

INORGANIC ANALYSIS.

Use of Textile Fibres in Microscopic Qualitative Chemical Analysis.
E. M. Chamot and H. I. Cole. (*J. Ind. and Eng. Chem.*, 1918, 10, 48-50.)—
 III. *The Detection of Boron by Means of Turmeric Viscose Silk Fibres.*—To obtain the characteristic blue colour with turmeric by the addition of alkali after drying down with boric acid, certain difficulties are encountered with ordinary turmeric paper, and the most usual result is a greenish-black coloration. The difficulty may be overcome by using individual fibres instead of paper, and observing the reaction microscopically. For dyeing the fibres, a 50 per cent. alcoholic alkaline solution is made by boiling 20 grms. of powdered turmeric with 50 c.c. of alcohol, filtering and adding an equal volume of water and 0.5 to 1.0 c.c. of 10 per cent. sodium hydroxide. The fibres are steeped in this solution, which is then evaporated on the water-bath to a syrup. The fibres are then quickly dipped in 95 per cent. alcohol, pressed between filter-paper, dipped in dilute sulphuric acid, washed and dried. Care must be taken to avoid the presence of unabsorbed turmeric, since this interferes with the formation of the blue colour. The delicacy and success of the test are largely influenced by the nature of the fibre employed. Viscose silk gives by far the best colour reaction, and flax comes next, but is not nearly so satisfactory. For performing the test, a drop of the solution containing boron is placed on a microscope slide, and acidified with dilute hydrochloric acid to decompose borates. A turmeric fibre about 5 mms. long is placed in the drop, which is allowed to evaporate completely to dryness, either spontaneously or by very gentle warming. The slide is cooled and the fibre examined under the microscope; a rose or violet-rose colour indicates boron, and when a drop of 1 per cent. sodium hydroxide solution is placed on the fibre the colour changes to Prussian blue, which gradually turns to violet. Too high a temperature in evaporation, failure to carry it to complete dryness, and too strong a solution of soda, interfere with the success of the test. The presence of hygroscopic salts is objectionable, since they prevent the complete drying of the fibre; large amounts of free phosphoric or silicic acid also introduce difficulties; any strong bleaching agents, if present, must first be removed. The test should not be performed on a borosilicate glass slide. The test is only valid for free boric acid; without the addition of mineral acid, borates do not respond. The test is sensitive to 1 drop of a $\frac{N}{10000}$ solution of boric acid; 1 drop of a solution containing 0.000025 mgrm. of boron gives a positive result.

IV. *The Detection of the Heavy Metals by Means of Zinc Sulphide Wool Fibres.*—Several natural and artificial fibres were tested as a vehicle for zinc sulphide, but the only fibres which could be caused to absorb sufficient of the reagent for satisfactory use were wool and mohair. The preliminary treatment of the wool fibre is important. The fat is removed by treatment with a mixture of alcohol and ether; the fibre is then swelled by soaking overnight at the room temperature in 1 per cent. sodium hydroxide solution. It is then washed and dipped five or six times alternately in solutions of 10 per cent. zinc acetate and 10 per cent. sodium sulphide, the excess liquid being pressed out each time but not washed. After the final dipping the impregnated wool is washed and dried by pressing between filter-papers. The

sodium sulphide solution is prepared by passing sulphuretted hydrogen into sodium hydroxide until no precipitate is formed with magnesium chloride. To apply the test, a drop of the solution to be tested is placed on a glass slide and a drop of dilute hydrochloric acid is added. A piece of the treated fibre about 5 mms. long is introduced and examined under the microscope. The liquid is evaporated to dryness, a drop of dilute ammonia solution is added, and the fibre again examined side by side with a new fibre for detecting slight differences of colour by comparison. The colour changes are yellow, orange, brown, or black. In acid solution the indications are: Straw-yellow, tin; lemon-yellow, arsenic or cadmium; orange, antimony; reddish-brown, bismuth; brown or yellow-brown, platinum, copper, mercury, antimony (sometimes cobalt, iron, manganese, or nickel); black or brown in very dilute solution, silver, lead, gold, mercury. With no colour in acid solution, the fibre may turn brown or yellow-brown in alkaline solution in presence of cobalt, iron, manganese, or nickel, but these elements rarely give good reactions. Since the fibre is viewed in transmitted light, a heavy precipitate of yellow or orange colour may appear brown or black owing to its density; conversely, a brown or black precipitate in very dilute form may appear pale brown or yellow. The zinc sulphide wool fibres are sensitive to 0.001 mgrm. of copper (*cf.* ANALYST, 1918, 48). J. F. B.

Notes on the Analysis of Exhaust Gas. G. R. Clare. (*J. Soc. Chem. Ind.*, 1918, 37, 51-52 T.)—For the control of gas engines, furnaces, etc., using producer gas, it is important to estimate the percentage of unburnt producer gas in the exhaust. This can be ascertained by a calculation from the percentages of CO_2 , CO, oxygen and hydrogen found in the exhaust gases, but the process may be very considerably shortened by omitting the estimation of the oxygen and employing a curve or table instead of calculation. The percentage of burnt producer gas in the exhaust is given by the ratio of the percentage of perfect exhaust gas present to the total perfect exhaust gas obtainable per 100 vols. of producer gas. This latter consists of carbon dioxide and nitrogen, the hydrogen being condensed as water vapour. The CO_2 formed is the sum of the percentages of CO_2 , CO, and CH_4 in the producer gas, while the nitrogen is the sum of that originally present in the producer gas and that in the air necessary for complete combustion.

The percentage of perfect exhaust present is :

$$\frac{100 \times (\text{CO}_2 \text{ in exhaust gases} - \text{CO}_2 \text{ due to unburnt gas present})}{\text{CO}_2 \text{ in 100 vols. of perfect exhaust}}$$

The CO_2 in 100 vols. of perfect exhaust is :

$$\frac{100 \times (\text{CO}_2 + \text{CO} + \text{CH}_4 \text{ in producer gas})}{\text{Volume of perfect exhaust from 100 vols. producer gas}}$$

Substituting and multiplying by

$$\frac{100}{\text{Vol. perfect exhaust per 100 of producer gas}}$$

gives the formula for the burnt gas, which works out to

$$\frac{100 \times (\text{CO}_2 \text{ in exhaust} - \text{CO}_2 \text{ due to unburnt gas})}{\text{CO}_2 + \text{CO} + \text{CH}_4 \text{ in producer gas}}$$

Taking a specific instance, where the mean composition of the producer gas is CO_2 , 16 per cent.; CO , 11 per cent.; H_2 , 26 per cent.; CH_4 , 3 per cent.; and N_2 , 44 per cent., the value $\frac{1.0}{4.0} \times$ percentage of combustibles in the exhaust may be substituted for the CO_2 due to unburnt gas present in the exhaust, and the above formula becomes :

$$\frac{\text{CO}_2 \text{ in exhaust} - 0.4 \times \text{combustibles in exhaust}}{0.3}$$

The percentage of unburnt gas in the exhaust being $\frac{1.0}{4.0} \times$ combustibles present, the percentage of producer gas which is rejected as unburnt gas is :

$$\frac{75 \times \text{combustibles in exhaust}}{\text{CO}_2 \text{ in exhaust} + 0.35 \times \text{combustibles in exhaust}}$$

Then for any fixed percentage of gas unburnt the value

$$\frac{\text{Combustibles in exhaust}}{\text{CO}_2 \text{ in exhaust}}$$

must also be fixed. Substituting values and plotting them, a regular curve is obtained with $\frac{\text{Combustibles}}{\text{CO}_2}$ as ordinates and percentage of producer gas unburnt as abscissæ. Given an analysis of exhaust gas in terms of CO_2 , CO , and H_2 , it is possible to see at a glance the percentage of the gas used which is rejected as unburnt, the formula and curve being sufficiently accurate for practical purposes even when the composition of the producer gas varies fairly considerably from the mean value assumed.

J. F. B.

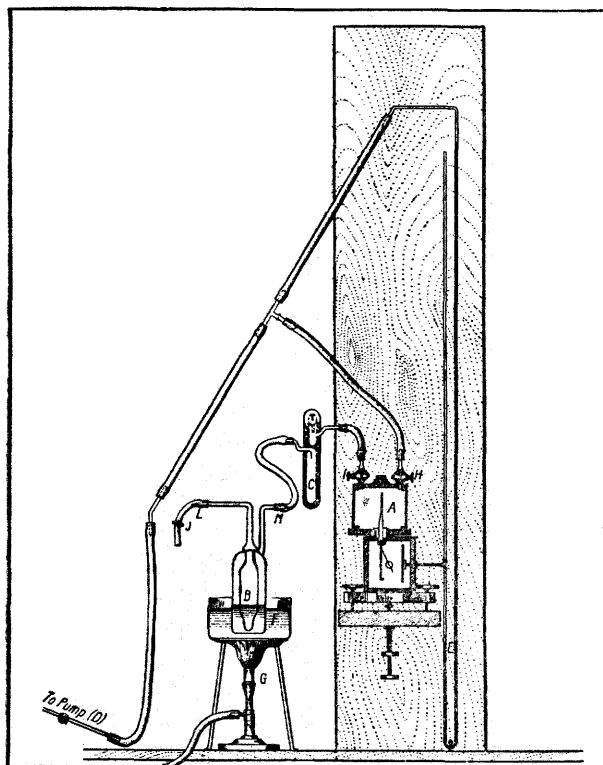
Estimation of Potassium by the Sodium Cobaltinitrite Method. C. V. Garola and V. Braun. (*Ann. Falsific.*, 1917, 10, 572-575.)—The following gravimetric application of this method is described : The reagent employed is prepared by dissolving 28.6 grms. of cobalt nitrate and 50 c.c. of glacial acetic acid in 500 c.c. of water ; 180 grms. of sodium nitrite are dissolved separately in 500 c.c. of water, the two solutions are mixed twenty-four hours before use, and filtered if necessary. The solution containing the potassium salt and free from bases other than sodium is evaporated to about 25 c.c., acidified slightly with acetic acid, and the reagent is added gradually ; 0.25 gm. of potassium chloride requires 25 c.c. of the reagent. The mixture is kept overnight in a stoppered flask, the precipitate then collected on an asbestos filter, washed with 10 per cent. acetic acid and once with alcohol, dried for about two hours at 100°C ., and weighed. The weight of the precipitate multiplied by 0.2074 gives the amount of K_2O present. The method yields accurate results, and may be used for the estimation of potassium in fertilisers, soils, wines, cider, etc.

W. P. S.

Radioactivity of Philippine Waters. J. R. Wright and G. W. Heise. (*Phil. J. of Sci.*, 1917, 12, 145-163.)—The radioactivity of about ninety different Philippine waters, chiefly from springs and flowing wells in the Island of Luzon, has been studied. The highest radium-emanation content encountered in a deep-well water was equivalent to $2,100 \times 10^{-12}$ grms. of radium ; the highest in the spring-water was equivalent to $1,300 \times 10^{-12}$ grms. of radium.

The actual radium content of about twenty typical samples showed that the radioactivity encountered was due to emanation absorbed from materials with which the ground-water had been in contact, and was not due to dissolved radium salts. One sample of water showed a scarcely detectable trace of activity due to radium salts in solution; all the others gave negative results.

The testing apparatus was a Spindler and Hoyer aluminium leaf electroscope provided with the usual equipment of tripod, shaking vessel, and circulation system



necessary for field work. It was found necessary in all determinations in the field or laboratory to have a calcium chloride tube introduced into the circulation system, so that all air and gases were dried before entering the ionisation chamber. Reliable readings were impossible without this precaution. The electroscope was charged by means of storage cells in the laboratory, or in the field by means of an ebonite rod, the standardisation being effected by means of radium bromide solution of known strength, which was kept sealed in a proper vessel for over a month. The emanation was then removed from the solution by boiling and by circulation of air, and was then drawn into the evacuated ionisation chamber (see Fig.).

After the instrument had been charged it was allowed to stand until the leak had become small and nearly constant. Readings both of the natural leak and that due to emanation content were taken at intervals of five minutes. The sealed vessel B,

containing the acidulated sample to be tested, was heated in a water-bath *F* to about 90° C., the ionisation chamber *A* having previously been evacuated by means of an electrically driven Geryk oil-pump. On completion of the vacuum the stopcock *H* leading to the pump was closed, and the vapours and gases from vessel *B* were caused to pass slowly through the drying-tube *C* into the chamber *A*. The liquid in the flask *B*, boiled under the decreased pressure, and the emanation was at once drawn into the chamber *A*. After equalising the pressure in the system the cock at *I* was closed, and readings of the leak were taken as described after fifteen minutes.

H. F. E. H.

Proximate Quantitative Method for the Estimation of Rubidium and Cæsium in Plant Ash. W. O. Robinson. (*J. Ind. and Eng. Chem.*, 1918, 10, 50-51.)—The method is based on the removal of the major portion of the potassium chloride by fractional precipitation with platinic chloride, and, further, by precipitation with strong hydrochloric acid. The resulting solution containing all the rubidium and cæsium chlorides and a large amount of potassium chloride is compared spectroscopically with a standard solution. Twenty grms. or more of the dry plant are incinerated in a muffle at a temperature not exceeding 525° C. The ash is dissolved in hydrochloric acid, and the excess evaporated off. An excess of freshly slaked lime is added to precipitate the phosphoric acid, magnesium, etc.; the mixture is boiled for a few minutes and filtered. The calcium in the filtrate is removed by precipitation with ammonia and ammonium carbonate; the calcium carbonate is filtered off, redissolved, and reprecipitated. The combined filtrates are evaporated to dryness and the ammonium salts carefully volatilised; the rare earth chlorides being readily volatile, this operation should be done in a muffle kept below red heat. The alkali chlorides are taken up with hot water and a few drops of hydrochloric acid, and treated with about 0.05 gm. of platinic chloride. The solution is stirred well and evaporated to pastiness. Meanwhile, a small carbon filter is prepared by drawing out a hard glass tube of $\frac{1}{2}$ inch or less diameter. A perforated platinum foil supports a small mat of asbestos. The unchanged potassium and sodium chlorides are rapidly dissolved in the minimum quantity of hot water, and the platinichlorides of the rare alkalis with some potassium platini-chlorides washed on to the asbestos pad with 80 per cent. alcohol. The platini-chlorides are reduced by connecting the carbon filter with a hydrogen generator and heating gently. The chlorides are washed through the filter with hot water, and the filtrate is evaporated to pastiness in a very small, lipped platinum dish. The mass is taken up with 4 drops of strong hydrochloric acid, and filtered through a very small filter into a tube holding 2 to 3 c.c. A number of these vials are graduated to hold the same volume. The rare alkali chlorides are taken up and filtered with two more portions of acid of 4 drops each, each successive portion being blown through the filter. The solution is made up to volume, and is ready for comparison with standards made up from rubidium, cæsium, and potassium chlorides with strong hydrochloric acid in the same way. For the spectroscope a Bunsen burner is used, carefully screened from the observer. The chlorides are so volatile that the flame reaction only lasts a few moments. Cæsium is identified by the lines 4,215.6 and 4,201.9, and rubidium by the double lines 4,593.3 and 4,555.4. These lines are

difficult to see, and the observer must remain in the dark room for at least an hour before the eyes become sensitive enough. The comparison is made by introducing a coil of platinum wire to withdraw a very large drop. The coil is carefully dried high above the flame, taking care to avoid spattering. The unknown solution is matched with standards by the brilliancy of the lines; an accuracy of 5 to 10 per cent. is easily obtained by different observers.

J. F. B.

Soil Acidity and the Hydrolytic Ratio in Soils. C. H. Spurway. (*J. Agric. Res.*, 1917, 2, 659-672.)—Recent investigations of soil acidity indicate the existence of a relationship between iron and aluminium compounds in the soil and its reaction to litmus-paper phenolphthalein indicator. The experimental work recorded by the author was carried out on twenty-nine samples of miscellaneous soils collected from the glacial formations of Michigan. Calcium, iron, aluminium, and silicon were determined by the solubility method, using $\frac{N}{5}$ hydrochloric acid. A definite relationship was found to exist between the ratios of calcium to iron and aluminium and the soil reaction. All the acid soils have ratios $\text{CaO} : (\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ above 1 : 1.3, and all the alkaline soils have ratios below this figure.

It is probable that the reactions of the soils studied depend chiefly upon hydrolytic ratios existing between hydrolysing compounds of the alkali earths and iron and aluminium.

A method for determining the calcium oxide required to neutralise a soil by indirect titration is described in which certain fixed quantities of a standardised calcium-hydroxide solution are allowed to react separately with varying amounts of soil. The concentrations of soil and solution giving a neutral reaction are chosen from the series by comparing the electrical resistance of the several solutions, also by means of phenolphthalein indicator. The greatest electrical resistance and faint colour of the indicator are coincident with the concentration giving a neutral reaction.

The quantities of lime required to neutralise the acid soils may be determined by computing the quantities of calcium oxide necessary to add to the acid soluble calcium oxide found in the soils to bring the ratios $\text{CaO} : \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ to 1 : 1.3. The quantity of calcium oxide required by this factor method corresponds closely to the quantities required when determined by means of the indirect titration method, and it appears that the titration method is accurate and convenient.

H. F. E. H.

Estimation of Tin in Low-Grade Ores. A. Adair. (*J. Ind. and Eng. Chem.*, 1917, 9, 1143.)—The method depends on the conversion of the stannic oxide into its phosphide, and has been devised on account of the difficulty of separating the tin from the large amount of silica in the ordinary fusion methods; loss of stannic chloride occurs during evaporation with hydrochloric acid to render the silica insoluble. The ore is roasted or treated with nitric acid, washed free from pyrites, dried, and ground to a very fine powder. Five grms. of this powder are mixed with 2 grms. of dry ammonium phosphate and 1 grm. of charcoal, and the mixture is heated in a closed crucible, at first gently for twenty minutes, and then at a red heat for thirty minutes. The fused mass, when cold, is powdered, moistened

with alcohol, and digested with 25 c.c. of warm hydrochloric acid for eighteen hours. The tin will now be all in solution, and is filtered from the gangue and charcoal.

W. P. S.

APPARATUS, ETC.

Method for Determining the Absorbency of Paper. E. O. Reed. (*J. Ind. and Eng. Chem.*, 1918, 10, 44-47.)—A common method for measuring the absorbency of blotting and other bibulous papers is the "mounting" test, according to which a strip of the paper is suspended vertically with the lower end immersed in water and the height to which the water rises in a given time is measured. The results of this test are independent of the width of the strip and the thickness of the paper. This test, although affording useful indications of the structure of the paper and purity of the fibres, is not performed under conditions corresponding to those under which a blotting-paper is used. A valid method ought to measure the rapidity with which a blot of ink is absorbed into the body of the blotting-paper in a horizontal position, such result depending not only on the structure and purity, but also on the thickness of the paper, since a given volume of ink will have to travel a shorter distance in a thick paper than in a thin one. The author has standardised a method for testing the rapidity of absorption, either of ink or water, in the following manner: A piece of the paper 4 inches square is placed over a beaker or tumbler, and a 1 c.c. pipette is arranged in a support so that its delivery end is $\frac{1}{2}$ inch above the centre of the surface of the paper, which is slightly dished so as to afford a shallow pool of liquid without buckling of the paper. The pipette is filled, clamped in position, and the liquid is discharged, while the time of absorption is measured by a stop-watch; observations are made in triplicate. To secure concordant results certain precautions must be observed. The temperature of the liquid must be constant (70° F. is specified); the paper must not be allowed to buckle, and the liquid must not spread as far as the annular support. If ink is used, it must be of standard composition, preferably made up as follows: Pure dry tannic acid, standardised by the hide-powder method, 23.4 grms.; gallic acid in crystals, 7.7 grms.; ferrous sulphate, 30.0 grms.; dilute hydrochloric acid (U.S.P.), 25.0 grms.; carbolic acid, 1.0 gm.; dyestuff "Bavarian Blue," 2.2 grms., made up to 1 litre. The ink should be kept in 50 c.c. dark bottles, tightly corked, in a cool place. Certain other factors influence the results, and should be standardised as far as possible. It is desirable to place the paper always with the wire side uppermost. The orifice of the pipette should be adjusted to deliver 1 c.c. of distilled water at 70° F. in four minutes. The height of the pipette from the surface of the paper should be from $\frac{3}{8}$ to $\frac{1}{2}$ inch. With very thin papers some of the liquid may filter through before it is absorbed; in such a case a pipette delivering 0.5 c.c. should be used. The results obtained with ink are of the most practical utility; the values obtained with water are not always the same as with ink. The rapidity of absorption bears no direct relation to the total absorptive capacity of a paper during repeated use. This may be tested by repeating the operation after allowing the ink to dry thoroughly between each observation. The rapidity of absorption of each 1 c.c. decreases until a point of final saturation is reached. Other things being equal, the total absorptive capacity tends to vary inversely as the ash content of the paper.

J. F. B.