

Inorganic

Colorimetric Determination of Bismuth with Dimercaptothiobiazole. A. K. Majumdar (*J. Indian Chem. Soc.*, 1944, **21**, 240-244)—Dimer-captothiobiazole gives a red ppt. with bismuth nitrate soln. If the reaction is conducted in presence of gum acacia a colour is produced by which bismuth may be detected at a limiting dilution of 1 in 6×10^6 , and which obeys Beer's law up to a concn. of 650 p.p.m. The peak of the absorption curve occurs at 470 $m\mu$. **Reagents**—Dimercaptothiobiazole (prepared and recrystallised according to Losanitsch, *J. Chem. Soc.*, 1922, **121**, 2544): 0.5% aqueous soln. Fresh solns. of freshly prepared reagent are more sensitive than fresh solns. of reagent a few months old or solns. a few days old. Gum acacia: 0.5% aqueous soln. **Method**—Add to a suitable vol. of bismuth soln., faintly acid with nitric acid, 5 ml of *N* nitric acid, 5 ml of gum soln., water, and a few drops of reagent soln. (sufficient to develop the colour fully) so that the final vol. is 20 ml. After 5 min. compare with a similarly treated standard soln. in a colorimeter, e.g., Duboscq. Excess of reagent or of gum soln. does not affect the colour. Extra gum soln. is sometimes necessary when the soln. contains large amounts of electrolytes. The following minimum quantities of other ions interfere with the determination of 0.26 mg of bismuth—Cu⁺⁺, 0.07 mg; Co⁺⁺, 2.5 mg; Ni⁺⁺, 9 mg; Cd⁺⁺, 3 mg; Pb⁺⁺, 5 mg; Hg⁺⁺, 1 mg; Ag⁺, 0.5 mg; As⁺⁺⁺, 5 mg; Sb⁺⁺⁺, 0.2 mg; Sn⁺⁺, 1 mg. At least 50 mg of Zn⁺⁺, Mn⁺⁺, Fe⁺⁺, sulphate, oxalate, tartrate, chloride, sulphite and phosphate do not interfere. The method may be applied to bismuth after separation as phenylarsonate. Notes are given of the solubility of dimercaptothiobiazole compounds of several metals in organic liquids. Separation of the bismuth by solvent extraction of the coloured compound is being studied. L. A. D.

Titration of Nickel. S. Sen (*J. Indian Chem. Soc.*, 1944, **21**, 311-312)—A volumetric procedure, useful for the analysis of non-ferrous alloys, depends on titration of an ammoniacal soln., free from copper, tin and lead, with 1% alcoholic dimethylglyoxime soln. **Method**—Dissolve 0.2 g of the sample in 50 ml of nitric acid, evaporate almost to dryness, add 50 ml of water and filter off the tin ppt. Remove copper and lead either with hydrogen sulphide or by electrolysis with platinum electrodes. Boil out hydrogen sulphide, if used, dilute to 200 ml, add 20 ml of 25% ammonium chloride soln., 10 ml of 20% citric acid soln. and 50 ml of ammonia soln. Warm to 55-60° C. for 5 min., add 5 ml of ammonia soln. and titrate with dimethylglyoxime soln. Use a filter-paper soaked in dimethylglyoxime soln. as external indicator. While any nickel remains in solution a red colour is produced which near the end-point can only be seen by transmitted light. After 3 or 4 drops more this colour is not produced, and this is taken to indicate the end-point. Standardise the dimethylglyoxime soln. against a known nickel soln. Use an automatic burette to avoid loss of alcohol by evaporation. Iron is prevented from interfering by the citric acid, although the end-point is sharper when iron is absent. Up to 40% of zinc in the alloy does not interfere. L. A. D.

Recovery of Dimethylglyoxime from Nickel Precipitate. S. Sen (*J. Indian Chem. Soc.*, 1944, **21**, 312)—Suspend the ppt. in water, or preferably alcohol, warm and pass hydrogen sulphide until cold, stirring if the gas stream is not sufficient to break up the mass. Digest under pressure for 1 hr., filter, and concentrate the filtrate to recover the dimethylglyoxime, which may then be recrystallised. L. A. D.

Rapid Volumetric Determination of Aluminium. L. T. Snyder (*Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 37-38)—In neutralised tartrate soln. the reaction $\text{Al}(\text{OH})_3 + 6\text{KF} \rightarrow \text{K}_3\text{AlF}_6 + 3\text{KOH}$ can be made the basis of a reliable and rapid acidimetric method. To the chloride soln. free from ammonium ions (0.025 to 0.13 g Al) add standard barium hydroxide soln. until there is a slight turbidity, then add 30 ml of 30% sodium potassium tartrate soln. and continue the titration to the phenolphthalein end-point. Add 30 ml of 30% potassium fluoride soln. (neutral to phenolphthalein) and titrate with 0.3 *N* hydrochloric acid until the colour does not return after 30 sec. An accuracy of ± 0.1 mg is claimed. The acid must be standardised against a soln. obtained from pure aluminium wire dissolved in carbonate-free *N* sodium hydroxide; the alkaline soln. is slightly acidified with hydrochloric acid and diluted to known volume. If primary standards are used a consistent negative error of 0.8% results. For an unexplained reason, titration with sodium hydroxide gives lower results than with barium hydroxide. Phosphate, silicate, sulphate, ammonium, and chromium interfere, whilst carbonate, chloride, potassium and sodium do not. Small amounts of copper, iron, manganese, magnesium and zinc (in a molar ratio to Al of 1 : 100) are harmless. W. R. S.

Specific Spot Test for Vanadium. G. Ashburn and J. H. Reedy (*Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 63)—Mix a drop of the test soln. with one of 85% phosphoric acid and, after a few seconds, one of 10% sodium tungstate soln.; vanadium gives a yellow to orange colour. Sensitivity 4 μg , or 8 μg in presence of 1000 parts of other metals unless the soln. is strongly coloured. The vanadium must be present as vanadate, and may be oxidised by warming with bromine if necessary. Reducing agents and strong acids interfere. The reaction may be due to the formation of a labile heteropoly acid; phosphoric acid is not essential, although it intensifies the colour while bleaching that of ferric salt. W. R. S.

Volumetric Determination of Calcium. J. J. Lingane (*Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 39-41)—The procedure consists in a direct single oxalate pptn. at controlled acidity without separation of other metals and subsequent permanganate titration. If a limestone contains organic matter, ignite 0.4 g in a platinum crucible over a blast burner. Dissolve the residue, or the original material (dolomite) in 5 ml of water and 10 ml of strong hydrochloric acid; heat to dissolve, dilute to ca. 50 ml, heat almost to boiling, and filter 100 ml of hot 5% ammonium oxalate soln. into the assay soln. Add methyl orange and ppt. by dropwise addition of diluted ammonia (1+1), with continuous stirring over a period of 5 to 10 min. until the tint is pinkish-yellow ($\text{pH } 4 \pm 0.3$). Set aside to settle for 20 to 30 min., collect the ppt. in a Gooch crucible, and wash thoroughly with 8 to 10

small portions of ice-cold water (not over 100 ml). Return the crucible to the pptn. vessel, add *ca.* 100 ml of water and 5 to 6 ml of strong sulphuric acid, and titrate at 90° C. with permanganate standardised against 0.3 g of sodium oxalate dried at 110° C. A duplicate determination can be made within 2 hr. Ferric oxide and alumina (0.1 g) do not interfere, but 0.2 g causes a positive error of 0.5%. There is no interference from 0.5 g of phosphorus pentoxide. If the amount of manganese exceeds 2 mg, it is co-pptd. and causes a positive error which is not proportional to the total amount present. Titanium gives slightly high results and the error is not eliminated by its pptn. as phosphate, but the normal small amount of titanium present in calcareous materials will not cause a material error.

W. R. S.

Fractionations in the Rare-Earth Group by Means of Sodium Sulphate. T. Moeller and H. E. Kremers (*Ind. Eng. Chem., Anal. Ed.*, 1945, 17, 44-45)—Sodium sulphate, a familiar group-reagent, is capable of effecting a convenient concentration of the terbium and yttrium earths by systematic fractionation. The authors heat the filtrate from double-sulphate ppts. produced in the cold, whereby a further fraction is obtained. In the last stages, however, when the cerium group is eliminated and the fractions become small, only one pptn., from hot soln., is carried out. Monazite residues (1710 g; 5% of yttrium earths) were added to hot strong nitric acid and the soln. was filtered, which eliminated *ca.* one-third of the ceria as an insoluble basic salt. The cold filtrate, diluted to contain 8.5% of oxides, was pptd. by slow addition of powdered sodium sulphate until the neodymium absorption bands in the mother-liquor became almost invisible. The ppt., containing 1230 g of earths almost free from yttria, was discarded. The filtrate was heated, yielding 208 g of earths in a secondary ppt., and a filtrate from which 55 g of earths were recovered by means of oxalic acid. These oxides were separated into 5 main fractions by pptn. with sodium sulphate from cold 10% nitrate soln. and heating of the mother liquors, each fraction being re-treated. In this way 65 fractionations were made in series of 2 to 5 fractions, those from the insoluble end being discarded when the yttria dropped below 15%, and those from the soluble end when the resulting oxides were almost colourless. Serial re-pptn. of the first main fraction gave 2 fractions and a mother-liquor containing the terbium earths with a few % of cerium earths and less than 15% of yttria; total weight 35 g, average atomic weight *ca.* 150. The 3rd, 4th and 5th main fractions yielded 6 fractions free from cerium earths, containing 95 to 99% of yttrium earths; balance terbium earths; total weight 66 g, average atomic weight 95. The oxides were recovered from the double-sulphate ppts. by solution in 10% ammonium acetate soln. and pptn. as oxalates. Fractions were combined on the basis of analyses. The latter involved determination of the average atomic weight (ANALYST, 1944, 69, 30) and absorption spectrophotometry in the range 400 to 700 $m\mu$ of nitrate solns., with an instrument calibrated against the pure oxides. Praseodymia, neodymia, samaria, erbia and holmia were estimated from absorption data, and yttria from the average atomic weight after estimation of the coloured earths. The terbium earths with dysprosia were estimated like yttria and reported together; lanthana by difference.

W. R. S.