may be present. If the precipitate is black, all the metals of Class II. must be looked for.

I. The precipitate formed by sulphide of ammonium is well washed and treated with caustic potassa, filtered and edulcorated. The filtrate may contain alumina and oxide of chromium (see p. 37). The residue is dissolved in hydrochloric acid with a little nitric acid, heated and filtered, precipitated by excess of caustic potassa, and the filtrate tested for zinc (see p. 36). The residue is treated with carbonate of ammonia, which will dissolve oxides of cobalt and nickel and leave those of iron and manganese. A portion of the residue is tested for manganese by tests 4, 5, or 6, and the remainder, dissolved in hydrochloric acid, is tested for iron by tests 5 and 6.

The solution, in carbonate of ammonium, is evaporated to dryness and heated. A portion of the dry mass is tested for cobalt by test 5; the remainder is dissolved in hydrochloric acid, neutralized as completely as possible, treated with excess of cyanide of potassium and hydrocyanic acid, and the solution tested for nickel by the addition of an acid (test 5).

II. The precipitate is thrown on to a filter, and after being well washed is drenched with dilute hydrochloric acid; if a black residue remains, the presence of nickel or cobalt or both is indicated. (A small portion of the residue may be examined for cobalt by the blowpipe test.) Nitric acid is added, and the solution thus obtained is boiled for some time, to peroxidize the iron and drive off hydrosulphuric acid.

Potassa is added in excess and the whole boiled for a few minutes, filtered, and the precipitate well washed out. The filtrate is tested for zinc and aluminum by sulphide of ammonium and sal ammoniac.

The residue is dissolved in as small a quantity of hydrochloric acid as possible, and the solution mixed with an excess of sal ammoniac and ammonia, filtered, boiled, and the precipitate washed. The residue may contain iron and chromium; the filtrate, cobalt, nickel, manganese, and a trace of zinc.

The solution is slightly acidulated with acetic acid, and treated with hydrosulphuric acid; a black precipitate indicates cobalt or nickel or both. The filtrate may contain manganese, detected by evaporating to dryness and the blowpipe test. A portion of the black precipitate is tested for cobalt by the blowpipe, and the remainder dissolved in nitrohydrochloric acid, neutralized with potassa and boiled with cyanide of potassium. Nickel is detected in this solution by test 5.

The residue, containing iron and chromium, is tested for the latter by test 4, and for the former by solution in a little acid, dilution and addition of ferrocyanide of potassium.

This process is preferable to the former, as oxide of chromium is with difficulty extracted from the mixed sulphides.

It has been recommended to dissolve the precipitated sulphides and oxides in water, to precipitate with excess of potassa, and to test the filtrate for zinc, aluminum and chromium, &c. &c. This process is open to the objection, that when oxides of iron, nickel, or cobalt, are present, most if not all of the oxide of chromium may remain undissolved; and when large quantities of chromium are mixed with iron, a great portion, sometimes the whole, of the oxide of the latter metal is dissolved in the potassa, and the solution is of a reddish yellow colour.

Class I.—These metals may be divided into three groups (see table), or as follows:

Sulphides soluble in sulphide of ammonium (Gr. II. p. 27).

Sulphide is orange—antimony.
" yellow—arsenic.
" yellow—binoxide of tin.
" brown—protoxide of tin.
" black—gold.
" black—platinum.

Sulphides insoluble in sulphide of ammonium (Gr. III. p. 27).

Sulphide is black—dinoxide of mercury.
" black—oxide of mercury.
" black—silver.
" black—lead.
" black—copper.
" black—bismuth.
" yellow—cadmium.

Lead, silver, and dinoxide of mercury, are precipitated from their solutions as white chlorides by hydrochloric acid (Gr. I. p. 27). If, after washing by decantation, ammonia be added :

The precipitate dissolves—silver.
" remains unchanged—lead.
" is turned black—mercury.

Silver and mercury can be thus entirely removed from a solution, but a portion of lead remains dissolved, the chloride not being absolutely insoluble.

Hydrosulphuric acid may cause in the acid solution a white precipitate of sulphur, which remains suspended for a long time.

The solution is nearly colourless and contains protoxide of iron —peroxide of iron.

The solution is green and contains oxide of chromium—chromic acid.

$$Fe^2\,Cl^3 + H\,S = Fe^2\,Cl^2 + H\,Cl + S$$
$$Fe^2\,O^3 + 3\,S\,O^3 + H\,S = Fe^2\,O^2 + 3\,S\,O^3 + H\,O + S$$
$$Cr^2\,O^6 + 3\,S\,O^3 + H^3\,S^3 = Cr^2\,O^3,\ 3\,S\,O^3 + H^3\,O^3 + S^3$$

It must be remembered that a separation of sulphur may also be caused by free chlorine bromine, iodine, sulphurous, nitrous, hypochlorous, chloric, bromic, and iodic acids. The hydrochloric acid of commerce not unfrequently contains sulphurous acid.

GROUP II.

LEAD.

1. Potassa throws down a white precipitate from salts of lead, soluble in excess.

2. Ammonia acts in the same manner, but the precipitate is quite insoluble in excess, and is not produced in solution of the acetate.

3. Hydrosulphuric acid produces a black precipitate, insoluble in dilute acids and alkaline sulphides. By boiling nitric acid it is decomposed, and a portion is converted into white insoluble sulphate of lead.

4. Hydrochloric acid produces a white precipitate soluble in a large excess of water, especially on the application of heat. The chloride is not blackened or dissolved by ammonia.

5. Iodide of potassium produces a bright yellow precipitate, soluble in a large excess of boiling water.

6. Chromate of potassa produces a yellow precipitate, soluble in potassa.

7. Sulphuric acid produces a white precipitate almost insoluble in water, especially if a considerable quantity of sulphuric acid be added.

8. Any salt of lead heated on charcoal with carbonate of soda gives soft malleable globules of the metal, and the charcoal is covered with a yellow incrustation.

SILVER.

1, 2. Potassa and ammonia produce a brown precipitate, insoluble in the former, but easily soluble in the latter.

3. Hydrosulphuric acid produces a black precipitate, soluble in strong boiling nitric acid, with separation of sulphur.

4. Hydrochloric acid produces a white curdy precipitate, blackened by light, insoluble in nitric acid, easily soluble in ammonia.

5. Salts of silver heated on charcoal with carbonate of soda give brilliant white malleable globules of the metal. The charcoal is not incrusted.

MERCURY.—(DINOXIDE.)

1, 2. Potassa and ammonia produce black precipitates insoluble in excess.

3. Hydrosulphuric acid forms a black precipitate insoluble in strong nitric acid, and dissolved by a hot solution of sulphide of potassium, with separation of metallic mercury.

4. Hydrochloric acid produces a white precipitate, blackened by ammonia. The calomel is converted by long boiling with hydro-

chloric acid into soluble corrosive sublimate, and metallic mercury, and by aqua regia it is rapidly dissolved.

7. Salts of mercury heated with dry carbonate of soda in a glass tube closed at one end, yield a ring of a grey colour, which consists of globules of metallic mercury; by rubbing the ring with a piece of wood, larger and more distinct globules may be produced.

MERCURY.—(OXIDE.)

1. Potassa in small quantities produces a brown precipitate, larger quantities produce a bright yellow one. If ammoniacal salts are present, the colour of the precipitate is white.

2. Ammonia produces the same white precipitate.

3. Hydrosulphuric acid in small quantities forms a white precipitate; on adding more and agitating, the colour passes into yellow, orange, brownish red, and finally becomes black when an excess has been added. The precipitate is insoluble in nitric acid, but soluble in aqua regia and sulphide of potassium, not in sulphide of ammonium.

4. Iodide of potassium added in sufficient quantity produces a brilliant scarlet precipitate, easily soluble in excess of the precipitant.

5. Same as with dinoxide.

6. Protochloride of tin produces at first a white precipitate of calomel, when added in excess a grey precipitate of mercury.

7. Same as with dinoxide.

All salts of mercury are volatile.

COPPER.

1. Potassa produces a light blue precipitate, if excess be added and heat applied it becomes black.

2. Ammonia produces a greenish blue precipitate, very readily soluble in excess, forming a magnificent blue solution.

Carbonate of ammonia acts in the same way.

3. Hydrosulphuric acid produces a blackish brown precipitate, readily soluble in hot nitric acid and not absolutely insoluble in sulphide of ammonium.

4. Ferrocyanide of potassium produces a reddish brown precipitate, insoluble in acids, decomposed by potassa.

5. Metallic iron becomes covered with copper when introduced into a solution of that metal, especially if the solution is acid.

6. When any salt of copper is fused with carbonate of soda on charcoal for some time, and the soda and adhering charcoal scraped out and ground with water in an agate mortar, on pouring off the light particles, brilliant red spangles of metallic copper will be visible.

7. Oxide of copper tinges a bead of borax green in the outer flame. The action of the reducing flame (aided by tin) is to form a bead which is colourless when hot, but opaque red when cold.

CADMIUM.

1, 2. Potassa and ammonia produce white precipitates easily soluble in excess of the latter, but insoluble in carbonate of ammonia.

3. Hydrosulphuric acid produces a bright yellow precipitate, insoluble in ammonia, dilute acids, or alkalic sulphides.

4. Heated with carbonate of soda on charcoal, salts of cadmium produce a reddish yellow incrustation.

BISMUTH.

1, 2. Potassa and ammonia produce white precipitates insoluble in excess.

3. Hydrosulphuric acid a black precipitate.

4. Chromate of potassa a yellow precipitate insoluble in potassa.

5. Salts of bismuth are decomposed by water; white basic salts are produced, which are insoluble in tartaric acid. The salts must not contain too much acid, as no decomposition will be effected by water in that case; the excess of acid can be driven off by gentle heat. The basic iodide is red.

6. Salts of bismuth heated on charcoal with carbonate of soda give metallic globules which are quite brittle; the charcoal receives a slight yellow incrustation.

In a mixture of the oxides of this class, the lead, silver, and dinoxide of mercury may be precipitated by hydrochloric acid. The precipitate boiled with a large amount of water, and filtered; the filtrate tested for lead. The residue is treated with excess of ammonia and filtered, the filtrate tested for chloride of silver by the addition of nitric acid. The residue can be tested for mercury by the reduction test.

The filtrate from the precipited chlorides is saturated with hydrosulphuric acid, the precipitate thrown on to a filter and well washed, nitric acid is then added, which dissolves all but the sulphides of mercury. The nitric solution is divided into several portions.

One is tested for lead (some chloride may have remained in solution) by test 7.

Another portion for bismuth, by evaporation and mixing with water, test 5.

Another portion is treated with excess of ammonia; a blue colour indicates copper, but the solution may also contain cadmium, but cannot contain lead or bismuth; it is filtered, neutralized with nitric acid, and tested for cadmium by carbonate of ammonia, which dissolves the salt of copper, but not that of cadmium.

GROUP I.

The sulphides of the remaining metals may be divided into two classes.

Those which are insoluble both in hydrochloric and in nitric acid —gold, platinum.

Those which are dissolved or decomposed by either nitric or hydrochloric acid—tin, arsenic, antimony.

GOLD.

1, 2. Potassa and ammonia produce reddish yellow precipitates in concentrated solutions.

2. Protochloride of tin, if partially oxidized, produces a purple red precipitate or coloration.

3. Protosulphate of iron precipitates a fine brown powder of metallic gold; the liquid appears blueish by transmitted light.

4. Oxalic acid at a boiling temperature causes the precipitation of brilliant metallic gold on the surface of the test tube.

In testing for gold with the protosalt of iron, care must be taken that the solution contains no free nitric acid, as this of itself is apt to produce a brown colour.

PLATINUM.

1, 2. Potassa and ammonia produce in solutions of platinum, acidulated with hydrochloric acid and not too dilute, yellow crystalline precipitates soluble in excess of the precipitants aided by heat.

2. Protochloride of tin produces an intense brownish red colour.

3. Iodide of potassium produces an intense brown or black colour.

TIN.—(PROTOXIDE.)

1, 2. Potassa and ammonia form white precipitates soluble in excess of the former. On boiling this concentrated solution, metallic tin precipitates and binoxide remains dissolved.

3. Hydrosulphuric acid produces a dark brown precipitate, soluble in boiling hydrochloric acid, converted into insoluble binoxide by nitric acid, soluble in alkalic sulphides, especially if a little sulphur be added, by which it is converted into bisulphide. Old sulphide of ammonium generally contains an excess of sulphur.

4. Water added to neutral solutions of protoxide of tin causes a turbidity, removed by addition of hydrochloric acid.

5. Perchloride of gold (see under gold).

6. Chloride of mercury (see under mercury).

7. Salts of tin are reduced by heating on charcoal with carbonate of soda and borax, and more easily by a mixture of the carbonate with cyanide of potassium. The ready oxidation of the metallic globules is a good test for tin, the produced oxide not being volatile.

TIN.—(BINOXIDE.)

This oxide exists in two modifications; the one obtained by the action of potassa on persalts of tin, is soluble in acids and in excess of potassa; the other, produced by the oxidation of tin by means of heat or nitric acid, is quite insoluble in acids, and only dissolved by potassa or its carbonate on employing fusion.

1, 2. Potassa and ammonia; white precipitates soluble in excess of the former.

3. Hydrosulphuric acid produces a yellow precipitate, soluble in boiling hydrochloric acid, in potassa, and in alkalic sulphides, difficultly soluble in ammonia, converted into insoluble binoxide by nitric acid.

4. Zinc precipitates metallic tin from solutions not containing nitric acid; the precipitate is easily soluble in hot hydrochloric acid, forming a solution of the protochloride.

ANTIMONY.

1, 2. Potassa and ammonia produce a white precipitate, readily soluble in excess of the former. The oxide is not precipitated at once from solutions of tartar emetic.

3. Hydrosulphuric acid produces an orange coloured precipitate in acid solutions. The sulphide is easily soluble in potassa and alkalic sulphides, very little soluble in ammonia, still less in bicarbonate of ammonia, insoluble in dilute acids, but soluble in moderately strong hydrochloric acid. The sulphide, dissolved in potassa and heated with oxide of copper or bismuth, gives an alkaline solution of oxide of antimony. Fused with nitre, it gives antimonate of potassa.

4. Neutral salts of antimony are decomposed by water, the insoluble basic salt is soluble in tartaric acid, and this solution is not altered by further addition of water.

5. Zinc precipitates black pulverulent metallic antimony from all solutions not containing nitric acid.

6. Copper foil or gauze boiled with an acid solution of antimony becomes coated with the metal.

7. If a salt of antimony be added to a mixture of zinc and dilute sulphuric acid, the hydrogen evolved contains antimoniuretted hydrogen, $Sb\,H^3$, and burns with a blueish flame. If a piece of porcelain be held in the flame, a black velvety spot is produced. If the gas be passed through a glass tube heated to redness at one point, a metallic ring is formed just beyond the heated portion.

8. Compounds of antimony fused with carbonate of soda and cyanide of potassium give brittle globules of metallic antimony. These globules evolve fumes of oxide even when removed from the flame, and become incrusted with acicular crystals.

The crystals of oxide of antimony are usually elongated prisms, but sometimes octohedra.

ARSENIC.—(ARSENIOUS ACID.)*

1, 2. Potassa and ammonia produce no precipitate, the arsenites of these alkalies being soluble.

3. Hydrosulphuric acid produces a bright yellow precipitate in acid solutions; without excess of acid the sulphide remains dissolved, giving to the liquid a yellow colour. The sulphide is soluble in

---

* Although the oxides of arsenic are true acids, yet it is more convenient to treat of them under the head of bases. Arsenic while possessing some of the properties of a metal, in many respects assimilates to phosphorus.

alkalies, their carbonates and bicarbonates, and alkalic sulphides, but insoluble in hydrochloric acid. Oxidized by boiling in nitric acid. Fused with nitre it gives sulphate and arsenate. Boiled with potassa and oxide of copper it gives sulphide of copper and arsenate of potassa; if oxide of bismuth be used, arsenite is formed.

4. Heated in a tube with a mixture of cyanide of potassium and carbonate of soda, the sulphide evolves arsenic which condenses as a metallic ring; a portion of the sulphide escapes decomposition, remaining behind in combination with sulphide of sodium.

5. Nitrate of silver produces no precipitate in solutions of arsenious acid, as the nitric acid set free holds the arsenite of silver in solution; the careful addition of dilute ammonia causes the production of a yellow precipitate, easily soluble both in ammonia and nitric acid. (Hume's test.)

6. Sulphate of copper acts in the same way. The careful addition of ammonia produces a yellowish green precipitate, soluble in ammonia and any free acid (Scheele's test.)

7. Arsenious acid boiled with excess of potassa and a few drops of solution of sulphate of copper, reduces the oxide and causes a red precipitate of suboxide of copper; the reaction is the same as with grape sugar.

8. Any compound of arsenic (excepting the sulphides) added to a mixture of zinc and sulphuric acid, causes the evolution of arseniuretted hydrogen, which burns with a blueish white flame, and forms brownish black spots of a bright metallic lustre on pieces of porcelain held in the flame. If a portion of the tube be heated red hot, a brilliant metallic ring will be formed.

9. Arsenious acid heated in a tube with charcoal, and an arsenite heated with charcoal and carbonate of soda, evolve metallic arsenic, which condenses into a ring which may be metallic, or, if the quantity is very small, only blackish brown.

10. Arsenious acid heated with acetate of potassa evolves alkarsine,* which is recognized by its horrible odour. The addition of a little protochloride of tin and renewed heating causes the no less characteristic chloride of cacodyl to be evolved.

11. In reducing arsenious acid, the particle to be examined is

---

* Alkarsine is excessively poisonous.

dropped into a tube closed at one end, a splinter of charcoal (heated to drive out moisture) is put on the top of it, the charcoal is then made red hot by the blowpipe flame, and the tube inclined so as to cause the arsenic to be heated. The ring when formed can be readily driven farther up the tube.

12. Copper foil or gauze boiled with a solution containing arsenious acid, and to which hydrochloric acid has been added, becomes coated with metallic arsenic, acquiring a steel grey colour (Reinsch's test); when the quantity is very small, the boiling must be continued for a quarter of an hour. The copper can be removed and heated in a reduction tube, when a sublimate of arsenious acid will be formed if the arsenical coating is of any thickness. Nitric acid and nitrates, chlorates, and all substances evolving chlorine or bromine, interfere with this reaction. The copper in such cases should be proved to be free from arsenic, as the copper would be dissolved, and hence arsenic might be brought into the solution.

13.' A metallic ring having been obtained by either of the above processes, the following confirmatory experiments may be made, to prove that the sublimate is arsenic and not antimony, the only substance for which it can possibly be mistaken. The tube having been cut off:

a. The ring is gently heated. A garlic odour is evolved, which is peculiarly characteristic of arsenic. Pure antimony gives no such odour.

b. The ring is gently heated, the tube being held in a slanting position, the dark coloured or metallic ring disappears and a white ring is produced higher up in the tube. This is found to consist of octohedral crystals. If these crystals are not sufficiently distinct even when seen by a magnifier, the tube may be closed at the point from which the metal has been volatized; if the white ring be now very gently heated, it will generally be found that large and distinct crystals will be deposited in the lower part of the tube.

c. The crystals are dissolved in water, and examined by tests 3, 5 and 6. When very small quantities are acted on, these tests are rather difficult, especially 5 and 6.

d. A drop of nitric acid is allowed to run into the tube and gently heated, or the ring is scraped out and heated in a white capsule with nitric acid; effervescence is observed, and the solution is carefully evaporated to dryness. Nitrate of silver now produces a brick red precipitate or coloration of arsenate of silver. If dilute nitric acid has been used, and the solution has not been evaporated to dryness, the precipitate from the neutralized solution will be yellow, viz., arsenite of silver.

e. A tube containing a metallic ring is attached to an apparatus evolving dry hydrosulphuric acid, gentle heat is applied to the ring, when it turns of a yellow colour. With antimony the colour is orange. It is now attached to a flask evolving gaseous hydrochloric acid, the yellow arsenical ring is not affected, the orange antimonial deposit disappears. This test, although rather troublesome, is very accurate.

f. If a tube containing an arsenical ring closed below is heated in an oil bath to a temperature of 500° F., the arsenic is sublimed while antimony is not affected. In this way a ring composed of the two metals can easily be examined for both.

g. The spots of arsenic obtained on plates of porcelain are easily soluble in solution of hypochlorite of soda (obtained by precipitating the so-called chloride of lime by carbonate of soda), and also by solution of iodate of potassa, a faint reddish tinge being perceptible at the moment of solution.

Antimonial spots are not acted on by either of these reagents.

The spots may be dissolved in nitric acid and examined by test *d*, care being taken that all nitric acid is driven off, a brick red colour is produced.

Antimonial spots give no red colour.

ARSENIC ACID.

1. Hydrosulphuric acid produces no precipitate in neutral and alkaline solutions of arsenic acid. In acid solutions, a precipitate of persulphide ($As\,S^5$) is produced after a time, especially if the mixture be heated. This sulphide exhibits properties similar to those of the tersulphide.

2. Heated with carbonate of soda and charcoal or cyanide of potassium, a larger quantity of arsenic remains in the residue than when the lower sulphide is employed.

Sulphurous acid readily reduces arsenic to arsenious acid if gently warmed with it; hence, where rapid precipitation is desired, it is better to digest the solution with sulphurous acid before treating with hydrosulphuric acid.

2. Nitrate of silver produces, with arsenate, a characteristic reddish brown precipitate, easily soluble in nitric acid and in ammonia. Hence with free acid no precipitate is formed. The arsenate of silver is more difficultly soluble in acetic acid than the arsenite, and the presence of an arsenate in an arsenite may be detected by precipitating with nitrate of silver and adding a slight excess of acetic acid; the yellow arsenite dissolves, the arsenate remains.

3. Chloride of magnesium and ammonia produce a crystalline precipitate of the ammoniaco-magnesian arsenate, corresponding to the phosphate.

Tests 8, 9, 10, 12 and 13, apply as well to arsenic as to arsenious acid.

The production of arseniuretted hydrogen, in either case, is shown by the following formulæ :

$$\mathrm{As\,O^3 + Zn^6 + 6\,S\,O^3 + H^3\,O^3 = Zn^6\,O^6,\ 6\,S\,O^3 + As\,H^3}$$

$$\mathrm{As\,O^5 + Zn^8 + 8\,S\,O^3 + H^3\,O^3 = Zn^8\,O^8,\ 8\,S\,O^3 + As\,H^3}$$

The presence of sulphur and of nitric and chloric acids must be guarded against, as they interfere with the reaction.

The separation of the sulphides of gold and platinum from those of tin, arsenic and antimony, has been already shown.

The three latter sulphides may be recognized as follows:

The mixed precipitate is dried and heated strongly in a tube, the sulphide of arsenic sublimes and may be recognized by the appropriate tests. The residue is digested with nitric acid, washed, and the insoluble matter treated with tartaric acid, which dissolves oxide of antimony and leaves binoxide of tin; the former detected by tests 3 and 6, the latter by the reduction test, and solubility of the bead in hot hydrochloric acid.

Or the mixed sulphides may be treated with strong nitric acid, an excess of carbonate of soda added, evaporated to dryness, the mixture fused, the mass treated with water, which dissolves out arsenate of soda (Arsenic, ch. iii.) and leaves antimonic acid and oxide of tin. This having been washed is fused with carbonate of soda and cyanide of potassium, a metallic bead is obtained, which is boiled with hydrochloric acid. The solution is tested for tin (3 and 6), and the residue or a portion of the bead either heated on charcoal, when the characteristic antimonial incrustation is formed, or boiled with nitric acid, the resulting white body digested with tartaric acid as above described, and the solution tested for antimony by tests 3 and 4.

DETECTION OF ACIDS.

PRELIMINARY EXAMINATION.

1. A fragment of the salt is heated on charcoal by the blowpipe flame. Deflagration shows the presence of nitric, chloric, bromic or iodic acids.

2. A portion is heated on platinum foil. Charring shows the presence of some organic acid.

3. A portion is drenched in a tube with sulphuric acid.

a. The salt acquires a yellow colour accompanied by crackling detonation—chloric acid.

b. Effervescence takes place—carbonic or hydrosulphuric acid.

4. A portion is heated in a tube with sulphuric acid.

a. Brownish red vapours are evolved, especially on adding a little metallic copper—nitric acid.

b. Brownish vapours are evolved, which turn starch paste reddish yellow—hydrobromic acid.

c. Purple or violet vapours are evolved, which turn starch paste blue—hydriodic acid.

d. Colourless vapours with smell of vinegar—acetic acid.

e. Colourless vapours which act on a moistened glass rod held in them—hydrofluoric acid.

f. Colourless vapours of pungent smell not acting on glass—hydrochloric acid.

g. Colourless vapours smelling of—hydrocyanic acid.

h. The solution becomes very dark coloured—tartaric acid probably.

i. Effervescence takes place—oxalic, citric, or tartaric acid, or a cyanide.

j. If no change takes place, the solution may be poured into a dish, a little alcohol added and ignited—a green flame shows boracic acid.

The previous determination of the base very much simplifies the search after the acid, especially in this portion of the course where the salt is soluble in water, certain bases precluding the possibility of the existence of certain acids in a soluble salt.

Baryta excludes the metallic acids, sulphuric, carbonic, hydrofluoric, boracic, phosphoric, oxalic, tartaric, citric, iodic; in acid solutions, all but sulphuric may be present.

Strontia excludes the same; the sulphate is not utterly insoluble.

Lime excludes the same; the sulphate however is only difficultly soluble.

Lead excludes hydrochloric, hydriodic and hydrobromic acids, the corresponding salts being difficultly soluble; it totally excludes sulphuric acid; the rest may be present in acid solutions.

Silver and mercury (dinoxide) totally exclude the first three.

The oxides of the heavy metals generally exclude carbonic, phosphoric, boracic, oxalic, iodic, and sulphur.

These laws apply only to salts which react neutral to test papers, as some acid carbonates, phosphates, &c., are soluble.

There are also some exceptions, as in the iodates and the combinations of oxalic acid with oxides of the formula R^2O^3.

They do not apply at all to double salts, and are not therefore of much value, unless it is known that the substance under examination is merely a simple compound.

TABLE FOR THE DETECTION OF ACIDS.

I. Precipitated by $Ba\,Cl$ from neutral solutions.	II. Precipitated by $Ca\,Cl$ from neutral solutions.	III. Precipitated by $Ag\,O.\,N\,O^5$ from neutral solutions.	IV. The addition of $Fe^2\,Cl^3$ to the neutral solution, produces:
Insoluble in $H\,Cl$ or $N\,O^5$	Precipitated at once	Insoluble in $N\,O^5$	A white precipitate
$S\,O^3$	Insoluble in $\overline{Ac}$	White $H\,Cl$	$P\,O^5$
	$C^2\,O^3$	$H\,Cy$	
Soluble in $H\,Cl$ or $N\,O^5$	$H\,F$	H^2Cfy	A blue precipitate
$C\,O^2$	Soluble in $\overline{Ac}$	$H\,Csy$	$H^2.\,Cfy$
$P\,O^5$	$C\,O^2$	Yellowish $H\,Br$	
$B\,O^3$	$P\,O^5$	$H\,I$	A brownish green colour
$C^2\,O^3$	$B\,O^3$	$H^3\,Cfdy$	$H^3\,Cfdy$
$Cr\,O^3$	$\overline{Tar}$	Soluble in $N\,O^5$	
$H\,F$	$As\,O^3$	White $C\,O^2$	A red colour
$\overline{Tar}$	$As\,O^5$	$B\,O^3$	$\overline{Ac}$
$\overline{Ci}$		$C^2\,O^3$	$H\,Csy$
$As\,O^3$	Precipitated after boiling	$\overline{Tar}$	
$As\,O^5$	$\overline{Ci}$	$\overline{Ci}$	
		Yellow $P\,O^5$	
		$As\,O^3$	
		Red brown	
		$Cr\,O^3$	
		$As\,O^5$	
		Black	
		$H\,S$	

This Table is by no means as useful as the one for the Detection of Bases, the student must rely more upon the special tests for each acid. The test I. ($Ba\,Cl$) is quite useless except as detecting $S\,O^3$. After the application of II. the liquid is filtered, and III. applied to the filtrate. The precipitate formed is thrown onto a filter, the filtrate may contain $\overline{Ac}$, but cannot contain any of the other acids mentioned under IV.

ACIDS.

The acids may be classed in two great divisions.

1. Those acids the salts of which are not blackened on the application of heat.

2. Those acids the salts of which are blackened on the application of heat, and when the base is an alkali or an earth form carbonates. All the acids of this division are organic.

FIRST DIVISION.

Class I.—Acids which are precipitated from neutral solutions by chloride of barium.

$$\mathrm{As\,O^3,\ As\,O^5,\ Cr\,O^3,\ S\,O^3,\ P\,O^5,\ Bo\,O^3,\ C\,O^2,\ C^2\,O^3,\ Si\,O^3,\ H\,F.}$$

The first two have been already disposed of under the head of arsenic.

CHROMIC ACID.

The salts of chromic acid are distinguished by the following characteristics:

1. They are all yellow, red, or brownish red.

2. They are reduced by hydrosulphuric acid in acid solutions to the form of sesquioxide of chromium, which together with the basic oxide remains dissolved, and sulphur is precipitated. The change of the yellowish red solution to green is very characteristic.

3. They are reduced by heating with hydrochloric acid and alcohol, green sesquichloride of chromium being formed.

4. The soluble salts give a yellow precipitate with acetate of lead.

5. Heated with sulphuric acid and dry chloride of sodium, dark red fumes are evolved.

The chromic acid is detected during the examination for the base.

SULPHURIC ACID.

1. The white precipitate formed by chloride or any other salt of barium is quite insoluble in nitric or hydrochloric acids.

2. Sulphates heated on charcoal with a little carbonate of soda, until the mass fuses, form a hepar, which when moistened with water on a polished silver coin produces a brown stain. If it be

dissolved in water and an acid added, hydrosulphuric acid is evolved. The solution gives a splendid purple colour with nitroprusside of sodium.

SULPHUROUS ACID.

1. Sulphites are decomposed by heating with sulphuric acid and effervescence produced; the gas has the well-known smell of burning sulphur.

2. The nature of the gas may be further proved by holding in it a piece of paper soaked in a solution of starch and iodic acid, iodine is set free and turns the starch blue.

3. Sulphurous acid or sulphites boiled with hydrochloric acid and protochloride of tin evolves hydrosulphuric acid, which can be detected by its blackening action on lead paper.

$$Sn^3\,Cl^3 + S\theta^2 + H^3\,Cl^3 = Sn^3\,Cl^6 + H^2\,O^2 + H\,S$$

PHOSPHORIC ACID.

1. The white precipitate produced by chloride of calcium in neutral solutions is soluble in acetic acid, without effervescence.

2. When chloride of ammonium, ammonia and sulphate or chloride of magnesium, are added to a soluble phosphate, a crystalline precipitate is formed, especially on violent shaking. The precipitate is soluble in acids, even in acetic.

3 Nitrate of silver produces a yellow precipitate, readily soluble in nitric acid and in ammonia.

4. Molybdate of ammonia, added to a solution of a phosphate acidulated with nitric or hydrochloric acid, produces a yellow precipitate, especially on standing. If the quantity is small, only a yellow colour is produced, and the precipitate is formed after a considerable time.*

5. If to a solution containing phosphoric acid hydrochloric acid be added to acid reaction, then a few drops of perchloride of iron, and finally acetate of potassa in excess, a flocculent white precipitate of perphosphate of iron ($3\,P\,O^5, 2\,Fe^2\,O^3, 3\,HO$) is produced. If excess of iron has been added the solution will be red, on boiling for some time the whole of the iron will be precipitated, containing

---

* It has been shown that silicic acid produces a similar reaction, but may be readily distinguished from phosphoric acid (see Test I. for silicic acid).

all the phosphoric acid. The perphosphate of iron is soluble in hydrochloric acid, but not in acetic; hence the use of acetate of potash, which produces chloride of potassium and sets free acetic acid.

BORACIC ACID.

1. Strong acid added to concentrated solutions of borates causes the separation of boracic acid on cooling, in form of crystalline scales.

2. Borates mixed with sulphuric acid and alcohol and ignited, cause the flame to acquire a greenish colour.

3. Turmeric paper dipt into a mixture of a borate with excess of hydrochloric acid, acquires a bright red colour.

CARBONIC ACID.

1. The white precipitate caused by salt of barium is readily soluble in acids with effervescence.

2. Carbonates are decomposed by acids with effervescence; the escaping gas is inodorous, and if conducted into lime water renders it turbid; excess of the gas redissolves the precipitate.

OXALIC ACID.

1. The acid itself, and its salts in a dry state, when heated with sulphuric acid, evolve a mixture of carbonic acid and carbonic oxide; the latter burns with a blue flame.

2. The acid and its salts precipitate salts of lime, even gypsum, and the precipitate is insoluble in acetic acid.* Ammonia assists the precipitation when the solution is acid.

3. The precipitate so formed is soluble in hydrochloric acid without effervescence, but if previously ignited it dissolves with effervescence, all the oxalate of lime being converted by heat into carbonate, evolving carbonic oxide.

SILICIC ACID.

1. The alkalic silicates, which alone are soluble, are decomposed by acids. If the solutions are concentrated silicic acid is separated in gelatinous flakes, if dilute it remains in solution in its soluble

---

* When oxalic acid is in combination with sesquioxide of chromium it is not precipitated by salts of barium or calcium; the detection of the acid, especially in the chromo-oxalates, is somewhat difficult. The first test may be used.

modification. If the acid solution be evaporated to dryness and washed with water the silicic acid remains behind as a white gritty powder, quite insoluble in acids or water, this being the insoluble modification.

2. Finely divided silicic acid is dissolved on boiling with caustic soda or its carbonate.

3. Silicic acid dissolves to a clear bead in carbonate of soda when heated before the blowpipe, carbonic acid being evolved.

HYDROFLUORIC ACID.

1. The acid and its soluble salts produce a transparent gelatinous precipitate in a solution of chloride of calcium, ammonia promotes its formation, it is insoluble in nitric and hydrochloric acid.

2. When a fluoride mixed with sulphuric acid is evaporated to dryness on a piece of glass, the spot where the mixture lay will be found corroded.

3. If a piece of glass be coated with wax, and fine lines scratched through the wax so as to expose the glass, and the plate thus prepared be placed over a platinum or leaden capsule containing the above mixture, and the whole be gently warmed for some time, the glass will be found to be corroded on the parts where the wax has been removed. The wax can be partly melted off, and the glass cleaned with oil of turpentine.

4. If a fluoride be heated with pounded glass and sulphuric acid, and the gas evolved be passed into water, gelatinous silicic acid will be separated and the water will acquire a strong acid reaction. (Hydrofluosilicic acid.)

In a mixture of salts containing all these acids, the first three will have been detected in the examination for the base. Sulphuric acid would be detected by test 1 applied to the solution, sulphurous acid by tests 1 and 2, boracic acid by test 2 applied to the dry mixture, carbonic acid by tests 1 and 2 applied to either the solution or the dry mass without heat, oxalic acid by test 1, silicic acid by test 1, hydrofluoric acid by test 3.

Further, the arsenious and arsenic acid might be removed by hydrosulphuric acid from an acid solution, and the oxide of chromium afterwards by ammonia. One portion of the solution could then be tested for phosphoric acid by tests 2 and 4, and another portion for oxalic acid by test 2. (See note to oxalic acid.)

In presence of sulphites this method would be preferable.

Class II.—Acids which are precipitated by nitrate of silver from solutions acidulated with nitric acid, but not by chloride of barium.

H Cl, H I, H Br, H Cy, H S, H^2 Cfy, H^3 Cfdy, H Csy.

HYDROCHLORIC ACID OR CHLORINE.

1. Nitrate of silver produces a white curdy precipitate insoluble in nitric acid, soluble in ammonia, and reprecipitated on the addition of nitric acid.

2. Sulphuric acid and black oxide of manganese heated with chlorides, evolve chlorine, recognizable by its odour and bleaching properties.

3. Sulphuric acid alone evolves from chlorides hydrochloric acid, recognisable by its pungent odour and by forming dense fumes with ammonia.

4. Heated with sulphuric acid and ~~fused chloride of sodium~~ chromate of potassa, the chlorides evolve dark red fumes which dissolve in ammonia with a reddish yellow colour.

HYDRIODIC ACID OR IODINE.

1. Nitrate of silver produces a yellow precipitate insoluble in nitric acid and in ammonia, the yellow colour becomes lighter by the action of the latter reagent.

2. Nitric acid (fuming) and chlorine, added to a solution of an iodide, cause a separation of iodine as a brown powder.

3. If the solution is very dilute only a yellow colour will be produced.

4. If a few drops of chloroform or of bisulphide of carbon be added to this solution (3) and well shaken, the chloroform, &c., on subsiding, will exhibit a beautiful pink tinge.

5. A solution of starch added to the liquid (No. 3) produces a fine blue colour, which disappears on boiling.

6. Sulphuric acid alone, heated with an iodide, causes evolution of violet coloured vapours of iodine.

7. Acetate of lead produces a beautiful yellow precipitate in solutions of iodides; the precipitate is soluble in excess of boiling water, and separates on cooling in golden spangles.

HYDROBROMIC ACID OR BROMINE.

1. Nitrate of silver produces a faintly yellow precipitate, not so soluble in ammonia as the chloride.

2. Bromides heated with oxide of manganese and sulphuric acid evolve brownish red vapours of bromine, recognizable by its odour and by turning starch of a reddish yellow colour.

HYDROCYANIC ACID OR CYANOGEN.

1. Nitrate of silver gives a white precipitate soluble in ammonia, insoluble in cold nitric acid, but dissolved on boiling for some time.

2. If to a solution containing hydrocyanic acid a few drops of an old solution of protosulphate of iron (*i. e.* containing some persulphate) be added, and then potassa in excess, a dirty green precipitate is formed; on the addition of hydrochloric acid a fine blue colour is produced, owing to the formation of ferrocyanide.

3. If hydrocyanic acid be mixed with a few drops of sulphide of ammonium, and the mixture boiled until quite inodorous, or evaporated to dryness, the residue will give a blood red colour with perchloride of iron, owing to the formation of sulphocyanide.

HYDROSULPHURIC ACID.

1. Is evolved from soluble sulphides on the addition of a stronger acid, producing effervescence. The gas is recognizable by its smell and by its blackening action on salts of lead spread upon paper. Strips of paper may be soaked in acetate of lead.

2. Soluble sulphides give a magnificent purple colour with nitroprusside of sodium.

3. Many sulphides when heated in a tube open at both ends, evolve sulphurous acid, which can be recognized by its action on paper soaked in a mixture of iodic acid and starch.

4. Insoluble sulphides, when heated with nitric acid, cause the evolution of red fumes; a yellow substance (sulphur) is separated, and the liquid is found to contain sulphuric acid.

HYDROFERROCYANIC ACID.

HYDROFERRICYANIC ACID.

SULPHOCYANIC ACID.

See tests for protoxide and peroxide of iron.

It is not likely that a mixture of all these acids could occur, the last three would be detected by the iron tests, hydrosulphuric by test 1, hydrocyanic by test 3. In presence of the four following acids, the whole might be precipitated by nitrate of silver and the precipitate treated with ammonia, the ammoniacal solution acidulated with nitric acid, and the precipitate tested for cyanogen as recommended in Chap. III. The remainder ignited to destroy cyanide, and the residue treated with nitric acid, and the solution thus obtained tested for silver, the detection of which further indicates the presence of a cyanide. The part insoluble in nitric acid is decomposed by mixing with water, sulphuric acid and metallic zinc. The solution obtained after a short time is carefully neutralized with carbonate of soda, evaporated to a small bulk, mixed with starch paste, and a drop of strong nitric acid or chlorine water added; a yellow coloration indicates bromine, its absence chlorine.

The residue insoluble in ammonia can be decomposed as above, or by boiling with caustic potassa and a little sugar. The solution can then be tested for iodine. Ferro and sulphocyanide of silver might be treated in the same way.

The presence of a chloride can be determined by distilling with sulphuric acid and chromate of potassa, brownish red vapours are formed which condense in water, forming a reddish solution the colour of which is not destroyed by ammonia, and in which chromic acid may be detected.

Class III.—Acids which are not precipitated by either chloride of barium or nitrate of silver, but which form salts deflagrating when heated on charcoal.

$N\,O^5$, $Cl\,O^5$, $I\,O^5$

NITRIC ACID.

1. All nitrates with the exception of some few basic salts are soluble in water, some are difficultly soluble in nitric acid, hence the addition of this latter to a salt of baryta causes a precipitate which dissolves in excess of water.

2. A nitrate mixed with cyanide of potassium and heated produces ignition and detonation.

3. If a nitrate in solution (not too dilute) be mixed with sulphuric acid and a few drops of solution of indigo, and the whole heated, the blue colour is destroyed, the resulting tint is generally yellow.

4. A nitrate heated with sulphuric acid and a little metallic copper evolves red fumes.

5. If a solution of a nitrate be mixed with about one-fourth of its bulk of sulphuric acid and cooled, and a crystal of protosulphate of iron be thrown in, a brown colour will appear around the crystal.

CHLORIC ACID.

1. All chlorates are soluble in water, when heated give off oxygen and are converted into chlorides, which are precipitated by nitrate of silver.

2. Chlorates mixed with cyanide of potassium and heated, produce ignition and violent detonation.

3. Same as with nitrates.

4. Chlorates treated with sulphuric acid produce a yellow colour and evolve a yellowish gas (peroxide of chlorine) which readily explodes on heating.

IODIC ACID.

1. The iodates of potassa are sparingly soluble in cold water, the iodates of baryta insoluble and lose oxygen when heated.

2. Iodates mixed with cyanide of potassium and heated detonate feebly.

3. When heated on charcoal they deflagrate and evolve violet fumes.

4. Acid solutions of iodates mixed with starch produce a blue colour on the addition of sulphurous acid.

5. Iodates heated with sulphuric acid and protosulphate of iron evolve violet fumes.

If all three acids should be present in a mixture, the iodic may be detected by tests 3, 4 or 5, and by its giving a precipitate with salts of baryta; the chloric by strongly heating a portion and testing the solution of the residue with nitrate of silver, the precipitate must be partially soluble in ammonia, the filtered solution being reprecipitated by nitric acid, and the nitric acid by test 5.

SECOND DIVISION.

Acids forming salts which blacken on the application of heat.
$\overline{\mathrm{Tar}}$ $\overline{\mathrm{Ci}}$ $\overline{\mathrm{Ac}}$.

TARTARIC ACID.

1. The acid and its salts blacken when heated, evolving a peculiar and characteristic smell.

2. When treated with sulphuric acid, blackening takes place with effervescence, and the evolved gas can be made to burn with a blue flame at the mouth of the tube.

3. The acid in excess gives with potassa or its salts a crystalline precipitate.

4. Chloride of calcium produces in neutral solutions of tartrates a white precipitate (presence of ammonical salts prevents or retards its formation) soluble in caustic potassa, reprecipitated on boiling.

5. Lime water produces in neutral tartrates, or with the acid if used in excess, the same white precipitate.

CITRIC ACID.

1. The acid and its salts are blackened on the application of heat, emitting a peculiar odour quite different from that evolved by the tartrates.

2. Same as with $\overline{\mathrm{Tar}}$, excepting that the colour of the liquid is yellow and not black.

3. Citric acid forms soluble salts with the alkalies.

4. Chloride of calcium produces a white precipitate with neutral citrates, insoluble in potassa, soluble in solution of sal ammoniac, and reprecipitated on boiling.

5. Lime water in excess produces no precipitate in the cold, but only on boiling.

ACETIC ACID.

1. The acid itself being volatile is not blackened by the application of heat; the acetates are blackened, but not to such an extent as the salts of the preceding acids.

2. The acetates are all soluble in water, with the exception of some few basic salts.

3. Neutral acetates mixed with sesquichloride of iron give a red colour. On boiling a precipitate is formed. Corrosive sublimate does not alter the colour.

4. Acetates heated with not very concentrated sulphuric acid evolve acetic acid, recognisable by its odour.

5. Acetates heated with a mixture of equal parts of sulphuric acid and alcohol evolve acetic ether, very readily recognisable by its agreeable odour.

If these three acids were present together, the acetic might be detected by tests 4 and 5, the tartaric by test 3, and the citric by heating the solution from which the tartaric acid had been previously precipitated by lime water.

BODIES INSOLUBLE IN WATER.

In examining any substance which is not a metal, an alloy, a metallic ore, or a mineral (very few of which are soluble in water), about twenty grains in state of powder are boiled with eight or ten times the weight of water. If the whole is dissolved, the testing is conducted as already described. If a residue remains after boiling for some time, the liquid is allowed to settle; a few drops poured out and evaporated on platinum foil; if no residue is left, the substance is quite insoluble; if any is perceptible, the liquid is poured off, the residue in the tube again boiled with fresh water, the whole filtered, washed out, and the filtrate examined as above.

The residue in the tube is drenched with hydrochloric acid and heated, if entirely dissolved the examination may be proceeded with as hereafter described. If a residue remains, a fresh portion should be treated with nitric acid, as the presence of lead, silver or dinoxide of mercury would prevent solution by hydrochloric acid.

If neither acid causes solution, a mixture of the two is tried. Whether the acid employed dissolves anything is ascertained in the same way as described above for water. The nitro-hydrochloric solution must be evaporated on glass.

The acid solution is diluted with water. The formation of a precipitate or milkiness would indicate antimony and bismuth, and in some cases lead and tin.

If on treatment with nitric acid red fumes are evolved, and after continued boiling a yellow substance (sulphur) floats on the surface, the presence of a metallic sulphide is indicated. If at the same time a white sediment is formed, lead, tin and antimony may be expected.

METALS AND ALLOYS.

1. Gold and platinum are insoluble in nitric acid, but soluble in nitro-hydrochloric.
2. Antimony and tin are oxidized, but the resulting oxides remain undissolved.
3. All the other metals are dissolved by moderately strong nitric acid, on application of heat.

DETECTION OF THE BASES IN THE ACID SOLUTION.

When the solution has been made in hydrochloric acid, lead, silver and mercury ($Hg^2 O$), will remain undissolved as chlorides.

When the solution has been made in nitric acid, the process is to be conducted exactly as already described; but in the application of the test with sulphide of ammonium other points must be regarded.

The white precipitate formed by this reagent in aqueous solutions can only be sulphide of zinc or alumina; but in solutions obtained by means of acids it may contain phosphates of alumina and the alkaline earths, and the oxalates of the latter. In order to detect them, the following modification must be introduced.

A portion of the solution is freed from hydrosulphuric acid by heating, excess of caustic potassa added, and the whole gently warmed.

1. If the white precipitate dissolves completely, no phosphates or oxalates of the earths can be present; if other coloured metallic oxides are precipitated, the potassa solution must be examined for zinc, alumina and chromium.
2. The precipitate does not dissolve. After being well washed, it is boiled for some time with a strong solution of carbonate of soda, and filtered. The filtrate is acidified with acetate acid, and tested

for oxalic acid by test 2. Another portion is tested for phosphoric acid by test 2, after acidification with nitric or hydrochloric acid.

Phosphoric acid may readily be detected in an insoluble phosphate by applying test 4 to the solution in dilute hydrochloric acid, or by the careful application of test 3 to the nitric solution, and neutralization with ammonia.

DETECTION OF THE ACID.

No chlorates can be present, as all these are soluble in water. Iodates and iodides are detected by the evolution of violet vapours when the substance is acted on by nitric acid. Sulphides are detected by the separation of sulphur, as above mentioned, and by the formation of sulphuric in the liquid. (When lead is present, sulphate of that metal will be formed.) Nitric acid can only be present in the form of a subnitrate, and its presence may be detected by test 4.

Phosphoric and oxalic acids are separated from metallic oxides by hydrosulphuric acid or sulphide of ammonium (a salt of ammonia being formed), and can be detected by the usual tests, after heating. From the earths they are separated as above described. From alumina, phosphoric is best separated by fusion with carbonate of soda, or the phosphate may be dissolved in acid, tartaric acid added to prevent precipitation of the earth by ammonia, and the application of test 2.

SUBSTANCES INSOLUBLE IN WATER AND ACIDS.

Of these the most commonly occurring are sulphates of lead, baryta, strontia and lime, of which the lime salt is sparingly soluble in water and more so in hot hydrochloric acid; the lead salt also is soluble in the latter. Silica and silicates, only a small proportion of the latter being acted on by acids. Chloride, bromide and iodide of silver. The compounds of lead might be included, as they are all sparingly soluble in water. Calomel is not included, as it is converted into metallic mercury and chloride by boiling hydrochloric, and completely into chloride by nitro-hydrochloric acid.

Alumina and oxide of chromium in certain forms, oxide of tin and antimonic acid.

The sulphates are analysed by boiling (or better by fusion) for some time with carbonate of soda, washing with water, filtering and edulcorating the precipitate. In the filtrate the sulphuric acid can be detected after acidification, and the base can be found by dissolving the precipitate in hydrochloric acid and testing in the usual way. If sulphate (or chloride, &c.) of lead be heated with carbonate of soda on charcoal a bead of soft lead is formed and a hepar produced. See tests for lead and sulphuric acid.

A mixture of the sulphates of $Ba\,O$, $Sr\,O$ and $Ca\,O$ may also be analysed as follows. The finely powdered mixture is boiled for 10 or 15 minutes with a mixture of 1 part $K\,O, C\,O^2$ and 3 parts $K\,O, S\,O^3$, filtered and the residue well washed out until all $S\,O^3$ is removed. By drenching with $H\,Cl$ and washing, all the $Sr\,Cl$ and $Ca\,Cl$ is dissolved, and $Ba\,O, S\,O^3$ remains. The filtrate is evaporated to drive off free acid, and divided into two parts, in the one the $Sr\,O$ is detected by means of $Ca\,O, S\,O^3$, and to the other a little $As\,O^3$ and $N\,H^3$ are added. An immediate precipitate indicates $Ca\,O$, as this oxide forms an insoluble arsenite, while no such precipitate is produced in solutions of $Sr\,O$. Excess of $As\,O^3$ and $N\,H^3$ must be avoided.

The silver salts are best analysed by fusion with carbonate of soda in a porcelain crucible, when metallic silver is separated. Silica and silicates are treated in the same way in a platinum crucible, if containing no easily reducible metals, the fused mass dissolved in water, acidified with hydrochloric acid, evaporated to dryness to render the silicic acid insoluble, washed with water, and the bases detected in the solution. To detect the alkalies, the mineral must be ignited with pure carbonate of lime and sal ammoniac, the alkalies can then be extracted by water alone.

Alumina and oxide of chromium are rendered soluble by fusion with bisulphate of potassa; oxide of tin and antimonic ~~lead~~ acid by fusion with carbonate of soda, after which they will dissolve in hydrochloric acid, or by fusion with cyanide of potassium and carbonate of soda, when a metallic bead will be formed. (See tests for tin and antimony.)

CHAPTER III.

DETECTION OF POISONS.

The most commonly occurring poisonous substances which the chemist may be called upon to detect are the following: Sulphuric, nitric, hydrochloric, oxalic and hydrocyanic acids; salts or combinations of lead, copper, mercury, tin, bismuth, arsenic and antimony; opium or morphine, strychnine, and other alkaloids. The first three acids are seldom used as poisons, but it is sometimes necessary to examine for the first in cases where oil of vitriol has been thrown over persons.

SULPHURIC ACID.

In its normal state, or diluted with water, is detected by the tests already mentioned; by its complete volatility when heated, whereby it is distinguished from the bisulphate of potassa and soda; by its acid properties, which are also possessed by the above named salts; by its power of charring paper when used as ink, the paper being afterwards held before the fire, and by its power of turning black cloth red or brown and destroying the fibre.

If mixed with animal or vegetable matter, or if on cloth, the substance must be digested with water and a little pure acetic or hydrochloric acid, filtered, and the sulphuric acid detected as above.

If chalk has been administered as an antidote, the lime salt must be collected and examined as described at page 69.

It must be borne in mind that almost all animal fluids contain minute traces of sulphates.

NITRIC ACID.

Is best detected by neutralizing with pure carbonate of potassa, the suspected liquid, or that obtained from the organic mixture, as described under the preceding head, evaporating to crystallization, and testing for a nitric acid as described at page 63.

Dilute nitric acid does not char paper on drying, as is the case with sulphuric, but communicates a yellow tinge. It does not destroy the fibre of cloth in so powerful a manner.

HYDROCHLORIC ACID.

Whether free or in combination is detected as described at p. 61. It must be borne in mind that the gastric juice reacts acid, and that chloride of sodium is a common constituent of animal matters.

OXALIC ACID.

May come under examination either in a free or combined state, as a solid or in solution. The forms most likely to occur are the free acid and the binoxalate or quadroxalate of potassa. The acid itself crystallizes in prisms which are striated, and which are not therefore so transparent as the smooth-faced crystals of Epsom salts, for which oxalic acid has often been mistaken.

The solid acid when heated volatizes entirely, which is not the case with Epsom salts.

The solution has an acid reaction.

The potassa salts when mixed with hydrochloric acid do not effervesce; by heating they are converted into the fusible carbonate which effervesces with acid.

The characteristic tests are described at page 59.

If organic matter is present, the whole must be digested or boiled with water; the solution filtered and precipitated with acetate of lead, the precipitate collected and washed. The oxide of lead is mixed with water and treated with excess of hydrosulphuric acid, in which case the sulphide of lead is sometimes separated with difficulty even after long warming, or the precipitate is digested with a little sulphuric acid; in either case the whole is filtered, and the proper tests for oxalic acid applied to the filtrate. The filtrate may also be evaporated to dryness and the oxalic acid extracted with alcohol, the solution evaporated, redissolved in water, and the tests applied to the solution.

It must be borne in mind that sorrel and some other vegetable substances contain an oxalate of potassa. When only small quantities are detected, it must be proved that these articles have not been used in food.

In most cases the greater part of the oxalic acid is removed from the stomach by vomiting.

If lime or magnesia has been administered as an antidote, the insoluble substance can be tested for oxalic acid as described at page 68.

HYDROCYANIC (PRUSSIC) ACID.

This acid may exert its poisonous action when administered in a free state or in combination with some metallic oxide.

The proper tests have been described at page 62.

If the acid is mixed with organic matter, the mixture may be distilled, and the distillate tested as already described; or the mixture may be placed in a dish, and a watch glass suspended over it moistened either with sulphide of ammonium, nitrate of silver, or the precipitate obtained by adding potassa to a mixture of a proto and a persalt of iron, or an old solution of protosulphate. In the first case sulphocyanide of ammonium is formed, in the second a white film of cyanide of silver, and in the third ferrocyanide of iron (prussian blue), on the addition of a drop of hydrochloric acid.

The mixture may also be filtered, the filtrate precipitated by nitrate of silver, and the precipitate examined as already described.*

The odour of hydrocyanic acid is very characteristic to most but not to all persons, it soon disappears, and this poison cannot be detected after the lapse of any very considerable period. Twenty days may be taken as the extreme limit, the escape of the vapour depends greatly on the way in which the substances have been kept.

Those cyanides or double cyanides in which the metals can be detected by the ordinary tests are poisons; when the reverse is the case, as in the ferrocyanides, they are not poisonous.

There is no reason to assume that this acid is ever generated spontaneously in the body, nor is it produced by distillation. Amygdaline, the principle of bitter almonds, would of course produce it; it is not generated from apple pips. (See Taylor on Poisons.)

LEAD, COPPER, TIN, BISMUTH, MERCURY.

These metals, if presented for examination in the form of salts or of solutions tolerably free from organic matter, may be detected by

---

* See Addenda.

the tests already described under their several heads; while if present in a complex organic mixture, they are eliminated during the process for the detection of arsenic hereinafter described. The processes for their detection may therefore be deferred for the present.

DETECTION OF ARSENIC.

It is a very fortunate circumstance for the interests of humanity that arsenic always has been and still remains the most favourite poison. Were this the case with many other poisonous bodies, crime would escape unpunished much more frequently than at present, from the simple circumstance of many of these substances being undiscoverable by chemical tests; but in the case of arsenic, whether we have to operate upon pounds or thousandths of a grain, upon the pure substance or a complex mixture, upon the body of the poisoned person immediately after death or after the lapse of many years, our tests are still capable of detecting the arsenic with absolute accuracy.

It may be questioned whether the recent stringent regulations adopted in England with regard to the sale of arsenic may not lead to the use of other more insidious poisons, and thus render the task of the toxicologist more arduous and his results less reliable than they have been heretofore.

The methods for its detection are among the easiest processes of analytical chemistry, the results palpable to the senses and the same to all. No great experience in chemical manipulation is required by the operator; all that is necessary is a careful attention to directions and a rigid examination into the purity of the reagents. It has been well observed by Wöhler, that the difficulty of detecting arsenic does not lie in the elimination of the poison itself, but in the proof of its non-existence in the materials employed for its detection.*

---

* The element arsenic is very widely distributed in the mineral kingdom, and in the form of sulphide and as arsenious acid has been known from a very early period. Its chemical nature was first accurately examined by

Arsenic may be brought to us for detection in one of the following forms :

1. As a solution, free from impurities—such as a solution of arsenious acid, arsenite of potash or soda, Donovan's solution, arsenate of alkali. No other forms are likely to occur.

2. As a solid—arsenic or arsenious acid itself, insoluble arsenites of earths or metallic oxides, arsenates of the same, arsenical sulphides, or complex minerals containing arsenic.

3. As a fluid or solid, but mixed with organic matter—as in the

---

Brandt in 1733, and more especially by Scheele in 1775, he having discovered the arsenic acid and the compound with hydrogen.

It occurs under the following forms :

Metallic arsenic As, arsenious acid AsO^3, arsenates: Haidingerite $Ca^2O^2.HO, AsO^5 + 2 aq$, Pharmacolite $Ca^2O^2.HO, AsO^5 + 5 aq$, Berzeliite $Ca^3O^3, AsO^5 + Mg^3O^3, AsO^5$, Skorodite $Fe^2O^3, AsO^5 + 4 aq$, Cobalt bloom, Olivenite, Euchroite, Erinite, &c. &c.

Small quantities of arsenic have also been found in other ores, and consequently in the products derived from them. Thus iron pyrites often contains arsenic, and hence its occurrence in the sulphur made from pyrites, and in the sulphuric, hydrochloric and phosphoric acids of commerce, as well as in phosphorus itself. Arsenic has also recently been detected in the artificial manure obtained by acting on bones with sulphuric acid, and its presence is of course owing to the employment of an impure acid. It has also been stated that arsenic has been detected in plants growing in soils watered with a solution of arsenious acid, or manured with the above mentioned superphosphate. It frequently accompanies sulphide of antimony, and hence the antimonial preparations are seldom perfectly free from traces of arsenic, with the exception of tartar emetic. It exists according to Rumler in some meteoric stones, as in the olivine accompanying the meteoric iron of Siberia and of Atacama. It has been found in very minute quantities in certain mineral springs, as in those of Hammam Berda, and Hammes Koutin, in Algiers, and of Rippoldsau. The following quantities of arsenious acid were found by Will, in the springs of Rippoldsau :

Joseph spring	1 grain	in	144	bottles.
Wenzel "	1	"	216	"
Leopold "	1	"	96	"

Walchner has also proved its existence in the deposit from the Wiesbaden and many other springs, probably as an arsenate ; and it has been found in several iron ores, such as spathic and lenticular, hydrated oxide of iron, &c. &c. The same chemist detected it in some soils, marls and clays, but always in exceedingly minute quantities

Some years since the idea was started that arsenic was still more widely distributed, and existed in the animal and vegetable kingdoms, as for instance in bones and flesh, replacing it was supposed the phosphoric acid in the form of arsenic acid. This seemed very natural, as the arsenates are isomorphous with the phosphates ; but the deductions were proved afterwards to have depended on erroneous experiments, and we have no reason to suppose the existence of the smallest trace of arsenic as a normal constituent in the human, the animal or the vegetable kingdoms.

contents of the stomach, vomited matter, food, &c., or absorbed into the system as in the coats of the stomach itself, the liver and other organs of the body, the blood, the bile, and the urine.

I. If the arsenic occurs in any of the forms mentioned under the first head, it may be detected by the tests described at pages 50-51. In Donovan's solution it is mixed with mercury, and may be separated by precipitating with $H\,S$, and treating the mixed sulphides with $N\,H^4.\,S$ or with $N\,H^3$, which dissolves the arsenical sulphide. The solution is examined as described at pages 50-51.

II. The solid may be metallic arsenic, as in the so-called *cobalt* or fly powder. A portion may be heated in a tube and the sublimed ring examined, as described at page 52, or it may be heated in an open tube and the sublimate of arsenious acid examined. Most of the metallic arsenides may be treated in this way.

The solid may be arsenious acid, which can be examined by the usual tests. The following properties of the acid are of importance:

Arsenious acid is sometimes met with as a colourless or slightly yellow transparent or opaque amorphous glass, more generally as a white powder more or less crystalline. When slowly sublimed in a tube, regular octohedra of great brilliancy are formed. Water at 60 F. dissolves about 1.3 per cent ; by long boiling as much as 11 per cent. may be taken up, and the solution on cooling will retain a large proportion. Owing to the difficult solubility of arsenious acid, it floats on the surface of water and does not mix readily. It volatizes without fusion and is readily reduced by charcoal or cyanide of potassium on the application of heat, and from acid solutions by zinc and copper. The vapour of arsenious acid is inodorous; the garlic odour observed in the above reduction experiments is owing to metallic arsenic, or perhaps to a suboxide.

The insoluble arsenites and arsenates may be dissolved in acids and the arsenic separated as already described. They are all decomposed by digestion with caustic potassa; and the alkaline solution, after acidification with sulphuric acid, may be used in Marsh's test or for the separation of the sulphide. It is better to separate the arsenic by either of these means than to attempt the reduction with charcoal or cyanide of potassium. The sulphides of arsenic are volatile; they may be reduced by heating with a mixture of $Na\,O.\,C\,O^2$ and $K\,Cy$, but a portion of the arsenic remains behind.

If mixed with an excess of sulphur, all of it may remain in the residue. Hence for reduction experiments it is better to digest the sulphide repeatedly with nitric acid, so as to oxidize the sulphur completely (if any remains undissolved after long boiling, the solution may be filtered off), evaporate to dryness, and to heat this residue with the above mixture. The sulphides are readily soluble in caustic potassa, and the solution when boiled with oxide of bismuth or copper gives sulphide of the metal and arsenite or arsenate of potassa.

$$\mathrm{As\,S^3 + K\,O + Bi\,O^3 = Bi\,S^3 + K\,O, As\,O^3}$$

III. Arsenious acid is the substance which must generally be sought for in all cases of this class; but whatever the nature of the arsenical compound may be, the arsenic can be discovered by the process about to be described.

The first step of the operation is not needed when the examination is made of the liver, kidneys, spleen, blood, bile, or urine; but when food, vomit, evacuation, or contents of the stomach are to be investigated, the substance should be put into a clean glass, a quantity of distilled water added, well stirred, allowed to settle for a few seconds and then poured off. The same operation is repeated with the small quantity left behind, and fresh water added several times if necessary.

Where large quantities of arsenic have been administered, a granular substance will remain, which must be washed on to a filter, edulcorated and dried. (The washings must be preserved and added to the rest of the decanted matter.) The dry powder is then examined by the tests described at page 50.

If the sediment is obtained apparently free from any organic matter, it may be thrown on to a filter previously dried at 212° F. and weighed. After drying the filter with the sediment its weight can be again ascertained, and the difference gives the amount of arsenious acid, supposing the same to be pure.

The matter which has been decanted from the sediment, to which the washings have been added, is then evaporated over a water bath until it acquires the consistency of a thick syrup. The blood and bile are evaporated in the same manner; the stomach, intestines, liver, spleen, kidneys, or other parts of the body, are cut up into small pieces, and the mass thus obtained mixed with about an equal weight of hydrochloric acid free from arsenic.* The urine may be evaporated in the same way, or it may be acidulated with hydrochloric acid, and submitted at once to operation 3.†

1. To this mixture, contained in a perfectly clean porcelain dish, heated over a water bath, powdered chlorate of potassa is added in portions of about one drachm at a time, the effervescence caused by each being allowed to subside before the next is added. The operation must be conducted under a chimney, or in some locality where the evolved vapours of chlorine can be rapidly removed, and the temperature must never be higher than that obtained by the steam of water. In that case no chloride of arsenic can be volatilized.

This gradual addition of the chlorate is continued until the whole of the solid mass is dissolved, and only a white substance floats in a clear liquid. If on the addition of a new portion of chlorate no effervescence is produced, it may be necessary to add more hydrochloric acid.

The liver and kidneys, or any very solid portion of the body, are usually more difficult to dissolve than the contents or the stomach. When a perfectly homogeneous white or yellowish mass has been obtained, water is added in about equal bulk, and the heating continued until the liquid no longer smells of chlorine.

2. The whole is then filtered through white paper, and the residue washed with hot water. If the solution is more than a pint, it is better to evaporate it to about this amount.

---

* Good commercial (Glasgow) hydrochloric acid is generally free from sulphurous and sulphuric acids. In order to free it from arsenic and to render it fit for the above operation, it must be mixed with an equal bulk of water, and treated for hours with a current of hydrosulphuric acid. It is then allowed to stand for some days in a warm place, until it no longer smells of hydrosulphuric acid. The clear acid is then poured or filtered off, and is sufficiently strong for the above purpose.

† The process here described is not that recommended by Dr. Taylor, in his work on poisons, but it is one which is almost universally adopted by continental chemists, and for ease of execution and accuracy of result certainly surpasses all that have hitherto been proposed. The writer's reasons for adopting it, after many years' experience, in preference to the plans recommended by Dr. Taylor, have been published in the *Canadian Journal* for July, 1859, and the recent revelations on the Smethurst trial have only confirmed his opinions.

3. Hydrosulphuric acid is then passed through the hot solution for some hours. The gas must be washed according to the directions given at page 15.

4. The liquid is filtered and the precipitate well edulcorated. The filtrate on standing often deposits more sediment, and a further proportion is sometimes obtained on gently evaporating it. In most cases however this will not be found to be necessary, and need only be adopted when the amount of arsenic is very small. It must be remembered that even when no arsenic is present a precipitate of a slightly yellowish tint will be formed. When any quantity of arsenic is present the yellow colour of the precipitate is immediately perceptible.

An orange coloured precipitate would indicate antimony, but does not preclude the presence of arsenic. A black precipitate may indicate lead, mercury, copper, and bismuth.

5. The precipitate while on the filter is drenched with ammonia; it will generally dissolve readily, but if it adheres to the paper it may be gently stirred off with a feather. The residue is washed out and the filtrate allowed to run into an evaporating basin.

Sulphide of antimony will dissolve to only a very small extent, and the other metallic sulphides are perfectly insoluble in ammonia. Hence an orange or black residue will indicate one or more of these metals, the examination for which will be described hereafter.

6. The filtrate is evaporated to dryness and the residue heated with strong nitric acid. It is not absolutely necessary to digest until all the sulphur is oxidized.

7. The mixture containing an excess of nitric acid is neutralized with pure carbonate of soda, perfectly free from chlorine.

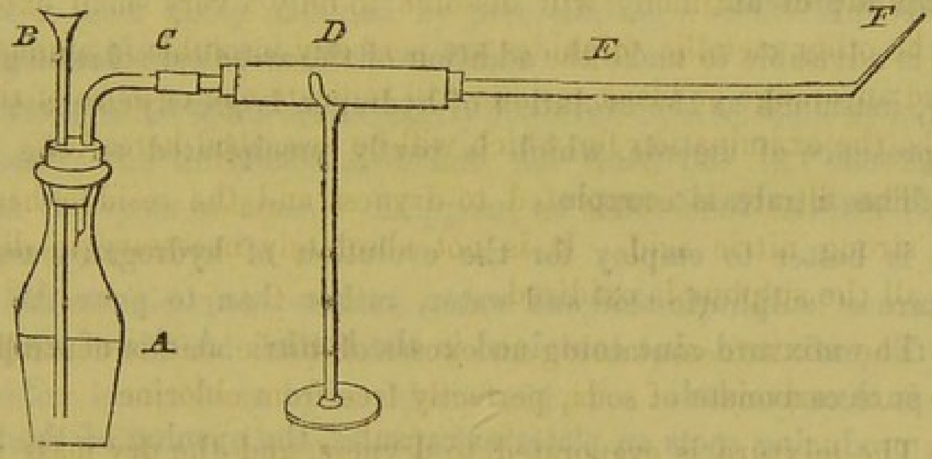
8. The mixture is evaporated to dryness, and the dry mass projected in small portions into a porcelain crucible in which a little pure nitrate of soda is kept in fusion. If a sufficient quantity of nitric acid has been employed the mixture will become black, but speedily lose its colour; if it does not, but remains black, or if violent deflagration takes place, the dry residue of the former operation must be mixed with more pure nitrate of soda. The whole mass having been fused to a perfectly colourless liquid, is allowed to cool.

9. Pure sulphuric acid is now added, and gentle heat applied, fresh portions of acid being added from time to time until red fumes are no longer evolved, but dense white vapours of sulphuric acid, and the solid mass is entirely dissolved.

10. After cooling, the mass is dissolved in water, the crucible washed out, and the solution introduced into a graduated tube and its volume observed (say 25 measures of the alkalimeter, page 91).

By the operation described in Section 1, the organic matter is partly removed; by Section 3 the arsenic is precipitated as sulphide, still containing a small portion of organic matter; by Section 5 the sulphide is dissolved, but the organic matter still accompanies it; by Section 6 more organic matter is destroyed, but not all, and the arsenic is converted into arsenic acid; by Section 8 the whole of the organic matter is removed, and the mixture contains nitrate, sulphate, arsenate and carbonate of soda, the latter only when an excess of the salt has been used; by Section 9 the nitric and carbonic acids are evolved, and the mixture contains only sulphate and arsenate.

The following apparatus is now required:



A is a flask or bottle containing pure zinc, granulated or in sheet; this must be free from arsenic, which fact is proved in the course of the experiment. B a long funnel; C a bent tube connected with D, a tube filled with dry caustic potassa, connected with E, a glass tube bent at right angles at F, and drawn out to a point, and covered with copper foil or gauze at E, to prevent bending when heat is applied at this point. Pure sulphuric acid, diluted with three times its bulk of water, is now poured in through the funnel

B. After the hydrogen gas has been evolved for some time, and there is no further danger of any explosion, the gas is kindled at F, and a porcelain plate or crucible cover held over the flame. If no spots are produced, the absence of arsenic is proved; but in order to confirm this, heat is applied at E until the tube is red hot. If after a quarter or half an hour no black or metallic ring is observed beyond E, the absence of arsenic is certain.

Any quantity (5 measures) of the solution obtained in 10 is now introduced into the bottle A, the tube at E being still kept red hot. If arsenic is present, a metallic ring will be quickly formed a little beyond the heated portion. If the heat is very intense, the colour of the flame at F will not change, generally however it will acquire a blueish white tint.

After a distinct ring has been formed in the tube, the flame may be withdrawn from E, and several pieces of porcelain held over the flame at F, so as to form a number of spots.

After about six porcelain plates have been thus spotted, the tube may be bent downwards and the evolved gas conducted into a solution of nitrate of silver; a black precipitate will be produced if arsenic is present.

It is advisable to make the addition of the arsenical solution gradually, inasmuch as the evolution of hydrogen is greatly increased by the presence of arsenic, which is partly precipitated on the zinc and forms a galvanic couple.

It is better to employ for the evolution of hydrogen a cooled mixture of sulphuric acid and water, rather than to pour the acid into the water and zinc contained in the bottle. A rise of temperature is thus avoided.

In producing spots on plates or capsules, the opening of the tube must not be too small, and the current of gas must not be so strong as to cause a pointed flame. The porcelain is held close to the opening of the tube, and must not be kept there too long, otherwise the spot may be volatilized.

Chlorine, hydrochloric and nitric acids, must be excluded, as they prevent or interfere with the evolution of arsenuretted hydrogen.

Antimonuretted hydrogen produces very similar appearances, and the following experiments may be made to distinguish the spots or rings obtained, or the nitrate of silver solution through which the gas has been passed.

If the sulphide has been extracted by ammonia (5), antimony is almost totally excluded.

If the fusion with nitrate of soda has been effected (9) and the resulting mass has been extracted with water, instead of being treated with sulphuric acid, all the antimony remains behind as antimonate of soda.

The ring or mirror formed by arsenic is easily volatilized, and a garlic odour is perceptible; that formed by antimony is much less volatile, and no odour is evolved.

The arsenic ring is brilliantly metallic and solid; the antimony ring is generally fused into small globules near the heated point, and of a silvery white colour.

The arsenic spots are brown and lustrous; those from antimony are black and velvety. If produced from exceedingly minute traces of either metal there is not much difference between them.

The arsenic spots are readily dissolved by a solution of hypochlorite of soda; the antimony spots are not acted on. This solution is most easily obtained by precipitating a solution of so-called chloride of lime by carbonate of soda.

The arsenic spots are instantly dissolved by a solution of iodate of potassa; the antimony spots are not acted on. At the moment that the spots of arsenic disappear, an evanescent reddish tinge is observed.

The arsenic spots, warmed with a drop of sulphide of ammonium, are dissolved, and the solution leaves on evaporation a bright yellow residue insoluble in hydrochloric acid; the antimony spots leave an orange residue easily soluble in hydrochloric acid.

The arsenic spots, dissolved in fuming nitric acid and evaporated carefully to dryness so as to remove every trace of nitric acid, give with nitrate of silver a brick red precipitate of arsenate of silver; the antimony spots do not exhibit this reaction. For the success of this experiment, it is necessary that the spots should not be too thin.

The arsenic spots may be dissolved in cold nitric acid of s. g. 1.3, and the solution tested for arsenious acid.

The ring or mirror formed in the tube may be examined by the various tests described at pages 51-52.

When arsenuretted hydrogen is passed through a solution of nitrate of silver, that metal is precipitated and arsenious acid dissolved, which can be detected by the addition of ammonia (Hume's test). When antimmuretted hydrogen is used, all the antimony is precipitated with the silver.

The process above described is applicable in almost all cases; the only exceptions are perhaps those in which the body has undergone great decay, and the whole mass has to be examined. In such cases a somewhat different process is adopted, for a description of which the reader is referred to "Taylor on Poisons," and more especially to "Otto on the Detection of Poisons," in which excellent work will be found all requisite information with regard to the subject of arsenic. The above may be considered as a short abstract of Otto's description.

All the materials used must be proved to be free from arsenic. An instructive experiment for the student is to operate on a piece of flesh or other organic matter, going through the whole of the above operation. If no indication of arsenic be found, the materials must be pure. The operation may then be repeated, a small quantity of arsenic having been mixed with the organic matter.*

The materials most likely to contain arsenic are the sulphuric and hydrochloric acids, and the zinc. By examining a few specimens of sheet sinc it is generally possible to obtain a pure sample. The hydrochloric acid is purified as already described, and the sulphuric acid can be freed from arsenic by diluting with water and passing hydrosulphuric acid through it for some hours. A pure strong acid can be obtained by placing the acid in a retort, and heating nearly to boiling, while a current of hydrochloric acid (page 14) is passed through it. The distillate is tested from time to time with hydrosulphuric acid, until no yellow precipitate is formed. The sulphuric

---

* Although in the preceding description the employment of the apparatus figured at page 79 is recommended for very accurate investigations, the experiment can also be made in most cases in a common 8 oz. phial, furnished with a *wide* tube, drawn out to a point, and cut obliquely at the lower end to prevent drops of the acid collecting in the tube and interfering with the flame of the gas. The arsenical solution must be introduced by removing the cork.

acid itself should then be tested in Marsh's apparatus. In presence of sulphuric acid, hydrochloric acts on arsenious acid and forms volatile terchloride of arsenic.

The chemist is often called upon to report on the quantity of arsenic present in the stomach and intestines, or absorbed into the tissues, as in the liver. No difficulty is met with when the examination is effected by the above process. The whole of the stomach with its contents, and the intestines with their contents, may readily be dissolved and examined as above described. When operating on the liver, blood, urine, or other substance, a weighed quantity is taken for the experiment. The pure solution of arsenate of soda finally obtained, is as above mentioned introduced into a graduated tube and a certain portion employed for Marsh's test; the remainder (arsenic having been found) is gently warmed with a strong solution of sulphurous acid, which reduces the arsenic to arsenious acid. Hydrosulphuric acid now precipitates tersulphide of arsenic, which is thrown on to a tared filter, washed, dried and weighed. Or the sulphide, before drying, is dissolved in ammonia, the filter washed out, and the filtrate, having been allowed to run into a tared dish, is evaporated to dryness and again weighed. 100 parts correspond to 80.4 of arsenious acid. The quantity contained in the whole of the solution may then be readily calculated, &c. &c. The quantity of arsenic can also be ascertained by adding to the solution of arsenate, without previous treatment with sulphurous acid, a mixture of chloride of ammonium, sulphate of magnesia and ammonia. The granular precipitate of $Mg^2 O^2 . N H^4 O, As O^5 + H O$ is collected on a filter, washed with ammoniacal water, dried at 212° and weighed. 100 parts correspond to 52.10 parts of arsenious acid.

ANTIMONY.

In the preceding process for the detection of arsenic, the precipitated sulphides (4) are thrown on to a filter, washed with water and treated with ammonia. The sulphide of antimony remains behind, and can be dissolved in hydrochloric acid. The solution may be tested for antimony by the tests described at page 49. If any sulphide of antimony has been dissolved, then, on washing the fused mass (9) with water, a white residue remains, which dissolves in hydrochloric acid, and can be tested for antimony.

The presence of antimony is generally indicated at once by the orange colour of the precipitated sulphide.

The characters of antimonuretted hydrogen and of the spots obtained from it have been already described.

TIN.

Salts of this metal are poisonous, but are not likely to be used as poisons, unless accidentally. The protosalts of tin would be converted into persalts by the treatment with chlorate of potassa, &c., and consequently the precipitated sulphide would be yellow. When treated with nitric acid it would be converted into insoluble binoxide, which might be mistaken for oxide of antimony and might contain it. When fused with carbonate and nitrate of soda a portion would be dissolved, but a large quantity would remain insoluble in water. This residue may be fused with cyanide of potassium, and treated as directed at page 53.

COPPER.

The precipitated sulphide is black, dissolves in nitric acid, forming a blue solution. See tests for copper, page 45.

LEAD.

The precipitated sulphide is black, dissolves partially in nitric acid, leaving a white residue of sulphate of lead (see page 44). The solution can be tested for lead by the reactions mentioned at page 44.

MERCURY.

The precipitated sulphide is black, insoluble in nitric acid if previously well edulcorated, easily soluble in nitrohydrochloric acid. The solution may be tested for mercury as described at page 45.

Calomel, which may have been administered medicinally, will by the above process have been converted into corrosive sublimate; hence the detection of mercury does not prove that corrosive sublimate had been administered. The detection of chlorine in the filtered contents of the stomach is also of no value. In cases of poisoning by corrosive sublimate it often happens that small crystals of the salt may be discovered in the folds of the stomach. A small portion being found soluble in boiling water proves that the substance was not calomel; on evaporating to dryness, mixing with carbonate of soda, and heating in a tube, the presence of mercury is proved by the sublimation of the liquid metal (see page 45.)

If the poisonous sublimate is mixed with food, it must be extracted by digestion with water, avoiding the use of acids. To the solution the ordinary tests for mercury may be applied.

ZINC.

Salts of this metal are poisonous, but are not often used for criminal purposes. In the general process for the detection of metallic poisons, it would remain in solution unprecipitated by hydrosulphuric acid. On neutralizing the solution with ammonia, the sulphide would be precipitated, generally of a greenish colour from presence of iron. The precipitate can be tested for zinc by the process described at page 41.

BISMUTH.

The precipitated sulphide is brownish black. It may be dissolved in nitric acid, the solution evaporated to dryness, mixed with water, and the bismuth detected by the tests mentioned at page 46. The salts of bismuth can scarcely be reckoned among poisons.

OPIUM.

This substance being generally administered in solution, is detected by its smell and by the reactions which indicate the presence of meconic acid, which is a constituent of all opiums.

Sesquichloride of iron added to a solution of meconic acid, or to a solution of opium so far diluted with water as to render it of a light colour, produces a blood red colour.

This colour is not destroyed by boiling, which would be the case if it were caused by the presence of an acetate.

It is not destroyed by the addition of a solution of corrosive sublimate, as is the case with the colour produced by a sulphocyanide.

If the opium is mixed with organic matter, a clear solution must be obtained by filtration. The addition of acetate of lead causes the precipitation of meconate of lead; this is collected, washed, decomposed by a little sulphuric acid, and filtered. The filtrate is tested with the chloride of iron.

ALKALOIDS.

Although the recognition of these bodies when in a state of purity is not attended with any difficulty, the detection of them when mixed with organic matter, and when in such small quantities as they generally are when used as poisons, is one of the most delicate chemical operations. The reactions of many of the alkaloids are so exceedingly similar, that unless they can be obtained in a state of absolute purity, their characters are partially or completely masked. Fortunately most of these bodies are exceedingly rare and expensive; but it may be doubted whether the recently imposed restrictions on the sale of arsenic may not tend to increase their employment for criminal purposes.

MORPHINE

Is scarcely soluble in ether, while its salts are readily soluble. It is little soluble in water, while its salts are mostly easily soluble, especially in presence of acids.

Concentrated nitric acid added to morphine or its salts produces a blood red colour, passing to yellow.

Iodic acid is reduced by morphine and its salts, iodine being set free.

Neither of these tests are of much value, as other substances act in the same way.

Neutral sesquichloride of iron produces in neutral solutions a greenish blue colour.

If morphine is dissolved in sulphuric acid and a little nitrate of potassa added, a greenish brown colour is produced, with bichromate of potassa.

For the separation of morphine from mixed liquids see page 88.

NARCOTINE

Is much more soluble in ether than morphine. It gives no blue colour with chloride of iron. With sulphuric acid and a little nitric acid it gives a blood red colour, destroyed by excess of nitric acid.

STRYCHNINE

Is very little soluble in water or ether, readily soluble in chloroform and boiling alcohol, readily soluble in water when acids are present. It forms brilliant prismatic or octohedral crystals by slow evaporation.

Its solution is intensely bitter. One part of strychnine communicates sensible bitterness to 40,000 parts of water.

Nitric acid produces a red colour; but this is only seen when the strychnine contains brucine, which is generally the case with the commercial alkaloid.

If strychnine is dissolved in sulphuric acid, and a drop of a solution of bichromate of potassa added to the cold solution, a splendid blue or violet colour is produced, passing to deep red. Instead of the solution it is better to employ a small crystal of the bichromate, when the colour is produced round it, and on moving it from one place to another streaks are formed.

The chloroform solution of strychnine may be dropt on to a glass or porcelain plate, and the drop evaporated. A small quantity of sulphuric acid is then added to each dried particle, and a minute fragment of bichromate added. In this way a most minute fraction of a grain may be detected.

The presence of any impurity is very apt to prevent the reaction.

Young frogs placed in very dilute solutions of strychnine or its salts become tetanic after an hour or two. It has been stated that $\frac{1}{5000}$th of a grain has been detected in this way. The action is much more rapid if the suspected liquid is injected into the thoracic or abdominal cavity of the frog.

VERATRINE

Gives with concentrated sulphuric acid a yellow colour, which by gentle heat passes to yellowish red, and finally into a beautiful violet red.

NICOTINE

Is left on evaporation of its ethereal solution as an oily drop, becoming yellow by exposure. When distilled with water it volatilizes and evolves a peculiar odour. Its salts are insoluble in ether, and can thus be freed from fatty matters.

Chloride of gold gives a reddish yellow precipitate, soluble in excess of nicotine.

Chloride of platinum produces a yellow precipitate. Salts of ammonia must have been previously removed by alcohol, in which they are insoluble, while the nicotine compounds are soluble; the oxalate is specially adapted for this method of purification.

For tests for the other alkaloids the reader is referred to "Otto's Detection of Poisons."

SEPARATION OF ALKALOIDS FROM MIXTURES.

Although the detection of some alkaloids when in a pure state is not attended with difficulty, the separation of them from mixtures containing organic matter is by no means easy. The process detailed below is that originally proposed by Stass, and modified by other chemists.

It depends on the power possessed by ether and chloroform of extracting the *free* alkaloids from their solutions. It has been observed that the alkaloid (especially morphine) is only soluble in ether and chloroform when freshly separated from its combinations and before it has assumed its crystalline form. Indeed, morphine when crystallized may be freed from narcotine and other impurities by washing with alcohol, ether and chloroform.

The suspected substance is mixed with 2 parts of strong alcohol and from 10 to 30 grains of oxalic or tartaric acid, and gently heated for some time. Solid bodies, as the liver, &c., may be moistened with the acidulated alcohol, pressed, and the operation repeated. (It may be remarked that the absorption of the undecomposed alkaloid into the tissues, and its passage into the urine, is still a disputed point.)

The solution is filtered, the residue washed with alcohol, and the filtrate evaporated.

The extract is treated with water, the solution filtered and evaporated.

The residue is again treated with cold strong alcohol, and the solution evaporated.

The residue is dissolved in water, ammonia added, and the mixture well shaken with a drachm or two of chloroform or a considerable quantity of ether.

(Otto recommends shaking with ether and removing this when coloured, *previous* to the addition of ammonia. By this means colouring matters are removed. Ammonia is then added, &c. &c.)

The ether or chloroform is now removed by a pipette (a glass tube drawn out to a point at one end, and having a vulcanized caoutchouc ball fastened on to the other), and the solution evaporated at a low temperature. The addition of two parts of alcohol to the chloroform will often cause the better crystallization of strychnine. The solution may be divided into several portions in separate capsules, and the residue tested by the various reactions already described.

If the residue still contains organic matter it may be moistened with sulphuric acid, treated with water after some hours, and the alkaloid extracted by means of ammonia and chloroform, as already described. This process may be repeated as long as carbonization takes place.

Strychnine (and probably many other alkaloids) may be extracted from their solutions by animal charcoal, which after filtration is boiled with alcohol, the solution evaporated, the residue dissolved in water, and the test then conducted as above.

ALCOHOL

May be detected by distilling the contents of the stomach, lungs, &c., with water. The distillate is again distilled with carbonate of potassa or chloride of calcium, and the first portions which pass over heated with a mixture of chromate of potassa and sulphuric acid. The solution acquires a green colour. If this mixture be heated in a retort, and caustic soda added to the distillate, a yellow or brownish colour will be produced owing to the presence of aldehyde.

CHLOROFORM.

May be separated in the same manner and recognized by its odour. Other tests are scarcely necessary.

PHOSPHORUS.

Only a few instances are known of this substance having been administered for criminal purposes, several accidents have however resulted from its accidental admission into the stomach.

If phosphorus is present in the contents of the stomach, its peculiar odour will generally be perceptible.

If a part of the contents is gently dried on an iron plate, portions will take fire.

If some of the contents are mixed with a little sulphuric acid and heated in a flask, the vapours being conducted through a rather long delivery tube, into another rather wide perpendicular tube kept cold by water, and opening into a receiver, a luminous appearance will be observed at the mouth of the wider tube.

If any quantity of phosphorus is present, small globules will be collected in the receiver. These may be digested with nitric acid, and the produced phosphoric acid detected by the proper tests, as described at page 58.

It has also been recommended to put into the flasks a few pieces of sulphur; on removing them at the end of the operation they will be found to be luminous, having absorbed some of the phosphorus.

CHAPTER IV.

MISCELLANEOUS.

ALKALIMETRY.

The determination of the quantity of caustic alkali present in a sample of commercial potash, soda, or their carbonates, is often of great importance, and this operation is termed alkalimetry. It may also be applied to the determination of the strength of solutions of potassa, soda, or ammonia, and to the analysis of several salts.

An alkalimeter or burette capable of containing 1000 grains of water and divided into 100 divisions is required. Various forms have been recommended; but the simplest kind, which in careful hands will answer all purposes, is constructed as follows:

A glass tube about ¾ inch in diameter and 16 inches long is selected, one end is closed by the blowpipe flame, and after cooling 1000 grains of water are poured in; the tube is then cut off, leaving about an inch or less unoccupied by the water. After drying, the rough edge is heated and pressed out into a shallow lip or spout at one side.

A portion of water weighing 50 grains, or, what is better, an equal bulk of mercury which will weigh 678.4. grains, is then introduced into the tube, and the height to which it rises marked with a three-cornered file or marking diamond. Another portion is introduced, and the same operation repeated until 20 such divisions have been obtained. Each of these divisions can then be divided into five by the eye, the smaller portions being marked with shorter file scratches. If these marks be made to proceed from a line scratched the whole length of the tube, the operation will be found to be easier. Each of these smaller divisions will contain 10 grains of water. The larger divisions are now numbered, beginning from the upper end of the tube, 5, 10, 15, &c. The last mark will then be 95.

To prepare the test acid, one part of pure sulphuric acid is mixed with five parts of water, and the mixture allowed to cool. An ounce or more of pure bicarbonate of soda is heated strongly for half an hour, by which means it is converted into neutral carbonate. Of this, 170.6 grains (containing 100 grains of Na O) are dissolved in water in a porcelain dish, a few drops of litmus solution added, and the mixture gently warmed over a lamp.

The above dilute acid is poured into the graduated tube till it stands at 0, and this solution is now gradually added to the alkaline liquid, until the blue colour changes to bright red. After each addition the effervescence must be allowed to subside, and towards the close the acid must be added drop by drop. In order to render the pouring easy, and to prevent the acid running down on the outside of the tube, the lip or spout may be greased.

As soon as the red colour is produced and remains on heating, the quantity of acid is read off; it will probably be somewhere near 90. If fresh dilute acid be now poured into the tube until it stands at 10 (100–90), and water be poured in up to 0, and the whole well mixed, an acid is obtained of which 100 measures will neutralize 100 grains of caustic soda, or one measure one grain. When no great quantity of the test acid is required, this operation may be repeated until the whole of the test acid has been diluted to the proper strength; but when a larger amount is desired, a cylinder must be specially graduated for the purpose, each of the 100 divisions containing 500 or 1000 grains of water. A large quantity of the acid can thus be diluted to the proper strength at one operation.

In examining any sample of soda (*i. e.* carbonate) 100 grains are treated exactly as above described. The number of divisions of the acid used indicate the number of grains of Na O contained in the sample; and as a half or even a quarter of a division can very easily be read off, the process is susceptible of great accuracy.

100 grains of crystallized carbonate of soda would require 21½ measures of the acid, hence the salt contains 21.5 per cent. of soda. The amount of dry carbonate of soda can be derived from the equation $\text{Na O} : \text{Na O}, \text{Co}^2 :: 21.5 : x$, or $31 : 53 :: 21.5 : 36.7$

Borax, biborate of soda can be examined in this manner.

In examining potash samples, an allowance must be made for the difference between the equivalents of potassa and soda. The quantity of potassa neutralized by 100 measures of the test acid is larger than that of soda, in the proportion of $NaO : KO$, i. e. 31 : 47.

Hence if the salt under examination were bicarbonate of potassa, and the quantity of acid employed were 31 measures, the amount of potassa would be 47. If any other number of measures were used, such as 28, the amount of potassa would be obtained from the equation $31 : 47 :: 28 : x$. If instead of using 100 grains of the sample, we employ 151.5, then the number of volumes of acid consumed indicate at once the per centage of potassa.

Some samples of potash and soda contain portions of the caustic alkalies. In that case two trials must be made, one with 100 grains of the crude mass, and another with the same quantity of the salt, dissolved in water, precipitated by chloride of barium, the carbonate of baryta filtered off and washed as rapidly as possible, and the filtrate tested for its amount of alkali by the alkalimetric process. The latter operation gives the amount of caustic alkali present, and the former the quantity of alkali both caustic and carbonated.

When the sample does not dissolve perfectly in water, the solution must be filtered and the filter and residue well washed out, before applying the test to the filtrate.

The sample may contain traces of sulphide and hyposulphite, both of which would neutralize a portion of the acid. The presence of the former is detected by the solution causing a black or dark coloured precipitate with acetate of lead, the latter by the clear solution becoming turbid on the addition of an acid. In these cases the solution of the sample is mixed with a little chromate of potassa, gently warmed, filtered and washed out; the filtrate is then examined. By this means the sulphide and hyposulphite are converted into sulphate.

In these experiments blue litmus paper may be used, instead of the infusion of litmus.

ACIDIMETRY.

The strength of acids is determined by means of a titrated solution of carbonate of soda. 170.6 grains (containing 100 grains of soda) are dissolved in 1000 grains of water, every 10 grains (one division) contain one grain of soda. 100 grains of the acid is weighed out, mixed with a few drops of solution of litmus, and the alkaline solution added until the clear red colour is changed to a wine-red tint, caused by free carbonic acid, and which turns to blue on boiling. The number of measures used having been read off, a simple calculation gives the amount of acid, as 31 parts of soda neutralize 40, 54, 36.5 of sulphuric, nitric and hydrochloric acids respectively, &c. &c.

Owing to the difficulty which exists with us of obtaining suitable flasks and tubes, the excellent process of Fresenius and Will has been omitted. It depends on the determination of the quantity of carbonic acid present, and is preferable to the process described in so far as no alkalimeter is required, an instrument which if not made by the experimenter himself should always be carefully examined as to the correctness of its graduation. This process is applicable to the investigation of both acids and alkalies. (See "Fresenius' Analytical Chemistry.")

Mohr's alkalimeter is infinitely more convenient than any other and is made as follows: a tube of the dimensions above mentioned, is drawn out into a point, the contraction being made gradual, and care being taken that the glass is not rendered too thin. After the small end has been closed, mercury is poured in until it rises above the shoulder, and the graduation is now effected as already described. The closed end being cut off, a thin tube of vulcanized indian rubber is fastened on to it, and a small pointed tube of glass fastened into the other end of the vulcanized tube. A small wire clip is now placed on the indian rubber, by which it is closed, but can be opened more or less by pressing the arms of the clip. The tube can be supported in a common holder attached to a retort stand.

The alkalimeter being now filled with test acid, the clip is opened and the liquid allowed to run out until the upper surface has sunk to 0. The flow of acid into the sample to be tested can now be regulated with the greatest nicety, by opening the clip to a greater or less extent. (See Mohr's excellent work "Die Titrirmethode.")

STRENGTH OF HYDROCYANIC ACID.

This important medicinal agent is very apt to vary in its strength, partly from its mode of preparation and partly from gradual decomposition or evaporation. It is therefore of great importance to be able to ascertain the strength of any sample, *i. e.* the quantity of anhydrous H Cy per cent.

Of the older processes, the only one which can be at all recommended is that which consists in using a certain weight (100 grs.) of the acid to be examined, and adding solution of $AgO.NO^5$ until no further precipitation is observed, collecting the precipitate on a tared filter, washing, drying and weighing. Every five grains of the dry cyanide corresponds to or indicates one grain of anhydrous hydrocyanic acid.

$$HCy + AgO.NO^5 = AgCy + HO, NO^5$$

$$AgCy = 134.1, \quad HCy = 27, \quad 27 \times 5 = 135$$

which is very nearly the equivalent of nitrate of silver.

This process is however objectionable on account of the time required in its performance, and is much inferior to Liebig's process, which requires only one weighing, supposing a titrated solution of $AgO.NO^5$ to be kept ready for use, and may be executed in about five minutes.

Ag Cy has a great tendency to unite with K Cy, forming a soluble double salt K Cy. Ag Cy, and when H Cy, K O and any salt of silver are brought together, this compound will be formed, to the exclusion of all others. Hence if to a solution containing H Cy and excess of K O and Na Cl, we add gradually a solution of $AgO.NO^5$, no precipitate of Ag O or Ag Cl will be formed until the whole of the H Cy present has entered into combination with Ag O and K O, and formed the double salt Ag Cy, K Cy. As soon as all H Cy has been thus employed, any further addition of $AgO.NO^5$ will cause a precipitate of Ag O, or of Ag Cl if Cl be present.

The equivalent of $AgO.NO^5$ is 170.1, that of H Cy is 27. Consequently, if 170.1 grains of AgO, NO^5 are employed before a permanent precipitate is obtained from such a solution, it is evident that it must have contained 54 grains of H Cy, because two equivalents of H Cy are required to form the above double salt. If to 54 grains of anhydrous H Cy we add K O in excess, which generally contains some chlorine, but a little common salt may be added, we should use 170.1 grains of Ag O, N O^5 before producing any permanent precipitate.

If therefore we dissolve 170 grains of Ag O, N O^5 in 1000 grains of water in a common alkalimeter, and add this gradually, stirring repeatedly, to the 54 grains of acid, we should use the whole 1000 grains without producing a precipitate; any further addition would produce a turbidity, and it would be evident that the acid under examination contained 100 per cent. of H Cy. If it required only 500 grains, it would indicate 50 per cent.; if only 10 grains, 1 per cent. But if we reduce the strength of the Ag O, N O^5 solution ten times, *i. e.* use only 17 instead of 170, then 10 grains would indicate 0.1 per cent.; and as five measures, or even one, can easily be poured out of the alkalimeter, we can determine the strength of the acid to a very small fraction.

The process then is simply this. To introduce into a graduated tube, capable of containing 1000 grains of water, 17 grains of pure Ag O. N O^5, to fill the tube with water up to the 0 mark, and to dissolve the salt by closing the aperture with the thumb and shaking, taking care to avoid loss of the solution on removal of the thumb.

A small glass containing a little potassa solution, to which if required some Na Cl has been added, is then tared on a balance, and into this the H Cy is dropt, until the weight added is 54 grains. Into this solution the above test liquor is added gradually, with constant stirring, until a permanent turbidity is produced. The number of measures used is now read off; and as such tubes are generally divided into 100 parts, each division will indicate 0.1 per cent. of H Cy. Suppose 27 measures have been used, the strength of the acid is 2.7. If 20½ have been employed, the liquid under examination contains 2.05 of H Cy.

CHLORIMETRY.

EXAMINATION OF CHLORIDE OF LIME.

This substance varies so much in quality, containing from 0 up to 30 per cent. of bleaching chlorine, that the method of determining its strength is of great importance.

The process depends on the observation of the conversion of sulphate of the protoxide of iron into the corresponding salt of the peroxide, by means of the active chlorine contained in the so-called chloride of lime.

$$2\,FeO + Cl + HO = Fe^2O^3 + HCl$$

Hence 5 grains chlorine oxidize 39 grains of the sulphate.

The change is shown by the action of the iron salt upon ferricyanide of potassium. The protosalt produces a blue coloured precipitate, the persalt only a brownish colouration.

The protosulphate is prepared for this purpose by dissolving clean iron nails in dilute sulphuric acid, precipitating with alcohol, and drying on blotting paper.

For the preparation of the ferricyanide see page 16.

In order to make the experiment, 39 grains of sulphate are dissolved in about one ounce or more of water, and acidulated with sulphuric acid. A quantity of the bleaching powder, amounting to 50 grains, is carefully rubbed up to a thin cream with water in a mortar; this liquid is poured into an alkalimeter (see page 91), the mortar rinsed with water, the tube filled up to 0, and the contents well mixed by agitation.

This solution is now gradually poured into the sulphate solution until no more protoxide remains unchanged. Some of the ferricyanide is dissolved in water, and a number of drops allowed to fall on a glass plate; the solution to which the chloride is being added is stirred with a very thin glass rod, and from time to time a drop taken out and mixed with the ferricyanide on the plate. As soon as a brown colouration is observed and no blue precipitate, the operation is finished, and the number of volumes used read off.

The quantity employed to effect perfect oxidation must have contained five grains of active chlorine; and if 36 divisions have been used, the amount in the 100 is easily calculated.

$$36 : 100 :: 5 : x = \quad x = 13.89.$$

As 50 grains of bleaching powder were used, this number must be multiplied by 2 to give the per centage, viz., 27.78. The amount of active chlorine in 100 parts can also more readily be ascertained by dividing 1000 by the number of divisions employed.

$$\tfrac{1000}{36} = 27.78$$

When the chloride is very strong, the quantity of sulphate may be doubled, in order to render unavoidable errors of observation as small as possible; and in the reverse case, when it is very weak, 100 or 200 grains of the chloride may be used instead of 50. The calculation has then to be slightly altered. (Otto's "Lehrbuch." Mohr's "Titrirmethode.")

EXAMINATION OF BINOXIDE OF MANGANESE.

The value of black oxide of manganese depends upon the quantity of oxygen it is capable of evolving, or upon the amount of chlorine it will yield when acted on by hydrochloric acid. 43.5 parts will evolve 35.5 of chlorine, $Mn\,O^2 + 2\,H\,Cl = Mn\,Cl + 2\,H\,O + Cl$, and this quantity of chlorine is sufficient to oxidize 278 parts of protosulphate of iron (see Chlorimetry), this number representing two equivalents: $2\,(Fe\,O.\,S\,O^3 + 7\,aq.)$ From this it appears that 50 grains of the binoxide yield chlorine sufficient to oxidize 319 grains of protosulphate.

50 grains finely powdered oxide are mixed in a flask with half an ounce of water and 1½ ounce of strong hydrochloric acid. The sulphate is now added, from a weighed portion of 319 grains, the additions are made gradually, and the mixture well shaken, until a drop being taken out and added to ferricyanide of potassium, begins to show a blue colour, *i. e.* indicates an excess of protoxide of iron. If the binoxide were pure, all the 319 grains of sulphate would be oxidized, and the sample would be said to contain 100 per cent. of black oxide; if only 300 grs. were used, then as $319 : 300 :: 100 : x$ $x = 94.04$, *i. e.* the sample contains 94.04 per cent. pure peroxide.

Another method, sufficiently accurate for most purposes, is to place in a flask with water and sulphuric acid 50 grains of the finely powdered binoxide, the flask is placed on the pan of a balance, with 150 grains of crystallized oxalic acid, and the whole tared. The oxalic acid is now added and the flask well shaken, carbonic acid escapes, and its quantity is ascertained by observing the loss of weight. This indicates almost exactly the quantity of pure binoxide in the specimen.

$$Mn\,O^2 + C^2\,O^3 = Mn\,O + 2\,C\,O^2$$

$$Mn\,O^2 = 43.5 \qquad 2\,C\,O^2 = 44.0$$

ANALYSIS OF MINERAL WATERS.

The bases and acids which are generally met with in mineral waters are contained in the following list; the last eight being more rarely found, or existing only in small quantities.

$K\,O$, $Na\,O$, $Ca\,O$, $Mg\,O$, $Fe^2\,O^3$, $Fe\,O$, $S\,O^3$, $P\,O^5$, $Si\,O^3$, $C\,O^2$, $H\,Cl$, $H\,S$, $H\,I$, $H\,Br$, $B\,O^3$, $N\,O^5$, $H\,F$, $Al^2\,O^3$, $Li\,O$, $Sr\,O$.

About one quart is required for the analysis, and should be collected at the spring in well stoppered bottles.

Free carbonic acid is detected in one portion (3 or 4 ounces) of the water, by the precipitate formed on the addition of lime water, or by the precipitate formed in lime water by boiling some of the water in a flask and passing the evolved vapours into that solution.

Hydrosulphuric acid is detected by its smell and its action on lead paper, or on a hydrochloric solution of arsenious acid.

As in many mineral waters the earthy carbonates are held in solution by free carbonic acid, it is necessary to boil a pint of the water for some hours in order to drive it off. A precipitate is formed, which may contain $Ca\,O.\,C\,O^2$, $Mg\,O.\,C\,O^2$, $Fe^2\,O^3$, $Si\,O^3$; this is dissolved in hydrochloric acid, and tested for the above substances according to the general plan. The filtrate is evaporated to about one eighth, and tested for the other probable constituents according to the methods already described.

In testing for magnesia, after the precipitation of the lime by oxalate of ammonia, and addition of phosphate of soda, it is necessary to allow the mixture to stand for at least 24 hours, as, owing to the small quantity of magnesia generally present, the precipitate does not form at once, but only after standing, and is then generally very crystalline.

The quantities of the last eight substances mentioned in the above list are usually so small that it requires the evaporation of large volumes of the water, and an examination of the mother liquor, in order to detect them. (The reader is referred to Fresenius's "Treatise.")

Iodine and bromine may be detected in the concentrated water, or in the mother liquor, obtained by evaporating several quarts to a small bulk and allowing some of the salts to crystallize out. The iodine may be detected by chloride of palladium, which gives a black precipitate, or a small quantity of hyponitric acid (from starch and nitric acid) may be added. The iodine is set free and may be extracted from the solution by shaking with bisulphide of carbon, which acquires a splendid pink colour. The colourless liquid is now treated with chlorine, and tested for bromine by means of starch. Chloroform may be used instead of bisulphide of carbon.

ANALYSIS OF SOILS.

The following substance must be sought for in soils:

Potassa.
Soda.
Ammonia.
Lime.
Magnesia.
Alumina.
Manganese.
Iron.

Sulphuric Acid.
Silicic "
Carbonic "
Phosphoric "
Hydrochloric "
Organic Matter.
Water.

The soil should be allowed to dry by exposure to the air for a day or two, rubbed in a mortar (all large particles being taken out), and passed through a fine sieve or piece of muslin.

As most soils even when air-dried still contain water, a weighed portion is heated in a water bath for some hours. A loss of weight indicates retained water, and its amount may be ascertained by reweighing.

The dried residue is heated on platinum foil or in a crucible. Organic matter is detected by the blackening, and, if nitrogenized, by the peculiar smell and evolution of ammonia. By using a weighed portion the amount can be ascertained, if the heating is continued until all the carbon is burnt off, the residue moistened with carbonate of ammonia, and again gently heated.

A portion of the original soil is tested for ammonia by heating with potassa.

The analysis is divided into three parts.

1. Of the portion soluble in water.
2. Of the portion soluble in hydrochloric acid.
3. Of the insoluble residue.

I. Any convenient quantity, not less than half a pound, is boiled for about an hour with twice its weight of water, the solution filtered, evaporated to a small bulk, and examined for bases and acids in the manner already described in the general plan.

II. About an ounce of the residue is heated for a quarter of an hour with hydrochloric acid, a large quantity of water added, again boiled, the solution filtered, and examined for bases and acid as already described. The larger portion must be used for the detection of phosphoric acid, as that substance is usually present in very minute quantities.

III. The insoluble residue is examined by the process already recommended for the analysis of silicates. Alkalies must be sought for, the easiest method of analysis being by means of carbonate of lime and sal ammonia.

In each of these processes, if rather a small weighed quantity is taken, and the residue in each case well washed, dried and weighed, we obtain a proximate quantitative analysis of the soil. A correct determination of the quantities of all the several ingredients is attended with much difficulty, and the description of the process does not fall within the scope of this work. (See Fresenius' "Quantative Analysis," Abel & Bloxam's " Handbook," &c., &c.)

BLOOD STAINS.

If the stain is on a piece of steel, gentle heat may be applied. Spots of dried blood will peel off, while rust stains remain unaltered.

A portion of the stain which has peeled off by heat, or has been scraped off, is heated in a small tube closed at one end, a strip of turmeric or reddened litmus paper being held in it. An odour of burnt horn is evolved from blood, and the turmeric paper becomes brown, the litmus blue, from evolution of ammonia. Vegetable juices evolve acids.

The knife or article on which the stains exist is suspended in a small quantity of water and allowed to stand for several hours. A red solution is thus obtained.

To one portion of this solution ammonia is added. No change takes place with blood. Most vegetable reds are turned blue.

Another portion is boiled. The solution becomes colourless, and a dirty brown precipitate is formed. Vegetable colours are not altered.

To another portion nitric acid is added. A precipitate indicates albumen.

Through another portion gaseous chlorine is passed for a few minutes.

If the colour is owing to blood, the solution acquires a faint greenish tinge, and a flocculent precipitate is formed.

With vegetable infusions the colour is simply destroyed.

The solution after having been filtered is boiled to evolve chlorine, and sulphocyanide of potassium added. A red colour indicates iron, which is a constituent of the colouring matter of the blood. To observe this red tinge it is better to look down the tube, and not through it.

By the aid of a good microscope, blood may be recognized either by the form of the blood corpuscules or by the formation of crystals under the action of acetic acid.

If a portion of the stain be scraped off, mixed on a slide with a little syrup or dilute glycerine (sg. 1.028) the corpuscules will become visible under a high magnifying power.

A few drops of the aqueous solution obtained as above are mixed with a little chloride of sodium, and evaporated under the air pump with sulphuric acid. Under the microscope it exhibits no appearance of Teichmann's crystals. It is now treated with glacial acetic acid, and evaporated to dryness at a temperature of 212° Fahr. A drop or two of water is added, and on examination crystals will now be visible.

Another method is to mix the suspected substance, or the evaporated solution, or even the cloth containing the spots, with carbonate of potassa, and to calcine the mixture. The fused mass is boiled with a little water and a few particles of iron or of sulphide of iron. The solution is filtered, acidulated with acetic acid, and sesquichloride of iron added. A greenish or blue colour indicates the presence of ferrocyanogen, and hence of nitrogen. It is of course necessary to prove the absence of nitrogen from the cloth. Wool must not be treated in this way, as it contains nitrogen.

If the blood stains on steel are very old, and are mixed with rust, the hœmatine becomes insoluble in water, and must be extracted by digestion with a solution of potassa. To this extract chlorine is added, and the iron detected as already described.

BILE.

Bile is detected by reagents which act either upon the true biliary matter or upon the colouring substances contained in it. Urine, which is sometimes called biliary, contains only the colouring matters, biliphœine and biliverdine, which are detected by nitric acid. These substances, or at least the first, can be extracted from the bile by chloroform, and the solution exhibits the peculiar reaction with nitric acid. The residual bile itself, however, appears from recent experiments to behave in the same way.

The substance suspected to contain bile is mixed with a few drops of strong nitric acid; a peculiar play of colours is produced, green, pink, violet and yellow. Ordinary nitric acid may be used if a little sulphuric acid is afterwards added. This sinks to the bottom, and the colours are produced in the strata of liquid above it.

Bile is mixed with water containing a little sugar; to this sulphuric acid is gradually added, until the mixture becomes hot. A deep purplish crimson colour is produced. This test (Pettenkofer's) is not applicable to the detection of the colouring matters.

Biliary calculi usually consist principally of cholesterine, which may be extracted by boiling them with ether or alcohol, and crystallizes in fatty scales on evaporation of the filtered solution.

URINARY CALCULI.

These may be divided into two classes.

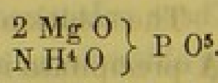
1. Calculi which are destructible by heat, leaving only a very small earthy residue.
2. Calculi which are indestructible by heat, leaving a large amount of earthy residue.

It must be remembered that all organic calculi contain a certain amount of inorganic matter, while the earthy calculi are sure to contain sufficient organic matter to cause them to blacken on the application of heat. This separated carbon, however, burns away, and leaves a large residue of a more or less pure white colour.

In examining these bodies it must be borne in mind that they are seldom uniform. Frequently the central portion or nucleus is quite different in composition from the external coating. Urate of ammonia frequently forms the kernel of phosphatic calculi, &c. &c.

To the first class belong those calculi consisting of Uric Acid, Urate of Ammonia, Cystine, Xanthic Oxide.

To the second, Ammonio-magnesian Phosphate $\left.\begin{matrix}2\,\mathrm{Mg\,O}\\ \mathrm{N\,H^4O}\end{matrix}\right\}\mathrm{P\,O^5}$.



Phosphate of Lime $3\,\mathrm{Ca\,O.\,P\,O^5}$, almost always associated with the former. When in about equal proportions the calculus is readily fused before the blowpipe flame, and is termed fusible calculus. Oxalate of lime, which on heating leaves a residue of carbonate, mixed with caustic lime. Urates of lime and soda may also occur, generally in combination with other calculi, leaving after incineration a residue of carbonate.

ANALYSIS.

A small portion of the calculus, or of its several strata, is heated on platinum foil. Cystine evolves a very peculiar odour. If it burns away, leaving only a very small ash, it must consist of uric acid, urate of ammonia, or cystine.

A portion is boiled with water, and the solution filtered. The filtrate may contain urate of ammonia, soda, and lime. If entirely soluble, the calculus is in all probability urate of ammonia.

A portion is boiled with caustic potassa. It dissolves without evolution of ammonia—uric acid. It dissolves with evolution of ammonia—urate of ammonia.

If any considerable residue had been left on incineration, this evolution of ammonia might have been owing to the presence of the phosphate. Hydrochloric acid added to the potassa solution and allowed to cool, causes the precipitation of granular uric acid.

A portion of this precipitate is heated in a porcelain capsule, with a little nitric acid, and evaporated to dryness. A red colour indicates uric acid. Exposure to the vapours of ammonia sometimes increases this colour. Water produces a beautiful purple solution.*

The calculus is wholly or partly insoluble in caustic potassa. After having been well washed, the residue is treated with hydrochloric acid.

Effervescence indicates the probable presence of carbonate of lime.

If the calculus dissolves without effervescence before incineration, but with effervescence after being strongly heated, oxalate of lime is indicated. The hydrochloric solution is neutralized with ammonia as far as possible without causing precipitation. The addition of acetate of soda or ammonia causes the precipitation of oxalate of lime, if any be present, as that salt is insoluble in acetic acid.

The solution is filtered off and precipitated by oxalate of ammonia. A precipitate indicates lime.

The solution is filtered off and mixed with ammonia. A crystalline precipitation indicates magnesia.

The phosphoric acid in the hydrochloric solution may be detected by the tests described at page 58.

Xanthic oxide and cystine calculi are of exceedingly rare occurrence.

---

* Gouty concretions usually contain urate of soda.

URINARY DEPOSITS.

Most urine deposits a flocculent substance on standing, which generally consists of mucus globules and epithelial scales. On allowing it to settle perfectly and then pouring off the lighter portions, minute octohedral crystals of oxalate of lime may often be detected.

A more or less coloured deposit is often formed, which redissolves on the application of heat. The deposit is usually urate of ammonia, sometimes urate of soda. The uric acid and the base may be detected by the tests already described.

A crystalline dark red deposit usually consists of uric acid.

A deposit which does not dissolve on the application of heat, but is readily soluble in hydrochloric acid, usually consists of the phosphate of lime, or more generally of the phosphate of ammonia and magnesia.

URINE.

The specific gravity of healthy urine is about 1.025, but in disease it may be found much less, and sometimes rises as high as 1.050. The determination of the specific gravity is therefore of considerable importance, and may be effected by means of the urinometer or the ordinary S G bottle. A simple and much more accurate method is the following: A glass stopper or heavy rod of glass of about 100 or 200 grains in weight is attached to a piece of fine silk, hair, or fine wire, as in the ordinary process for taking the gravities of solids. It is first weighed in air and then in water, the respective weights marked on the glass by a diamond, or by the method described at page 112. The quantity of glass abraded by the latter process is so small that it may be left out of account. On examining a specimen of urine, it is only necessary to ascertain the weight of the glass when in the urine.

Let $A =$ weight in air.
$B =$ weight in water.
$C =$ weight in urine.

Then $\frac{A-C}{A-B} =$ specific gravity of the urine.

Mucus and Epithelium. The urine on standing usually allows a light flocculent matter to subside, which when examined under the microscope is found to consist of epithelial scales and mucus globules. Not unfrequently the secretion is turbid, in which case it is desirable to filter it previous to the application of other tests.

Urea. Abnormal urine is sometimes so rich in this substance that a crystalline precipitate is formed on the addition of nitric acid. Generally it is necessary to concentrate to about one-fourth, when the addition of nitric acid causes the whole to solidify to a mass of scaly crystals of nitrate of urea.

Pure urea may be obtained as follows: the urine is evaporated to a syrup, extracted with alcohol, filtered, the filtrate digested with animal charcoal, filtered, the filtrate mixed with an excess of oxalic acid. The precipitate which forms is pure oxalate of urea. This is dissolved in water, and chalk added as long as effervescence ensues. The solution filtered and evaporated gives crystals of urea.

Uric Acid. May be detected by concentrating the urine to about one half its bulk, adding a little hydrochloric acid, and allowing the mixture to stand for some hours. Reddish brown crystals will form on the sides of the glass, which may be scraped off, washed with water, dissolved in caustic potassa, and again precipitated by the addition of acid. It forms a crystalline powder which exhibits the reactions described at page 105.

Uric acid is best prepared from the urine or excrements of large serpents; but as this substance is difficult to obtain, and the quantity contained in human urine is very small, the following process may be adopted.

One pound of pigeons dirt is boiled with a large quantity of water and three ounces of borax, the liquid strained off and boiled up with 2½ ounces of sal ammoniac. On cooling, the precipitate which has formed is separated, and repeatedly washed by decantation. It is again dissolved by boiling with a very dilute solution of borax, and filtered through a cloth if necessary. Sulphuric acid being now added, causes a precipitation of uric acid, which may be further purified by solution in potassa, filtration, precipitation by carbonic acid, solution of the precipitate in a large quantity of water, and final precipitation by hydrochloric acid.

Hippuric Acid. This acid is a constant ingredient in the urine of horses and cows, and appears to be of frequent occurrence in human urine. In some diseases, as chorea, it occurs in large quantities, and is always found after the administration of benzoic acid.

It is detected in the urine by acidulating with hydrochloric acid, evaporating to a small bulk, cooling, and boiling the precipitate which is formed with water. The hippuric acid is readily recognized by its crystalline form.

Hippuric acid may be obtained in quantity from cows urine, by adding to it, when fresh, sufficient hydrochloric acid to render it sensibly sour. On standing for 12 hours, the hippuric acid crystallizes out, and may be purified by boiling with a large quantity of water and some animal charcoal. On filtering rapidly, the acid will crystallize in nearly colourless needles.

Most of the inorganic constituents of urine may be detected by the direct application of the proper tests to the liquid itself, but the organic matter may also be removed by evaporating to dryness and incinerating the residue. The substances to be sought for are phosphoric, sulphuric, carbonic, hydrochloric, and silicic acids, lime, magnesia, potassa and soda. They may be detected by following the usual plan of analysis.

Urine sometimes contains biliary colouring matter, sugar and albumen.

The colouring matter is detected as described at page 103.

The sugar is detected by adding to the urine a few (12–15) drops of solution of sulphate of copper, and then excess of caustic potassa, by which the precipitate first formed is dissolved. On gently heating, the yellowish red suboxide of copper is precipitated. Sometimes no precipitate is produced, but the urine acquires a bright yellowish red colour. The heat should not be raised to a boiling temperature.

Saccharine urine, heated with excess of potassa, acquires a reddish yellow colour.

Saccharine urine mixed with yeast is capable of fermentation.

If urine containing sugar be mixed with an equal bulk of a solution of carbonate of soda (1 part crystallized salt, 3 parts water), and boiled with a small quantity of subnitrate of bismuth, a blackening or greyish colouration is produced in the latter salt. Albumen will produce the same effect, and hence if present must be previously removed by boiling and filtration.

Albumen is detected by heating the urine when it becomes turbid from coagulation of the albumen.

Nitric acid also causes a precipitate. Too much acid must be avoided.

Corrosive sublimate precipitates the albumen.

ADULTERATIONS.

The detection of adulterations in chemical products is often of the greatest importance, and is very instructive to the student of practical chemistry. The methods of detecting the impurities in the usual reagents have been already described, and any extended enumeration of adulterations generally lies beyond the scope of this work. A few examples are appended for practice.

CARBONATE OF LEAD.

The white lead of commerce is a mixture or compound of hydrated oxide of lead, with variable quantities of the true carbonate. It not unfrequently contains or is adulterated with the following salts: sulphate of lead, sulphate of baryta, sulphate of lime, and carbonate of lime.

A pure specimen should be perfectly reduced to metallic lead when heated on charcoal.

Dilute nitric acid should dissolve it perfectly. If a residue is left it may be examined for $Pb\,O.\,S\,O^3$, $Ba\,O.\,S\,O^3$, $Ca\,O.\,S\,O^3$, by the processes already described.

The nitric solution, when precipitated by hydrosulphuric acid and filtered, should exhibit no traces of lime in the filtrate, which would result from the presence of chalk.

Dilute solution of potassa dissolves white lead, but leaves carbonate of lime undissolved.

IODIDE OF POTASSIUM.

This salt, being prepared in several ways, may contain different impurities from imperfectly conducted processes of manufacture, or from wilful adulteration.

The following formulæ show the different methods of preparation:

1. $K^6 O^6 + I^6 = K O . I O^5 + K^5 I^5 =$ by heating $K^6 I^6 + O^6$
2. $Zn + I = Zn I + K O . C O^2 = Zn O . C O^2 + K I$
3. $K O . C O^2 + I + S H = C O^2 + H O + S + K I$

In the first case the salt may contain iodate of potassa from imperfect heating; the salt generally turns brown on keeping; its solution is immediately turned brown by tartaric acid, owing to separation of iodine from the iodic acid, and it precipitates salts of baryta.

In the second and third cases it may contain carbonate of potassa. This is recognized by its insolubility in alcohol, and by the effervescence produced by the addition of an acid.

Chloride of potassium is sometimes used as a means of adulteration. To detect it a portion of the salt is *fully* precipitated by nitrate of silver, the precipitate washed out, treated with ammonia, and the filtrate supersaturated with nitric acid, which precipitates chloride of silver. The chloride is soluble, the iodide insoluble in ammonia.

OXIDE OF MERCURY

May be adulterated with red lead or with some red earthy substance, such as brick dust. On strongly heating for some time until all the mercury has been volatilized, a yellow residue will remain if red lead were present. This residue is perfectly soluble in nitric acid, to which the usual tests for lead may be applied. If any residue remains insoluble it is probably some earthy adulteration.

CALOMEL

Sometimes contains traces of corrosive sublimate, which may be extracted by means of hot water, and detected as described at page 44. It should be borne in mind that calomel, when heated with hydrochloric acid, is rapidly converted into corrosive sublimate and metallic mercury. By this reaction the presence of mercury instead of its suboxide, in some medicinal preparations, may be proved. Metallic mercury being quite insoluble in hydrochloric acid, the substance under examination when thus treated will yield a solution free from metal; if however it contains suboxide, it will be first converted into subchloride, and by further action into mercury and chloride, which remains dissolved.

$$Hg^2 O + H Cl = Hg^2 Cl + H O \qquad Hg^2 Cl = Hg + Hg Cl.$$

CHLOROFORM

May contain alcohol and ether, hydrochloric and hypochlorous acids, sulphurous acid when the chloroform has been treated with sulphuric acid and has not been left in contact with binoxide of manganese previous to its final rectification, and some exceedingly injurious methyl compounds when it has been prepared from wood spirit instead of alcohol.

Alcohol and ether may be detected by adding water to a measured quantity of chloroform contained in a graduated tube. On shaking and allowing the mixture to settle, the volume of the chloroform will be found to have diminished. A green colour will also be produced on treating the adulterated article with chromate of potassa and sulphuric acid.

Hydrochloric acid may be detected by its acid reaction, and by extraction with water and application of the usual tests.

Hypochlorous acid by its bleaching power.

Sulphurous acid by the iodic acid test.

Methyl compounds by shaking the chloroform with sulphuric acid, when a brown colouration will be produced.

The specific gravity should be 1.496 or 1.500.

SULPHATE OF QUININE.

Salicine may be detected by warming with sulphuric acid, when a red colour will be produced.

Starch by a solution of iodine, or by boiling for a few minutes with a drop of sulphuric acid, cooling, adding sulphate of copper and excess of potassa, and heating gently, when red oxide of copper will be precipitated.

Sugar by the same test, or by precipitating with carbonate of potassa, evaporating the filtrate nearly to dryness, extracting with alcohol, and testing the filtrate for sugar.

Stearine by treating with dilute acid, which dissolves the quinine and leaves the fat, which melts on the application of heat.

Earthy impurities may be detected by incinerating the mixture and thoroughly burning off the carbon, which requires long heating. Their nature can then be determined. Carbonate and sulphate of lime are sometimes employed.

ADDENDA AND ERRATA.

Page 23—From the native molybdate of lead the acid can be obtained by digesting the finely powdered mineral with sulphuric acid, filtering, evaporating the filtrate with a little nitric acid, and heating until all sulphuric acid is driven off. The dry residue is then dissolved in ammonia.

" 26—line 3, add "silver."

" —line 6, add "bismuth."

" 34—Test 5 for magnesia may be omitted.

" 56—Column III., for H Cfy read H^2 Cfy.
for H Cfdy read H^3 Cfdy.
for Hs read H S

" 72—The H Cy may be precipitated by Ag O, NO^5, the Ag Cy placed in a watch glass, moistened with H Cl, and the evolved vapours made to act on N H^4 S.

" 77—It has been lately proposed to modify the process here described, by heating the K O. Cl O^5 with H Cl in a flask, and passing the evolved gas into the organic mixture. The operation thus becomes more complicated without any equivalent benefit resulting.

" 85—Mercury in solution may be detected by introducing a piece of gold wire round which some strips of tin-foil have been twisted. The metal is deposited on the gold, and by heating the wire in a small tube the mercury may be volatilized and condensed in globules.

" 92—In lieu of a marking diamond, the end of a three-cornered file may be used, having been previously heated red-hot, cooled rapidly by immersion in water or mercury and ground to a sharp point.

√