

Organic Analysis.

Detection of Oxygen in Organic Compounds. J. Piccard. (*Helv. Chim. Acta*, 1922, **5**, 243-244.)—The test is based on the fact that iodine dissolves in oxygen-free solvents and gives a violet coloration, whilst it gives a brown colour with liquids containing oxygen. The sensitiveness is increased by making the ratio Iodine:Oxygen as small as possible, and by viewing a long column of the liquid. A solution of iodine (1 in a million) in pure benzene is observed in a flat-bottomed glass tube 90 cm. long; on the addition of a soluble substance containing oxygen the violet colour changes distinctly to brown. A quantity of oxygen considerably less than can be estimated by combustion may be detected in this way.

H. E. C.

Titration in Ethyl Alcohol as Solvent. E. R. Bishop, E. B. Kittredge and J. H. Hildebrand. (*J. Amer. Chem. Soc.*, 1922, **44**, 135-140.)—Hydrogen-electrode titration curves are given for a number of reactions in ethyl alcohol solution, together with a table of indicators for use in such reactions. The hydrogen ion concentration was measured by means of a hydrogen electrode against a standard mercurous bromide electrode. The values are given in terms of electromotive force. Colour changes of indicators in ethyl alcohol solution are as follows, the figures giving the E.M.F. (in volts) of the change:—Bitter almond oil green: green, 0.69 colourless; brom-phenol blue: yellow, 0.34 green, 0.47 blue; cresol red: 0.20 pink, 0.30 orange; curcumin: greenish-yellow, 0.66 red, 0.85 orange, 0.91 golden; cyanine: colourless, 0.24 blue; gallein: rose, 0.68 violet-blue; iodeosin: golden-brown, 0.20 pink; methyl green: blue, 0.66 lavender; methyl orange: pink, 0.20 orange, 0.23 yellow; methyl violet: violet, 0.95 colourless; methyl red: red, 0.54 orange, 0.62 yellow; naphthol-benzoin: light brown, 0.70 blue; *p*-nitrophenol: colourless, 0.61 yellow-green; phenolphthalein: colourless, 0.68 red; resorcinol blue: red, 0.39 blue; rosolic acid: golden, 0.58 orange, 0.65 pink; sodium alizarin sulphonate: greenish-yellow, 0.50 orange, 0.57 rose, 0.82 violet; thymol blue: red, 0.30 golden; thymolphthalein: colourless, 0.82 blue; trinitrobenzene: colourless, 0.68 golden-orange; tropæolin: salmon pink, 0.20 orange, 0.23 golden; tropæolin 00: pink, 0.15 orange, 0.20 yellow.

W. P. S.

Relation between the Refractive Index and the Chemical Characteristics of Oils and Fats. G. F. Pickering and G. E. Cowlshaw. (*J. Soc. Chem. Ind.*, 1922, **41**, 74-77 T.)—Owing to the effects of oxidation and polymerisation, there is no obvious relation between the iodine values of commercial oils and their refractive indices, but, when freshly prepared oils from good material

are examined, the higher iodine value corresponds with the higher refractive index. Factors which affect the refractive index are: the acid value (A.V.), saponification value (S.V.), oxidised and hydroxylated acids, and unsaponifiable matter. It is shown on theoretical grounds that the following equation connects the refractive index and the iodine value (I.V.):—

$$n_D^{40} = 1.4643 - 0.000046(\text{S.V.}) - 0.0096(\text{A.V./S.V.}) + 0.0001171(\text{I.V.}).$$

If it is found that the refractive index of a sample is higher than that calculated from this equation, it indicates that the oil is not fresh, or has been prepared from damaged material. Experiments on the oxidation of the fatty acids of oils with permanganate show that the refractive index of the total fatty acids rises, and that of the normal (*i.e.* soluble in petroleum spirit) fatty acids falls. With the acids from the distillation products of fatty acids, the refractive index of the total fatty acids rises, and that from the normal fatty acids first rises, then falls, possibly as a result of polymerisation.

H. E. C.

Extraction of Oils and Fats from Chrome-Leather. D. Woodroffe. (*J. Soc. Leather Trades Chem.*, 1922, 6, 97–102.)—After a review of previous work on this subject it is suggested that petroleum spirit, the solvent usually employed at present, should be replaced by chloroform, which is a more efficient solvent than the former for the materials usually employed for fat-liquoring chrome-leathers (chrome-sole, box-calf, glacé kid, etc.). These materials include neatsfoot, rape, fish and linseed oils, dégras, wool-grease, resin and sulphonated oils. Ether is not desirable on account of its solubility in water. Carbon tetrachloride, benzene, and trichlorethylene are unsuitable because of their higher boiling points, and the consequent necessity for heating the extracted substances to 105° C., which might cause increase of weight through oxidation.

R. F. I.

Estimation of Free Sulphuric Acid in Leather. C. van der Hoeven. (*Collegium*, 1921, 458; *J. Soc. Leather Trades Chem.*, 1922, 6, 117.)—This estimation is becoming more important now that synthetic tannins are being more widely used. The method of Thomas (*J. Amer. Leather Chem. Assoc.*, 1920, 504) is modified as follows:—A weighed quantity of fine leather-parings is treated in an extraction apparatus, at a definite temperature, with a solution of sodium dihydrogen phosphate, which, after some hours, extracts the whole of the sulphuric acid. The extract is made up to a definite volume, and the total sulphuric acid estimated in an aliquot portion by means of barium chloride. The neutral sulphuric acid is estimated in the ash of the original sample, care being taken to oxidise any reduced sulphate by means of iodine or bromine water. The difference between the two figures gives the free sulphuric acid.

R. F. I.

Quantitative Method for the Separation and Estimation of Phenols. M. T. Hanke and K. K. Koessler. (*J. Biol. Chem.*, 1922, 50, 271–288.)—The following method is applicable to the examination of media in which bacteria have been grown in the presence of salts, glycerol or glucose, but is not adapted to the investigation of urine or blood. The liquid containing the phenols is acidified

and distilled under ordinary pressure. Phenol and *p*-cresol distil quantitatively, and, if one only is present, it may be estimated by the method already described (see preceding abstract), but this procedure is useless if the distillate contains both. The residue, after evaporation to a small volume, is extracted ten times with ether, which removes the aromatic hydroxy-acids quantitatively, and they are then dissolved in dilute phosphoric acid and estimated. The particular hydroxy acid present (if one only) may be identified, and the amount estimated, by the colour developed on the addition of the reagents and the time required for the development of its maximum intensity. The aqueous solution, after extraction with ether, is made alkaline with sodium carbonate and extracted six times with amyl alcohol, which removes tyramine, this extract afterwards being shaken several times with *N* sulphuric acid, in which the colorimetric estimation of the phenol is made. The aqueous residue from the amyl alcohol extraction contains tyrosine; it is treated with excess of concentrated hydrochloric acid, evaporated, the residue dissolved in water, and the tyrosine estimated colorimetrically. Experimental details are given of work carried out in the development of these methods

T. J. W.

Electrometric Titration of Azo Dyes. D. O. Jones and H. R. Lee. (*J. Ind. Eng. Chem.*, 1922, **14**, 46–48.)—Sufficient (approximately one grm.) of the finely powdered dye to require for reduction from 30 to 45 c.c. of 0.25 *N* titanous chloride solution is weighed out, 25 c.c. of distilled water are added, and the flask is heated on a steam bath for about 10 minutes. Twenty-five c.c. of 40 per cent. sulphuric acid are run in, the flask is stoppered, and a current of carbon dioxide is passed through it for five minutes. From 35 to 50 c.c. of 0.25 *N* titanous chloride solution are added, the mixture is boiled for five minutes and cooled to 30° C., and the excess of titanous chloride titrated with 0.05 *N* ferric alum solution as follows:—The reaction flask, provided with one calomel electrode and one platinum electrode, is connected with a potentiometer, and the voltage produced by each addition of the ferric alum solution is noted. On reaching the end point the connections with the electrodes are reversed, and the addition of the ferric alum solution continued. A curve of the reaction is drawn with voltage readings as ordinates and c.c. of ferric alum solution as abscissæ, from which the end point is determined and the amount of titanous chloride solution used is deduced. For routine work sufficient accuracy will be attained by taking a large deflection of the galvanometer needle as the end point, after adjustment to zero at the commencement of the back titration.

T. J. W.

Estimation of the "Bromine Figure" or "Chlorine Factor" of Pulp. A. Tingle. (*J. Ind. Eng. Chem.*, 1922, **14**, 40–42.)—An investigation of the action of approximately normal solutions of bromine upon cellulose and on unbleached sulphite spruce pulp has shown that accurate results are obtainable only when the substance under examination is in solution; no reaction occurs between bromine and cellulose within thirty minutes; pulp containing lignone appears to react with bromine in definite steps, one of which is completed in thirty minutes, and the

results obtained bear a definite and simple ratio to the amount of chlorine used in bleaching. For the method adopted the following solutions are used:—*Bromine solution*: Eight grms. of bromine are added to 100 c.c. of *N* sodium hydroxide solution, and the mixture is shaken until solution is complete and is then boiled. After cooling, the liquid is made up to one litre, and is then standardised by the addition of hydrochloric acid and potassium iodide and titration with 0.1 *N* sodium thiosulphate solution. *Acid solvent*: Fifty c.c. of concentrated sulphuric acid are slowly added to 450 c.c. of hydrochloric acid (sp. gr. 1.19). From 0.6 to 0.75 gm. of the dry pulp, contained in a stoppered bottle, is dissolved by agitation with 30 c.c. of the acid solvent until a homogenous mixture is obtained. To the solution 20 or 25 c.c. of the bromine solution are added, and the bottle thoroughly shaken, and subsequently gently agitated at intervals for thirty minutes. Twenty-five c.c. of 8 per cent. potassium iodide solution are run in, and the mixture is well diluted and titrated with 0.1 *N* sodium thiosulphate solution, starch solution being added as partial indicator. The end point is indicated by the disappearance of the red tint due to the combination of iodine with the cellulose, which occurs shortly after the vanishing of the starch-iodide blue. The “bromine figure” is obtained by dividing the weight of pulp taken by the number of c.c. of sodium thiosulphate solution used, and the “chlorine factor” from the expression

$$\frac{\text{C.c. of thiosulphate solution} \times 0.00355 \times 100}{\text{Weight of pulp taken}}$$

T. J. W.