ORGANIC ANALYSIS.

Elementary Analysis by Means of a Calorimetric Bomb. H. L. Higgins and A. Johnson. (*J. Amer. Chem. Soc.*, 1910, **32**, 547-558.)—In carrying out elementary analyses by means of a calorimetric bomb, a number of difficulties arise, notably in getting the interior of the bomb perfectly dry at the beginning of the combustion, and the operations are very time-consuming. Following up suggestions made by Hempel (*Ber.*, 1897, **30**, 202) and by Zuntz and Frentzel (*Ber.*, 1897, **30**, 380), the authors have developed the following method, according to which the weight of carbon dioxide in the gases resulting from the combustion is determined by weighing these gases and analysing a portion of them, whilst the greater part of the water is weighed in the bomb itself, no attempt being made to collect it in a calcium chloride tube. In addition to the bomb, the necessary apparatus consists of a balance which, with a load of 3 kilogrms., turns to 0·01 grm., and a gas analysis apparatus, such as Haldane's, by means of which the carbon dioxide (usually 15 to 20 per cent.) in the gas mixture can be estimated with an error not exceeding 1 in 500.

The bomb containing the substance, ignition thread and kindler, and full of air at atmospheric pressure, is weighed to 0·01 grm. It is then charged with oxygen to 20 to 25 atmospheres and again weighed, after which the combustion follows in the usual way. The gas is then released from the bomb, passed through a sulphuric acid U-tube, and a portion collected in the Haldane apparatus and analysed. When the gas in the bomb reaches atmospheric pressure, the bomb is closed and weighed. It is then opened, the ash (if any) weighed, and the rinsings titrated for nitric acid.

The weight of carbon $= (c + 0{\cdot}14a)/(1 + 266{\cdot}7/b)$, where c, the weight of gas in the bomb at the end of combustion, equals the weight of the bomb immediately after the combustion, less the weight of the bomb after all but one atmosphere of the combustion gas has been released, plus the weight of this atmosphere of gas (calculated from the known volume of the bomb and the results of the gas analysis), less the weight of water passed out of the bomb and collected in the sulphuric acid U-tube, a, the weight of nitrogen gas in the bomb at the end of the combustion, is the sum of the weights of nitrogen in the oxygen supplied, in the substance burned, and in the air with which the bomb is filled at the commencement of the experiment, less that of the nitrogen oxidised to nitric acid; and b is the volume percentage of carbon dioxide in the final gas mixture. The constant 0·14 is the approximate numerical value of the expression $\frac{O}{N} - 1$, where O and N represent the atomic weights of oxygen and nitrogen, and 2·667 is similarly derived from the expression $\frac{100\ O_2}{C}$.

The weight of water formed $= d - e + f$, where d represents the weight of the bomb proper and the water it contains, and is found by subtracting from the weight of the bomb at the end of the combustion (after releasing the pressure) the combined weights of the nitric acid, ash, and gaseous contents; e represents the weight of the empty bomb, and is found by subtracting from the weight of the bomb at the beginning of the experiment—(1) the weight of air which it contains, (2) the weight of substance burned, and (3) the weight of the ignition thread and kindler; and f is the weight of water leaving the bomb on releasing the pressure and collected in the sulphuric acid U-tube. This amount approximates so closely to 0·02 grm. in all experiments that the authors have abandoned the use of the drying-tube, and substitute the constant 0·02 for f in the above equation.

From the weights of carbon and hydrogen thus determined, the amounts due to the ignition thread and kindler are, of course, deducted. The degree of accuracy of the carbon determination depends principally on the accuracy with which the gas analysis is conducted; that of the hydrogen determination depends on the sensibility of the balance. Working with 1·5 grms. of a substance containing 40 per cent. of carbon and 7 per cent. of hydrogen in a bomb of 250-300 c.c. capacity, the combustion gases will contain about 20 per cent. of carbon dioxide, and the water will weigh less than 1 grm. The error in the case of the water may be ±0·02 grm., whilst an error of 0·1 per cent. in the determination of carbon dioxide will cause the carbon to be incorrectly estimated by ±0·5 per cent. G. C. J.

Moist Combustions by Means of "Caro's Acid." W. Migault. (*Chem. Zeit.*, 1910, **34**, 337.)—Monopersulphuric acid, otherwise known as "Caro's acid," is prepared by adding slowly to 1 part of "perhydrol" (30 per cent. hydrogen peroxide) 3 or 4 parts of concentrated sulphuric acid. This reagent is a powerful oxidising agent, and evolves large quantities of oxygen, ozone, and sulphur trioxide on heating. At temperatures below 100° C. the production of sulphur trioxide may be controlled, whilst nearly all substances of an organic nature undergo a rapid and complete combustion. The reagent is of general application for the destruction of organic matter in the wet way for analytical purposes—*e.g.*, Kjeldahl determinations, estimation of metals, etc. In order to control the evolution of vapours and to avoid losses, the combustion is best effected in a flask with a long neck, with a reflux condenser fused on. A dropping-funnel without a tap, but fitted with a long capillary stem, is inserted in the upper end of the condenser, and serves for the introduction of the hydrogen peroxide on pressure of a rubber ball. The substance to be destroyed is placed in the flask, together with some concentrated sulphuric acid, and subjected to a preliminary decomposition by heating at 100° C. The flame is then extinguished, and the "perhydrol" is added gradually until the solution becomes colourless. If the combustion is not complete, the liquid may be further heated to 140° C., cooled again to 100° C., and treated with a further quantity of the peroxide. According to the nature of the material, 1 grm. requires 2 to 4 c.c. of "perhydrol" and 6 to 12 c.c. of sulphuric acid. If permissible, the addition of a small drop of mercury acts as an oxygen-carrier, and facilitates the oxidation. As a rule, the whole operation is complete in thirty minutes. J. F. B.

Quantitative Determination of Cane-Sugar by the Use of Invertase. C. S. Hudson. (*U.S. Dept. of Agric., Bureau of Chemistry, Circular No.* 50.)—The use of invertase as a substitute for hydrochloric acid in the estimation of cane-sugar by Clerget's method presents the advantage that, with the exception of raffinose, all the other readily hydrolysable carbohydrates remain unaffected. For the preparation of a stock solution of invertase, 5 pounds of pressed yeast are broken up and treated with 30 c.c. of chloroform in a closed flask, at a temperature of 20° C., for about sixteen hours. The yeast is thereby liquefied and the fluid is filtered. Sufficient lead acetate is then added to produce complete defecation, the solution is filtered, and the excess of lead removed by potassium oxalate. The liquid so obtained is treated with 25 c.c. of toluene, and dialysed in a pig's bladder with running water. The dialysed solution, after filtration, may be preserved indefinitely, in presence of a little toluene, at the temperature of the ice-safe. It possesses a slight dextro-rotatory power, which may be allowed for when extreme accuracy is required. In performing the analysis the clarified sugar solution is freed from excess of lead, and acetic acid is added drop by drop to 50 c.c. of the filtrate, until the reaction is acid to litmus; 5 c.c. of the stock solution of invertase are added, and the volume is made up to 100 c.c. A few drops of toluene are added, and the liquid is allowed to remain at any temperature between 20° and 40° C. overnight, and polarised at a temperature of 20° C. The factor, when invertase is used, is somewhat lower than the factor used in Clerget's formula for inversions by hydrochloric acid. The formula for calculating the percentage of cane-sugar is

$$\frac{S - I}{141{\cdot}7 - \frac{T}{2}} \times 100$$

in the case of invertase.

Invertase is only active in faintly acid solutions, and acetic acid is selected in preference to hydrochloric, because a relatively large excess of the former has but little retardative effect on the inversion. In solutions inverted by invertase the variation of the rotation of the lævulose with a change of temperature shows a lag which is not observable in solutions inverted by acid. At a temperature of 20° C. this lag lasts for about ten minutes. It is necessary, therefore, after adjusting the temperature for polarisation, to maintain the liquid at that temperature until the rotation becomes constant. Raffinose interferes with the determination of cane-sugar by invertase, just as it interferes in the ordinary method with hydrochloric acid. On the other hand, the invertase method gives more accurate results than the acid method, in the presence of other carbohydrates which are affected by acids, and of products which are decomposed at the temperatures which the acid methods of inversion involve. J. F. B.

Estimation of Cellulose by Lange's and Simon and Lohrisch's Methods. A. Scheunert and E. Lötsch. (*Zeit. physiol. Chem.*, 1910, **65**, 219-231.)—The authors have investigated these methods for the estimation of cellulose, and find that neither process yields quantitative results. Simon and Lohrisch's method (ANALYST, 1904, **29**, 371) yields results which in certain cases are 50 per cent. too low, and the same may be said of Lange's method (ANALYST, 1895, **20**, 283). They show that the cause of the deficiency lies in the action of the highly concentrated potassium hydroxide solution on the cellulose. When hydrogen peroxide is employed in addition to potassium hydroxide, the cellulose undergoes still further decomposition. The two methods are, therefore, quite useless for the accurate estimation of cellulose. (See also ANALYST, 1900, **25**, 218.) W. P. S.

Co-efficient of Expansion of Glycerol. A. M. Comey and C. F. Backus. (*J. Ind. Eng. Chem.*, 1910, **2**, 11-16.)—As the result of an elaborate investigation concerning the thermal co-efficient of expansion of glycerol of sp. gr. between 1·254 and 1·264 at 15·5°/15·5° C., the following values are given: At 20° C., $c = 0{\cdot}004612$; at 25° C., $c = 0{\cdot}000617$; and at 30° C., $c = 0{\cdot}00622$. G. C. J.

Characteristics of Certain Kinds of Gum. E. Meininger. (*Arch. Pharm.*, 1910, **248**, 171-201.)—The gums derived from different species of *Acacia* differ considerably in their chemical and physical characteristics. In the following table are given the results obtained by the author in the examination of samples of the gums from *Acacia pycnantha* (Australia), *A. horrida* (South Africa), *A. arabica* (Africa, Arabia, India), and *Melia azadirachta* (India, Ceylon, Malay Archipelago). In each case galactose and arabinose were detected in the products of hydrolysis.

Gum from	Water.	Specific Rotation $[\alpha]_D$ in Aqueous Solution.	Insoluble Matter.	Ash.	Calcium.	Magnesium.	Nitrogen.	Galactan.	Pentosans.	Methyl Pentosan.
	Per Cent.		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Acacia pycnantha	13·55	-19·39°	0·64	0·92	0·28	0·123	2·19	58·72	16·98	2·92
A. horrida - -	15·34	+53·94°	0·98	2·59	1·06	0·345	1·51	27·36	36·50	2·83
A. arabica - -	14·39	+	—	2·41	0·76	0·106	1·39	21·85	50·43	—
Melia azadirachta	15·41	-57·16°	0·27	2·99	0·76	0·294	4·49	11·11	26·27	—

C. A. M.

Error in Estimation of Degree of Tannage of Leathers. J. G. Parker and M. Paul. (*J. Soc. Chem. Ind.*, 1910, **29**, 315.)—For the complete analysis of leather, Von Schroeder's method is generally used (*J. Soc. Chem. Ind.*, 1898, **17**, 164). This method consists in determining the actual moisture and "ash" in the leather after cutting into thin shavings (or rasping into powder), extracting another portion of the sample with petroleum ether for estimation of oil, and then washing out the water-soluble matters, including uncombined tannins, from the oil-free residue by percolation with warm water, and, finally, on another portion of the sample, determining the nitrogen by Kjeldahl's method, from which the amount of hide substance present can be calculated. The difference between the sum of the amounts of moisture, ash, fat, and soluble matters, and 100 was then taken as pure leather substance; and, further, the "degree of tannage" of a leather was calculated by subtracting the amount of hide substance from the leather substance, thus obtaining the tannin; the ratio $\frac{\text{tannin combined}}{\text{hide substance}}$ = the degree of tannage of the leather. This factor is of value for ascertaining the quality of the leather, and indicates whether the article is likely to give a good yield in dressing, its possibility of re-tannage, and whether the tannin process has been rationally conducted.

The authors point out that Von Schroeder's method of calculation involves an error, insomuch as the soluble mineral matters are twice calculated, once in the "ash," and again in the water-soluble matters, and the amount of "leather" found is too low. Instead, therefore, of determining the leather substance by difference in this way, the authors propose to regard it as equal to the dry leather residue (after removal of water-soluble matters, etc.) minus the ash of this residue. The slight error due to alteration in composition of the ash constituents on incineration is negligible. Von Schroeder's calculations are thus shown to be low in degree of tannage by 0·5 to 2·4 per cent., and examples are given showing that the error in certain cases may, with the old method of calculation, amount to 6 or 7 per cent. in the case of modern leather.

In order to determine correctly the leather substance, the authors have devised a method in which the leather is washed by water slowly passing through a "serpentine" glass tube immersed in a water-bath provided with a thermo-regulator, and kept at 55° to 60° C. Twenty grms. of leather, contained in an inverted Procter's filter-bell plugged at each end, with washed and tanned cotton-wool, are by this means treated for twenty-four hours with 1 litre of water at the above temperature, the flow of water being regulated by means of a clamp. In the case of under-tanned leather, or leather tanned in a drum (incomplete tanning), the temperature must not exceed 55° C. The residue of leather substance plus insoluble mineral matters is dried and weighed, and the pure "leather" determined by subtracting the weight of the ash of this residue from the total weight. The paper contains numerous analyses of leather tanned without extract, leathers of mixed tannage, and of adulterated leathers. A. R. T.

Quantitative Estimation of Quinones. R. Willstätter and R. Majima. (*Ber.*, 1910, **43**, 1171-1175.)—The authors have developed the method proposed by Willstätter and Dorogi (*Ber.*, 1909, **42**, 2165) for the estimation of quinones by means of hydriodic acid and thiosulphate. The reaction $C_6H_4O_2 + 2HI = C_6H_6O_2 + I_2$ in ethereal solution is not quite complete, and means have to be adopted to destroy the equilibrium which tends to be set up. The hydriodic acid employed must be fairly concentrated and the ethereal solution of the quinone must not be too dilute; some of the hydriodic acid must be allowed to remain in the ethereal solution, so that it may complete the reduction of the quinone whilst the iodine is being absorbed by thiosulphate. If the colour of the solution permits, the liberated iodine is best determined by direct titration; but, since the solutions are generally coloured, it is necessary to add excess of thiosulphate and to titrate back. The influence of the ether tends to introduce an error the reverse of that due to incomplete reaction, since pure ether will liberate iodine from hydriodic acid in the presence of air. This error may be minimised by adhering to the concentration of hydriodic acid specified below, also, by preference, working in an atmosphere of carbon dioxide. For the analysis, the ethereal solution of the quinone, containing 0·2 to 0·4 grm. per 100 c.c., is treated in a stoppered separating funnel with 2 c.c. of a 30 per cent. solution of potassium iodide, and 1 c.c. of 30 per cent. sulphuric acid for every 0·2 grm. of quinone present. The liquid is shaken for about two minutes until the aqueous layer no longer becomes cloudy in a few seconds; 50 to 60 c.c. of water are then added, without shaking, since it is necessary to avoid the complete removal of the hydriodic acid from the ether. $\frac{N}{10}$ thiosulphate solution is then added in portions of about 10 c.c. each time, the contents of the funnel being slightly agitated for a short time after each addition. Care must be taken to ascertain, by colour or by external tests, when a slight excess of thiosulphate has been added; such excess should not be more than 2 c.c. The aqueous layer is then drawn off and the excess of thiosulphate is titrated back with iodine in presence of starch. The above reaction proceeds rapidly in the case of benzo-quinone, and the results show over 99 per cent. But in the case of xylo- and thymoquinones it is necessary to shake for five to eight minutes, and even then the reaction is not complete. Good results may, however, be obtained by increasing the quantity of hydriodic acid threefold, and by working in an atmosphere of carbon dioxide with ether previously saturated with the gas. J. F. B.

Composition of a Natural Scammony Resin. A. Goris and G. Fluteaux. (*Bull. Sciences Pharmacol.*, 1910, **17**, 15-16; *Chem. Zentralbl.*, 1910, **1**, 1255.)—A sample of scammony resin had the following composition: Water, 5·0; ash, 7·18; substances soluble in alcohol, 78·82; soluble in ether, 66·7; and insoluble in alcohol, 8·0 per cent. The ash contained iron, aluminium, silica, and calcium. The optical rotation of the portion soluble in alcohol was $[\alpha]_D = -21° 47'$, and that of the portion soluble in ether was $[\alpha]_D = -24° 26'$. No trace of starch was present.

C. A. M.

Examination of Asphalt. K. G. Mackenzie. (*J. Ind. Eng. Chem.*, 1910, **2**, 124-127.)—Richardson and Forrest (*J. Soc. Chem. Ind.*, 1905, **24**, 310) have pointed out that, whereas the true asphalts are as readily soluble in carbon tetrachloride as in carbon disulphide, native bitumen which has been weathered and residual pitches from petroleums which have been overheated in refining, though almost completely soluble in carbon disulphide, may leave notable residues on treatment with tetrachloride. Accordingly they regard the percentage of matters soluble in disulphide, but not in tetrachloride, as a valuable index of degree of weathering or of overheating, as the case may be, and Richardson has proposed to call these bodies "carbenes." It is now shown that the insoluble residue is, in part at least, not a constituent of the original bitumen, but the product of a reaction between this and carbon tetrachloride, and that the reaction proceeds farther and more rapidly in bright light. Gilsonite and refined asphalts, however, yield no residue or less than 0·1 per cent., whereas such products as Texas pitch may yield residues up to 10 per cent. It is shown conclusively that overheating in refining may lead to this figure being much exceeded, and, though the solubility test must now be recognised as merely an empirical one, its retention is recommended. Having regard to the discovery that time as well as light influences the result, it is important that approximately uniform conditions be secured. If solution be effected overnight, and filtration commenced seventeen hours later, exposure to bright sunlight being avoided, closely concordant and useful results may be obtained. Contrary to the statement of Richardson and Forrest, the use of carbon tetrachloride containing as much as 5 per cent. of disulphide as impurity does not affect the results. G. C. J.

Analysis of Vulcanite. I. Simple Method for the Estimation of Sulphur of Vulcanisation in Hot Vulcanised Rubber. G. Hübener. (*Gummi. Zeit.*, 1910, **24**, 213-214; *Chem. Zentralbl.*, 1910, **1**, 1390-1391.)—In the method previously described by the author (ANALYST, 1909, **34**, 170) for the analysis of vulcanite, a portion of the total caoutchouc has to be calculated from the estimation of the sulphur of vulcanisation. The latter value was obtained from the difference between the total and the free sulphur. In the case of samples containing insoluble sulphates as loading, these minerals are included in the value found for total sulphur by Henriques' (alkali fusion) method, and they have to be separately estimated in the ash and deducted. This necessity introduces a complication and an error. According to the following method of procedure a value is obtained for total sulphur with the exclusion of insoluble mineral sulphates : 1 grm. of the rasped sample is treated with 15 c.c. of concentrated nitric acid, and boiled, first on a sand-bath, and lastly in a water-bath, until most of the acid is evaporated. The solution is diluted and treated with 3 c.c. of bromine, the excess of the latter being finally expelled by boiling. The solution is filtered off from the insoluble residue, and the sulphuric acid in solution is precipitated as barium sulphate. The sulphur of vulcanisation is then found as the difference between this value and the free sulphur and sulphide sulphur determined in the manner described (*loc. cit.*). The results found by Henriques' method for total sulphur are slightly lower than those obtained by the above method, owing to the solubility of barium sulphate in presence of large proportions of sodium chloride. J. F. B.

Estimation of Caoutchouc as Tetrabromide. T. Budde. (*Gummi. Zeit.*, 1910, **24**, 212-213; *Chem. Zentralbl.*, 1910, **1**, 1389.)—The author defends the tetrabromide method against suggestions made by Harries and Rimpel that the results are too low. He contends, on the other hand, that the nitrosite method of the latter author gives results which are too high, and that Harries' method of purification does not yield a pure caoutchouc. The following improved procedure is indicated for carrying out the tetrabromide method : 0·15 to 0·20 grm. of the finely chopped, dry sample is digested with 50 c.c. of carbon tetrachloride for twenty-four hours. The swollen caoutchouc is then treated for six hours with 50 c.c. of the brominating reagent (1,000 c.c. of carbon tetrachloride, 6 c.c. of bromine, and 1 grm. of iodine), with occasional agitation. The liquid is then treated with half its volume of alcohol, shaken vigorously, and allowed to stand overnight. The liquid is decanted off through a paper filter, and the precipitate is washed with a mixture of 2 parts of carbon tetrachloride and 1 of alcohol, next with pure alcohol, and is then treated with 30 to 40 c.c. of carbon disulphide. After standing for three to four hours the liquid is mixed with 50 c.c. of petroleum spirit and filtered off through the same filter. The precipitate in the flask and the filter are completely freed from residues of bromine by washing with alcohol; the filter and its contents are returned to the flask, 25 c.c. of $\frac{N}{5}$ silver nitrate solution and 20 c.c. of nitric acid (sp. gr. 1·40) are added, and the whole is boiled until the caoutchouc tetrabromide is completely decomposed and converted into silver bromide. The excess of silver nitrate is titrated back with ammonium thiocyanate, and the bromine value is calculated ; the latter × 0·425 = caoutchouc. The author shows that dammar resin behaves, on bromination, in exactly the same manner as the supposed higher brominated caoutchouc of Harries and Rimpel. J. F. B.

Estimation of Caoutchouc as Tetrabromide: Influence of the Protein. E. Spence. (*Gummi. Zeit.*, 1910, **24**, 212-213; *Chem. Zentralbl.*, 1910, **1**, 1390.)—The author shows that all the known varieties of latex yield caoutchouc contaminated with coagulated protein, no matter how carefully it may have been prepared and washed. In some varieties of washed and dried caoutchouc, particularly in Ceara and Manicoba varieties, the protein frequently amounted to 8 to 10 per cent. The proteins obtained from the latex of *Funtumia elastica* react with bromine. It is not yet known whether, or in what degree, the proteins interfere with the estimation of caoutchouc as tetrabromide, but the possibility should certainly be taken into account. J. F. B.

The Adamkiewicz-Senex Test for Casein in Paper. C. E. Waters and J. C. Beneker. (*J. Ind. Eng. Chem.*, 1910, **2**, 28.)—The Adamkiewicz test for casein sizing in paper consists in extracting the paper with borax solution, precipitating the dissolved casein with acid, drying, and warming gently with a mixture of 2 parts of glacial acetic acid and 1 part of concentrated sulphuric acid. The gradual development of a purple coloration indicates the presence of casein. This test has been simplified by Senex, who moistens the paper with the reagent and warms slightly. The authors have investigated the test, and find that paper sized with rosin also gives a purple coloration. Further experiments showed that powdered resin, wood-pulp, and pine shavings, as well as casein, respond to the test. It is evident, therefore, that, before testing a sample of paper for casein, the paper must be thoroughly extracted with alcohol acidified with acetic acid in order to remove any rosin which may be present. W. P. S.

Melting-Point of Trinitrotoluene. A. M. Comey. (*J. Ind. Eng. Chem.*, 1910, **2**, 103.)—Though the melting-point of trinitrotoluene is given in many books of reference as 82° C. on the authority of Wilbrand, the best attested value hitherto was that of Mills, who finally decided that this should be 78·8° C. The present author has prepared trinitrotoluene which melts sharply at 80·6° C., and finds that many samples of commercial trinitrotoluene melt as high as 80·5° C. G. C. J.

Ylang-Ylang Oil from Réunion. E. Tassilly. (*Bull. Sciences Pharmacol.*, 1910, **17**, 20-27; *Chem. Zentralbl.*, 1910, **1**, 1254-1255.)—A sample of ylang-ylang oil from Réunion had the following characteristics: Sp. gr. at 15° C., 0·939; specific rotatory power $[\alpha]_{D17}^{\circ} = -64^{\circ}$; $[n]_{D20}^{\circ} = 1{\cdot}510$; saponification value, 97. The oil was soluble in 1·5 times its volume of alcohol, the solution becoming turbid on the addition of more alcohol. It contained only 1·28 per cent. of substances not volatile with steam. When cooled, it became slightly turbid. Two oils from the Seychelles had sp. grs. of 0·958 and 0·924, and $[\alpha]_{D17}^{\circ}$ of $-45^{\circ}\ 27'$ and $-18^{\circ}\ 46'$ respectively. A Réunion sample contained 9·05 per cent. of benzoic acid, 4 per cent. of acetic acid, 25·5 per cent. of alcohols (linalool and geraniol), and 31 per cent. of cadinene.

C. A. M.