Inorganic Analysis.

Applications of Ceric Sulphate in Volumetric Analysis.   N. H. Furman. (*J. Amer. Chem. Soc.*, 1928, **50**, 755–764.)—Dilute sulphuric acid solutions of ceric sulphate were found to possess at least a moderate degree of stability, and the reaction between such solutions and a standardised ferrous sulphate solution was suitable for the accurate potentiometric determination of either ion.   The reaction is applicable to the standardisation of ceric solutions.   These may also be standardised by titrating them, while hot, with standardised oxalic acid, but the reverse reaction is not satisfactory.   A potentiometric study of the determination of cerium shows that oxidation of bismuthate or persulphate, followed by potentiometric titration with ferrous sulphate, is rapid and satisfactory.   D. G. H.

Antimony Enamels.   K. Beck and W. A. Schmidt.   (*Z. Unters. Lebensm.*, 1928, **55**, 1–24.)—Antimony trioxide or sodium antimoniate ("Leukonin") are often used as cheaper substitutes for zinc oxide in white enamels.   Antimony is detectable in such cases by the orange-yellow precipitate produced on the addition of sulphuric acid to a solution of the enamel in a 3 per cent. solution of tartaric acid, and 1 mgrm may be detected in 100 c.c. of solution, even in the presence of zinc and zirconium oxides.   The change in valency during the heating process of antimony compounds, both in the pure state and mixed in an enamel, has also been investigated for various methods of heating in order to find the most suitable solvent for the antimony, and a method is described for the accurate determination of small quantities of tri- and penta-valent antimony in the presence of one another.   For enamelled vessels of 1 litre capacity, 200 c.c. of a 3 per cent. solution of tartaric acid are used.   The solution is boiled in the vessel over a naked flame for 30 minutes, with a round-bottomed flask full of cold water as a combined cover and condenser, well shaken, and made up to a suitable volume with the tartaric acid.   (1) Fifty c.c. are then titrated with 0·001 N potassium bromate solution in the presence of 20 c.c. of hydrochloric acid (sp. gr. 1·126), and one drop of methyl orange (1:1000), till the colour disappears.   (2) This solution, or another 50 c.c. portion with 20 c.c. of acid, is then heated almost to the b.pt., 10 drops of a 10 per cent. solution of phosphotungstic acid added immediately, and then enough of a 0·1 N solution of titanium trichloride to produce a cobalt blue colour permanent for 2 minutes.   After a further 3 minutes, 2 drops of a 0·01 per cent. solution of copper sulphate are added, and, after a further 5 minutes, the red colour produced on the addition of a drop of methyl orange solution may again be removed by titration with the bromate solution.   The titrations (1) and (2), in c.c., less those given by the respective blank experiments, give the trivalent and total antimony, respectively, in 0·001 mgrm. equivalents, and this, multiplied by 0·0609, gives the amount in 50 c.c. of solution.   The potassium bromate should be recrystallised and dried at 125° C., and a 0·1 N solution (2·784 grms. per litre) standardised iodimetrically against a 0·1 N solution of potassium dichromate.

The titanium chloride solution is made from 100 c.c. of a commercial 15 per cent. solution and 200 c.c. of hydrochloric acid (sp. gr. 1·126), diluted to 1 litre.   J. G.

Determination of -SOOH (sulphinic) Group and of Ferric Iron.   S. Krishna and H. Singh. (*J. Amer. Chem. Soc.*, 1928, **50**, 792–798.)—Sulphinic acids yield insoluble ferric sulphinates and the formation is quantitative. A known volume of ferric chloride solution of definite concentration is acidified with hydrochloric acid, a known volume of the sulphinic acid added, the orange-coloured precipitate filtered off, washed, and the iron determined. The strength of the sulphinic acid is then calculated according to the equation $3R\text{SOOH} + \text{FeCl}_3 = (R\text{SOO})_3\text{Fe} + 3\text{HCl}$. Ferric iron in ferric chloride was determined by titrating a known volume of ferric chloride solution against a standard sulphinic acid solution in the presence of dilute hydrochloric acid with a dilute solution of potassium thiocyanate as external indicator. The error ranged from 0·0001 to 0·0004 grm. of ferric iron. Ferrous iron may also be determined in the presence of ferric iron and *vice versa*, and ferric ions in the presence of aluminium, chromium, nickel and cobalt.   D. G. H.

Detection and Determination of Beryllium. H. Fischer. (*Z. anal. Chem.*, 1928, **73**, 54–64.)—1.2.5.8.-Tetrahydroxyanthraquinone, which forms a bright blue lake with magnesium salts (ANALYST, 1925, **50**, 35), reacts in the same manner with beryllium, an alkaline solution of which strikes a cornflower-blue coloration with a few drops of the 0·05 per cent. dye solution in 0·25 N caustic soda ; the reagent should always be freshly made. The alkaline solution of the dye is violet. The limit of sensitiveness is 1:2,000,000 ; for the detection of small quantities it is recommended to use two test tubes, one containing the test, the other an equal volume of caustic soda of the same concentration as that in the test ; the same amount of reagent is added to each tube. The colours are compared against a white background. Alkali salts do not interfere, but ammonium salts decrease the sensitiveness. The presence of aluminate at any concentration is immaterial ; it is only necessary to increase the alkalinity of the liquor (to about 0·5 N) for large quantities. An admixture of 0·03 per cent. of beryllium in aluminium can be readily detected. Phosphoric acid, lead, zinc, and tin are likewise without influence. Cyanide does not interfere, tartrate only in so far as it depresses the sensitiveness to 1:335,000. On the other hand, the simultaneous presence of tartrates and aluminium spoils the reaction, as it causes a violet coloration ; iron should not be present in a tartrate solution in quantities exceeding 0·001 grm. per c.c. In presence of magnesium, beryllium is detected as follows : The nearly neutral solution (10 c.c.), free from aluminium and iron, is treated with about 1 grm. of ammonium chloride and a few drops of a 0·05 per cent. solution of the dye in $2N$ ammonia, next with 10 drops of strong ammonia and, during agitation, with 5 c.c. of saturated bromine water. If magnesium only is present, the colour is entirely discharged, but beryllium causes a stable violet-blue coloration ; after some time the beryllium lake flocculates. The test detects 1 part of beryllium in presence of 1000 parts of magnesium.

Determination. The principle underlying the determination is a matching of tints, not comparison of the same tint at varying intensities. Two standard solutions are required : (1) pure beryllium nitrate in 0·25 N caustic soda (0·1 grm. BeO in 1000 c.c.) ; and (2) a 0·05 per cent. solution of the dye in 0·25 N caustic soda, made on the day the determination is made. The dye solution (theoretically 0·0332 mgrm. Be per c.c.) is standardised as follows : (*A*) Ten c.c. are diluted in a conical flask with a suitable volume of 0·25 N caustic soda (*e.g* to 200 c.c.). (*B*) The solution serving as the colour standard is prepared like the preceding, but with an excess of the standard beryllium solution as well ; it has a pure blue colour. The standard beryllium solution is now added in small quantities to solution A, and a sample withdrawn after each addition and compared in a colorimeter with a sample of solution B. The sample from A is returned to the bulk before each addition of standard beryllium solution. The operations are repeated until the blue tint of B is matched by that of A. The unknown solution (0·25 N alkali) is tested by being added to another 10 c.c. of the standard dye solution, and the liquid again made up to 200 c.c. with the alkali (solution A') ; this is matched against B in precisely the same manner as A. A smaller volume of standard beryllium solution is now required to equalise the tints, from which data the unknown is calculated. The error is stated to be smaller than in most other colorimetric determinations. Its great advantage is applicability in presence of much aluminium. With more than 100 parts of aluminium, the tint of the assay does not coincide with that of the standard ; in that case a solution containing aluminium must be used as the standard. Sufficient sodium hydroxide is added to re-dissolve the alumina precipitate ; the solution is then diluted to the desired bulk with 0·25 N alkali. Alloys of copper or nickel with beryllium (3 per cent.) are analysed as follows : 0·1 grm. of sawings is dissolved in a little cold hydrochloric acid and hydrogen peroxide, and the solution evaporated to dryness on the water-bath. The residue is dissolved in a little water and treated with cyanide until the precipitate first formed has re-dissolved and the liquid is colourless. It is diluted in a graduated flask with 0·25 N caustic soda and an aliquot portion assayed colorimetrically. For the determination of beryllium in beryl, 0·2 grm. of the very finely powdered mineral is fused with sodium carbonate (twice). The melt is taken up with hydrochloric acid, and the silica rendered insoluble by evaporation. The filtrate is made up to 200 c.c. with alkali, etc., as above. The small quantity of ferric hydroxide does not interfere ; it is left to settle, and the clear liquid pipetted off for the colorimetric assay.   W. R. S.

Determination of Fluorine in Blende. L. Fresenius, K. Schroder, and M. Frommes. (*Z. anal. Chem.*, 1928, **73**, 65–69.)—A critical examination of the methods proposed led to the conclusion that Olivier's etching test (" funnel " method, *Z. anal. Chem.*, 1923, **62**, 299) is the best process for fluorine percentages of 0·05 and less. For high percentages (0·5 per cent. and more), a volatilisation method gives the best, but always low results, due to traces of moisture ; for this reason the method is not reliable for the lower percentages (ANALYST, 1923, **48**,

628). For the interval 0·5 to 0·05 per cent., the authors recommend their modification of Steiger's colorimetric method, based upon the bleaching action of fluorine upon pertitanic acid. It gives fair results even with quantities of 0·5 to 1 per cent. The sample is first submitted to the etching test, which gives an approximate figure. For the colorimetric determination, 2 grms. of the fine powder are fused with sodium peroxide and carbonate (5 grms. of each). The product is extracted with hot water, and the liquid evaporated to 50 c.c. after addition of 8 grms. of ammonium carbonate. The precipitate is filtered off and washed with hot water, the cold filtrate is acidified with an excess of 10 c.c. of sulphuric acid (1 : 1), violent stirring being avoided. The solution should remain perfectly clear ; if lead sulphate is precipitated in the acidification, the liquid should be made feebly alkaline, and filtered. For the standard, the same quantity of flux is dissolved in water and evaporated with the same amount of ammonium carbonate, etc., as with the assay sample. The solutions are placed side by side in hemispherical 500 c.c. porcelain dishes, and treated with 5 c.c. of 3 per cent. hydrogen peroxide and 5 c.c. of titanic sulphate solution (1 c.c. = 0·001 grm. TiO_2). The standard is titrated with a solution of sodium fluoride (0·0010 grm. F per c.c.) until the tint matches that of the assay. The method is stated to be sensitive to 0·0001 grm. F ; the quantity present should not exceed 0·003 to 0·004 grm. ; if it does, the liquid should be divided into halves. W. R. S.

Iodimetric Determination of Phosphorous Acid, and the Use of Sodium Hydrogen Carbonate in Iodimetry. P. Carre. (*Compt. rend.*, 1928, **186**, 436–438.)—Rupp's method of determining phosphorous acid by treating the aqueous solution with excess (5 to 15 mols.) of sodium hydrogen carbonate and excess of 0·1 N iodine solution, and, after the lapse of 90 minutes, titrating the residual iodine with sodium thiosulphate (*Ber.*, 1902, **35**, 3691), is found to give practically exact results only when the excess of iodine used is small (less than 5 c.c. of 0·1 N iodine) and the amount of sodium hydrogen carbonate less than 5 mols. (per mol. of phosphorous acid). This result is due to the fact that the action of iodine on the excess of the carbonate yields iodate, so that it is necessary to acidify the liquid with hydrochloric acid before determining the excess of iodine with thiosulphate. Moreover, during the oxidation of the phosphorous acid by the iodine, the mixture should be kept in a flask with a ground stopper, since otherwise the carbon dioxide gradually escaping entrains appreciable amounts of iodine. Similar precautions are advisable in all cases when excess of iodine is left in contact with bicarbonate, the latter being used in minimum quantity. The above method serves for the determination of free phosphorous acid when mixed with mono-esters of the acid, these remaining unoxidised by the iodine. T. H. P.