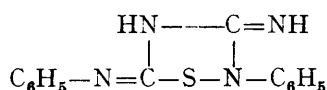


## Inorganic Analysis.

**Detection of Carbon Disulphide.** F. Feigl and K. Weisselberg. (*Z. anal. Chem.*, 1931, 83, 93–104.)—The methods for the detection of carbon disulphide were re-investigated and compared. The most sensitive of the published tests is the precipitation of cuprous xanthate. Two new tests are described: (I) Hector's base,



is derived from phenylthiourea by oxidation with hydrogen peroxide. When a solution containing carbon disulphide is treated with the base and a few crystals of nickel acetate and gently warmed, a violet-red precipitate is produced, or a pink coloration, according to quantity. If the nickel salt is insoluble in the liquid to be tested, 5 to 10 drops of water are also added. The reaction is exceedingly sensitive, still more so if volatilisation is prevented by working in a closed tube. The precipitate has the composition  $\text{C}_{30}\text{H}_{22}\text{N}_8\text{S}_6\text{Ni}$ . (II) The formation of lead sulphide in an alkaline lead solution is considerably hastened by the presence of formaldehyde: one drop of the test solution, 2 to 3 of formalin, and one of plumbite solution are stirred together on a spot plate. A darkening occurs in a few seconds. If hydrogen sulphide is thought to be present, the drop to be tested is first treated with bromine water till yellow, after which a tiny crystal of sodium sulphite is

stirred in to effect decolorisation. Working with larger quantities in a test tube allows of the detection of smaller quantities of carbon disulphide. If the liquid is immiscible with water, a ring of lead sulphide will be formed at the zone of contact.

W. R. S.

**Cobaltic Sulphate as an Oxidising Agent.** S. Swann and T. S. Xanthakos. (*J. Amer. Chem. Soc.*, 1931, **53**, 400–404.)—A study has been made of the preparation of cobaltic sulphate by electrolytic oxidation of cobaltous sulphate, and its use as an analytical reagent for the wet oxidation of certain organic compounds to carbon dioxide. For the preparation of cobaltic sulphate a saturated solution of cobaltous sulphate in 10 *N* sulphuric acid, contained in a porous cell which dipped into a beaker containing the same liquid, was oxidised anodically, using an anode of platinum sheet, a sheet of copper surrounding the porous cell serving as the cathode. A good yield of cobaltic sulphate was obtained by electrolysis for about 4 hours with an anode current density of 0.01–0.2 amp. per sq. cm., provided that the temperature was kept below 10° C. by cooling the electrolyte vessel in ice. The cobaltic sulphate was not isolated in the tests of its oxidising power on organic compounds; the suspension of the solid in sulphuric acid, which was the product of the electrolytic preparation, was used. The organic compound was stirred mechanically with an excess of this product for an hour at the ordinary temperature in a three-necked flask, which was fitted with an absorption train for carbon dioxide; air was then aspirated for half an hour through the apparatus, while the flask was heated on a water-bath. By this means it was found that, whereas amylenes, benzene and glycerin gave no carbon dioxide, and acetic acid, ethyl alcohol and acetone gave only a little, formic acid, tartaric acid, citric acid and malic acid gave the theoretical yield. Ethylene glycol gave a 96.05 per cent. yield of carbon dioxide. Formic acid remained unoxidised in the presence of amylene and glycerin.

S. G. C.

**Study of Spacu's Reaction. Volumetric Determination of Copper.** J. Golse. (*Bull. Soc. Chim.*, 1931, **49**, 85–100.)—The author has studied Spacu's reaction (the precipitation of copper as cupric pyridine thiocyanate by the addition of pyridine and an alkali thiocyanate) with a view to making it the basis of a volumetric method of determination of copper. The methods proposed involve the precipitation of the copper by the addition of a regulated excess of the reagents, filtering off the precipitate, and determining the uncombined thiocyanate ions remaining in the solution, either (*a*) by precipitation by a known quantity of silver nitrate, the excess of which is determined by titration with standard ammonium thiocyanate, using iron alum as indicator; or (*b*) by oxidation with a known quantity of sodium hypochlorite, the unused excess of which is determined by addition of potassium iodide and titration of the liberated iodine with sodium thiosulphate. Even under the most favourable conditions which could be found, a certain proportion of the copper—about 2 per cent.—remained unprecipitated, and this necessitates the application of empirical corrections in the calculation of the amount of copper from the quantity of volumetric solution employed. The

methods, as so far worked out, cover the determination of copper in pure copper sulphate solutions only over a limited range of concentration, and they break down in presence of zinc, nickel, etc., owing to the pyridine thiocyanates of these metals being insoluble. On account of these limitations the details of the methods are not abstracted.

S. G. C.

**Separation of Beryllium from Aluminium.** A. Travers and Schnoutka. (*Compt. rend.*, 1931, **192**, 285–287.)—The following modification of the method of Berthier was used for the separation of the two metals and the extraction of beryllia from beryl: the freshly-precipitated hydroxides are dissolved in excess of alkali, the solution saturated with sulphur dioxide and boiled for 10 minutes, and left in the cold for some hours. The alumina is quantitatively precipitated, occluding a little beryllia. The precipitate is, therefore, re-treated, when it yields nearly all the remaining (“*la presque totalité*”) beryllia. The advantages claimed are, that the alumina precipitation is quantitative, and that a high yield is secured in the extraction of beryllia from the mineral. No numerical data establishing the completeness of the separation are given.

W. R. S.

**Rapid Colorimetric Estimation of Potassium.** E. R. Caley. (*J. Amer. Chem. Soc.*, 1931, **53**, 539–545).—The following method is proposed for the determination of amounts of potassium between 0.01 and 0.001 grm.; it depends on the precipitation of potassium as picrate, which is separated, dissolved in water, and the yellow solution thus obtained matched colorimetrically: The solution containing the potassium as chloride (sulphates must be absent) is evaporated to dryness in a 25 c.c. beaker, the residue is dissolved in 1 c.c. of water, and 7.5 c.c. of a saturated solution of picric acid in 95 per cent. alcohol are added. The liquid is stirred until a precipitate forms, and kept for 40 minutes, with stirring at 5-minute intervals, the beaker being placed in a dish containing water at 20° C., to maintain a definite temperature during the precipitation. The potassium picrate is filtered off on a sintered glass filtering funnel having a medium porosity (filter paper will not do), and the precipitate is washed with successive 1–2 c.c. portions of ether until the washings are colourless. The ether having been removed by drawing air through the funnel, the precipitate is dissolved by pouring several successive quantities of water through the funnel, the solution being received in a 50 c.c. volumetric flask. The intensity of colour of the solution is compared in a plunger-type colorimeter with that of a standard solution of potassium picrate, containing practically the same amount of potassium as is being determined, prepared by submitting a measured volume of standard potassium chloride solution (1.907 grm. KCl per litre; 1 c.c. = 0.0010 grm. K) to the same procedure. This condition can be fulfilled only by preparing a range of standards, and choosing the one which is nearest to the unknown in colour for the final matching in the colorimeter; the standards keep well if protected from evaporation. The range of standards is called for to compensate for the solubility of potassium picrate. The method breaks down for amounts of potassium below 0.001 grm. Ammonium,

caesium and rubidium give insoluble picrates just like that of potassium. More than 0.007 grm. of sodium gave high results in the determination of 0.001 to 0.005 grm. of potassium. The presence of 0.005 grm. of lithium, magnesium, calcium, barium, strontium, aluminium or ferric iron caused no interference.

S. G. C.

**Decomposition of Refractory Silicates by Fused Ammonium Fluoride and its Application to the Determination of Silica in Glass Sands.** A. C. Shead and G. F. Smith. (*J. Amer. Chem. Soc.*, 1931, 53, 483–486.)—Berzelius noted the fusibility of ammonium fluoride, and Rose and Jannasch had independently employed ammonium fluoride for decomposing silicates, but, it is here suggested in such a way as to obscure the peculiar advantages of the reagent. The following process was tested with good results on two samples of glass sand, the silica content of which was known: The sample is thoroughly mixed with 5 grms. of crystalline ammonium fluoride in a weighed 25 ml. platinum crucible provided with a well-fitting lid. The crucible is placed in a hole through a heavy asbestos board so that about one-third of the surface of the crucible projects underneath. This part is maintained at a dull red heat for about 10 minutes. Experience showed that about 1 grm. of quartz (passing one hundred mesh sieve) should be volatilised within this time, but that a repetition of the process is necessary to complete the decomposition. Towards the end of the fume evolution, the burner is held in the hand with the flame impinging on the lid; this causes the detachment of the deposit of ammonium salt, which falls into the crucible, carrying with it any residue which may have been projected upwards during the decomposition. Before the crucible is allowed finally to come to redness, after the fluoride has been volatilised, it is recommended to add a drop or two of concentrated sulphuric acid, or a few fragments of ammonium persulphate, to prevent the escape of traces of aluminium or iron as halide. The residue is weighed, the loss in weight being due to silica.

S. G. C.

## Gas Analysis.

**Analysis of Mixtures of Hydrogen, Methane and Ethane.** O. J. Walker and S. N. Shukla. (*J. Chem. Soc.*, 1931, 368–370.)—The method depends on the removal of ethane by condensation (cf. *Trans. Faraday Soc.*, 1931, 27, 35), and of hydrogen by absorption on palladium. The apparatus consists of a Topley pump connected through a 3-way tap to (1) a U-tube which may be cooled in a vacuum vessel with liquid air, and (2) a steam-jacketed palladium absorption-tube containing 3 grms. of palladium-sponge. Each of these 2 tubes is connected also to a train consisting of a mercury-trap, a transferring-pipette, and a bent capillary tube dipping into a mercury trough. The mixture (5 to 10 c.c.) is measured in a Bone and Wheeler burette and transferred, by means of a small tube inverted over mercury in a crucible, to the capillary tube at the end of the apparatus nearest the U-tube (1), and thence to the latter by manipulating the pump and the transferring pipette. After 5 minutes at the temperature of

liquid air the residual hydrogen and methane are removed and measured (the absorption giving the ethane), and passed to the palladium-tube, where they are heated for 20 minutes at 100° C. The steam is then replaced by cold water, and the residual gas measured to determine the hydrogen. A complete analysis takes 1½ hours, and the mean errors for mixtures containing ethane (10 to 45), hydrogen (31 to 64), and methane (16 to 50 per cent.) were  $\pm 0.8$ , 1.1 and 2.6 per cent., respectively. The percentage by volume found for any constituent seldom differs by more than 1 per cent. from the amount taken. Owing to the small volume of sample, no error arises from solution of methane in the condensed ethane (cf. Mulders and Scheffer, *Rec. trav. Chim. Pays Bas*, 1930, **49**, 1057), but a check is provided if the methane and ethane are freed from hydrogen and exploded separately, and the ratio *contraction after explosion/contraction after absorption* in potassium hydroxide solution determined. This is essential if nitrogen is present.

J. G.

## Microchemical.

**Micro-Chemical Tests for Benzoic Acid, Salicylic Acid and Esters of *p*-Hydroxybenzoic Acid in Food and Drugs.** R. Fischer and F. Stauder. (*Mikrochem.*, 1930, **7**, 330–338.)—The analysis is carried out on 1 to 2 grms. of material, such as jam, fruit juice, preserved vegetable, or syrup, which may contain 0.05–0.1 per cent. of the preservative to be identified. The material is acidified with hydrochloric acid, and, if the consistence is too thick, diluted with hot water. Fats are melted and digested with 2 to 3 c.c. of dilute sodium bicarbonate solution, and then the aqueous solution is poured off and acidified. The acid solution is extracted with a few c.c. of ether, and the ethereal solution is transferred, drop by drop, to a sublimation tube in a paraffin bath at a temperature not higher than 50° C. The different compounds are then separated by fractional sublimation, and the sublimates are identified by their crystalline form, their reactions, or melting points.

J. W. B.