

INORGANIC ANALYSIS.

The Iodometric Estimation of Aluminium Hydroxide and of Free Acid in Aluminium Sulphate and Alums. S. E. Moody. (*Zeit. anorgan. Chem.*, 1907, **52**, 286-291.)—The filtered aqueous solution of 15 grams of the finely powdered material is diluted to a litre, and the insoluble matter dried at 100° C. and weighed. An aliquot portion (25 c.c.) of the filtrate is titrated with potassium permanganate solution to obtain the amount of iron in the ferrous condition. A second portion of 25 c.c. is then reduced with zinc in the usual way, and titrated with the permanganate solution; the difference between the two titrations is a measure of the amount of iron in the ferric condition. For the estimation of zinc 25 c.c. are diluted to 50 c.c., and the solution treated with 3 grams of sodium acetate and 1 c.c. of acetic acid, and electrolyzed, by means of a current of 2 ampères, for thirty minutes with a rotating cathode. The deposit, which may contain some iron, is washed with alcohol, dried, and weighed, after which it is dissolved in sulphuric acid, the solution titrated with potassium permanganate solution, and the amount of iron thus found deducted from the weight of the zinc precipitate. The amount of iodine liberated from a mixture of potassium iodide and iodate by 25 c.c. of the original solution is then determined.

The total iodine, less the amounts corresponding to the total aluminium, the

ferrie sulphate, ferrous sulphate, zinc sulphate, and ammonium sulphate, is termed the "iodine difference." If this difference be positive—

$$\text{Iodine difference} \times \left(\frac{98.08}{2 \times 126.97} \right) (0.386) = \text{free acid};$$

and if negative—

$$\text{Iodine difference} \times \left(\frac{102.2}{6 \times 126.9} \right) (0.134) = \text{free alumina.}$$

C. A. M.

Methods for the Control of the Electrolytic Refining of Copper.

H. Koch. (*Zeit. anal. Chem.*, 1907, **46**, 29-37.)—Ulke objected to the method of determining the free acid in an electrolyte by means of an ammoniacal solution of copper, owing to the end-point of the reaction being rendered uncertain by the solutions in some cases becoming turbid on standing; but the author describes a method of obviating this. The double salt— $\text{CuSO}_4 \cdot 4\text{NH}_3 + \text{H}_2\text{O}$ —reacts with 2 molecules of sulphuric acid, so that for preparing a normal solution 61.36 grams per litre are required. Owing to the moisture in the commercial salt, it was found necessary to use 65 grams, and the stability of the solution was insured by the addition of 6 grams of ammonium sulphate. The solution, prepared in this way with water boiled until quite free from carbon dioxide, kept unaltered for months, provided that the crystalline salt had been used. The addition of the ammonium sulphate has no injurious effect upon the solubility of the copper hydroxide in the titration of the acid by Kieffer's method. Details are given for the estimation of copper and arsenic.

C. A. M.

The Electrolytic Precipitation of Gold with the Use of a Rotating Anode.

J. R. Withrow. (*Journ. Amer. Chem. Soc.*, 1906, **28**, 1350-1356.)—The electrolytes used in the investigation were (1) potassium cyanide and (2) sodium sulphide. The rate of precipitation of the metal was especially studied. Using an apparatus similar to that described by Ingham (*ANALYST*, 1905, p. 67), it was found that as much as 0.5 gram of gold could be completely deposited in from ten to twelve minutes, employing a current not exceeding 10 ampères at about 10 volts, 5 grams of potassium cyanide, and a dilution of 60 c.c. On substituting 30 c.c. of sodium sulphide solution of specific gravity 1.165 for the cyanide, it was found that 0.5 gram of gold could be deposited in a period of time not exceeding twelve minutes. W. P. S.

The Volumetric Estimation of Mercury. **E. Rupp.** (*Berichte*, 1906, **39**, 3702-3704.)—The solution of the mercury salt, containing about 0.2 gram of mercury in 25 to 50 c.c., is treated with excess of potassium iodide (1 gram) so that the mercuric iodide that forms is redissolved. The liquid is next rendered alkaline with sodium hydroxide, treated with 2 or 3 c.c. of 40 per cent. formaldehyde solution diluted with 10 c.c. of water, and allowed to stand for about a minute. It is then acidified with acetic acid, 25 c.c. of $\frac{N}{10}$ iodine solution added, and the excess of free iodine titrated with $\frac{N}{10}$ sodium thiosulphate solution. The formaldehyde precipitates the mercury, which combines with the iodine to form mercuric iodide, and the excess

of iodine is titrated as described. If the mercury be in the form of mercurous salts, it must be brought into the mercuric state before precipitation. In the case of mercuric cyanide, sulphuric acid should be used instead of acetic acid for the acidification, so as to decompose any cyanogen iodide that may have been formed.

C. A. M.

On Some Reactions of Mercuric Iodide. N. A. Orlov. (*Chem. Zeit.*, 1906, 30, 1301.)—Mercuric iodide converts palladious chloride quantitatively into the iodide in methyl alcohol solution. Freshly precipitated silver chloride reacts with a methyl alcohol solution of mercuric iodide to form a yellow body, apparently a double compound of AgCl and HgI₂; no chloride passes into solution. An aqueous solution of thallous chloride precipitates the red mercuric iodide from a methyl alcohol solution of the latter, whilst an aqueous solution of bismuth chloride causes no precipitation. An aqueous solution of thallous chloride is not acted on even by a large excess of freshly precipitated silver bromide or iodide. A. G. L.

The Specific Gravity of Aqueous Solutions of Perchloric Acid. K. van Emster. (*Zeit. anorgan. Chem.*, 1907, 52, 270-280.)—The perchloric acid was prepared by distilling a mixture of solid potassium perchlorate with sulphuric acid of 96 to 97·5 per cent. strength, at a pressure of 50 to 70 mm. Redistillation under reduced pressure of the crude acid thus obtained yields pure perchloric acid, boiling between 14° and 17·3° C. under a pressure of 15 to 20 mm. The pure acid was poured immediately over chemically pure ice, or into already diluted acid, and then further diluted by suitable additions of water. The strength of each of the solutions was determined by titration with standard baryta solution, and the specific gravity by means of a Sprengel tube. The results given in detail are also plotted in the form of a curve, and for practical purposes the author has constructed a table of the corresponding values from which the following is condensed :

Specific Gravity at 15°/4° C.	HClO ₄ .	Specific Gravity at 15°/4° C.	HClO ₄ .	Specific Gravity at 15°/4° C.	HClO ₄ .	Specific Gravity at 15°/4° C.	HClO ₄ .
	Per Cent.		Per Cent.		Per Cent.		Per Cent.
1·005	1·00	1·090	14·56	1·320	42·03	1·580	63·00
1·010	1·90	1·100	16·00	1·340	43·89	1·590	63·74
1·015	2·77	1·125	19·57	1·355	45·26	1·600	64·50
1·020	3·61	1·165	24·94	1·375	47·05	1·610	65·26
1·025	4·43	1·180	26·82	1·390	48·37	1·620	66·01
1·030	5·25	1·190	28·05	1·410	50·10	1·640	67·51
1·040	6·88	1·210	30·45	1·450	53·31	1·655	68·64
1·045	7·68	1·250	34·95	1·475	55·18	1·660	69·02
1·050	8·48	1·270	37·08	1·500	57·06	1·665	69·40
1·055	9·28	1·290	39·10	1·540	60·04	1·670	69·77
1·060	10·06	1·300	40·10	1·570	62·26	1·675	70·15

C. A. M.

Preparation of Standard Sulphuric Acid. F. W. Richardson. (*Journ. Soc. Chem. Ind.*, 1907, **26**, 78.)—In the method proposed, a known quantity of the dilute acid is neutralized with barium hydroxide solution, the mixture is evaporated, and the residue of barium sulphate weighed. The procedure is as follows: 5 c.c. of the dilute sulphuric acid are weighed in a platinum basin and exactly neutralized by the addition of a filtered saturated barium hydroxide solution, phenolphthalein being used as indicator. The neutralized solution is evaporated to dryness, and the residue is ignited, at first gently and afterwards at a bright red heat. From the weight of the residue the amount of sulphuric acid may be calculated and the solution diluted to the required strength. The specific gravity of the dilute sulphuric acid serves as a check on the accuracy of the results obtained by the method given above, as does also a determination of the strength of the acid by means of the immersion refractometer (*ANALYST*, 1903, **28**, 91).

W. P. S.

Phosphotungstic Acid as a Reagent for Potassium Salts. G. C. Meyer. (*Chem. Zeit.*, 1907, **31**, 158-159.)—Phosphotungstic acid, like phosphomolybdic acid (*ANALYST*, 1907, **32**, 64), can be used as a reagent for potassium salts. Sodium phosphotungstate gives sparingly soluble precipitates with salts of potassium, ammonium and lead, but no precipitate with salts of calcium and magnesium. The potassium compound presents insuperable difficulties in filtration, but useful results may be obtained by comparative precipitations at different dilutions. The reagents employed are 20, 15, 10, 5, and 2·5 per cent. solutions of sodium phosphotungstate, which should be stored in brown bottles. The salt to be analysed (in the form of a mixture of potassium and sodium chlorides) is dissolved at a concentration of 20 grams per 100 c.c. For the test, 1 c.c. of reagent and 1 c.c. of the salt solution are placed in one of a series of shaking cylinders 10 cm. high and 8 mm. in diameter, and the mixture is shaken vigorously. In this way a series of tubes is obtained in which precipitates appear at different times with different concentrations of reagent, according to the percentage of potassium chloride in the salt mixture. This percentage can then be estimated by reference to a table prepared as the result of similar experiments with mixtures of known composition. For instance, 0·7 per cent. of potassium chloride in the salt can be detected with the 20 per cent. reagent, 1·0 per cent. can be detected with the 20 and the 10 per cent. reagents, 2·5 per cent. with the 10 and the 5 per cent. reagents, and 4·0 per cent. with the 5 and the 2·5 per cent. reagents. The time required by the precipitates to reach certain stages of density is also taken into account in comparing the results. By using a 1 per cent. solution of sodium phosphotungstate the scale can be extended with a fair degree of accuracy up to 10 per cent. of potassium chloride, but beyond that the method is inapplicable.

J. F. B.

An Absorption Compound of Basic Praseodymium Acetate and Iodine. N. A. Orlov. (*Chem. Zeit.*, 1907, **31**, 45.)—The precipitate obtained with ammonia from a solution of praseodymium acetate, as free as possible from lanthanum, gives a violet-blue colour with iodine solution and with solid iodine, resembling in this respect basic lanthanum acetate and solid potassium acetate.

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The Solubility of Potassium Permanganate. G. P. Baxter, A. C. Boylston, and R. A. Hubbard. (*Journ. Amer. Chem. Soc.*, 1906, **28**, 1336-1343.)—The following results were obtained, the figures being the averages of many concordant determinations :

Temperature (C.°).	Percentage of KMnO_4 .	Parts of KMnO_4 to 100 Parts of Water.
0	2.75	2.83
9.8	4.13	4.31
19.8	5.96	6.34
24.8	7.06	7.59
29.8	8.28	9.03
34.8	9.64	10.67
40.0	11.16	12.56
45.0	12.73	14.58
50.0	14.45	16.89
55.0	16.20	19.33
60.0	20.02	25.03

W. P. S.

Detection and Estimation of Sodium Chloride in Stannic Chloride.

P. Heermann. (*Chem. Zeit.*, 1907, **31**, 27.)—An approximation of the quantity of sodium chloride present in solutions of stannic chloride may be obtained by adding to different portions of the solution in question four or five times their volume of—(a) alcoholic hydrogen chloride, obtained by saturating 99.5 per cent. alcohol with dry hydrogen chloride; (b) fuming hydrochloric acid (specific gravity, 1.19); and (c) ordinary 96 per cent. alcohol. In a solution of 1.67 specific gravity, alcoholic hydrogen chloride will give a cloudiness after a few minutes' standing with 0.1 per cent. of sodium chloride; fuming hydrochloric acid will produce a precipitate after a few minutes with 1.0 per cent. of sodium chloride; and alcohol a precipitate] (on cooling and scratching) with 4 per cent. of sodium chloride. Five per cent. of sodium chloride is not soluble in stannic chloride of the above-mentioned concentration in the cold.

In a solution of 1.53 specific gravity, alcoholic hydrogen chloride will give a cloudiness with 0.2 per cent. of sodium chloride; fuming hydrochloric acid gives a definite cloudiness after one or two minutes with 1.5 per cent.; and alcohol gives a precipitate after several minutes with 8 per cent.

A. G. L.

The Estimation of Tungsten in Tungsten-Steel. G. v. Knorre. (*Stahl. u. Eisen*, 1906, **26**, 1489; through *Chem. Zeit. [Rep.]*, 1907, **31**, 79.)—The method is based upon the fact already recorded by the author (*Berichte*, 1895, **28**, 783) that tungstic acid is quantitatively precipitated by benzidine hydrochloride. For the determination of tungsten in tungsten steel a weighed quantity of the sample is treated with hydrochloric or sulphuric acid, with precautions to exclude air,

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and the undissolved tungsten filtered off, washed, and converted into tungsten trioxide by ignition. The contents of the crucible are next fused with sodium hydroxide, and the mass extracted with water and filtered from the iron oxide. The filtrate is rendered just acid with hydrochloric acid (methyl orange being used as indicator), and the tungsten precipitated with the benzidine solution. This is prepared by triturating 20 grams of benzidine with water, washing the mixture into a beaker with 300 to 400 c.c. of water, adding 25 c.c. of fuming hydrochloric acid (specific gravity 1.19), heating the whole, filtering, and making up to a litre. Of this solution 50 c.c. are used for the precipitation of 0.25 gram of tungsten trioxide, and the precipitate is washed with a dilute benzidine solution prepared by adding 5 to 10 volumes of water to the reagent. It is important that air should be completely excluded in preparing the solution of the sample, that too large an excess of acid should not be employed, and that the liquid should be cold before being filtered. For technical analyses the author recommends removal of the free hydrochloric acid by neutralization with sodium hydroxide (or by evaporation), followed by the addition of a little sulphuric acid or alkali sulphate before precipitation of the tungsten by the benzidine. Any oxidation after precipitation of the tungsten is negligible. When cold the precipitate is collected on a filter, washed with the dilute benzidine solution, ignited while still moist in a platinum crucible, and the residue fused with anhydrous sodium hydroxide in a platinum crucible. The mass is extracted with water, the solution filtered from the iron oxide, and the filtrate rendered just acid with hydrochloric acid, and then treated with 10 c.c. of $\frac{N}{10}$ sulphuric acid. The tungstic acid in the solution is now reprecipitated with 40 to 60 c.c. of the benzidine reagent, and the benzidine tungstate collected, washed with the dilute benzidine solution, and converted into tungsten trioxide by ignition. The presence of phosphorus in the steel does not interfere with the results.

C. A. M.

The Analysis of Zinc Ores. J. A. Muller. (*Bull. Soc. Chim.*, 1907, [iv.], 1, 61-63.)—The following method is only accurate in the absence of notable quantities of fluorine or phosphorus; but the author asserts that none of the zinc ores he has examined have contained more than traces of these elements. The sulphides precipitated from the hot hydrochloric acid solution are digested with sodium sulphide, the resulting solution acidified with dilute hydrochloric acid, and the precipitate washed successively with water, alcohol, and with a mixture in equal parts of alcohol, ether, and carbon bisulphide. It is then detached from the filter with the aid of an alcohol washing-flask, evaporated to dryness, and the residue treated with nitric acid (specific gravity 1.38) in a covered crucible. The mass is taken up with water, and the residue, after removal of the soluble portion, treated with hot *aqua regia*. Finally, tartaric acid is added to the solution, which is then rendered alkaline with ammonia and the arsenic determined as ammonium magnesium arsenate. The filtrate will still contain about 1 mgm. of the double arsenate per 20 c.c., and this arsenic is precipitated together with the antimony from the acidified solution by means of hydrogen sulphide. The antimony is then determined as sulphide, and the difference between the result and the amount of the precipitate gives the quantity of arsenic sulphide.

The sulphides insoluble in sodium sulphide solution may contain lead, copper, and cadmium. They are treated with nitric acid, the excess of which is subsequently evaporated, and the lead separated by means of sulphuric acid and alcohol. The alcoholic filtrate is evaporated to dryness, and the excess of sulphuric acid expelled by heating the residue more strongly, after which a little nitric acid is added, the solution diluted so as to contain 3·4 per cent. of free acid, and the copper separated electrolytically, the platinum basin serving as the cathode. Lastly, the liquid is treated with a little sulphuric acid, and evaporated to dryness, and the cadmium determined in the form of cadmium sulphate. Slight traces of lead, copper, and zinc may be present in this sulphate. The acid filtrate from the original hydrogen sulphide precipitation is boiled to expel dissolved gases, and the iron, aluminium, and manganese precipitated by means of hydrogen peroxide and ammonia. The mixed hydroxides are dissolved in hydrochloric acid, the solution boiled to convert the whole of the manganese into manganous chloride, and the manganese then separated from the iron and aluminium by means of ammonium succinate added to the hot, nearly neutral solution containing sodium acetate. After standing for twenty hours, the liquid is heated to about 90° C., then cooled and filtered, and the precipitate washed with water and with ammoniacal water, dried, ignited, and weighed. The aluminium is separated by fusion with potassium hydroxide in a silver crucible. The manganese in the filtrate is precipitated with hydrogen peroxide and ammonia, and determined as Mn_3O_4 . The filtrate from the iron, manganese and aluminium is boiled to expel the excess of ammonia, a little more aluminium being separated during the process. The cold filtrate is treated with a little ammonia, and the zinc precipitated with hydrogen sulphide. Lastly, calcium is determined in the form of oxalate, and magnesium by precipitation with magnesia mixture. The accuracy of the method is shown by test analyses. C. A. M.

A Delicate Test for Zinc. G. Bertrand and M. Javillier. (*Bull. Soc. Chim.*, 1907, [iv.], 1, 63-66.)—On adding ammonia in excess to a solution containing zinc and a sufficient quantity of calcium, and filtering the liquid if necessary, a clear solution is obtained which, when boiled, slowly deposits microscopic crystals of calcium zincate. This precipitate is so sparingly soluble that it enables traces of zinc present in a large amount of liquid to be concentrated into a small volume: In separating 0·001 gram of zinc, for instance, from $\frac{1}{2}$ litre of water, not less than 50 c.c. of milk of lime are added, followed by 10 to 15 per cent. of strong ammonia. The filtrate is boiled, and the crystalline deposit collected and dissolved in hydrochloric acid, the excess of which is subsequently expelled by evaporating the solution to dryness. The residue is dissolved in water, the calcium precipitated by means of ammonia and ammonium oxalate, and the zinc converted into sulphate by ignition with sulphuric acid. The zinc sulphate can then be weighed, and, if necessary, the presence of zinc confirmed. The precipitation is practically quantitative, and the reaction is capable of detecting 1 part of zinc in 5,000,000. C. A. M.

The Detection of Traces of Zinc in Commercial Alcohols. G. Guérin. (*Journ. Pharm. Chim.*, 1907, 25, 97-98.)—Commercial methyl and ethyl alcohols

frequently contain traces of zinc derived from the action of the small amount of acid they may still retain upon zinc in the vessels in which they are kept or transported. The ordinary reactions are not sensitive enough to detect this zinc without concentration of the alcohol, but slight traces are readily found by the urobilin test : From 2 to 3 c.c. of a chloroform solution of urobilin are treated with 25 to 50 c.c. of the alcohol, followed by half the quantity of water. On adding 3 or 4 drops of ammonia solution, a green fluorescence will be immediately produced in the presence of zinc, whilst the liquid will appear rose-coloured by transmitted light. The reaction is capable of detecting 0.05 mgm. of zinc.

C. A. M.