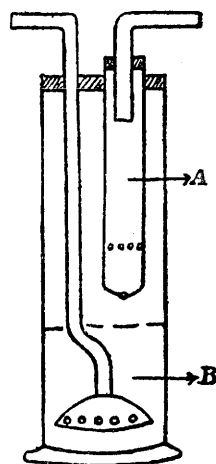## ORGANIC ANALYSIS.

Estimation of Carbon in Carborundum and the Like. S. A. Tucker and A. Lowy. (*J. Ind. and Eng. Chem.*, 1915, **7**, 565-571.)—This method was devised for the analysis of "silundum," which is shown to exist in two modifications, approximating to the composition SiC (a variety of carborundum) and Si_4C_4O, the title of the paper in which the method is described being "The Preparation, Properties, and Composition of Silundum."

The difficulty in estimating carbon in such materials lies in their resistance to decomposition by ordinary methods. After trying other methods with indifferent results, the authors found that litharge was an excellent flux for decomposing and partially oxidising the material, complete oxidation being effected by means of a stream of oxygen. The sample (0·2 to 0·25 grm.) is mixed with 5 grms. litharge, the carbon content of which has been determined in a blank test under the same conditions as the analysis. The mixture is placed in a combustion-boat of vitrified clay, 120 mm. long and 15 mm. wide. These boats, designed by C. M. Johnson

and made by Eimer and Amend, New York, were the only ones found suitable, porcelain, nickel, iron and copper all being fused by the molten litharge. The boat is placed in a silica tube in an electric furnace, a current of dry oxygen, free from carbon dioxide, is passed through the tube and the temperature raised cautiously, switching off the current if the rate of evolution of gas tends to become too rapid. The temperature is kept at about 600° C. for forty-five minutes and then gradually raised to 1,000° C., any carbon monoxide formed at this temperature being oxidised by passing over a heated coil of cupric oxide. The gases are dried by means of sulphuric acid and the carbon dioxide is absorbed in a suitable apparatus containing potassium hydroxide, the authors preferring Vanier's apparatus. With large crystals of carborundum as test material, the method appears to be accurate to 1 per cent. on the carbon, assuming that the carborundum was pure silicon carbide. One of the forms of silundum gave results much nearer the theoretical (found C = 29·89; required by SiC, 29·78). Duplicates agree well, for example 29·89, 29·95, 29·84.

<div align="right">G. C. J.</div>

Estimation of Benzol in Gas. **A. Krieger.** (*Chem. Engineer*, 1915, **21**, 252-253.)—By benzol in this connection is understood the sum of the benzene, toluene, xylenes, etc. Earlier methods are reviewed, and it is pointed out that, however satisfactory they may be in gas works, they are insufficiently exact for coke oven works. Even crude coke oven gas contains less benzol than ordinary illuminating gas, and washed gas should only contain about 7 per cent. of the amount present in the crude gas. The constant problem of the coke oven manager is to see that his washers, usually guaranteed to extract 90 per cent. of the benzol, are in fact working efficiently. None of the earlier methods are of service in such circumstances, and most of them require the presence of a skilled chemical manipulator.

The method recommended is condensation by washing with a suitable oil, cooled to − 18° C. A tar oil distilling between 240° and 260° C., or paraffin oil boiling between 200° and 300° C., is suitable. Such oil will absorb nearly one-tenth of its weight of benzol, but in practice should not be required to absorb more than 2 per cent. of its weight. A suitable washer is figured. The cylinder is 9″ × 2″, and is charged with 50 c.c. of oil. The outlet tube (*A*) is 6″ × ½″, is packed with glass beads (2 mm.), and has a hole in the bottom, and a ring of small holes for the inflow of gas. The beads prevent mechanical loss of oil. Two such washers are used in series, and gas is passed through them at the rate of 40 litres per hour. The duration of the test will depend on the concentration of benzol in the gas and other local conditions. In the author's practice, an eight hours' run is made, about 0·8 grm. benzol being absorbed by the first washer and 0·05 grm. by the second. With the speed of gas indicated and providing the oil in the first washer has not absorbed more than 1 grm. of benzol, a third washer shows no

increase in weight. The only other apparatus required is a meter and a balance sensitive to 0·01 grm. G. C. J.

Detection of Cinnamic Acid. D. Schenk and H. Burmeister. (*Pharm. Zeit.*, 1915, **60**, 213-214; through *J. Chem. Soc.*, 1915, **108**, II., 382.)—The test recommended depends on the oxidation of the cinnamic acid to benzaldehyde, and the identification of this by its odour and by its reaction with phenol and sulphuric acid. The substance to be tested is acidified with phosphoric acid and extracted with ether; the ethereal solution is then shaken with sodium carbonate solution, the aqueous layer is separated, extracted twice with ether (this is essential, particularly in the case of fruit juices, in order to remove small quantities of furfural compounds), and very dilute potassium permanganate solution is added, drop by drop, until the pink colour is only just discharged. The solution is now extracted with ether, the ethereal solution is treated with 10 drops of an ethereal 5 per cent. phenol solution, allowed to evaporate at the ordinary temperature, and a few drops of concentrated sulphuric acid are added to the residue. A yellow coloration is obtained, even when the quantity of benzaldehyde formed from the cinnamic acid is too small to be identified by its odour. The furfural compounds which may be present give, if not removed completely, a faint orange coloration, which cannot be mistaken for that yielded by benzaldehyde.

Reagents for Use in Gas Analysis. I. Alkaline Pyrogallol. R. P. Anderson. (*J. Ind. and Eng. Chem.*, 1915, **7**, 587-596.)—The report of an elaborate investigation as to the best composition for this reagent. A solution of 15 grms. pyrogallol in 100 c.c. of potassium hydroxide solution of specific gravity 1·55 is recommended. Solutions containing more potassium hydroxide are less easy to prepare and less easy to manipulate, whilst solutions containing more pyrogallol tend to foam. It is desirable to use solutions as concentrated as is convenient, not only because the life of such solutions is longer, but because several observers have called attention to the fact that solutions of pyrogallol of relatively low alkali content tend to react with oxygen with production of carbon monoxide. The solution recommended is free from this defect, so far as can be judged using Hempel's apparatus for technical analysis. When used at 20-24° C., a solution that has already absorbed 26 times its volume of oxygen will still absorb the whole of the oxygen from a sample containing 90 per cent. of that gas in two minutes, when shaken in a Hempel double pipette. If three minutes be allowed the specific absorption is somewhat higher (30), whilst it is higher still (31) if the reagent is not required to absorb the oxygen from samples richer in that gas than air is. The author is unable to confirm Hempel's statement that potassium hydroxide purified by alcohol should not be used. As that statement was made as long ago as 1887, it is possible that differences in method of manufacture explain the discrepancy. Sodium hydroxide cannot be substituted for potassium hydroxide. Using a solution of sodium hydroxide as concentrated as was practicable, it was found that only 10 per cent. of the oxygen in a sample of gas was absorbed as the results of three minutes' shaking. G. C. J.

Volumetric Estimation of Nitro-Compounds. A. J. Berry and C. K. **Colwell.** (*Chem. News*, 1915, **112**, 1-2.)—The method is the known one of reduction by means of a known amount of stannous chloride and titration of the excess of stannous chloride, the novelty consisting in the manner in which the excess of stannous chloride is estimated. For this purpose a standard solution of copper sulphate is employed, and, to determine the endpoint, advantage is taken of the fact that, in presence of much hydrobromic acid, a very small amount of a cupric salt imparts a pronounced orange-yellow colour to a comparatively large volume of solution.

The copper solution conveniently contains about 40 grms. copper per litre, and is made by dissolving a weighed amount of copper sulphate and about 100 grms. of potassium bromide in 1,000 c.c. of dilute (1:1) hydrochloric acid. The stannous chloride solution is made up roughly equivalent to the copper solution.

A suitable quantity of an aqueous solution of the nitro-compound (only water soluble compounds are dealt with) is measured out, 25 c.c. of stannous chloride solution, 35 c.c. of a 50 per cent. solution of potassium bromide, and a considerable excess of hydrochloric acid, are added, and the mixture boiled for fifteen minutes in an atmosphere of carbon dioxide. The excess of stannous chloride is then titrated with the copper solution as described. The difference between the volume of copper solution required in this experiment and in one similar, except that water is substituted for the solution of the nitro-compound, is the measure of the latter. In the author's test experiments, these differences were small (7 to 14 c.c.), and their results only accurate to ±2 per cent. G. C. J.

Analysis of Chinese Wood-Oil Varnishes. E. E. Ware and C. L. Schu-**mann.** (*J. Ind. and Eng. Chem.*, 1915, **7**, 571-573.)—In the study of the polymerisation of China wood-oil in presence of rosin, it became necessary to devise a method for separating the various possible constituents of the final mixture. Twitchell's method, depending on formation of the ethyl esters of the fatty acids, and their subsequent separation from the rosin and from each other, gave a fair separation of the oils from the rosin, but the esters of the polymerised and unpolymerised oils did not show sufficiently pronounced differences upon which to base a method for their separation. The following method served well:

The sodium soaps of the fatty acids of both the raw and heat-treated oils are insoluble in absolute alcohol, whilst sodium resinate is soluble. If proper precautions (not specified in the paper) be taken for the control of temperature and concentration, the soaps of the fatty acids precipitate in a sufficiently granular form to permit of ready filtration and washing. The subsequently freed fatty acids may be dissolved in warm 80 per cent. alcohol, from which the comparatively insoluble elæomargaric acid may be crystallised by cooling. These characteristic crystals of elæomargaric acid may be filtered and weighed, or the residue acids may be weighed and the elæomargaric acid computed by difference. The oxyacid present may be separated from the residue by precipitation from petroleum ether. In this way it is possible to estimate total fatty acid, unpolymerised acid, oxyacid, polymerised acid, and unsaponifiable matter. G. C. J.

Demulsification Values of Mineral Lubricating Oils for Use in Steam Turbines. A. Philip. (*J. Soc. Chem. Ind.*, 1915, **34**, 697-701.)—The leakage of water into the oil system in steam turbines tends to form emulsions which cause trouble in the lubrication, especially when the water contains large proportions of salt derived from sea-water or shore-water. Electrolytic corrosion of the machinery may then occur. It has been found in practice that two samples of lubricating oils may differ but slightly in their chemical and physical properties, and yet one will be suitable and the other useless as a turbine lubricant. In order to test the suitability of oils for this purpose, the author determines the "demulsification value" in a special apparatus. This consists of an agitator, driven at high definite speed (350 to 400 revolutions per minute) for a definite time (five minutes) by means of an electric motor, in a mixture of 500 c.c. of the oil with 500 c.c. of water at 100° C. At the end of the given period the mixture is transferred to a graduated glass measure, and after a fixed period (twenty-four hours) the volume of the separated oil is read off and calculated as a percentage of the oil originally present. Oils giving demulsification values of 90 per cent. or over have been found to give no trouble due to formation of emulsions under the practical conditions of use of a forced lubricating system on steam turbines. The addition of 1 per cent. of undistilled fuel oil to a high-grade lubricating oil lowers the demulsification value, possibly owing to the bitumen in the former. The following table gives the actual analysis of a mineral lubricating oil of high grade, and the imaginary results of an oil fuel and of a mixture of the lubricating oil with 1 per cent. of the oil fuel:

	1. High-Class Special Mineral Lubricating Oil.	2. Imaginary Oil Fuel, all Results being Extreme Values.	3. Calculated Values for Mixture 1 per Cent. of 2 with 99 per Cent. of 1.
Sp. gr. at 60° F.	0·8870	0·9685	0·8779
Flash-point	403° F.	180° F.	400·7° F.
Viscosity at 70° F. (seconds) ...	675	2586	694·1
Free acidity to water (as oleic acid)	nil.	0·5 per cent.	0·005 per cent.
Sulphur	0·109 per cent.	3·98 per cent.	0·147 per cent.
Iodine value...	16·2	100·0	17·03
Saponification value	0·28	6·0	0·33
Bitumen	nil.	38·0	0·38
Paraffin wax...	nil.	27·5	0·275
Demulsification value	96 per cent.	nil.	nil.

In cases where contamination of an oil with minute quantities of fuel oil has been suspected, the demulsification test has been found to afford the only clear proof of difference between the oil as accepted and as delivered. The addition of paraffin wax has not been found to decrease the demulsification value, and in some cases may even increase that value. C. A. M.

Specification of Vulcanised Rubber Gum by Volume and its Estimation by a New Solution Method. F. Gottsch. (*J. Ind. and Eng. Chem.* 1915, **7**, 582-586.)—It is said that the physical properties of a rubber compound and its quality are more properly related to the percentage by volume of vulcanised rubber gum present than to the percentage by weight, that the large majority of rubber goods are sold by bulk and used by bulk rather than by weight, and that this volume conception is necessary to an understanding of rubber mixings. The author would therefore introduce this conception into specifications and into analytical reports to show whether goods comply with the specification. The specific gravity of vulcanised rubber is so nearly unity that it suffices to multiply the percentage of vulcanised rubber-gum found by analysis by the specific gravity of the sample.

Whether the percentage of vulcanised rubber be specified by weight or by volume, the specification must include methods of analysis or a reference to known methods. The author describes the methods in use in the City of New York Department of Water Supply, Gas, and Electricity.

Vulcanised rubber-gum by weight is defined as the difference between 100 and the sum of the free sulphur, organic acetone extract, mineral fillers and " corrected foreign matter."

In the estimation of mineral fillers many solvents for rubber were tried, and the best found to be salol. Many of the fillers used ("fume pigments") are in such an extremely fine state of division that without a coagulant it is extremely difficult to filter them off. Such a coagulant is found in a solution of soluble cotton in amyl acetate. One grm. of the sample is extracted with acetone for four hours, dried in a steam oven and transferred to a 100 c.c. becker. The thimble is burnt and the ash added to the contents of the becker. Melted salol (about 50 grms.) is next added and the mixture heated to 120° to 150° C. until the rubber is dissolved. About 2 c.c. of a 1 per cent. solution of soluble cotton in amyl acetate are added, the mixture cooled and coagulated by stirring in 75 c.c. or more redistilled turpentine. After allowing the flock to settle, the supernatant liquid is decanted through an alundum crucible. The insoluble matter is washed by decantation and on the filter with turpentine, finally using a little acetone to dissolve the soluble cotton. The crucible is dried at 105° to 110° C. All filtrates and washings are evaporated, the residue ignited and weighed, and the weight of mineral matter thus recovered added to that in the crucible.

The usual methods for the estimation of free sulphur are criticised and a new one proposed. It is an application to this purpose of a well-known method for the estimation of total sulphur, the organic matter in the acetone extract being destroyed by fusion with sodium peroxide and potassium carbonate, the sulphur then being estimated as barium sulphate with the precautions usual when such an estimation follows a peroxide fusion.   G. C. J.

Analysis of Tanning Materials. T. Callan. (*J. Soc. Chem. Ind.*, 1915, **34**, 646-647.)—In the course of a number of analyses of various tanning materials, it was found that the non-tannin filtrates obtained in Bennett's method (ANALYST, 1915, 132), using standard American hide powder, showed in many cases distinct

traces of tannin, even after shaking for twenty minutes with hide powder, when tested by concentrating 6 c.c. of the detannised solution to 3 c.c. and applying Stiasny's test (addition of 1 c.c. of saturated sodium chloride solution, 2 drops of 1 per cent. metaphosphoric acid solution, and 2 drops of 5 per cent. gelatin—5 per cent. sodium chloride solution). Tannin could not, however, be detected in the solution by means of the official test (addition, drop by drop, of a 1 per cent. gelatin —10 per cent. sodium chloride solution). It would appear that the alterations proposed by Bennett, designed to reduce absorptions of non-tannins, have been carried too far, and although in all probability the gain in accuracy, owing to reduced absorption of non-tannins, is more than the error introduced by the non-absorption of traces of tannin, the presence of this latter error will prove a strong objection to the method.   W. P. S.