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THE USES OF ELECTROLYSIS
IN
QUANTITATIVE CHEMICAL ANALYSIS.

BY

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CONTENTS.

INTRODUCTORY AND HISTORICAL.

Sir Humphry Davy was the first to utilise the fact that electricity can occasion chemical decomposition, in the preparation of Potassium and Sodium; and since his day many other elements, Calcium, Strontium, Magnesium and so on have been obtained in the same way. Scientific attention seems to fix itself for periods in certain paths, which are nnduly trodden, while others are neglected. But neglect of the possibilities of electricity is no part of the practice of the present. Industrially, medically and scientifically it is always meeting wider applications; and the following pages will be directed to illustrating its use in Quantitative Chemical Analysis.

Qualitatively electric force has been employed as a test very usefully; more usefully than many students, who have overlooked its value, are aware of. The detection of Antimony with Platinum and Zinc, of Mercury with Copper, and of Copper with a steel needle are all cases in point. Quantitatively researches dating principally from a period some twenty years back have at all events opened for discussion the question how far the testtube may be replaced in our laboratories by a more delicate, more cleanly and less cumbersome agent—to wit the electric battery. The new analysis is only in its infancy, and remains still sub judice. There are great difficulties in the way which may in the long run prove fatal to its wider employment. But there are cases where it renders us such undoubted service that we are bound to weigh its claims, and decide whether it may not be at the least a useful aid in analysis volumetric and gravimetric; in a word whether we may not divide quantitative chemical analysis into volumetric, gravimetric and electrolytic in relation to its methods.

Professor Wolcott Gibbs of Harvard was the first to publish results of analyses by electrolysis. In a paper in which he urged the value of acetate of sodium in the separation of aluminium from the alkaline earths, he gave a series of very exact analyses of Cupric Sulphate which be wrote $CuO . SO_3 + 5 HO$ and of coins containing Copper. His results were obtained in from one to three hours with a battery of two feeble Bunsen's cells. This was in 1864. Next year Luckow commenced a series of researches which culminated in his receiving a prize at the hands of the Mansfeld'schen Ober-Berg- und Hütten-Direction in Eisleben for a paper presented in 1869 containing practical proposals for analysing ores for Copper and also for Nickel and Cobalt. From that time numerous researches have been undertaken so that the electrolytic Chemistry of all the chemical Elements has been investigated. Among the many Chemists who have since made additions to our knowledge Dr. A. Classen deserves especial mention both for his original work, his assiduity in pressing the claims of, and his excellent treatise upon, the New Analysis.

PART I.

PHYSICAL DISCUSSION OF THE BEHAVIOUR OF BODIES UNDER THE ACTION OF THE ELECTRIC CURRENT.

Conductors of the electric current are divisible into two classes: bodies conveying the current without themselves undergoing any change, whose conductivity be it mentioned is diminished by the application of heat, such as the metals, peroxides and some sulphides; and secondly bodies termed electrolytes conveying the current but undergoing decomposition in the process, such as the various chemical salts. Bodies of this class have an increased conductivity as the temperature is raised; for example two Bunsen's cells may not suffice to force a current through a solution containing the double oxalates of Zinc and Nickel but immediately on the application of heat decomposition commences.

The same current passing through a series of electrolytes will decompose chemically equivalent quantities of each.

In the case of water hydrogen is decomposed at the negative pole which will be termed the Kathode; being the electro-positive element: while oxygen passes to the positive pole which will be termed the Anode being the electro-negative element.

Ammonic oxalate is decomposed into hydrogen and ammonium bicarbonate the latter forming then ammonia and carbonic acid.

Sodium pyrophosphate separates into one equivalent of sodium and one equivalent of $P_2O_5 + O$.

Salts of the organic acids separate at the anode one equivalent of O and one equivalent of the acid anhydride and a the kathode one equivalent of the metal.

Finally the following facts in regard to nitric acid may be mentioned. It commonly yields HNO_2 at the anode, but in the acid s. g. 1.2 this decomposition does not occur. In the presence even of H_2SO_4 no formation of NH_3 occurs: but if $CuSO_4$ is in solution $(NH_4)_2SO_4$ is separated. Ammonia is also formed in concentrated solutions of nitrates. If free alkali is present in a solution of nitrates, no NH_3, but HNO_3 forms at the anode.

Interesting investigations have been mode of the physical structure of the metal separating. Mixed solutions of metallic salts are placed upon a slide under the microscope, and are electrolysed by a current conveyed to the poles by delicate wires. Solutions containing chlorides of Tin and Zinc yielded the metals in well defined form separated by a right line almost by way of demarcation; on one side being the Zinc in winding threads maintaining a generally parallel direction, upon the other the Tin in cubical bodies of varying size connected in rows. From solutions containing nitrates of Barium and Lead there crystallized out leaf-like modifications of Lead upon the one hand and as representing Barium a scum of $Ba(OH)_2$ only. The separation of the metal appeared to be as if from a supersaturated solution.

Without observing such facts in working quantitatively the characters of the metallic deposits is worthy of attention. Zinc is very prone to form a mal-adherent mass reminding of a charcoal surface. Copper separates in a beautifully metallic layer when the solutions are properly prepared, and the current employed of a strength represented by 2—3 cc. Knall-gas per minute. But in too strong solutions, solutions not sufficiently acid, and with powerful currents it separates in a spongy form, black in colour, very absorbent, and impossible to free from enclosed salts. Iron separated upon a wire from a solution containing Manganese and pyrophosphates in particles, standing out from the wire as the filings stand out from a magnet. On the other hand it separated from a solution containing Tartaric acid in very compact form, appearing almost to form an alloy with platinum.

APPARATUS REQUIRED IN APPLYING THESE PRINCIPLES TO QUANTITATIVE CHEMICAL ANALYSIS.

BATTERIES AND RESISTANCES.

Various, in fact all, forms of battery have been employed, as well as thermopiles and magneto-electric machines, for producing current. Clamond's Thermopile was chosen in many of the earlier researches as by Wrightson. It consists of Zinc-Antimony couples with Iron as connecting material and Asbestos for insulation: the junctions being heated by gas. After heat has been applied for an hour such a pile with yield 7—8 cc. Knallgas per minute.

Noe's Thermopyle has been preferred to Clamond's from its readiness, constancy and duration; being inferior to it however for technical purposes. It likewise consists of Zinc-Antimony conples with Iron connections.

Neither of these instruments however is as convenient as an ordinary battery, and once damaged very difficult of repair.

Meidinger's Hydro-electric battery is recommended by Luckow. There are two metals, Copper and Zinc; and two fluids containing Sulphates of Magnesium and Copper in solution. The battery becomes constant at the and of three weeks delivering then a current of 3 cc Knallgas per minute, at commencing it yields a current af .5 cc Knallgas per minute; in a few days the current reaches a strength of 1.5 cc and 2.5 cc Knallgas.

Bunsen's Battery was employed by Lecoq de Boisbaudran, in the preparation of the new metal Gallium by Electrolysis. It was recommended for use by Riche for the estimation of Manganese, one or two cells, one cell if only a small amount of the element was present. Beilstein and Jawein used four cells for the separation of Zinc.

It consists of a carbon pole immersed in strong nitric acid contained in an inner porous cell, and a plate of amalgamated Zinc of cylindrical form in dilute sulphuric acid in an outer vessel. Ordinarily a Bunsen's Battery will be found as convenient as any; though it must of course be placed in a draught-cupboard. The gases evolved corrode the wires and copper screws very speedily, so that they require frequent cleansing with dilute nitric acid, or rubbing with a file or sand-paper. On once replenishing with acid the current will continue to flow for 60 hours in quantity sufficient to induce the simpler decompositions. If two cells with carbon plates 8 in by 2 in by 1 in and a Zinc cylinder 8 in high and 4 in diameter be taken about 20 cc of Knallgas are delivered per minute, far more than is required for separation of Copper, and equal to the requirement in the cases of most of the elements. The complete electrolytic separation of Iron however may require the application of three cells.

Classen mentions also Leclanché's battery, Daniell's battery and Grove's battery for very powerful currents. The electromotive forces of these batteries are

Leclanché	1.48	Volt.
Daniell	1.079	»
Grove	1.81	»
that of a Bunsen cell being	1.80	»

With others electric machines have found favour. Ohl recommends a Gramme's Machine with which he was able in 4 hours to separate 1 grm. of Cobalt and Nickel, and in 4 hours 1 grm. of Copper. Classen uses a machine supplied by Siemens and Halske worked by an engine of one horse power for which he claims the great advantage industrially of enabling numerous analyses, requiring all strengths of current, to be carried out simultaneously. A further refinement elaborated by him consists in the introduction of measured amounts of resistance, by means of a resistance coil. But for ordinary purposes it is quite sufficient to know within moderate limits the strength of the elements which we are employing, and to introduce solutions as for example of Zincic sulphate if required to add a resistance. In this way the 20 cc Knallgas delivered by two Bunsen's cells may be readily reduced to 5 cc or 3 cc.

ELECTRODES AND CONNECTIONS.

The battery is connected by means of insulated wires with the stand : which consists of Copper uprights on insulated feet. The wires are fixed in holes in these uprights by means of screws. When all the connections are complete excepting the fixation of one wire, it is readily seen if all is in order by touching with the wire the Copper of its upright when a spark passes. The uprights are apt to tarnish in the presence of gases from the battery and steam from the solutions being electrolysed. The Copper may then become converted into nitrate and this drop into the liquids under examination. Rubbing with Oleonaphtha or other mineral oil obviates the action of the gases upon the Copper, and the application of a lid to the basin containing the solutions prevents any foreign body mixing with them.

One upright carries a horizontal bar, from which usually the anode, less commonly the kathode hangs; the other carries a ring of metal in which a platinum basin rests: or it may carry a bar like its fellow for suspension of either anode or kathode where for example the whole decomposition is conducted in a beaker.

The earliest kathode employed was a platinum basin, the anode consisting of a platinum wire carrying a spiral immersed in the fluid. The basin should be large for especially when made the kathode it is desirable to have as much surface as possible. It ought to hold 500 cc of fluid and be a segment of a sphere in shape. A snitable beak is very convenient, admitting after anointing with Vaseline, the safe pouring of fluid from basin to basin. Moreover a couple of lips, one at either side for convenience of lifting into exsiccator, scales, and ring, is desirable. For the anode a couple of feet of stout platinum wire may be used, twisted at one end into a horizontal spiral of three or four turns which lies in the fluid; and may by changing the bar upon the upright be either raised out of the liquid altogether or brought within an inch of the platinum basin.

It is necessary to provide a cover for this apparatus in the shape of a large watch glass perforated with a hole in the centre through which the wire carrying the spiral passes. It ought to be convex towards the fluid, and the hole should have a lip. In this way drops falling from the stand, and containing copper are caught. If this precaution be not taken, the experimenter will find ever increasing quantities of that metal upon the kathode. This cover serves other purposes. Where strong currents are employed, large bubbles of gas carry portions of fluid outside the vessel altogether. Secondly when the aid of heat is songht for hastening the process this cover acts as a condenser obviating the necessity for repeatedly adding more liquid.

Where the experimenter desires to make frequent changes in the constitution of the fluid submitted to electrolysis the above apparatus may be replaced with a beaker containing the fluid into which two poles dip. The kathode consists of a platinum plate of sufficient surface bent into a cylinder, and within it hangs the anode in the form of a small spiral. The beaker is filled with the solution containing the electrolyte. For the sake of illustration let us suppose this solution to be one of Cupric Sulphate to which Tartaric acid and Caustic Soda in excess have been added. As the electrolysis proceeds the deep blue colour vanishes gradually and one can determine with the aid of a sheet of white paper the termination of the process. Furthermore one can readily apply heat, and readily alter the constitution of the fluid. When the reaction has advanced by addition of dilute nitric acid the colour changes to a pale green, and the reaction becomes acid. But the deposition of copper advances as well, and better than before. A point however may be reached when the current still passing, no Copper separates, and what had separated is redissolved. This illustrates the fact that certain agents are unfavourable to the electrolytic separation of elements. Among such are principally hydrochloric acid and chlorides.

MEDIA FOR THE SOLUTION OF SUBSTANCES UNDER EXAMINATION.

The solutions submitted to electrolysis are of paramount consequence. By a snitable choice of solutions we may divide the metals into groups. From acid solutions only a few metals separate—to wit copper, silver and platinum; and peroxides as of lead, manganese and bismuth: whereas most metals deposit from alkaline solution. The preparation of solutions requires assiduous care, and measurement. The approximate amount of metal, the amount of acid or alkali and the amount of water onght to be known. Moreover various media are conveniently present. Dilute sulphuric acid is a very convenient medium from which to electrolyse salts of copper. Lead separates well upon the anode from solutions containing free nitric acid. The various organic acids have been very widely and successfully employed, a fact in relation with the peculiar electrolytic behaviour of salts of organic acids already referred to. Acetic acid, citric acid, tartaric acid and oxalic acid have been most made use of. Very often it is best to use a saturated solution of ammonic oxalate. On adding this reagent to the metallic compounds a precipitate forms which redissolves in excess. The resulting liquid is submitted to electrolysis.

Pyrophosphate of Sodium does not appear to yield such good results as the Oxalate of Ammonia at all events in the case of Zinc and Nickel. A saturated solution is added to the solution containing the metal until the precipitate first formed is redissolved. Farther additions of ammonia or ammonic carbonate are recommended.

The termination of the reaction may be inferred by using the ordinary qualitative reagents for the several metals. A drop is taken from the liquid upon white bibulous paper and the reagent applied.

Where a beaker is used, and the liquid possesses highly distinctive colour the conclusion of the electolysis is very evident. It remains to be seen whether, when the liquids are not highly coloured, an index may not remain in the solution throughout; for example sulphocyanide of potassium in solutions of ferric salts.

A simple method for reaching the same end, and involving no loss of fluid consists in exposing a fresh surface of platinum, for example by tilting the platinum basin, to the fluid being electrolysed. If at the end of half-an-hour or so no fresh metal has been thrown down it may be concluded that the reaction is at an end.

In using a platinum basin as one pole for the separation of iron and manganese it is convenient to make it the anode, and to replace the wire spiral by a more snitable apparatus by way of kathode. The spiral has been recommended, but it is not to he employed. A wider surface holding the Iron better ought to he used. This may consist of a platinum cylinder, a platinum cone or a platinum plate. The latter form laid flat under the surface of the solution is excellent; for it offers a wide surface, and opposes the carrying away of deposited metal by currents of gas. The metal employed for the electrodes is accordingly in most instances platinum, which must be scrupulously clean and of an even surface. It is well to wash with strong hydrochloric, and fuming nitric acid at intervales; then with distilled water; and finally with ether. To prevent destruction of the metal for at times alloys form containing platinum and the metal deposited such as Zinc or Iron, it is desirable to overlay the platinum surface with a thin surface of Copper or of Silver. This is indispensably necessary in separation of Zinc and Nickel by volatilizing the former from a mixture containing the two metals. An alloy of platinum-zinc forms which does not dissolve out in the strongest acids, with difficulty after melting with sulphide of potassium, and requiring in the end the use of sand.

When the metal has been separated upon the surface of the platinum basin, the latter is washed out with distilled water, —the washings being of course added to the original remnant of solution when other elements remain to separate—and then with absolute alcohol and then dried in the airbath at about 100° C. Where the metal has deposited well these operations do not take 10 minutes in all.

There is an advantage here in employing a plate or cone of moderate dimensions as the kathode: it is small in size, and easy of weighing; in washing it only requires dipping into, and stirring round first in distilled water, then in absolute alcohol, to become adequately washed; and in the rare instances where particles do detach they are not mixed with the solutions which undergo further examination but are at hand in distilled water and can be taken up upon a filter and estimated gravimetrically.

PART II.

BEHAVIOUR OF THE INDIVIDUAL METALS.

A complete system for the separation of the various chemical elements by electrolysis alone cannot be formulated, although certain broad groups may be determined. Nor is this necessary for the purposes of Quantitative Chemical Analysis which deals rather with a few elements already known, than with a large unknown quantity which it is the province of Qualitative Analysis to dissect.

Electrolytically the elements are divisible into two primary classes; those which separate on the anode as peroxides and those which separate upon the kathode in metallic form. The latter group again falls into two divisions; metals depositing from alkaline solution and metals depositing from acid solution.

CLASS I.—METALS SEPARATING AS PEROXIDES.

[1] Manganese under all circumstances; usually lead, thallium and bismuth. Peroxides result from the formation of ozone at the anode. Their amount is less when the solution is warm and alkaline. A number of other metals may deposit partially in oxides upon the anode; including silver, nickel, cobalt, uranium, palladium, molybdenum and tin.

CLASS II.—METALS SEPARATING CHIEFLY FROM ACID SOLUTIONS.

Copper, silver, mercury, platinum, palladium, indium, cadmium, tin, as well as selenium and tellurium. Several other

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[1] To this peroxide the formula $MnO . MnO_3$, less probably $Mn_2O_7 . 3MnO$, has recently been assigned.

elements may separate from solutions which are not alkaline: —viz, antimony, arsenic, nickel, iron and zinc.

CLASS III.—METALS NOT DEPOSITED FROM STRONGLY ACID SOLUTION, FALLING HOWEVER FROM ALKALINE SOLUTION.

This group properly includes zink, nickel, cobalt, iron, uranium and the remaining elements which have not been indicated above.

It now remains to state briefly what is known of the electrolytic chemistry of the principal elements.

SILVER.

This metal separates well from its chloride or cyanide dissolved in potassic cyanide. This forms the basis of an excellent method for estimating chlorine, bromine and iodine which are first obtained in combination with silver and then electrolyzed from solutions in the cyanide.

If alkaline solutions are used the metal is mostly obtained in flocculent form.

Bergmann recommends as most convenient the separation from liquids containing free nitric acid as follows

200 cc fluid
·03—·04 grm silver
3—6 grm free nitric acid

the electrodes being half an inch apart and a current represented by 1·5 to 2·5 cc knallgas being employed.

Double pyrophosphatic solutions to which ammonia or nitric acid has been added are suitable.

MERCURY.

It has long been known that mercury separates in regular form on the kathode from acid solutions and it remains still true that mercury is best electrolyzed in the presence of free nitric or sulphuric acid. Where the former acid is employed the current should have a strength represented by ·5—1 cc knallgas.

Mercuric, not mercurous, salts may be electrolysed from their double pyrophosphates after addition of ammonia or ammonic carbonate.

LEAD.

In solutions containining 10°/₀ of free nitric acid lead separates well on the anode as peroxide and may be weighed as PbO; or estimated as CO_2 after treatment with oxalic acid.

The following facts also deserve to be brought into review. It has been separated as metal when present as tartrate in alkaline solutions containing acetates of the alkalies: also when oxalic acid has ben added to the nitrate in excess. Where the lead has been obtained as sulphate this may be dissolved in alkali with addition of sodic tartrate, the solution rendered acid with HCl till a slight precipitate forms, then neutralized with $NaOH$ and electrolysed after addition of $NaOH$ and $(NH_4)HO$.

Finally it is separable from the double pyrophosphate after addition of ammonic carbonate.

THALLIUM.

Behaves generally as lead; but even from acid solutions containing some nitric acid a certain proportion of metal comes down on the kathode, while the bulk appears as superoxide on the anode.

From alkaline solutions containing ammonia or potash thallium is deposited upon the kathode, and thallic oxide on the anode.

PLATINUM.

Separates readily upon the kathode from solutions acidified with hydrochloric or sulphuric acids, or from solutions prepared with ammonic oxalate. Care must be taken that the current is not too strong in which case the mètal separates as platinum-black. A single Bunsen's cell determines a separation in compact metallic form.

PALLADIUM.

This metal separates under similar conditions to the last. From the nitrate in nitric acid in forms on the kathode with the lustre of bronze there being deposited at the same time however some reddish oxide on the anode. From alkaline solutions deposition is slower, a certain amount of oxide in this case also forming.

INDIUM.

May be satisfactorily separated from sulphuric acid upon the kathode. It separates well also in the presence of organic acids.

GOLD.

The precious metal comes down upon the kathode from solutions in potassic cyanide. It is necessary for obvious reasons previously to cover the platinum basin with a thin layer of silver.

MOLYBDENUM.

The separation is unsatisfactory: molybdenons oxide or the hydrate of molybdenum sesquioxide $Mo_2O_3 . 3 H_2O$ depositing from ammonia.

URANIUM.

The acetate rendered acid with acetic acid, placed in a platinum basin as anode, at a temperature of 60—70° yields uranium hydroxide and then uranio-uranons hydroxide. It may be weighed as uranio-uranons oxide.

VANADIUM.

On electrolysis of solutions of vanadic chloride in hydrochloric acid the liquid changes colour and the vanadic acid is reduced to vanadious.

CADMIUM.

The satisfactory separation of this metal offerred difficulties to certain of the earlier experimenters. From ammoniacal solutions it separates in porous form. From its sulphate in acid solution it deposits upon the kathode, but in scales which soon pass across to the anode and break the current.

Better results are obtained on treating the nitrate or sulphate in succession with caustic alkali and with potassic cyanide. The liquid is electrolysed with three Bunsen's cells. It has been proposed to separate this metal from zinc by treating its acetate or sulphate with sodic bicarbonate and acetic acid, and then electrolysing with two Daniell's cells under heating.

Solutions prepared with sodic pyrophosphate and ammonia, the current being represented by 3—5 cc knallgas; or with potassic oxalate are very suitable for electrolysis.

GALLIUM.

This metal was separated electrolytically by Lecoq de Boisbaudran its discoverer from solutions of its oxide in caustic potash.

ANTIMONY.

The solutions of the double oxalate are not recommended for use in the separation of this element. It may be separated from the sesquisulphide dissolved in excess of potassic monosulphide, addition of ammonium sulphate having been made to increase the conductivity of the fluid. Likewise a solution of the chloride in ammonic tartrate may be employed or the sulphosalts-

The metal is very successfully separated from tin in con. centrated solutions of sodic monosulphide (s. g. 1·225) to which caustic soda has been added. The current required is represented by 1·5 to 2 cc knallgas per minute. Next the sulphide of sodium is replaced by sulphide of ammonium and the tin separated with a current of 9—10 cc knallgas per minute.

Furthermore it may be separated from arsenic where arsenic is present as arsenic acid by solution of the ore or alloy in aqua regia, dilution with water, and treatment with caustic soda and sulphide of sodium. The further determination is to be conducted as in the case of tin.

TIN.

This element may be electrolysed from solutions containing hydrochloric acid or prepared in the usual way with ammonic oxalate.

Stannous salts are separable conveniently from solutions containing pyrophosphates and treated with ammonic carbonate; the tin being in part however oxidised on the anode.

ARSENIC.

It remains here to add to what has been said of this metal under antimony that the most delicate of all tests for arsenic is by the preparation of H_3As electrolytically, and the subsequent detection of the same.

BISMUTH.

Bismuth is very difficulty separable from acid solutions, from those containing potassic bitartrate, or the ammonic double salt. If in small quantity, by using a very large basin, it may be estimated care being taken to weigh separately any portions of metal which become detached. It has been said to separate well frome its sulphate and citrate; also from solutions containing free citric acid. It has been likewise recommended to treat the bismuth salt with oxalates of ammonium and potassium and electrolyse with very feeble stream at 70—80°. Because of oxidation the metal must be redissolved in nitric acid, and the nitrate converted into oxide with the aid of heat.

Separation may, finally, be effected from pyrophosphatic solutions treated with ammonic carbonate and ammonic oxalate.

COPPER.

The electrolytic separation of copper can be readily effected from a great variety of solutions. Earlier observers met with difficulties attributed to re-solution of the metal in the acid which had been added to the liquid undergoing analysis. But this difficulty was got over by washing without break.

Sulphuric acid and nitric acid have een most widely employed as solvent media. Nothing can be more satisfactory than the separation from a solution containing 15% of dilute sulphuric acid (1 : 5) with a single weak Bunsen's cell. If the current have difficulty in starting a little more acid may be added, or some sulphate of ammonium, or heat may be applied.

The only drawback is slight oxidation on exposure of the metal in the moist state to the air.

Nitric acid may likewise be used 10% being present in the solution. An excess however prevents all action for the metal appears to be redissolved as rapidly as it is formed.

We may add hydric chloride so that 5—7·5% of the dilute acid is present in the liquid; or tartaric acid with either sulphuric acid or caustic soda.

Cuprous sulphide has been dissolved in potassic cyanide, ammonic carbonate added and the metal separated at 70° after a few minutes boiling.

Ammonic oxalate, or sodic pyrophosphate with or without further addition of ammonia ammonic carbonate or acid may be used in preparing the solutions.

ALUMINIUM.

In solutions containing salts of this metal, treated with ammonic oxalate no action occurs so long as the ammonic oxalate present remains in excess of the ammonic carbonate formed; this point overpassed aluminic hydroxide separates.

This property enables us to separate iron from aluminium.

MANGANESE.

This element is separable as peroxide on the anode from solutions containing nitric acid, less satisfactorily it has been said in the presence of oxalic acid, milksugar, or tartaric acid. As regards the latter it has been found that manganese separates well on the anode as peroxide from solutions containing also sulphate of iron, excess of ammonia, and tartaric acid.

In the presence of sulphuric acid the peroxide separates well, better with the aid of heat. With only traces of manganese present a violet-red colour forms in the liquid.

Occasionally some peroxide separates on the kathode.

The peroxide is brought to red heat, and weighed as MnO.

The double oxalates are very servicable in the case of manganese, enabling ns also to separate the metal from iron. In solutions containing both metals, treated with potassic or ammonic oxalate and with a further excess of ammonic oxalate no manganese comes down upon the anode until all iron has been deposited upon the kathode.

Solutions treated with pyrophosphate in excess and ammonia the peroxide adheres well to the platinum basin.

IRON.

This metal is separable electrolytically from solutions containing tartaric acid and ammonia in very adherent metallic form upon the kathode. Moreover manganese present separates as peroxide.

The deposition of iron occurs from solutions prepared with potassic and ammonic oxalate; and by use of a sufficiency of the oxalate the metal can be separated from beryllium, zirconium and vanadium as well as aluminium and manganese.

It falls from solutions containing the chloride in acid ammonic oxalate.

Sodic pyrophosphate may be employed but the metal separates in a form somewhat mal-adherent.

The course of procedure is as follows. Mixed sulphate of iron and manganese are treated with a saturated solution of sodic pyrophosphate until the precipitate first formed is redissolved. Then addition of ammonic oxalate is made, care being taken not to add excess which brings down a white precipitate. Three Bunsen's elements are put in circuit and heat applied. As anode the platinum basin serves, as kathode a cone or plate immersed in the fluid.

Thus ·4582 grm $FeSO_4.7H_2O$
·5365 » $MnSO_4.7H_2O$
Fe found gravimetrically . . . . 0·091
» » electrolytically . . . . 0·092

The sources of error being oxidation by the fluids and loss from maladhesion.

Where pyrophosphates are used the basin being the kathode, and heat applied there is liability to deposition of a layer of pyrophosphates upon the iron, a salt which cannot be removed without great oxidation of the metal. It is observable that the iron seems to separate best round the rim of the kathode when the kathode is a plate. An iron kathode prepared with hydric chloride presents disadvantages.

COBALT.

This metal is separable under the same conditions as nickel. In ores it is recommended to throw down copper and arsenic with H_2S bearing in mind that As_2S_3 is somewhat soluble in H_2S. Aq. The iron is got rid off, after oxidation with potassic chlorate and hydrochloric acid by treatment with caustic soda and boiling with acetic acid. Then after adding excess of ammonia the liquid may be electrolysed for cobalt.

In using pyrophosphates a subsequent addition of ammonic carbonate must be made.

ZINC.

Zinc may be electrolysed from acid and from alkaline solutions. In a solution from which Copper had been removed, containing tartaric acid and a residuum of nitric acid so that the whole was strongly acid Zinc came down showing a tendency to redissolve, and only semi-metallic in appearance, being black and not compact. Sulphate of Zinc treated with ammonic acetate and citric acid deposits the metal, the electrodes being near together and the current represented by 5 c.c Knallgas per minute. Solutions containing Zinc together with some free hydrochloric or sulphuric acid placed in a platinum basin with some metallic mercury deposit Zinc as an amalgam.

In alkaline solutions prepared with excess of ammonia, and although adhering well at first to the Kathode, and in part round its edges beautifully crystalline, it bridges across to the anode becoming very spongy; without however completely breaking the current. The adhesion to the anode is very loose so that the Zinc may be rubbed off with a feather an weighed separatly, after filtering and drying 4 gr. pure Zinc were taken and dissolved in dilute sulphuric acid, the whole being made of to 200 cc. of this solution 20 cc were taken, 10 cc of ammonia added, and water to 50 cc. Electrolysis was conducted with 3 Bunsen's cells in good order. Next morning the current still passing 397 Zinc (instead of 4) were deposited in all, partly spongy. The metal always forms a dark alloy with the platinum surface, very difficult of removal.

Additions of ammonic acebate enable the experimenter to obtain Zinc from ammoniacal solution in compact form.

Zinc, Nickel and Copper may be all separated together from ammoniacal solution. The Zinc is not spongy, but dirty in colour.

There remain to be mentioned separation from solutions containing the double oxalates, and pyrophosphate of sodium with subsequent addition of ammonia or ammonic carbonate. As regards the latter the metal has mostly been found to separate in indifferent and poorly adherent form; and to take long in the process 18 hours or more.

NICKEL.

Nickel has only been separated from alkaline solutions. It appears however that Nickel may come down with Zinc in acid solutions. Usually Ammonia is added to the Nickel solution, and the result is very satisfactury. A solution containing 005 crystallized sulphate of Nickel per cc was prepared: 20 cc wer-taken 10 cc of ammonia added and the whole diluted to 50 cc in a beaker. On electrolysis with 3 Bunsen's cells, the metal fell speedily without application of beat.

Ni =·02063 (found), ·0208 (calculated). The burk of the deposit fell upon the side of the Kathode facing the anode, and was silvery in appearance, on the other side the metal deposited principally on one edge black in colour.

The presence of hydrochloric acid and sal-ammoniac hinder this decomposition.

Nickel and Cobalt separate together 3 eg of Cobalt to 2 of Nickel it appears.

Nickel has been separated as phosphate the solution in dilate sulphuric acid being electrolysed.

In certain ores from New-Caledonia Maquesia present separates with the Nickel. It is therefore recommended to redissolve the precipitate in nitric acid, then drive off excess with sulphuric acid, supersaturate with ammonia and re-electrolyse. Unless sufficient ammonia is in the liquid a black precipitate forms on the Anode.

Ammonic Carbonate may be used instead of ammonia but the decomposition is slower. In the presence of Sodic phosphate likewise the decomposition is tardy.

Where Manganese is present as well as Nickel the former may be separated upon the anode as peroxide : but a portion passes to the Kathode with the Nickel.

In pyrophosphate solutions separation is slow and the metal of indifferent formation.

SELENIUM AND JELLURIUM.

These elements separate from acid solutions upon the Kathode. It has been said that the black colour of the Copper electrolysed from some ores is due to the presence of these two bodies. This black colour however is due to oxidation in presence of water and occurs where there is no selenium or tellurium whatever.

PART III.

THE ANALYSIS OF PHOSPHORITE.

The mineral having been finely powdered, so that it does not grate between the teeth, is dissolved in dilute nitric acid. Silica with a certain amount of ferric oxide remain undissolved which are separated by filtration and weighed together. Subsequently the ferric oxide is separated with hydrochloric acid and the silica weighed for itself. The iron present may be estimated as hydroxide after precipitation with ammonia.

The original filtrate containing iron, aluminium, calcium, magnesium and phosphoric acid is treated on the water-bath with tin-leaf so long as nitrous fumes are evolved, and then filtered. The residue contains the phosphoric acid, the liquid iron and aluminiun, and calcium. On addition of excess of ammonic oxalate and filtration the calcium is separated and the iron and aluminium remain to be separated electrolytically as already described.

THE ANALYSIS OF SPATHEISENSTEIN.

The mineral is brought into solution with dilute hydrochloric acid on the water-bath, and evaporation is then conducted to dryness. The silica is brought upon a filter and separated as such. The filtrate is treated with fuming nitric acid till oxidation of all iron is complete, evaporated to dryness and again brought into solution with water. On treatment with ammonic oxalate in excess the calcium is precipitated and the filtrate is analysed electrolytically for iron and manganese as already described. The magnesia and carbonic acid are separately estimated.

THE ANALYSIS OF NEUSILBER.

NEW-SILVER.

The cleaused alloy is dissolved in a little fuming nitric acid, and the solution then brought to dryness. Dilute sulphuric acid is added, and the nitrates again brought into solution. If tin is present it remains as stannic oxide after treatment with fuming nitric acid.

Lead remains undissolved as sulphate on solution in sulphuric acid, and is filtered off and weighed as such.

It now remains to estimate the copper, iron, nickel, cobalt, zinc and manganese. Dealing with these separately.

a) COPPER.

The solution prepared with 20 cc dilute sulphuric acid is brought to 250 cc and electrolysed with a single Bunsen's cell. Two platinum electrodes are used; one a platinum basin, the other a thick wire spiral. The metal at once begins to deposit of bright red colour and very adherent. Faint streaks of a black tint were noticable here and there upon the surface of the metal. On tilting the basin a fresh surface was found to be clean after half an hour. The liquid was then poured off and the deposit washed without breaking the current, then with alcohol, exposure to air benig avoided as far as possible, and dried in the air-bath at 100°.

·2685 Neusilber taken

Cu = ·1518 or 56·54 %

Again ·0965 of the alloy taken, dissolved in fuming nitric acid and diluted to 200 cc with addition of 15 cc dilute nitric acid and electrolysed with 2 feeble Bunsen's cells.

Cu = ·547 or 56·68 %.

Upon the whole the metal was notso compact as on treatment with sulphuric acid. The lead of the assay separated upon the anode.

Next ·958 of neusilber was taken and brought to solution in dilute hydrochloric acid. Electrolysis was conducted with two strong Bunsen's cells; and the poles were near together. Next morning the metal had separated out in beautiful frosted masses; that upon the platinum basin near the anode being pitted with holes where the current had passed in beautifully regular form. The metal was however spongy, difficult to wash and contained acid and salts in its pores.

Cu = ·546 or 56·99%.

Further 1·1697 were taken and treated with 5 cc of strong tartaric acid solution and 20 cc of caustic soda and made up to 250 cc.

The metal separated speedily; but of a more and more black colour. There is no doubt that this black colour is due to partial oxidation in the presence of water. If a surface of electrolysed copper be moistened with water, and rubbed with the finger this black deposit rapidly forms.

Cu = ·6638 or 56·75%.

Lastly 1·0922 grm treated with tartaric acid 5 cc and nitric acid 20 cc gave

Cu = 6204 or 56·8%.

Here also the metal came out black in colour.

Experiments were likewise made in separating the metal from ammonia.

b) IRON.

The solutions from which the copper has been separated, containing the remaining metals are altogether satisfactory for the determination of these same.

The iron is present in such small quantity that it may be most conveniently determined gravimetrically.

It was separated as succinate, converted into oxide after bringing to red heat with admission of air. It was likewise separated as ferric oxide in the electrolysed liquid for separation of zinc and nickel with the battery.

c) MANGANESE.

Appeared as a minute quantity of peroxide under these last circumstances.

d) NICKEL AND ZINC.

These metals were separated together from pyrophosphate solutions with ammonia, and likewise from sulphuric solutions simply treated with ammonia to excess.

The liquid after separation of copper from sulphuric acid was concentrated and placed in a beaker containing 100 cc. Ammonia was added to excess and two poles, a platinum spiral as anode and a platinum plate as kathode already covered with copper immersed in the fluid. Three Bunsen's cells were employed. Next day the manganese was deposited as peroxide upon the spiral, the iron was separated upon the surface of the liquid as ferric oxide to be estimated as such, and the nickel and zinc were thrown down together upon the kathode. Ammonic sulphide was used as an index. The reagent cannot be left in the fluid for if any nickel remains the whole becomes very dirty, and the deposited metal is converted into sulphide.

[1] It being proposed to estimate the zinc upon the one hand which melts at 412° and boits at 1040°, and the nickel (and cobalt) upon the other, which melts at 1450° by volatilizing the former in an atmosphere of hydrogen, the plate was taken from the wire and placed in a crucible and exposed to a bright red heat. In one experiment, where ·035 of the combined metals were taken, the residuum of weight was ·015.

This method when further perfected is calculated to yield satisfactory results, in a most difficult and tedious gravimetric process.

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[1] In a recent paper it has been proposed to separate zinc and nickel from neutral solutions containing sodic acetate with H_2S; but nickel comes down equally with zinc.

Results of the analysis of Neusilber.

Lead	·09 °/o	
Copper	56·54 °/o	
Iron	·19 °/o	(precipitated as succinate).
	·23 °/o	(precipitated as oxide).
Manganese a trace		
Zinc	26·23 °/o	
Nickel and cobalt	16·78 °/o	

PART IV.

What may we then conclude as to the future of analysis by electrolysis. Quantitative chemical analysis conducted upon the old lines was calculated to yield results often unsatisfactory, after long and laborious processes. There is no Royal road to knowledge and the student or investigator who precipitated, filtered and weighed became thorougly conversant with the properties of the compounds of the chemical elements, and with the methods by which they were to be obtained, and yet unknown compounds as well. At the same time be became possessed of much knowledge practically applicable in the sciences and arts. But in the great region of industrial occupation, in mining and manufacturing, in assaying he was handicapped by the complexity of bodies and the great delicacy and skill requisite to compass results.

The electric current there can hardly be a doubt simplifies difficulties greatly, reduces toilsome labour to a minimum, saves time, and permits skilled knowledge to devote itself to other work than the drudgery of making for the hundredth time a quantitative analysis. Any one however small his manipulative dexterity cun reach accurate results in the analysis of every variety of ore by electrolysis. He can conduct any number of analyses at the same time. Once commenced the process goes on of itself, and he is free to devote himself elsewhere, practically then it may be expected that electrolysis will in the future play a great part in analysis. Moreever it must not be forgotten that the most delicate of all tests for arsenic is the electrolytic test: and it is claimed that tin can be with certainty completely separated from antimony. It remains for our Professors and Teachers to determine how far they are prepared to go in replacing volumetric and gravimetric, always doing justice to their educational value in chemistry, by electrolytic ones.

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compts.

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