

INORGANIC ANALYSIS.

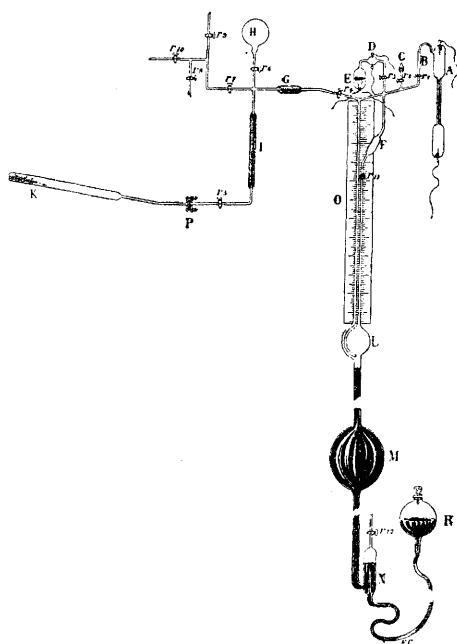
Detection of Bromides in Presence of Thiocyanates and Ferrocyanides : Action of Chromic Acid on Cyanogen Bromide. I. Guareschi. (*Zeitsch. anal. Chem.*, 1914, **53**, 490-495.)—The author has previously described a very sensitive reaction for bromine, depending on its liberation from its compounds by

means of chromic acid and its subsequent action in restoring the colour to fuchsin which has been decolorised by treatment with sulphurous acid (ANALYST, 1913, 38, 118, 518). This fails in presence of thiocyanates, if comparatively dilute chromic acid solution is added to the solution of bromide and thiocyanate. Under certain conditions, however, the test will detect 0.5 mgrm. of bromide in presence of 1 grm. of thiocyanate. For example, if 10 c.c. of 50 per cent. chromic acid be added slowly (on account of the violent reaction) to a mixture of solid potassium thiocyanate containing a trace of potassium bromide, and the mixture heated to incipient boiling, and a current of air then passed through it, sufficient bromine will accompany the air to affect a strip of paper treated with the fuchsin reagent. In the case of ammonium salts, the reaction with 50 per cent., or even 25 per cent., chromic acid is too violent, and it is better to use a large excess of 5 to 10 per cent. acid. Directions are given for the detection of traces of bromide in presence of the thiocyanates of silver and mercury and in presence of very large quantities of ferrocyanides. The test as originally described suffices when the ferrocyanide-bromide ratio does not exceed 1000 : 1. Cyanogen bromide itself is readily decomposed by chromic acid with liberation of bromine, the reaction being almost instantaneous with chromic acid concentrations above 15 per cent. With weaker acid it proceeds much more slowly, but a concentration as low as 0.2 per cent. suffices to bring it about.

G. C. J.

Analysis of Very Small Quantities of Gas : Application to Air Analysis. P. A. Guye and F. E. E. Germann.

(*Comptes rend.*, 1914, 159, 154-157.)—The principle of the method is the measurement of the pressure at which the sample (0.25 c.c. or less at *N. T. P.*) fills an apparatus of some 25 c.c. capacity, and the redetermination of this pressure after the sample has been subjected to the action of appropriate absorbents, etc. The method was first devised for studying the gases occluded in rocks, and the apparatus *K* represents a tube in which such rock can be heated and subjected to reduced pressure by means of the pump *R*, *N*, *M*. The dimensions of *K*, *I*, *G*, and *L*, are such that the space from r_4 to a mark below *L* is just equal to the space to the left of r_4 . The gas to the right of r_4 , half that in the sample, is usually taken for analysis, although nearly the whole could, if necessary, be drawn over by means of the pump. The initial pressure, preferably about 7 to 8 mm., is read, like subsequent pressures,



to within 0.01 mm. by means of the MacLeod gauge O , L , r_{11} . The manner in which the gas can be brought into contact with appropriate absorbents, etc., in A , B , C , D , etc., is clear from the drawing. For the authors' purposes, E contained an iron spiral, with electrical connections for raising it to such a temperature as is requisite to make it function as an absorber of oxygen. C contained potash, D platinum electrodes for sparking with oxygen or hydrogen, and B gold leaf to absorb mercury vapour, which would otherwise attack the aluminium electrodes of the Plücker tube A , which serves for the spectroscopic examination of the gas residue. It is suggested that the apparatus would be useful for the analysis of air from high altitudes of which it is difficult to obtain large samples. G. C. J.

Commercial Copper Sulphate. F. Mach and P. Lederle. (*Landw. Vers.-Stat.*, 1914, **84**, 129-143; through *Chem. Zentralbl.*, 1914, II., 352-353.)—In all cases the sum of the constituents amounted to somewhat more than 100 per cent.; possibly the fact that the copper was estimated electrolytically introduced a slight error. One sample examined contained 1.2 per cent. of manganese sulphate. Powdered copper sulphates examined not unfrequently contained considerable quantities (12 to 15 per cent.) of ferrous sulphate. The method described by Windisch (*ANALYST*, 1913, **38**, 75; see also p. 520) is suitable for the rapid estimation of copper, but tends to yield low results. Moser's method of estimating copper (*ANALYST*, 1912, **37**, 516) by titration with titanous chloride is trustworthy.

W. P. S.

Gas Analysis by Fractional Distillation at Low Temperatures. G. A. Burrell and F. M. Seibert. (*J. Amer. Chem. Soc.*, 1914, **36**, 1537-1548.)—A development of the method of Lebeau and Damiens (*ANALYST*, 1913, **38**, 121, 276). These authors obtained three fractions, one containing the whole of the hydrogen and methane and nothing else, another containing the whole of the ethane with some propane, and the third containing the rest of the propane with any butanes. The eudiometric analysis of these mixtures of only two gases was then easy. The present authors make a sharp separation of methane, ethane, and propane by fractional distillation, analysis of the separated gases by slow combustion showing that they were of 99.9 per cent. purity, and that the residual fraction in the case of natural gas was mainly butane. Methane is distilled at -185°C . (63 mm.). The distillate is always pure methane, but the residue, on being allowed to attain the gaseous state, then being liquefied and again distilled at -185°C . (63 mm.), usually yields about 1 per cent. more methane. The chief separation of ethane is effected as follows: The liquid is surrounded by a bath of "wild" gasoline, cooled by means of liquid air to -140°C . "Wild" gasoline is the condensate obtained from some natural gases by compressing them to 250 lbs./in.², and then cooling to air temperature, and remains quite fluid at low temperatures, unlike ether, etc. With the apparatus described and illustrated in the paper, the temperature of the "wild" gasoline bath rises about 5°C . to 10°C . per hour, after the surrounding liquid air has all evaporated, and it is allowed to rise to -125°C ., whilst the gas to be analysed is gradually deprived of nearly all its ethane and some propane by means of the pump, the

pressure finally falling to about 3 mm. Both distillate and residue are refractionated, the former after liquefaction, the latter after being allowed to attain the gaseous state and being reliquefied. The combined distillates now contain the whole of the ethane, but require to be fractionated twice more, at -155° to -140° C. and at -145° C., to eliminate the last of the propane. A still greater number of fractionations is necessary to obtain the propane free from butane, the temperature and pressure of separation ranging from -135° C. at 0.1 mm. to -110° C. at 1 mm.

G. C. J.

Permanganate Titration of Iron in Presence of Chlorides. O. L. Barnebey. (*J. Amer. Chem. Soc.*, 1914, **36**, 1429-1448).—The author finds that the Zimmerman-Reinhardt method gives exact results, and suggests that the small constant error found by Jones and Jeffery (*ANALYST*, 1909, **34**, 306) was due to a trace of iron in their stannous chloride. When titrating small amounts of iron in a volume of 400 to 600 c.c., the use of phosphoric acid, as directed by Reinhardt, is unnecessary, provided sufficient sulphuric acid and manganese are present. In general, the disturbing action of hydrochloric acid is inhibited if the volume of Reinhardt solution taken is equal to the volume of hydrochloric acid (sp. gr. 1.1) present. These were the proportions recommended by Jones and Jeffery (*loc. cit.*), and the statement of these authors is confirmed that the use of an unnecessary excess of stannous chloride, with subsequent formation of a notable amount of mercurous chloride, tends to give high results. Certain neutral sulphates and acid phosphate mixtures react with hydrochloric acid and prevent the latter from causing high results in the iron titration, acid phosphate solutions being especially serviceable, and such mixtures may replace Reinhardt's solution. The author discusses the various theories that have been brought forward to explain the function of manganese salts in the titration of iron with permanganate, citing some thirty papers, and expresses the opinion that Birch's view (*Chem. News*, 1909, **99**, 61; *ANALYST*, 1909, **34**, 315), that MnCl_2 is formed, is deserving of more general consideration than has been accorded it by subsequent authors.

G. C. J.

Note by Abstractor.—The results of Jones and Jeffery cannot be explained by the presence of iron in their stannous chloride, as this would not have introduced a constant error, widely varying amounts of stannous chloride having been used.

Analysis of Pyrophoric Alloys of Cerium and Iron. H. Arnold. (*Zeitsch. anal. Chem.*, 1914, **53**, 496-503).—In the analysis of these alloys it has been usual to separate the cerium earths first as oxalates, and then, after destruction of oxalic acid, to precipitate iron with ammonia. Often the percentage of iron is the figure most needed or the only figure required, as many of these alloys contain little besides iron and metals of the cerium group (Ce, La, Di, etc.), and as the sole object of analysis is sometimes to determine whether or not the alloy infringes Auer's patent for alloys of cerium metals with 30 per cent. or more of iron. The above method is slow, as the separation of the cerium metals as oxalates is not even approximately quantitative unless twelve hours or more be allowed before filtration, and the

subsequent iron oxide precipitate is invariably contaminated with cerium earths, the final separation of which is a very tedious operation.

The author has tried various methods for the direct determination of iron, to be followed, if necessary, by the estimation of the other constituents of the alloy. He recommends precipitation of iron as sulphide by addition of ammonia and ammonium sulphide to a tartaric acid solution. The alloy is covered with water and dissolved by means of hydrochloric acid and bromine, the latter preventing loss of silicon as hydride. Silica is separated in the usual manner, a little potassium chloride being added before evaporation to prevent volatilisation of antimony chloride during baking. The filtrate from the silica has 3 to 5 grms. tartaric acid added to it, and is then poured into 50 c.c. of strong ammonia and heated to about 60° C. Ammonium sulphide solution (15 to 30 c.c.) is added slowly, with constant stirring, and the mixture is kept covered on the water-bath for one and a half to two hours. The precipitate, which often contains notable amounts of copper, and occasionally some zinc as well as iron, is filtered through a dense filter, with the usual precautions against oxidation, and washed some fifteen times with a warm solution of ammonium sulphide containing ammonia and ammonium tartrate. If zinc is present, the filter must be treated with nitric acid before ignition to avoid loss by volatilisation. If the percentage of iron alone is required, the precipitate is dissolved in hydrochloric acid, with addition of potassium chlorate, and the iron estimated volumetrically. As copper up to 5 per cent. is present in some alloys, however, it will often be necessary to ignite and dissolve the precipitate in hydrochloric acid, and separate copper as sulphide in acid solution. Iron is then separated from any zinc in the usual manner. If manganese is present, the iron in the sulphide precipitate is best separated from accompanying metals by an ether separation of the chlorides. The filtrate from the sulphides should throw no further precipitate on standing one to two hours. If left overnight, it should have more ammonia added to it, and be covered to prevent any ambiguity due to separation of sulphur. The tartaric acid in the filtrate is best destroyed by heating the concentrated solution for an hour on the sandbath, with 10 c.c. nitric acid and 2 grms. potassium chlorate. The mixture is then evaporated to dryness, the residue taken up with a further 10 c.c. of acid, and, after addition of 1 gm. potassium chlorate, heated on the sandbath another fifteen to thirty minutes. The nearly dry residue is largely diluted, and the cerium earths precipitated by means of oxalic acid, and filtered off after twelve hours. In the filtrate, oxalic acid is destroyed by means of nitric acid, and any antimony precipitated as sulphide. In the filtrate from the antimony, aluminium is precipitated by means of ammonia.

G. C. J.

Determination of Iron in Presence of Phosphoric Acid. C. E. Corfield and W. R. Pratt. (*Brit. Pharm. Conference*, 1914, 19.)—Attempts to evolve an accurate gravimetric method for the determination of iron in presence of phosphoric acid failed. In investigating volumetric methods it was found that phosphoric acid retards the reduction of ferric salts and the liberation of iodine from hydriodic acid by ferric salts, rendering these methods tedious. Methods involving reduction by zinc are inaccurate apart from the presence of phosphoric acid, since the end-point

is obscured by the zinc salts; in dilute solution the blue ferrous ferricyanide is prevented from forming, and in concentrated solutions is obscured by the zinc ferricyanide. Reduction by amalgamated aluminium, tin, and stannous chloride gave good results. The stannous chloride method is recommended. O. E. M.

Manganese Sulphide and the Estimation of Manganese. A. Villiers. (*Comptes rend.*, 1914, 159, 67-70.)—The dense green form of manganese sulphide is most easy to filter and wash. The conditions requisite to insure precipitation of manganese in this state appear to differ from those which insure the formation of other metallic sulphides in a dense, easily filtered form. This is said to be due to the fact that the pink sulphide exists in at least two states, the least dense of which is readily converted into the green, crystalline sulphide, whilst the denser pink sulphide is quite stable even at 100° C. The directions usually given for precipitating manganese as the green sulphide are to make the precipitation at a temperature near 100° C., and to add ammonia after adding ammonium sulphide. The author finds that under certain conditions the precipitation may be made in the cold and without the presence of excess of ammonia, but when ammonia must be added—and this will usually be the case in ordinary analytical practice—it should be added before the ammonium sulphide. The green sulphide can always be obtained by making the solution strongly ammoniacal, heating to 100° C., and then adding ammonium sulphide. The transformation is complete in seven to eight minutes. In absence of other salts, such as ammonium salts resulting from the neutralisation of acids, or in presence of very large quantities of such salts, the precipitation may be effected in neutral solution. In absence of ammonia, however, moderate saline concentrations induce the formation of the stable pink sulphide, which cannot be transformed into the green modification by subsequent addition of ammonia and boiling. In very dilute, neutral solutions, free from foreign salts, the green sulphide may be obtained even at room temperature. The precipitate is then grey at first, becoming greenish in ten minutes, and quite green in twenty minutes, the transformation being complete in forty-five minutes. G. C. J.

Nickel Cooking-Vessels. M. Vuk. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1914, 28, 103-104.)—In view of contradictory statements as to the liability of nickel vessels to attack food substances by acid, the author has carried out a number of experiments, and finds the degree to which the vessels are attacked by dilute acetic acid depends on the character of the nickel used in making the vessels. The following quantities per sq. dm. were dissolved when different grades of nickel plate were heated on a boiling water-bath with 5 per cent. acetic acid for two and a half hours; rolled nickel, 16 mgrms.; cast nickel, 28 mgrms.; electrolytic nickel, 31 mgrms.; drawn nickel, 39 mgrms.; "pure" nickel, 65 mgrms. W. P. S.

Volumetric Estimation of Small Quantities of Potash. L. Zaleski. (*Landw. Vers.-Stat.*, 1913, 83, 221-255; through *Chem. Zentralbl.*, 1914, I., 2121.)—The author has tested the method described by Mitscherlich (*ANALYST*, 1912, 37,

588). Since in this process the evaporation of the liquid containing the potassium cobaltinitrite is objectionable, he has endeavoured to modify the method in such a way as to precipitate the potassium nitrite directly in the solution in presence of nitric acid with the reagent recommended by de Koninck (*ANALYST*, 1909, **34**, 114) for the detection of potassium. In order to obtain the best results possible by this modified method, the precipitation must be effected by a considerable excess of the reagent (0.5 to 1.0 c.c. for each 1 mgrm. of K_2O). The necessary quantity of the reagent is added slowly while stirring, and the precipitate filtered off after twelve to twenty-four hours. The potash-factor is determined at the same time and under the same conditions. Neither Mitscherlich's method nor the modification now described is quite accurate. By close adherence to all necessary conditions, however, very satisfactory results can be obtained by both methods. The Mitscherlich method presents certain difficulties, and the author's modification affords a simpler means for arriving at results of the same degree of accuracy.

J. F. B.

Quantitative Determination of Radium Emanation in the Atmosphere, and its Variation with Altitude and Meteorological Conditions. J. R. Wright and O. F. Smith. (*Philippine J. of Science*, 1914, **9** A, 53-76).—The method employed was essentially identical with that of Eve and Satterly (*Phil. Mag.*, 1907, **14**, 724; 1908, **16**, 584, 622), large quantities of air being drawn over coconut charcoal contained in a tube 100 cm. long and 1.5 cm. in diameter. Rutherford (*Nature*, 1906, **74**, 634) showed that this was a good absorbent for radium emanation, and it is now shown that, for quantities of the order of magnitude dealt with by the authors, the absorption is quantitative. When the charcoal is distributed as a short column of greater diameter, a phenomenon analogous to saturation manifests itself, and with much higher concentrations of the emanation this phenomenon might be expected to manifest itself even when a long column of charcoal is used. At the same time air is bubbled through a solution of radium bromide containing a known amount of radium (6.3×10^{-10} grm.), and the emanation from the solution and the air is collected in another charcoal tube. The emanation absorbed in the charcoal is then driven off by heating to a dull red heat, collected over water in aspirators, and finally measured by passing into an ionisation chamber connected either with an electroscope or an electrometer. The emanation in a given volume of air can then be calculated from the ratio—

$$\frac{\text{emanation generated in the standard solution in a known time}}{\text{emanation in a known volume of air}},$$

provided the charcoal tubes absorb the same fraction of the total amount of emanation passing through them. This point was left in doubt by earlier workers, but the present authors show that absorption, under their conditions, is substantially complete. On the other hand, bubbling air through a cold solution of radium bromide does not remove the emanation as rapidly as it is formed, as was assumed by both Satterly and Eve. Only about 80 per cent. of the emanation is removed at a temperature of 27° C.

Other workers, in different parts of the world, have reported radium emanation

equivalent to 60 to 100×10^{-12} gram. radium per cubic metre of air. The mean value in Manila is about 80×10^{-12} , but the diurnal variations are large, extreme values being about 40 and 160×10^{-12} . On Mount Panui, at an elevation of about $8,000$ feet, the mean value was about 20×10^{-12} , and the extreme values 10 and 40×10^{-12} . This suggests that the concentration of radium emanation in the atmosphere decreases as the altitude increases. The lower values were found during or shortly after rain had fallen. Night values are, on the average, twice as high as day values. No definite relation could be traced between the variation of emanation content and a rising or falling barometer. Changes in humidity, likewise, seem to have no effect on the radio-activity of the atmosphere, but the total wind movement is evidently an important factor in determining the variation.

G. C. J.

Detection of Small Quantities of Selenious Acid in Sulphuric Acid.

E. Schmidt. (*Arch. Pharm.*, 1914, **252**, 161-165.)—On shaking 10 c.c. of sulphuric acid with 0.01 gram. of codeine phosphate, a green coloration, changing to bluish-green in fifteen minutes, is obtained in the presence of traces of selenious acid (0.00005 gram.). The test is thus more sensitive than the sodium hydrosulphite test (red coloration due to separated selenium). Sulphuric acid containing sulphurous acid gives no coloration with codeine phosphate, while the characteristic coloration is produced on adding 0.0001 per cent. of selenious acid. Tellurous acid at first does not affect sulphuric acid containing codeine phosphate, but after some time a red or pale blue colour is produced. On now adding selenious acid the distinctive green coloration is obtained, though more slowly than in the absence of tellurium.

C. A. M.

Volumetric Estimation of Titanium and Chromium by Means of a Modified Reductor. C. Van Brunt.

(*J. Amer. Chem. Soc.*, 1914, **36**, 1426-1429.)—Shimer and Shimer's method for titanium (*ANALYST*, 1912, **37**, 590) is slow, especially when the only zinc available is finer than was specified by these authors. Moreover, the 3' reductor is inconvenient, and it is difficult to prevent reoxidation.

The author uses an ordinary Jones reductor with a column of amalgamated zinc about $8''$ high and $1''$ in diameter. The tube is wrapped with a few feet of resistance ribbon or iron wire, in series with a lamp or other resistance adapted to taking sufficient current from a lighting circuit to boil the solution in the reductor. With this device, not only titanous, but also chromous salts, can be reduced in a few minutes. The stopcock at the bottom is closed, and the tube partly filled with hot 5 per cent. sulphuric acid, which is followed by the solution to be reduced. The apparatus is closed at the top by means of a double-bored stopper, carrying a tap-funnel and a vent-tube. The solution is kept near the boiling-point for ten to twenty minutes, and the pressure of steam is then made to expel the reduced solution through the stopcock at the bottom and below the surface of a ferric solution. The resulting ferrous salt, being comparatively stable, does not need to be protected against access of air, as does a titanous solution. The zinc in the reductor is washed successively with 5 per cent. and 1 per cent. sulphuric acid, which are admitted by means of the tap funnel and expelled by steam pressure without access of air, and

also collected below the ferric solution. The ferrous salt is then titrated with permanganate.

Chromic salts may be reduced to chromous salts in a similar manner, which are then caused to react with ferric salts, and the resulting ferrous salt estimated as described. The application of the method to the estimation of iron, titanium, and chromium, when present together, is discussed. For the estimation of all three metals together, the procedure is as described above. Iron alone is estimated by passing the solution through a reductor in the ordinary manner, not collecting in ferric solution, but adding bismuth oxide to reoxidise any reduced titanium or chromium, or, the iron is reduced with hydrogen sulphide or sulphur dioxide, which do not reduce titanium or chromium. Chromium alone is estimated by oxidising to chromate with ammonium persulphate and titration in the usual manner with ferrous iron and permanganate. Titanium is then estimated by difference.

G. C. J.

Separation of Yttrium from the Yttrium Earths. Part II. H. C. Holden and C. James. (*J. Amer. Chem. Soc.*, 1914, **36**, 1418-1423.)—In addition to the methods previously investigated (*ANALYST*, 1914, 280), the authors have tried fractional precipitation with sodium nitrite as well as fractionation by boiling with sodium hydroxide. Fractional precipitation with sodium nitrite is the most efficient and rapid method found thus far, the yttrium being concentrated in the mother liquors. This method is also less costly than either the phosphate or chromate methods formerly described (*loc. cit.*), and seems well adapted for the separation of yttrium on a commercial scale. It will not separate yttrium from terbium, since this element also tends to become concentrated in the mother liquors. G. C. J.