

### INORGANIC ANALYSIS.

**Potassium Dichromate as an Analytical Standard.** G. Bruhns. (*J. prakt. Chem.*, 1916, **93**, 312-338; through *J. Soc. Chem. Ind.*, 1916, **35**, 908.)—The assertion of Wagner that the dichromates have a stronger oxidising action on hydrogen iodide than chromates, and that thereby the “excess value” of the former compared with sodium chloride or other reliable analytical standard can be explained, was not confirmed. Further, the hypothesis that chromic acid has an activating action on the dissolved oxygen towards hydrogen iodide, and gives lower results if the oxygen is previously expelled from the solution by carbon dioxide, is regarded as quite unjustified, as a diminished value of only 0·012 per cent. was found, a figure which lies within the limits of experimental error. From a series of experiments on the time reaction between very dilute dichromate solutions and hydrogen iodide, the conclusion is drawn that, in order to accelerate the oxidation and prevent a subsequent liberation of iodine, it is preferable to increase the concentration of the acid rather

than that of the iodide. Thus practically correct titrations were obtained after five minutes with dilute dichromate solutions to which only 1 c.c. of  $\frac{N}{2}$  potassium iodide, but 10 c.c. of 9.2 N-sulphuric acid, or 6 N-hydrochloric acid, were added. The use of hydrochloric acid is preferable, as the same quantity of sulphuric acid causes a considerably greater after-liberation of iodine.

**Detection of Nickel in Cobalt Salts.** A. R. Middleton and H. L. Miller. (*J. Amer. Chem. Soc.*, 1916, **38**, 1705-1711.)—The sensitiveness of the dimethylglyoxime test for nickel, especially in presence of large quantities of cobalt, is greatly increased by carrying out the reaction as follows: Alkali cyanide is added to the solution of nickel and cobalt until the precipitate first formed just redissolves. The solution is heated and rotated for five minutes after the change of colour is noted, diluted with water at 85° C. to about 50 c.c., and 1 c.c. of dimethylglyoxime solution added. Silver nitrate solution is then added drop by drop until a permanent precipitate results. When dimethylglyoxime and dilute silver nitrate are thus added to a solution containing alkali salts of nickelocyanide, cobaltcyanide and a small excess only of cyanide, precipitation of silver argenticyanide removes the cyanide ion and promotes decomposition of the nickelocyanide ion, increasing the concentration of the nickelous ion, while the cobaltcyanide ion is precipitated as  $\text{Ag}_3\text{Co}(\text{CN})_6$ , or, if not precipitated, is but slightly decomposed. Comparatively little dimethylglyoxime is then sufficient to precipitate the small amount of nickel present, in part at least. One mgrm. of nickel gives an immediate pink precipitate, whilst 0.02 mgrm. gives a distinct pink precipitate within half an hour, and the sensitiveness is not decreased by the presence of 8,000 times as much cobalt as nickel.

G. C. J.

**Use of Diphenylglyoxime as Indicator in the Volumetric Estimation of Nickel by Frevert's Method.** G. L. Kelley and J. B. Conant. (*J. Ind. and Eng. Chem.*, 1916, **8**, 804-807.)—The steel (1 grm.) is dissolved in 50 c.c. of hot, dilute nitric acid (sp. gr. 1.13), or, if much chromium is present, in 60 c.c. of dilute (1:1) hydrochloric acid, followed, when solution is complete, by nitric acid, drop by drop, until effervescence ceases. To the cooled solution, 12 grms. citric acid, 20 c.c. ammonia (sp. gr. 0.9), and enough of an ammoniacal solution of dimethylglyoxime to precipitate all the nickel, are added, followed by more ammonia to distinct alkaline reaction. After an hour the nickel precipitate is filtered off on an asbestos mat, well washed with water, and then dissolved by passing a mixture of 40 c.c. hydrochloric acid and 10 c.c. nitric acid through the mat, and following this with 100 c.c. of water. The filtrate is evaporated almost to dryness, which destroys the dimethylglyoxime and reduces the concentration of ammonium salts at a later stage, which is desirable. The solution is diluted to 150 c.c., made alkaline by addition of dilute (1:3) ammonia, of which 5 c.c. should suffice, and titrated by the new method. This consists in adding a measured and more than sufficient amount of standard alkali cyanide solution, then diphenylglyoxime as indicator, and finally titrating the excess of cyanide by means of a standard nickel solution. The standard cyanide is added until the opalescence (or bluish tinge) disappears, after which

about 15 c.c. more are added. Five c.c. of the indicator are added, and the titration with nickel solution proceeded with. The indicator is prepared by moistening 1 gm. of diphenylglyoxime with alcohol, dissolving it in 100 c.c. of 5 per cent. sodium hydroxide, and diluting to 1,000 c.c. As an indicator, it is preferable to dimethylglyoxime, because the lower solubility of its nickel complex makes it unnecessary to use it in as high concentrations as is necessary with dimethylglyoxime. Five per cent. of nickel in steel can be estimated with an error not exceeding 0.03 per cent. on the steel.

G. C. J.

**Volumetric Estimation of Nitrites. B. S. Davisson.** (*J. Amer. Chem. Soc.*, 1916, **38**, 1683-1687.)—The method described and recommended is a modification of that of Chabier ("Princip. and Pract. of Agric. Analysis," 2nd ed., vol. ii., p. 474). A special conical flask with wide neck is employed. This flask has a small tube fused through the side, and then extending downwards to the bottom of the flask, where it terminates in a horizontal limb, perforated on either side by small holes. Through the large rubber stopper pass a gas outlet, two burettes, and a tap funnel. The neutral or alkaline solution to be tested is introduced into the flask and diluted to about 150 c.c. Potassium iodide (0.5 gm.) and starch solution are added, the stopper inserted and the air displaced by carbon dioxide introduced through the side-tube. The current of carbon dioxide is then moderated and 10 c.c. of 15 per cent. sulphuric acid are added. After a short time the liberated iodine is titrated with thiosulphate. The second burette holds standard nitrite solution in case the end-point with thiosulphate is overstepped. The results with pure nitrite solutions are excellent. Fair results (about 5 per cent. too low) are recorded for solutions containing soil extract rich in organic matter. It is suggested that the influence of organic matter could be corrected by boiling a second sample with acetic acid and making a blank titration, but no experiments on these lines are described.

G. C. J.

**Estimation of Silver in Protein Preparations. H. Wastenson.** (*Pharm. Post*, 1916, **49**, 187-188; through *Chem. Zentr.*, 1916, i., 810.)—For the estimation of silver in protein preparations which contain chlorides, from 0.2 to 0.5 gm. of the substance is heated with a mixture of 10 c.c. of concentrated sulphuric acid and 2 c.c. of concentrated nitric acid until nitrous fumes are no longer evolved; the mixture is then cooled, diluted with 25 c.c. of water, heated to expel the water, and then boiled for a further thirty minutes. The clear solution is again cooled, diluted with water to about 100 c.c., and titrated with  $\frac{N}{10}$  ammonium thiocyanate solution in the presence of ferric alum (see also *ANALYST*, 1914, **39**, 279). W. P. S.

**Sodium Pyrogallate as Reagent for Estimation of Oxygen. J. W. Shipley.** (*J. Amer. Chem. Soc.*, 1916, **38**, 1687-1701.)—A number of solutions were prepared containing pyrogallol, sodium hydroxide, and water, in different proportions, several of which proved superior to any solution of potassium pyrogallate as absorbents of oxygen. The most effective solution was prepared by adding 40 c.c. of water to 100 grms. of pyrogallol and adding 100 c.c. of 49 per cent. sodium hydroxide solu-

tion. This solution has five times the absorptive capacity of Anderson's best solution of potassium pyrogallate (ANALYST, 1915, 40, 409), and absorbs oxygen at least as quickly. It is too viscous for use with capillaries of less than 1.5 mm. bore, but solutions containing as little as one-fifth the proportion of pyrogallol above recommended are quite as satisfactory as the best solution of potassium pyrogallate that can be prepared. No carbon monoxide was evolved from any of the series of solutions recommended by the author, but he confirms Lewes's statement (*J. Soc. Chem. Ind.*, 1891, 10, 407) that carbon monoxide is evolved when gases rich in oxygen are brought into contact with solutions as weak in pyrogallol and alkali as those used by Lewes.

G. C. J.

**Electrolytic Estimation of Silver in Solutions of Silver Chloride in Ammonia.** E. P. Schoch and F. M. Crawford. (*J. Amer. Chem. Soc.*, 1916, 38, 1682-1683.)—The solution, containing a slight excess of ammonia and about 20 grms. of ammonium chloride, and measuring about 150 c.c., is electrolysed at room temperature with an initial amperage of 0.35, using concentric electrodes of platinum wire gauze about 25 meshes to the cm., with a wire 0.1 mm. in diameter. The total area of the cathode employed is about 90 sq. cm. The electrodes are fixed, but a mechanical agitator is provided. The voltage is kept constant (1.1 between electrodes with the author's apparatus) until the current drops to zero. When the current has fallen almost to zero the voltage is raised to 1.3 or 1.4, and electrolysis continued until a total of twenty-five to thirty minutes has elapsed. This time suffices for 0.5 gm. of silver. Without disturbing the apparatus, about 3 grms. of oxalic acid crystals are added, and enough concentrated hydrochloric acid to make the solution faintly acid to litmus-paper. Without increasing the applied voltage, electrolysis is continued for about twenty minutes. During this stage the last 0.4 per cent. or so of the metal is deposited. The beaker containing the electrolyte is then rapidly replaced by one containing distilled water, and the deposit washed with alcohol and ether and dried high above a Bunsen flame. The deposits are purer than those obtained from cyanide electrolytes.

G. C. J.

**Estimation of Thiosulphate Sulphur in Lime-Sulphur Solutions by Iodine Titration.** P. L. Blumenthal and S. D. Averitt. (*J. Amer. Chem. Soc.*, 1916, 38, 1701-1704.)—The question of the accuracy of the so-called "iodine methods" for the estimation of thiosulphates and polysulphides in commercial lime-sulphur solutions has been investigated. It is found that an excess of iodine does react with tetrathionate in neutral or faintly acid solutions, upon standing. In every iodine titration on a lime-sulphur solution a small quantity of sulphate is formed; in some lime-sulphur solutions this is the only oxidation product found. The quantity of iodine used to form sulphate in an ordinary titration does not cause an appreciable error in the estimation of thiosulphate. The iodine values obtained after decomposing polysulphides by hydrochloric acid actually represent thiosulphate, since the barium sulphate obtained from such solutions after oxidation agrees very closely with the titration values. The presence of sulphites, which would also be titrated at this point, would tend to cause high results for thiosulphate as calculated from

the iodine value. If anything, the gravimetric results for thiosulphate are a trifle higher than the titration values, which points to an absence of sulphites, although this in itself is not absolute proof of the fact. G. C. J.

**Estimation of Tungsten by Fieber's Method. Separation of Tin from Tungsten. E. Dittler and A. von Graffenried.** (*Chem. Zeit.*, 1916, **40**, 681-682.) Fieber's method (*ANALYST*, 1912, **37**, 220) was found to be reliable for the estimation of tungsten in ferrotungsten, duplicate results agreeing within 0.1 per cent. In carrying out the estimation the authors recommend that a quantity of the finely powdered substance not exceeding 0.25 gm. be treated with bromine for twenty-four hours, the mixture then treated with 10 c.c. of concentrated hydrochloric acid, evaporated nearly to dryness, and again treated with 3 c.c. of hydrochloric acid and a few c.c. of nitric acid. After two hours the mixture is diluted, the precipitate is collected, washed, ignited at a low temperature, and weighed as  $WO_3$ . This method may also be applied to the analysis of tungsten concentrates containing not more than 10 per cent. of tin, but in this case the traces of tin oxide which remain in the tungstic acid must be removed by volatilisation with ammonium chloride. For the estimation of tin in tin ores containing tungsten 1 gm. of the ore is fused with 8 grms. of sodium peroxide, the melt is dissolved in water and diluted to 500 c.c. After filtration, 250 c.c. of the solution are used for the estimation of the tungsten (by the mercurous nitrate method); a further 200 c.c. of the solution are then treated with 10 grms. of sodium phosphate and acidified. If a slight precipitate forms at this point the mixture is filtered; the precipitate may be silica, or a trace of metastannic acid, and an evaporation with hydrofluoric acid will determine whether silica is present. The solution is now boiled to decompose the peroxide, and, while still boiling, the solution is treated with hydrogen sulphide. The precipitated tin sulphide is collected, washed with dilute ammonium acetate solution, dried, ignited and weighed as  $SnO_2$ , or the tin may be estimated electrolytically. W. P. S.

**Estimation of Total Hardness (in Waters) by Potassium Palmitate. M. Tilgner.** (*Chem. Zeit.*, 1916, **40**, 675.)—After the temporary hardness of a water has been estimated by titration with hydrochloric acid, Blacher has recommended (*ANALYST*, 1913, **38**, 127) the removal of the residual carbon dioxide by means of a current of air previous to the titration of the total hardness with potassium palmitate solution. As it is difficult to determine when the whole of the carbon dioxide has been expelled, the author prefers to neutralise the dissolved carbon dioxide with  $\frac{N}{10}$  potassium hydroxide solution, using phenolphthaleïn as indicator. The solution is then titrated with potassium palmitate solution as described. It is of advantage to add a little more phenolphthaleïn solution previous to the titration with the palmitate solution. W. P. S.