Inorganic

Reduction and Electrolysis of Perrhenate. G. E. F. Lundell and H. B. Knowles. (*U.S. Bureau of Standards J. of Research*, 1937, **18**, 629–637.)—Potassium perrhenate (16·6774 g.) was dissolved in 4 litres of 2·5 per cent. sulphuric acid, and aliquot portions were passed at 5° C. through an 18-inch Jones reductor (diameter 1 inch) filled with 20-mesh granulated zinc amalgamated with 5 per cent. of mercury. The solutions were previously boiled to expel air, and the operation was carried out in an atmosphere of carbon dioxide. The reduced solutions were titrated immediately with permanganate, or they were caught in excess of ferric sulphate or permanganate and then titrated. All the results indicate that the perrhenate is reduced to hydrorhenic acid: $HReO_4 + 8H = HRe + 4H_2O$. If the reduced solution, protected from oxygen, is warmed moderately and left to itself for 30 to 60 minutes, the reaction $HRe + H_2SO_4 = HReO + H_2O + SO_2$ appears to take place, with formation of hyporhenous acid.

Rhenium was deposited as such when a perrhenate solution containing 5 per cent. of sulphuric acid was electrolysed overnight between a sand-blasted platinum gauze cathode and spiral anode at 0·25 amp. per sq. dm. and 2·34 volts. The deposits were washed with water, alcohol and ether, and dried for 10 seconds at 105° C. Direct weighing of the deposit gave a positive error due to oxidation. The deposited metal does not oxidise appreciably in perfectly dry air, but it oxidises very rapidly in moist air, being quantitatively converted into perrhenic acid within 24 hours. The element can be determined by electro-deposition, conversion into perrhenic acid by exposure to moist oxygen, and alkalimetric titration of the perrhenic acid (phenolphthalein indicator). The small amount of rhenium that may escape deposition may be determined colorimetrically by Hurd and Babler's method (ANALYST, 1936, **61**, 500).   W. R. S.

Electro-deposition of Zinc from Citrate Solution. R. Winchester and L. F. Yntema. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 254–256.)—The zinc should be present in sulphate solution free from heavy metals, but aluminium, chromium and magnesium may be present. The solution, to which 1·5 g. of citric acid is added, is rendered neutral to methyl red—methylene blue indicator with sodium hydroxide. It is diluted to 200 ml. and electrolysed with a copper or copper-plated gauze cathode and a rotating platinum anode, the cathode current density

being about 1 amp. per sq. dm.   After $1\frac{1}{2}$ to 2 hours, a 1-ml. sample of the electrolyte is tested by the addition of 0·5 ml. of saturated hydrogen sulphide water. The electrolysis should be continued if more than a faint opalescence is produced. Finally the cathode is withdrawn and washed without switching off the current, dried and weighed.   Practically quantitative results were obtained with 0·2 g. of zinc taken.   Nitrate ions, dimethylglyoxime and urea interfere, also the following metals:—antimony, arsenic, bismuth, cadmium, copper, iron, lead, manganese, mercury, nickel and silver.   S. G. C.

Separation of Zinc from Cobalt by means of Hydrogen Sulphide. E. A. Ostroumow.   (*Ann. Chim. anal.*, 1937, **19**, 145–152.)—Zinc sulphide precipitated by hydrogen sulphide from buffered acid solution tends to be much contaminated with cobalt if that element is present.   Under similar conditions the entrainment of iron, manganese and nickel was much less marked.   The particular behaviour with cobalt is attributed to post-precipitation.   The effect can be reduced by the presence of acrolein in the liquid, which is considered to become adsorbed on the zinc sulphide particles and to take the place, to some extent, of the active layer of adsorbed hydrogen sulphide which is held to be responsible for post-precipitation phenomena.   It was further found that a slow current of hydrogen sulphide was desirable for minimising post-precipitation, the passage of the gas being continued only long enough to secure coagulation of the precipitate. A method suitable for a solution containing moderate amounts of zinc and cobalt (0·05 to 0·1 g.) is as follows:—The solution is neutralised approximately with dilute sodium hydroxide solution, and 10 ml. of chloroacetic acid (190 g. per litre) are added.   To the clear liquid 10 ml. of sodium acetate solution (136 g. per litre) are added, and the solution is diluted to 150 ml. and heated (temperature not stated). Five ml. of acrolein solution (4 per cent.) are added, and a slow current of hydrogen sulphide (about 60 to 80 bubbles per minute) is passed into the solution until the zinc sulphide coagulates (about 25 to 30 minutes are usually sufficient).   The zinc sulphide is filtered off, washed with dilute acetic acid (4 per cent.) saturated with hydrogen sulphide, and burnt off.   The residue is converted into zinc sulphate in the usual way and weighed.   Practically the theoretical recovery of zinc was obtained in test experiments, and the amount of cobalt in the zinc sulphate was found by colorimetric tests to be less than 1 mg.   With small amounts of zinc in presence of moderate amounts of cobalt, difficulties were experienced, because the precipitate did not coagulate well and was difficult to filter off.   The addition of paper-pulp suspended in water was satisfactory for collecting the precipitate, but was found to lead to serious contamination of the precipitate with cobalt.   It was concluded that this partial precipitation of cobalt was due to a kind of post-precipitation on the paper fibres promoted by the fact that the water absorbed in the added paper gave locally too low an acid concentration.   This drawback could be avoided by using pulp saturated with a buffered acid solution as follows:— Paper pulp prepared in the ordinary way is filtered off on a Buchner funnel, and then shaken up with 150 ml. of water containing 10 ml. of chloroacetic acid solution (190 g./litre), 10 ml. of sodium acetate solution (136 g./litre) and 5 ml. of acrolein solution (4 per cent.); quantities of this suspension are filtered off, as required, and

the impregnated paper is added for the purpose of collecting the zinc sulphide. With amounts of zinc of the order of 0·5 to 5 mg. in the presence of 0·1 g., of cobalt, it is desirable to pass hydrogen sulphide for about 15 minutes after the first signs of precipitation are seen; the impregnated paper pulp is added, and the passage of the gas is continued for a further 40 minutes, the determination being finished off as before. Quantitative results were obtained with zinc in amounts down to 0·5 mg. S. G. C.

Separation of Beryllium in the Presence of Complex Tartrates. **H. S. Miller.** (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 221.)—Beryllium may be precipitated from complex tartrate solution by the addition of a regulated quantity of ammonia. In this way it was possible to separate beryllium fairly quantitatively from elements, such as aluminium, iron, copper and chromium, that form complex tartrates from which the hydroxide is not precipitable by ammonia. No general directions for carrying out the method are given. The precipitate of beryllium hydroxide obtained is gelatinous and is stated to suffer from the disadvantage of readily adsorbing other substance from the solution, making repeated re-precipitation necessary. S. G. C.

Phosphotungstate Colorimetric Method for the Determination of Vanadium. E. R. Wright and M. G. Mellon. (*Ind. Eng. Chem. Anal. Ed.*, 1937, **9**, 251–254.)—The reaction on which the method is based involves the addition of sodium tungstate and phosphoric acid to an acid solution containing quinquevalent vanadium, whereupon a yellow or brownish colour is produced varying in hue and intensity with the vanadium concentration (*cf.* Willard and Young, *Ind. Eng. Chem.*, 1928, **20**, 764; Abst., ANALYST, 1928, **53**, 674). The preferred concentrations of reagents in the colorimetric solution are 0·025 M sodium tungstate, 0·5 M phosphoric acid and 0·6 N nitric, sulphuric, hydrochloric or perchloric acid; the concentrations are not critical; the amount of vanadium present in 100 ml. should be between 0·02 and 10 mg. Heating the solution to boiling is necessary for the full development of colour if more than 1 mg. of vanadium is present per 100 ml. The following substances were found to have no effect on the colour (in 100 ml. volume): sodium chloride (3 g.); sodium nitrate (5 g.); magnesium, calcium, strontium, barium, zinc, cadmium, mercury, aluminium, lead, arsenic, bromine, and acetate ion (0·5 g.); beryllium (0·025 g.); silver, lithium, chlorate ion, oxalate ion, citrate ion, tartrate ion (0·1 g.); silicate ion (0·05 g.); cyanide ion (0·02 g.). Ammonium and potassium give precipitates with the phosphotungstic acid and must not be present in more than traces. The following interfere by producing a precipitate: antimony, tin, titanium and zirconium, only small amounts of these being tolerable. Molybdenum tends to interfere, when present in fairly large amount, by forming a coloured compound. Ferric iron in the form of chloride gives a brown colour.

The following method is proposed for steel:—(*a*) *Chromium–Tungsten Steels containing 0·7 to 2·0 per cent. of Vanadium.*—A 150-mg. sample is dissolved, as far as possible, in 10 ml. of hydrochloric acid (1:1), by heating. Nitric acid is added, drop by drop, in amount sufficient to oxidise iron and tungsten. Perchloric acid (7 ml. of 60 per cent. acid) is added, and the liquid is evaporated until fumes of

perchloric acid are evolved, and kept boiling for 2 to 3 minutes after the orange-red colour, due to chromic acid, has appeared. After cooling, 40 ml. of water are added, the liquid is boiled, and 5 ml. of 0·5 M lead perchlorate solution are added. The precipitate of lead chromate and tungstic acid is filtered off from the cold solution, washed with a little cold water, and rejected (the small amount of vanadium occluded in the tungstic acid is ignored in this method). To the filtrate are added 10 ml. of nitric acid (1:1), 3 ml. of phosphoric acid (90 per cent.) and 5 ml. of 0·5 M sodium tungstate solution, the solution is heated to boiling, cooled, and diluted to 100 ml. The colour is compared colorimetrically with that of a solution containing 1·5 mg. of vanadium (as sodium vanadate), the same amount of reagents and about 60 ml. of water, which has been heated to boiling, cooled and diluted to 100 ml. (*b*) *Chromium–Tungsten Steels containing* 0·1 *to* 0·7 *per cent. of Vanadium.*—A 0·5-g. sample is dissolved, as far as possible, in 20 ml. of hydrochloric acid (1:1) by heating, 0·5 ml. of nitric acid is added, the liquid is evaporated to 10 ml., 5 ml. of hydrochloric acid are added, and the liquid is transferred to a separating funnel with not more than 5 ml. of water. The bulk of the ferric chloride is extracted by means of 30 ml. of ether. The aqueous layer is heated to remove dissolved ether and evaporated to fuming with 7 ml. of 60 per cent. perchloric acid, and the method continued as in method (*a*).   S. G. C.

Determination of Potassium in Soils and Silicates. J. E. Gieseking and H. J. Snider. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 232–233.)—A new flux is proposed for effecting the decomposition of soils, clays and similar materials when potassium is to be determined. It consists of a mixture of two parts of sodium carbonate with one part of lithium carbonate, and melts between 470° C. and 480° C. Potassium is finally determined by the cobaltinitrite method. A 1-g. sample of the 100-mesh material is first heated in a platinum capsule with perchloric acid in order to destroy organic matter. After removal of the perchloric acid by heating, the residue is mixed with 8 parts of the flux and covered with a layer of it. The mixture is fused at 500° to 600° C., with the capsule covered, until bubbling has ceased. The cooled melt is dissolved, as far as possible, in 75 ml. of 4 N hydrochloric acid; the liquid is evaporated to dryness, 10 ml. of conc. perchloric acid are added and evaporated to dryness. The perchloric acid treatment is repeated with the addition of 1 ml. of conc. hydrochloric acid, and 0·5 ml. of nitric acid to assist in dehydrating the silica and to decompose any traces of ammonium salts present. The residue is digested for a few minutes with 50 ml. of 5 per cent. hydrochloric acid, and the silica is filtered off, washed with 2 N hydrochloric acid, and ignited in the original crucible; the silica is volatilised with hydrofluoric acid and a little perchloric acid, and any residue is dissolved in a little dilute hydrochloric acid and added to the main solution, in which the potassium is now determined by the cobaltinitrite method, that described by Volk and Truog (*J. Amer. Soc. Agron.*, 1934, **26**, 537) being suitable.   S. G. C.

Determination of Rare Alkalis. J. C. Hillyer. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 236.)—The author discusses the applicability of Wells and Stevens' method (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 439) to the analysis of the mineral pollucite, which contains over 30 per cent. of caesium oxide. A modified

solvent-mixture is proposed for separating the alkali chlorides. It consists of 0·4 ml. of water and 10 ml. of alcohol, both saturated with hydrogen chloride, and will dissolve the following amounts of alkali chlorides at 25° C.:—potassium chloride, 0·0006 g.; rubidium chloride, 0·0027 g.; caesium chloride, 0·024 g.   S. G. C.

Analysis of Pollucite.   R. C. Wells and R. E. Stevens.   (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 236–237.)—The authors concur in the necessity for modifying their original method in dealing with samples containing a high proportion of caesium and indicate a further procedure applicable to pollucite (*cf.* preceding Abst.). This mineral, which occurs at Tin Mountain, S. Dakota, is unique, as it is the only mineral compound of caesium found in nature.   Caesium may replace potassium in minerals, but its amount seldom exceeds a few units per cent. and usually it is absent.   S. G. C.

Determination of Silicon in Aluminium and Aluminium Alloys. H. V. Churchill, R. W. Bridges and M. F. Lee.   (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 201–202.)—In order to examine the question whether silicon is lost as hydride when aluminium alloys are dissolved in acids, a number of representative aluminium alloys in different conditions of heat-treatment were submitted to three methods for the determination of silicon, involving attack with (*a*) sulphuric-nitric-hydrochloric acid mixture, (*b*) perchloric acid, and (*c*) sodium hydroxide. The results obtained by the tri-acid and sodium hydroxide methods showed satisfactory agreement for the silicon-contents of commercial aluminium, aluminium-manganese alloy (Mn, 1·25 per cent.), straight aluminium-silicon alloy (Si, 5 per cent.) and duralumin (Mn, 0·5; Cu, 4·0; Mg, 0·5 per cent.), irrespective of heat-treatment.   Except with the material in the fully annealed condition, marked differences were found between the results of these two methods with aluminium alloys containing magnesium-silicide hardener* (*e.g.*, Mg, 0·6; Si, 1·0 per cent.).   Examples of the results obtained with such an alloy are as follow:

Heat treatment	Silicon, per cent.		
	Tri-acid method	Perchloric acid method	Sodium hydroxide method
Fully annealed	0·93	0·92	0·94
"Solution heat-treatment"	0·85	0·75	0·94
"Solution heat-treated and aged at room temperature"	0·89	0·84	0·94

There was a general trend towards low results with perchloric acid attack with all the materials tested.   It was concluded that, whilst the tri-acid method is usually satisfactory, the sodium hydroxide method should be used when aluminium-magnesium silicide alloys are analysed for silicon.   The following methods were found satisfactory at the American Aluminium Research Laboratories:

Tri-acid method.—A 1-g. sample, contained in a 250-ml. beaker, is attacked with 35 ml. of acid mixture (485 ml. of water, 115 ml. of sulphuric acid, 200 ml. of hydrochloric acid and 200 ml. of nitric acid).   When no further action is evident, the liquid is evaporated until heavy fumes of sulphuric acid are evolved, the

* *Abstractor's Note.*—The alloy silmalec is a representative of this class of alloy in this country.

heating then being continued for 15 minutes. After cooling, 10 ml. of 1 : 3 sulphuric acid and 100 ml. of hot water are added, and the mixture is heated until the metallic salts are dissolved. Some paper-pulp is added and the residue is filtered off and washed with hot water. The filtrate is evaporated again as described above, in order to recover traces of silica, which are ultimately added to the first precipitate, the combined filters being ashed in a platinum capsule and the residue ignited. The residue is fused with 1 to 8 g. of sodium carbonate, and the cooled melt is dissolved in 50 ml. of 1 : 3 sulphuric acid. The solution is evaporated, and the residue is heated for 15 minutes while dense white fumes are evolved. The cooled residue is dissolved, as far as possible, in 100 ml. of hot water, prolonged digestion being avoided to minimise re-solution of silica. After the addition of paper-pulp, the silica is filtered off, and the filtrate is evaporated as before to recover traces of silica, which are then combined with the main portion. The filters are ashed in a platinum capsule, and the residue is ignited at 1000° C., cooled and weighed. It is moistened with a few drops of dilute sulphuric acid, hydrofluoric acid is added, the liquid is evaporated to dryness, and the residue is ignited and weighed. The difference between the two weights represents silica. A blank determination on the reagents is advised.

Sodium hydroxide method.—A 0·5 to 1·0 g. sample is dissolved, in a covered Monel-metal beaker, in 15 ml. of 30 per cent. sodium hydroxide solution. The liquid is then evaporated to 5 ml. If the solution is dark in colour, 2 to 3 ml. of 3 per cent. hydrogen peroxide are added, the liquid being then re-evaporated to 5 ml. The solution and any insoluble matter are transferred to a Pyrex beaker containing 65 ml. of 1 : 1 sulphuric acid and 20 ml. of 60 per cent. perchloric acid. The silica is recovered and determined in the usual way, with re-evaporation of the filtrate and use of the hydrofluoric acid volatilisation process. An alternative process is described involving acidification of the sodium hydroxide solution with hydrochloric acid, and evaporation with perchloric acid, as published by the Aluminium Research Institute (Standard Methods for Sampling and Analysing Aluminium and certain Aluminium Alloys, 1932). (*Cf.* Callender, ANALYST, 1933, **58**, 81.)   S. G. C.

Colorimetric Determination of Silicic Acid in the presence of Iron, Phosphorus and Fluorine. I. P. Alimarin and V. S. Sverev. (*Mikrochem.*, 1937, **22**, 89–101.)—The Diénert and Wandenbulcke method (*Compt. rend.*, 1923, **176**, 1478; Abst., ANALYST, 1923, **48**, 398) which consists in comparing the yellow colour formed from silicic acid and ammonium molybdate with a standard solution has been tested under various conditions. For visual comparison the lowest concentration for accurate matching is about 1 mg. per litre, and the highest 50 mg. per litre. For the comparison, varying amounts of standard sodium silicate are treated with 2 ml. of a freshly prepared 10 per cent. solution of ammonium molybdate for every 5 mg. of silica present, and 4 drops of 50 per cent. (by vol.) sulphuric acid, to bring the pH to about 1·2–2·0. The solution is then diluted to 100 ml. The colour reaches the maximum in 10 minutes at room temperature. A more intense and constant colour is produced if the solution is heated on the water-bath for 5 minutes. The intensity obtained at 50° to 66° C. remains constant

for 24 hours. The acidity of the solution is important and should be maintained within the stated limits of pH 1·2 to 2. Excess of mineral acid may be eliminated by buffering with sodium acetate and acetic acid. Ammonium molybdate should be added before the acid; this is especially important in dilute solutions of silica. Iron, if not present in excess of 20 mg. per litre, does not interfere. To remove excess of iron the best results are attained by fusing the substance with sodium carbonate and leaching the melt with a sodium carbonate solution, all the iron remaining in the residue and all the silicic acid passing into solution. The yellow colour given by phosphates reaches its maximum at 60 mg. of P_2O_5 per litre, and disappears if the P_2O_5 content is increased beyond 100 mg. per litre. If oxalic, citric or tartaric acid is added after the colour formation the yellow colour due to phosphate is destroyed, whilst that from silicic acid persists for several hours. In the presence of phosphorus and iron it is proposed to add to the coloured solution an excess of phosphoric acid, which destroys the colour of phosphomolybdate without affecting that of silicomolybdate, and which also combines with the iron present to form a colourless undissociated phosphate. The procedure is as follows:—Sodium acetate is added to neutralise any mineral acid present, then 2 ml. of 98 per cent. acetic acid, and for every 5 mg. of silica, 10 ml. of 10 per cent. ammonium molybdate are added. The solution is heated to 50° to 60° C. for 5 minutes, and after cooling and dilution 1 ml. of phosphoric acid (sp.gr. 1·7) is added. The coloured solution is diluted to 100 ml. and compared with a standard solution of sodium silicate treated by the same method. The colour persists for 30 minutes. The influence of the fluoride ion is eliminated by introducing aluminium chloride into the solution. If the fluoride tested is insoluble in water it may be dissolved in 10 ml. of 10 per cent. aluminium chloride solution, after which the other reagents are successively added.   J. W. M.

Studies in Fluorine Distillation. D. Dahle and H. J. Wichmann. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 297–303.)—The authors' previous work on the influence of certain factors on the recovery of fluorine by distillation with sulphuric acid (*J. Assoc. Off. Agr. Chem.*, 1936, **19**, 313) is extended to include distillations with perchloric and phosphoric acids. The effect of the presence of the salts of non-volatile acids is also studied. To determine the effect of "input volume" (*i.e.* the volume of liquid present in the distillation flask when the temperature at which the distillation is to be made is reached), mixtures of perchloric acid with water giving different input volumes but containing the same amount of sodium fluoride were distilled at constant temperatures, *viz.* 125° C. and 135° C. to a constant output volume of 25 ml. The input volume was varied in two ways, *viz.* by increasing the amount of acid and by adding salts of non-volatile acids (sodium perchlorate and calcium monophosphate). The amount of fluorine present in each experiment was 0·5 mg. The effects of the two methods of changing input volume are compared, and a similar comparison is made for sulphuric acid with sodium sulphate and ammonium persulphate. From the data obtained the following conclusions are drawn. The fluorine recovery decreases with increasing input volume; the change in recovery decreases with increasing input volume; the presence of soluble salts of non-volatile acids causes a decrease in the fluorine

recovery by a greater amount than is indicated by the corresponding increase in input volume. This retarding effect of soluble salts becomes important when material low in fluorine-content is to be analysed and relatively large quantities of sample must be used. The effect of input volume is almost twice as great when perchloric or phosphoric acid is used as when sulphuric acid is used. This is of practical interest when complete recovery in the smallest possible amount of distillate is required. Perchloric and sulphuric acids cause a more rapid rate of volatilisation of fluorine than does phosphoric acid. Comparisons made at constant input volumes show that both sulphuric acid and perchloric acid are more efficient at 125° C. than phosphoric acid at 135° C. This is of practical interest in the problem of the removal of fluorine from commercial phosphoric acid, as well as in the substitution of this acid for the other acids in distillation. The effect of varying temperature is the sum of two effects working in the same direction, *viz.*, the decrease in input volume and the rise in temperature. By deducting the first-named effect, which can be estimated at least approximately, the second effect is found. Apparently the recovery is greater if the distillation is carried out at higher temperatures. The temperature effect per degree is greater when large volumes are present during distillation than with small volumes. The temperature effect at similar input volumes is about twice as great for perchloric acid as for sulphuric acid, whilst phosphoric acid occupies an intermediate position. As with fluorine distillations with sulphuric acid, the quantitative recovery varies with the amount of distillate collected in accordance with the following equation—

$$ K = \frac{1}{t} \log \frac{c}{c - x} $$

where K is a constant, t is the number of ml. of distillate collected, c is the original concentration of fluorine, and $(c - x)$ is the concentration in the residue remaining in the flask after t ml. has been distilled. If c is taken as 100, x becomes the percentage recovery in t ml. of distillate.   A. O. J.

Hydrolysis of Rock-forming Minerals. A. Bramall and J. G. C. Leetch. (*Bull. Inst. Min. and Met.*, No. 391, April, 1937.)—Finely-divided powdered minerals are found to be very hygroscopic, and in the hydrolysed form many minerals are partly soluble in water; often alkali is leached out, and a mineral differing in structure from the original mineral may be obtained. A simple method of testing the solubility of a mineral to water is to grind it up very finely and test the reaction of the powder in water. Most of the common rock-forming minerals are reactive, *e.g.* various basic micas, hornblendes and other amphiboles (including asbestos); wollastonite, diopside, hypersthene, augite, aegirite, and other pyroxenes; olivine, apatite, sphene and some varieties of tourmaline; grossularite, melanite and some varieties of almandite; members of the chlorite and epidote groups; calcite, aragonite, magnesite, dolomite; brucite and chondrolite. Sericite, hydromuscovite and true muscovite are among the less reactive species. The reactivity and hygroscopic properties of the finely-divided dust may be explained from a knowledge of the crystal structure, and throw light on the problems of solubility of fine dust (*cf.* p. 645).   J. W. M.