

## ORGANIC ANALYSIS.

**Colour Reaction for Wood-Fibre.** A. Kaiser. (*Chem. Zeit.*, 1902, xxvi., 335.)—Equal volumes of amyl alcohol, free from furfural, and strong sulphuric acid are warmed on the water-bath to about 90° C., until a slight evolution of gas occurs; the faintly orange mixture is then cooled. This reagent, which may be termed “amyl-sulphuric acid,” has the property of turning wood-fibre red, violet, or dark indigo-blue, according to the quantity present. Newspaper or pine shavings moistened therewith strike first a greenish, afterwards a bright blue colour; while pure Swedish filter-paper only becomes red and commoner qualities violet. Appearance of the tint is hastened by a current of air and by gentle warming. As the colours vary with the

quantity, it is possible roughly to gauge the proportion of wood-fibre present in a sample of paper. The whole process is an adaptation of Vitali's reaction.

F. H. L.

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**The Alkalinity of Crude Sugar.** Herberger. (*Centralbl. Zuckerind.*, 1902, x., 552; through *Chem. Zeit. Rep.*, 1902, 92.)—The author states that phenolphthalein is useless for determining the alkalinity of crude sugar, since various salts and organic substances are present in the material which cause it to appear acid when it is really alkaline.

F. H. L.

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**Quantitative Estimation of Arabinose.** C. Neuberg and J. Wohlgemuth. (*Zeits. physiol. Chem.*, 1902, xxxv., 31; through *Chem. Zeit. Rep.*, 1902, 108.)—In the course of a research in which large quantities of the three arabinoses and their derivatives were required, the authors tested the following method. One hundred c.c. of urine, to which 1 gramme of arabinose had been added, was acidified with two drops of 30 per cent. acetic acid, concentrated on the water-bath to 40 c.c., and treated with 40 c.c. of hot 96 per cent. alcohol. After cooling for two hours the deposited salts were filtered off and washed with 40 c.c. of 50 per cent. spirit. The filtrate was mixed with 1.4 grammes of diphenylhydrazine, warmed in a boiling water-bath for half an hour, allowed to stand for twenty-four hours, and then filtered through a Gooch crucible, using the liquor for rinsing purposes. The crystals were then washed with 30 c.c. of 30 per cent. alcohol, which left them brilliantly white. The crucible was heated in the drying oven at 80° C. to constant weight, when the hydrazone assumed a faint violet tint, and the yield was found to be 2.1055 grammes of hydrazone, corresponding with 0.9993 gramme of *l*-arabinose, or 99.93 per cent. of the theoretical. Similar tests with *d*-arabinose gave a return of 99.80 per cent., and with *i*-arabinose 100.06 per cent. The method is therefore available for the separation of this sugar from other carbohydrates, especially xylose, even when the latter is present in considerable excess. It is necessary that 1 per cent. of arabinose be present; weaker liquids must be previously concentrated *in vacuo*.

F. H. L.

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**On Stahre's Reaction for Citric Acid.** A. Wöhlk. (*Zeit. anal. Chem.*, 1902, xli., 77-100.)—The sensitive reaction for citric acid discovered by Stahre (*Nordisk Farm. Tidsskrift*, 1895, ii., 141) is based upon the fact that on oxidizing citric acid with potassium permanganate and adding bromine a white precipitate insoluble in ether is obtained. Stahre concluded that in this reaction the citric acid was oxidized to acetone, which was converted by the bromine into a bromacetone.

In applying the test when less than 5 milligrammes of citric acid are present, the acid is dissolved in 2 c.c. of water, and heated to 30° C. after the addition of 2 to 4 drops of  $\frac{N}{10}$  permanganate solution. If any slight precipitation of manganese peroxide occur, 1 or 2 drops of a 4 per cent. solution of ammonium oxalate and about 1 c.c. of 10 per cent. sulphuric acid are introduced to clear the liquid. On now adding 2 drops of bromine water a distinct turbidity is produced.

When more than 5 milligrammes of citric acid are present the solution in 2 c.c. of water is treated with 5 drops of the permanganate solution, heated to 30° to 40° C., cooled, and mixed with 1 c.c. of dilute sulphuric acid. Should any precipitate be formed it can be removed by the addition of a little ammonium oxalate. Bromine water then added drop by drop gives a precipitate of extremely fine needles of pentabromacetone.

Stahre's reaction is obtained not only with pure solutions of citric acid and its salts, but also in the presence of other organic acids precipitated by calcium, such as tartaric, oxalic, malic acids, or inorganic acids, such as sulphuric and phosphoric acids. In such cases, however, more permanganate must be used, and it is best to make the test on a hot solution. Organic acids that react with bromine must obviously be removed.

The author confirms the statements of Henkel, Scheibe, and others as to the presence of citric acid as a normal constituent of milk. He has separated a compound which he has identified as citric acid by Stahre's reaction and other tests.

C. A. M.

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**The Determination of Mustard Oil.** P. Roeser. (*Journ. Pharm. Chim.*, 1902, xv., 361-364.)—The method recommended by the author is based upon the conversion of the allyl isothiocyanate into thiosinamine (as in the methods of Gadamer, etc.), adding standard silver nitrate solution to the ammoniacal liquid, and titrating the excess of silver by Denigés' method.

Five c.c. of a 1 per cent. solution of the commercial essence are mixed with 10 c.c. of ammonium hydroxide, and, after dilution with water, shaken with 10 c.c. of  $\frac{N}{10}$  silver nitrate solution. After standing for twenty-four hours, the liquid is made up to 100 c.c. and filtered, 50 c.c. of the filtrate treated with 5 c.c.  $\frac{N}{10}$  potassium cyanide solution, and the excess of cyanide titrated with silver nitrate solution, a few drops of a slightly ammoniacal 5 per cent. solution of potassium iodide being used as indicator.

The number of c.c. of silver nitrate solution taken up by the sulphur, doubled and multiplied by the factor 0.3137, gives the percentage of mustard oil in the essence.

For the determination of mustard oil in mustard flour, leaves, etc., 5 grammes of the sample are mixed with 60 c.c. of water and 15 c.c. of 60 per cent. alcohol, and distilled after standing for two hours. The distillate is received in a flask containing 10 c.c. of ammonium hydroxide, and after two-thirds of the liquid have passed over, it is mixed with 10 c.c. of  $\frac{N}{10}$  silver nitrate solution and diluted to 100 c.c., and the determination completed as described above.

It is stated that this method gives results almost identical with those obtained by the methods of Dieterich and Gadamer.

C. A. M.

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**Quantitative Separation of Cholesterin from Fats.** E. Ritter. (*Zeits. physiol. Chem.*, 1902, xxxiv., 430; through *Chem. Zeit. Rep.*, 1902, 100.)—The author has submitted his own process (this vol., p. 16) and that proposed by Bömer to a comparison, using in each case a fat relatively rich in phytosterin. He finds that his own method returns rather more phytosterin than Bömer's process, and considers that many of the objections to the latter are avoided. The product is also purer, but it is not absolutely pure phytosterin.  
F. H. L.

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**The Composition of Cacao Butter.** J. Klimont. (*Monatsh. für Chem.*, 1902, xxiii., 51-59.)—This paper is a continuation of the author's former communication on this subject (*ANALYST*, xxvii., 15), in which he stated that he had identified tripalmitin, tristearin, and a mixed glyceride containing the radicles of oleic, palmitic, and stearic acids, together with another mixed glyceride.

From a consideration of the elementary composition, iodine value, and saponification value of this last glyceride he has come to the conclusion that it contains the radicals of myristic, palmitic, and oleic acid, and possibly of some still lower fatty acids.

Neither arachidin nor arachidic acid could be detected in the specimen of fat examined.  
C. A. M.

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**A Note on the Use of the Bechi or Silver Nitrate Test on Olive Oils.** L. M. Tolman. (*Journ. Amer. Chem. Soc.*, xxiv., 396.)—Since some olive oils free from cottonseed oil give a brown coloration with the Bechi test as generally applied, the author recommends the following preliminary treatment, which, whilst not affecting the reducing action of the cottonseed oil, removes the free acid and other products of rancidity of the olive oil: To 25 c.c. of the oil, 25 c.c. 95 per cent. alcohol are added, and the whole is gently heated and then vigorously shaken; after allowing the liquids to separate, the alcoholic solution is decanted off, and the residue washed first with 2 per cent. nitric acid and finally with water. For the test, 10 c.c. oil, 10 c.c. amyl alcohol, and 5 c.c. of the reagent (2 grammes silver nitrate dissolved in 200 c.c. alcohol, with the addition of 40 c.c. ether and 2 drops nitric acid), are mixed in a test-tube. Half the mixture is kept for comparison, the other half being heated for ten minutes in a boiling water-bath. The above method of purification is stated to give very satisfactory results, and can be readily applied to lard and other fats.

A. G. L.

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**Comparison of Methods used to Determine the Iodine Value of Oils.** F. W. Hunt. (*Journ. Soc. Chem. Ind.*, 1902, xxi., 454.)—The methods compared were those of Hübl, Wijs, and Hanus (see *ANALYST*, xxvii., 15). He found that the Wijs solution (ICI in glacial acetic acid) lost 3 per cent. of its strength in two weeks, and the Hanus solution (IBr in glacial acetic acid) nearly 5 per cent. In determining

the iodine values, Hübl's solution was allowed to act for five hours, the other two for one hour. Each determination was done in duplicate:

	Hübl.	Hanus.	Wijs.
Pale seal ... ..	117.5	120.7	124.8
Whale ... ..	120.2	120.6	123.7
Olive ... ..	82.3	81.9	83.4
Castor (cold drawn) ... ..	82.6	84.4	85.6
Dogfish liver ... ..	134.7	141.2	143.2
Arachis (earth-nut) ... ..	91.8	91.6	93.4
Arctic shark ... ..	89.0	93.8	98.9
Pale rape ... ..	103.0	101.9	102.1
Coast cod ... ..	148.5	147.5	154.6
Newfoundland cod ... ..	144.8	150.0	154.7
Linseed ... ..	174.8	174.5	177.3
Cottonseed ... ..	108.5	107.0	110.0

The Wijs solution gave results higher than the Hübl solution, especially in the case of fish oils. The Hanus solutions gave results which were in some cases intermediate and in others agreed with those given by Hübl's solution.

Experiments were also made using a solution of iodine monobromide in carbon tetrachloride. The results obtained were:

	Iodine Value.	Corrected for Substitution.
Olive oil ... ..	82.0	—
Coast oil ... ..	153.9	—
Linseed ... ..	179.7	177.8
Arachis ... ..	90.8	89.5
Pale seal ... ..	125.4	124.5

The author does not recommend this solution, however.

A. M.

**On the Temperature Reaction of Oils with Sulphuric Acid—Maumené's Test.** H. C. Sherman, J. L. Danziger, and L. Kohnstamm. (*Journ. Amer. Chem. Soc.*, xxiv., 266.)—The authors have investigated the sources of errors in Maumené's test, especially as regards the drying oils, which give a violent reaction with the sulphuric acid, and come to the conclusion that if the oil is diluted with some non-drying oil the value calculated is always too high. They find that the use of a somewhat more dilute acid (89 to 90 per cent.) than is usually employed gives good results, which are directly comparable for both drying and non-drying oils. They recommend the statement of all results as "specific temperature reactions," according to the suggestion of Thomson and Ballantyne (*Journ. Soc. Chem. Ind.*, x., 233), which are obtained by multiplying the observed rise of temperature by 100, and dividing by the rise observed when 50 grammes water are treated with 10 c.c. of the same acid under the same conditions. Contrary to Thomson and Ballantyne, however, they find this value is slightly lower for a more dilute acid; but, still, their results agree reasonably well with those obtained by these authors.

A. G. L.

**Metallic Soaps from Linseed Oil. An Investigation of their Solubilities in Certain of the Hydrocarbons.** Hermann T. Vulté and Harriet Winfield Gibson. (*Journ. Amer. Chem. Soc.*, xxiv., 215.)—The authors have investigated the solubilities of a number of metallic soaps from linseed oil in various petroleum solvents and in turpentine, as well as the permanence of the solutions, and give tables showing the results obtained. They find that the lead soap separates from its solutions in all the petroleum solvents in less than one hour, the nickel soap only after several days, the iron soap only on the application of a gentle heat, and that the manganese soap is unique as regards its drying properties. They also find that no one solvent can be recommended for all the soaps, there being a maximum solubility for each one in some special solvent.

A. G. L.

**Characteristics of Butter from Human Milk.** Sauvaitre. (*Ann. de Chim. nat.*, 1902, vii., 143-145.)—The author has obtained the following results with a specimen of human butter, and compares the figures with those given by a sample of cow's butter :

	Cow's Butter.	Human Butter.
Specific gravity at $\frac{100^{\circ}}{15^{\circ}}$ C. ... ..	0.866 per cent.	0.870 per cent.
Critical temperature of solution in absolute alcohol ... ..	56° C.	59° C.
Coefficient of solubility in absolute alcohol ... ..	43.3 per cent.	34.7 per cent.
Melting-point of insoluble fatty acids ... ..	40.5° C.	40° C.
Solidification-point ,, ,, ... ..	39° C.	37° C.
Saponification value ... ..	221.2 per cent.	218.4 per cent.
Reichert-Wollny value ... ..	26.3 ,,	15.8 ,,
Hehner value ... ..	87.2 ,,	89.2 ,,
Iodine value ... ..	35.51 ,,	43.37 ,,
Total volatile acids ... ..	6.69 ,,	4.41 ,,
Ratio of butyric acid to caproic acid ... ..	2.2 : 1	2.4 : 1
Unsaponifiable matter ... ..	1.58 per cent.	4.68 per cent.
Melting-point of unsaponifiable matter ... ..	139° C.	143° C.

C. A. M.

**Detection of Indican in Urine.** Bertault. (*Journ. Pharm. Chim.*, 1902, [6], xv., 277; through *Chem. Zeit. Rep.*, 1902, 92.)—If the urine contains iodine (or bromine) as well as indican, the well-known test must be modified as follows: After the sample has been treated with an equal volume of hydrochloric acid, a few c.c. of chloroform, and a few drops of sodium hypochlorite, the acidified urine is pipetted off, the tube containing the chloroform is washed with water to remove the bulk of the acid, and then potassium hydroxide is added to alkalinity. The violet colour produced by the iodine disappears, and the chloroform remains blue if indican is present, or colourless in its absence.

F. H. L.

**Valuation of Rubber Goods.** A. Heintz. (*Chem. Zeit.*, 1902, xxvi., 247.)—The author suggests a method for the valuation of rubber goods, in which an attempt

is made, by ultimate analysis, to determine the proportion of true caoutchouc present. After a qualitative examination, the various foreign organic substances are removed by treatment with Henriques' solvents: unsaponifiable oils by ether, asphaltum by nitrobenzene, "substitutes" by alcoholic soda. The last traces of these liquids are next most carefully washed away, the residue is thoroughly dried, a combustion is carried out, and the amount of caoutchouc is estimated from the gain of the sulphuric acid tube, on the assumption that the body remaining after the above process is represented by the formula  $(C_{10}H_{16})_n$ . The method is not offered as an exact process, but one for commercial purposes only. It suffers from two possible sources of error: (1) That the caoutchouc originally used in the manufactured goods does not correspond in composition with the formula quoted, but contains some oxygen compound, resins, etc.; (2) that the solvents do not remove the whole of, or remove substances other than, those they are supposed to extract. As regards the first point, analysis of the washed rubber employed in the manufacture of boots has shown that on an average it consists of 97 per cent. of  $(C_{10}H_{16})_n$ , so that even if the finished wares contained 50 per cent. of caoutchouc, which is unlikely, the error would be only 1.5 per cent. In order to settle the second point, analyses have been made of several trade samples of finished goods and of materials prepared specially for the author, both by his process and by that of Henriques, etc. Two samples of Russian-made shoes gave 57.63 and 60.43 per cent. of inorganic matter, 1.51 and 1.57 per cent. of sulphur, 19.23 and 18.62 per cent. of organic substance, or 21.63 and 19.38 per cent. of caoutchouc, by difference respectively. By the author's process they gave 20.23 and 18.65 per cent. of caoutchouc, or, after correction for the 3 per cent. of oxygenated matter, 20.84 and 19.21 per cent. A material composed of ceresin and brown "substitutes," beside the rubber and sulphur, gave 75.11 per cent. (corrected) on ultimate analysis, whereas it contained 76.75 per cent.\* of caoutchouc. Another specimen containing inorganic matter, beside the sulphur and caoutchouc, gave 49.65 per cent. on combustion, the actual amount of rubber being 49.30 per cent.\*

F. H. L.

**The Determination of Sulphur in Plants.** G. S. Fraps. (*Journ. Amer. Chem. Soc.*, xxiv., 346.)—To 5 grammes of the material, placed in a  $3\frac{1}{2}$ -inch porcelain dish, 20 c.c. concentrated nitric acid are gradually added; the mixture is heated cautiously on the water-bath, then concentrated, and, after the addition of 10 c.c. of a 5 per cent. solution of potassium nitrate, evaporated to dryness; the residue is ignited, at first gently, finally over the blast-lamp, and the sulphur in it estimated as usual.

A. G. L.