

ORGANIC ANALYSIS.

Iodimetric Estimation of Acetone. W. Marriott. (*J. Biol. Chem.*, 1918, **16**, 281; through *J. Pharm. Chim.*, 1919, **19**, 133-136.)—With reference to the method described by Shaffer and Marriot (*ANALYST*, 1914, **39**, 184) for the estimation of acetone and β -hydroxybutyric acid in urine, in which use is made of Messingers' method for the estimation of acetone, the following work was done to control the accuracy of that method: A sample of acetone regenerated from the bisulphite compound was purified by distillation with permanganate and then with calcium chloride. The product was then submitted to fractional distillation, and the fraction distilling at 56° to 75° C collected. Very considerable care is required in making up and manipulating dilute aqueous solutions of acetone. The sample is weighed out in a small glass bulb of 2 to 3 c.c. capacity. The bulb is dropped into a 2-litre measuring flask and broken under water, the solution being then made up to the mark. Precautions are required to prevent loss of acetone in measuring off this dilute

solution for analysis. The flask is closed by a rubber stopper with two holes, through one of which is passed a 25 c.c. pipette. The pipette is filled by means of a rubber ball, and the measured liquid is transferred to a flask containing 500 c.c. of water, the point of the pipette being dipped below the surface of the water. To this solution 50 c.c. of $\frac{N}{10}$ iodine and 10 c.c. of caustic soda solution at 60 grms. per 100 c.c. are added. The flask is corked, shaken, and allowed to remain for five to ten minutes; 15 c.c. of hydrochloric acid are added, and the liberated iodine is titrated with $\frac{N}{10}$ thiosulphate. Each c.c. of $\frac{N}{10}$ iodine consumed is equivalent to 0.000968 gm. of acetone. The results are quite sufficiently accurate: for instance, acetone taken 30.62 mgrms., found 30.64 mgrms; taken 20.95, found 21.09 mgrms. Geelmuyden has stated that small quantities of acetone cannot be distilled from aqueous liquids without appreciable loss; the author has proved that, with suitable precautions, acetone can be distilled and collected quantitatively in a few minutes. Five hundred c.c. of an aqueous solution containing 33.7 mgrms. of acetone determined by the above method were placed in a Kjeldhal distillation flask of 800 c.c. capacity, with a tin condenser terminating in a glass tube dipping below the surface of 50 c.c. of water placed in a receiver. Distillation was continued for thirty minutes, but it was ascertained, by titrations made at intervals, that the whole of the acetone had distilled over after ten minutes, the distillate then containing 33.6 mgrms. of acetone by the Messinger method. The losses recorded by Geelmuyden did not occur, and it is suggested that that author did not have the end of the condenser dipping below the water in the receiver.

J. F. B.

Solubilities, Separation, and Purification of Anthracene, Carbazol, and Phenanthrene. J. M. Clark. (*J. Ind. and Eng. Chem.*, 1919, **11**, 204-209.)—A review of the method obtaining the "green salts" from crude coal-tar is given along with representative analyses of tars and oils and the effect of different tars and methods of distillation on the oils. The relative solubility of anthracene, carbazol, and phenanthrene in fourteen different solvents and at five different temperatures is shown. Procedures are described whereby anthracene and carbazol are obtained from 80 to 90 per cent. in purity by means of selected solvents and the proper control of temperatures. The solvents used are crude coal-tar naphtha and light coal-tar bases. A method for the preparation of pure anthracene is shown whereby the phenanthrene is removed by crude coal-tar solvent naphtha and the carbazol by fusion with a mixture of sodium and potassium hydroxides. The sublimed anthracene is then crystallised from pure benzol. A method for the preparation of pure carbazol is described whereby the phenanthrene is removed by crude coal-tar solvent naphtha and the anthracenes by the formation of a sulphonic derivative which is formed by the action of 98 per cent. sulphuric acid in the cold, and which derivative is soluble in water. The non-sulphonated carbazol is filtered and purified by sublimation. A method for the preparation of pure phenanthrene is described whereby the phenanthrene is separated from the anthracene and carbazol by dissolving in crude coal-tar solvent naphtha, boiled with animal charcoal and crystallised from 95 per cent. ethyl alcohol. The effect of different alkalis as agents for the removal of carbazol

is tabulated. A table is given showing the effect of different quantities of 98 per cent. sulphuric acid and water as agents for the removal of anthracene from carbazol.
G. C. J.

Testing Natural Gas for Gasoline Content. G. G. Oberfell, S. D. Shinkle, and S. B. Meserve. (*J. Ind. and Eng. Chem.*, 1919, 11, 197-200.)—The principle of the method recommended consists in absorbing the vapours in a solid absorbing medium such as charcoal, and subsequently recovering the gasoline by distillation. Apparatus for carrying out the test is described and illustrated in detail. The absorption apparatus is portable, so that the vapours from a measured volume of natural gas can be absorbed in charcoal in the field, and the charcoal sent to the laboratory for distillation.
G. C. J.

Estimation of the Methoxyl Group. J. T. Hewitt and W. J. Jones. (*J. Chem. Soc.*, 1919, 115, 193-198.)—In attempting to shorten the Zeisel process, the authors replace the alcoholic silver nitrate by pyridine, then estimate the pyridinium methyl iodide formed by diluting directly with water, acidifying with nitric acid, and adding a known amount of silver nitrate, the excess being then determined by thiocyanate according to Volhard's method. The hydriodic acid required is prepared by saturating an aqueous suspension of iodine with hydrogen sulphide, distilling the resulting solution, and collecting the fraction which boils between 123 and 127° C. (D. 1.7) for use. The pyridine used need not be completely freed from picoline, the fraction of the purified bases obtained from the commercial material distilling between 114° and 117° C. being collected for use. The apparatus employed consists of the usual CO₂ generator, decomposition flask heated in a glycerol bath to 130° C., and rectifying column. The CO₂ carrying the methyl iodide vapour is passed through two test-tubes in series, each containing 10 c.c. of pyridine. A suitable weight of the substance to be analysed is taken, and 20 c.c. of the hydriodic acid are added. After an hour the contents of the test-tubes are washed into a graduated flask, and the iodide estimated as already indicated. The yellow coloration which early develops in the pyridine and vanishes on dilution is without significance, as it is not due to free iodine finding its way into the pyridine; if, however, it should persist after dilution, it should be discharged with a little thiosulphate. The results of many analyses are recorded, which show the accuracy of the method when employed upon brucine hydrate, methyl alcohol, methyl oxalate, alcohol, and salicylates respectively; but unsatisfactory results were obtained with a sample of methyl benzoate and one of hydrated quinine sulphate. The method has many advantages when used for the products of wood distillation or other mixtures containing methyl alcohol, which hitherto has usually been estimated in these products by conversion into methyl iodide and measurement of the volume of the latter compound, but time may be saved and greater accuracy secured by combining the methyl iodide with a tertiary base and estimating the iodine volumetrically.

A suitable amount (see below) of the liquid to be analysed is heated with 20 c.c. of hydriodic acid (D. 1.7) for one hour. The contents of the test-tubes are then completely washed into a graduated flask and made up with water to 100 c.c. An

aliquot portion (see below) of the diluted solution is introduced into a glass-stoppered bottle of 250 c.c. capacity, 70 c.c. of water are added, and then, in order, 25 c.c. of $\frac{N}{10}$ silver nitrate solution and 30 c.c. of approximately $\frac{N}{10}$ nitric acid. The bottle is well shaken for five minutes, and 5 c.c. of concentrated ferric alum indicator are added. $\frac{N}{10}$ thiocyanate solution is now run in until further addition of one drop imparts a permanent orange colour to the liquid. Suitable amounts of liquids to be taken for analysis are given below.

a represents the volume of material to be operated on, and its dilution when necessary. *b* gives the volume of the diluted aqueous pyridine solution, obtained as described above, to be actually used in a titration. *c* is the formula to be used, giving the weight in grms. of methyl alcohol in 100 c.c. of the liquor analysed, where *t* is the number of c.c. of $\frac{N}{10}$ thiocyanate solution used in the titration.

Pyroligneous Acid.—(a) Take 5 c.c. of the original liquor; (b) 40 c.c.; (c) $0.16(25 - t)$.

Crude Wood Naphtha.—(a) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of the diluted solution for distillation with hydriodic acid; (b) 40 c.c.; (c) $1.6(25 - t)$.

Methyl Alcohol and Mixtures of the Alcohol with Acetone.—(a) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of this diluted solution for the estimation; (b) 20 c.c.; (c) $3.2(25 - t)$.

Artificial mixtures containing methyl alcohol and other products of wood distillation were made up and analysed by the method described, the results on the average being about 1 per cent. low, and Stritar and Zeidler (*ANALYST*, 1904, 29, 313) found that the maximum amount of methyl iodide obtainable from pure methyl alcohol in a Zeisel estimation corresponded to a 99 per cent. yield; while they also observed that the other constituents of wood distillates—acetone, formaldehyde, and acetaldehyde—give little or no methyl iodide on treatment with hydriodic acid. Methyl acetate gives one equivalent of methyl iodide, and methylal and dimethylacetal each give two. Guaiacol and other methyl derivatives of the phenols yield their equivalent of methyl iodide, but guaiacol may be eliminated from aqueous solutions of crude wood spirit by shaking with animal charcoal. The present method gives the total methyl alcohol, including both the free alcohol and that combined as methyl acetate; if desired, the ester may be determined by quantitative hydrolysis.

H. F. E. H.

Estimation of Nitro Groups in Organic Compounds by means of Stannous Chloride. J. G. F. Druce. (*Chem. News*, 1919, 118, 133.)—The reduction of aromatic nitro-compounds by stannous chloride in hydrochloric acid solution proceeds quantitatively, and has been used for the estimation of these compounds. The modification of this method employed by the author has given very satisfactory results in a number of cases. The procedure is as follows: A weighed quantity (0.2-0.6 grm.) of the nitro-compound is placed in an Erlenmeyer flask of 200 c.c. capacity, and about 30 c.c. of alcohol are added. The flask is connected with an apparatus generating carbon dioxide, and a slow stream of the gas is passed through the flask while the contents are warmed on the water-bath. When the air

has been displaced, 50 c.c. of stannous chloride solution of known strength are added, and the mixture is kept warm for two hours while a slow stream of carbon dioxide is passed through continuously. The liquid is cooled, the flask is disconnected, and the excess of stannous chloride titrated back with $\frac{N}{10}$ iodine in the presence of starch. The stannous chloride is prepared by dissolving 25 grms. of tin in 250 c.c. of strong hydrochloric acid and making up to 1,000 c.c. The solution is standardised with iodine immediately before use. Perfectly satisfactory results have been obtained with nitrobenzene, *o*-nitrotoluene, *m*-nitroaniline, *p*-nitroaniline, *m*-dinitrobenzene, and *p*-nitrotoluene.
J. F. B.

New Reaction of Paraffin Hydrocarbons. E. V. Lynn. (*J. Amer. Chem. Soc.*, 1919, **41**, 368-370.)—During the course of some experiments with nitrosyl chloride it was noticed that a saturated solution of this gas in normal heptane remained unchanged when kept in a dark place, but in sunlight the reddish-brown colour of the solution changed gradually to blue, and ammonium chloride was precipitated; the blue colour then disappeared, and the resulting turbid liquid deposited a yellow oil; at the same time hydrogen chloride containing a little nitric oxide was evolved. The process was repeated until 50 grms. of the oil had been collected. The oil had a very fragrant odour, was soluble in alcohol, and examination showed it to consist mainly of a mixture of the three ketones from heptane (methylamyl, dipropyl, and ethylbutyl ketones), dipropyl ketone predominating. It was found that petroleum spirit, *b.*-pt. 45° to 70° C., gave a similar reaction with nitrosyl chloride, and it appears that the latter will prove to be a useful reagent in the study of saturated chain compounds, and also of aromatic compounds, etc.

W. P. S.

Isolation and Examination of the Textile in Rubber-Proofed Cotton Fabrics. B. D. Porritt. (*J. Soc. Chem. Ind.*, 1919, **38**, 50-52 T.) The removal of the whole of the proofing from vulcanised and mineralised rubber-proofed fabrics is almost impossible by mechanical means. Solvents of high boiling-point will generally effect the desired result, but when very high temperatures are employed the cellulose is obviously damaged. A useful preliminary attack on the proofing composition is obtained by steeping in carbon bisulphide or extracting with this solvent in a Soxhlet apparatus. After this preparation the author recommends that the sample be heated for about an hour at 160° C. in a petroleum "white spirit" having a sp. gr. at 15.5°/15.5° C. = 0.7798, and a distillation range such that 48 per cent. distils at 170° C. and the whole at 225° C. Comparisons of the original and stripped fabrics according to their weight per square yard showed that in the case of "pure" coatings free from mineral matters the results were very satisfactory. A slight shrinkage in the width of the cloth takes place as the result of proofing, so that the weights of the stripped fabric may show a slightly heavier cloth than the original actually employed. On the other hand, fabrics are sometimes coated in the grey condition containing size, etc., in the warps, which is lost during the process of stripping; thus the stripped fabric may be slightly lighter than the original. The estimations are made in terms of dry cloth, and the weights are calculated back in terms of air-

dry material by applying the re-gain factor for moisture of 8.5 per cent. When mineral pigments, lamp-black, rubber substitutes, etc., are present, considerable variation in the treatment for stripping must be made. "Substitutes" require a subsequent treatment with N/1 alcoholic caustic soda for their complete elimination, and this is followed by boiling with dilute sodium carbonate and then treating with dilute acetic acid for removing basic matters of the ash. In some cases this may be repeated or varied by additional treatments with aqueous 2 N caustic soda and with tartaric acid solution. The completeness of the stripping is controlled by finally incinerating and estimating the ash. As a rule it is possible to obtain results sufficiently accurate for technical purposes with samples 3 inches square, although, on account of the unavoidable variability of textile fabrics, there is no guarantee that an accurate estimation of a small sample of the fabric really represents the average constitution of the whole piece. The results will tend to be less accurate the more severe and numerous the treatments with alkaline solutions necessary to render the mineral matters soluble in dilute acids. Certain mineral sulphides are very obstinate, and in some cases it is necessary to determine the cellulose by combustion after removing all the organic constituents.

J. F. B.

Study of Fatty Acids obtained from Varnish Oils and from Varnishes.
W. T. Pearce. (*J. Ind. and Eng. Chem.*, 1919, 11, 121.)—The object of the work was to obtain information which would assist in the detection and approximate estimation of China-wood and other oils that are being substituted for linseed in oil varnishes. The linseed oil used had been boiled two hours at 200° C. with oxides of lead and manganese. The acid mixtures were in most cases obtained by making up mixtures of the desired oils, saponifying with alcoholic potash, extracting the liberated acids with ether, and drying the solvent-free acids at 110° C. The refractive index of the fatty acids gives a good measure of the percentage of China-wood oil, advancing from 1.4666 at 20° C. for pure linseed oil to 1.4707 for oil with 5 per cent. China-wood oil, 1.4775 with 10 per cent., 1.4824 with 20 per cent., and 1.4895 with 50 per cent. Where the acids come from varnishes, however, the values are not in good agreement.

The jelly test, as described by Boughton (*U.S. Bureau of Standards, Technical Paper 65*), gives useful results, but the author uses the fatty acids instead of the oils, increases the time of heating to two hours and uses 5 grms. Mixtures of soya bean and China-wood oils and cottonseed and China-wood oils give just as good results as linseed and China-wood oils, while mixtures of linseed and soya bean oils and linseed and cottonseed oils give no jelly. Menhaden oil (100 per cent.) gives a small brown residue which in no way resembles China-wood jelly. Whilst China-wood oil gives 1 inch of jelly in a 6 inch by $\frac{5}{8}$ inch test-tube, a mixture of 50 per cent. China-wood oil and 50 per cent. linseed oil gives $\frac{1}{2}$ inch, and when the percentage of China-wood oil falls to 33 per cent., 20 per cent., 10 per cent., and 5 per cent., the jelly formed is $\frac{1}{4}$ inch, $\frac{1}{8}$ inch, a very small amount, and nil respectively. China-wood and menhaden oils in the ratio 1 : 1 give $\frac{1}{4}$ inch, and in the ratio 1 : 4 a very small amount. China-wood, menhaden, and linseed oils in the ratio 4 : 3 : 3 give $\frac{1}{8}$ inch, and China-wood, soya, and menhaden oils in the ratio 1 : 2 : 2 give $\frac{1}{8}$ inch. Fatty acids from a copal and rosin varnish made with China-wood, menhaden, and linseed oils in the ratio

1 : 2 : 2 gave $\frac{1}{4}$ inch jelly, whilst a varnish containing rosin and China-wood oil alone behaved like straight China-wood oil, and one containing copal and linseed gave a negative result.

The physical characteristics of some mixtures of fatty acids are given. Those from China-wood and linseed oils in the ratio 1 : 1 are largely solid and possess a characteristic odour, whilst the reduction of the proportion of China-wood oil to 1 : 4 leads to the disappearance of the odour and most of the solids. Mixtures of China-wood oil with soya or cottonseed oils behave similarly.

G. C. J.

Methods of Varnish Analysis. W. T. Pearce. (*J. Ind. and Eng. Chem.*, 1919, 11, 200-201.)—The author opens with the statement that “it is generally agreed that the following of any of the published methods will give results that . . . do not represent either the quantities or qualities of the materials used. . . . This opinion needs to be fully investigated.” As a result of experiments described in the paper it is shown that Boughton’s method for the separation and estimation of resins and oils, although long and tedious, does give the actual values within 3 per cent. Neither Darner’s nor Twitchell’s method can be relied on. Rosin can probably be estimated within 1 per cent. when 20 per cent. is present, or within 0.3 per cent. when 5 per cent. or less is present. For the estimation of rosin the author uses McIlhiney’s method, substituting Wolff’s esterification method for Twitchell’s. The experiments were made on varnishes of known composition, made by the author, and their preparation and the manner of calculating the final composition are described in detail. The oils used included linseed, China-wood, menhaden and soya-bean oils; the resins included Sierra Leone copal, East India copal, and kanni, whilst turpentine and benzine were used as thinners, and driers, the composition of which are not stated, were also used.

G. C. J.