

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

The Chemical Detection of Rancidity in Butter. P. Soltsien. (*Chem. Rev. Fett-u. Harz Ind.*, 1905, xii., 177, 178.)—The products causing the characteristic effects of rancidity can be distilled in a current of steam, and if the distillate is treated with alkali in excess to neutralize the fatty acids, and again distilled, they are obtained in a more concentrated form. The products from rancid lard give strong aldehydic reactions, such as the reduction of ammoniacal silver nitrate, but these hardly occur in the case of the distillate from rancid butter. Welman's phosphoric acid reagent is recommended as a reliable chemical test. It can be applied directly to a colourless fat, and on treating the mixture with ammonia in excess, a more or less pronounced blue coloration is produced, according to the degree of rancidity. In the case of a coloured oil or fat, such as butter, the test is applied to the distillate obtained as described above, and this should also be done whenever any green coloration is produced on the direct addition of the reagent to a colourless fat. The reaction with ammonia does not take place until after thirty seconds to a minute. The test can be carried out simultaneously with a determination of the free volatile fatty acids.

C. A. M.

Detection of Wood Spirit in Essences, Brandies, Tinctures, and Fluid Extracts. R. Peters. (*Chem. Zeit. Rep.*, 1905, xxix., 218.)—The wood spirit used to denature brandy for commercial purposes must contain 25 per cent. acetone. This fact makes the detection of wood spirit in brandy, etc., very easy. The author considers Légal's process the best; this is carried out as follows: 10 c.c. of the alcohol-containing material are mixed with water, and 20 c.c. of the mixture distilled off, using a small flame. To 10 c.c. of the well-mixed distillate there is added 1 c.c. of a freshly prepared 1 per cent. solution of sodium nitro-prusside (this must be kept from the light), and then 2 c.c. of an approximately 4 per cent. solution of caustic soda; a greater quantity of the latter must be used for strongly acid liquids. If acetone is present, a more or less deep red colour appears; in the absence of acetone, only a yellow colour is obtained. Colourless preparations—e.g., spirit of camphor, etc.—can be tested without previous distillation. The author hopes to succeed in modifying Légal's, or one of the other methods, so as to make it quantitative.

E. K. H.

The Determination of Glycerin in Wines. X. Rocques. (*Ann. de Chim. anal.*, 1905, x., 306-309.)—This is a method of direct determination based on the

solubility of glycerin in a mixture of acetic ether and alcohol. Acetic ether by itself will dissolve only 13·4 grams of glycerin per litre, but a mixture of 80 per cent. of acetic ether with 20 per cent. of pure alcohol dissolves 80·6 grams per litre at 20° C., without dissolving any appreciable quantity of other substances in the wine. In the determination 200 c.c. of the wine are evaporated to a syrup, and the residue mixed with a quantity of quicklime equal to that of the sugar present. The pulverized mass is allowed to stand twenty to thirty minutes, and then triturated with 50 to 200 c.c. of alcohol (96 to 97 per cent.), added little by little, until a homogeneous creamy fluid is obtained. This is allowed to stand for twenty to thirty minutes, and then filtered from the insoluble calcium sucates, the filter being subsequently washed with alcohol. The filtrate is rendered acid with tartaric acid, and the bulk of the alcohol distilled, a little pumice-stone being added to prevent bumping. The residue (15 to 20 c.c.) is mixed with 3 to 5 grams of quicklime and 10 grams of fine sand in a flat dish, and the evaporation completed *in vacuo*, which takes about twelve hours. The dry powder is shaken for two hours in a well-closed flask with 100 c.c. of the above-mentioned mixture of acetic ether and alcohol, after which it is allowed to stand, and then filtered. An aliquot portion of the filtrate (say 75 c.c.) is placed in a weighed dish, and evaporated *in vacuo* over sulphuric acid, and the residue of glycerin left for three days in the vacuum before being weighed. It will be found quite free from sugars and to contain only traces of mineral matter.

C. A. M.

A New Method of Estimating the Aldehydes in Oil of Lemon. E. Berté, (*Chem. Zeit.*, 1905, xxix., 805.)—The author refers to the controversy which took place in the *Chemist and Druggist* in the autumn of 1903, in which most of the authors were of opinion that the percentage of citral did not exceed 3 to 4 per cent.

Sadtler, however, used a process founded on an observation of F. Tiemann, in which a dilute aqueous solution of neutral sodium sulphite is shaken up with the aldehyde-containing liquid. Citral, under these circumstances, is transformed into citral dihydro-sulphonic acid, and the equivalent quantity of sodium hydroxide is liberated. Citronnellal does not give such a reaction. Tiemann found, by this method, 5·26 per cent. of citral; the total amount of aldehydes must be greater.

The author, whilst having complete confidence in the bisulphite method, as proposed by himself and Soldaini (*Chemist and Druggist*, September, 1903), has worked out a simple method for the estimation which depends on the difference in optical activity of the oil before and after treatment with one of the general reagents. The process is carried out as follows: The rotation due to the original oil was first determined. Ten c.c. of the oil and 50 c.c. of a saturated solution of potassium bisulphite were placed in a 250 c.c. Erlenmeyer flask; the flask was closed by a cork provided with one hole, through which passed a glass tube 40 to 45 centimetres in length. The mixture was shaken to an emulsion, kept on a boiling water-bath for ten minutes, and repeatedly shaken. It was allowed to cool, again heated for five minutes with vigorous shaking, and then again allowed to cool. The mixture was then transferred to a separating funnel of 100 c.c. capacity; it was allowed to stand some time for the upper layer of oil to separate from the lower layer containing

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the combined aldehyde. The separated terpene was twice washed with a small quantity of distilled water, separated, dried by addition of a small amount of anhydrous sodium sulphate, and filtered. The clear liquid was then examined polarimetrically. The percentage of aldehyde is given by the formula—

$$C = \frac{100 (A - a)}{A}$$

where a is the rotation of the original oil, and A that of the oil after removal of the aldehyde. The author performed several series of experiments to test the method. He first tried whether the rotatory power of the terpene was affected by the action of the ordinary aldehyde reagents or by heat. These experiments were performed with a terpene of specific rotation $+66^\circ$ at 20° C., and specific gravity 0.85190 at 15° C. No change could be observed.

Some experiments were next performed on genuine oil of lemon, obtained by favour of the producers. Different samples gave values of 6.85 to 7.40 per cent. of aldehyde.

Another series of determinations was made on lemon oils adulterated with known quantities of a specially prepared terpene, or mixtures of this terpene and olive oil such as to give a specific gravity about that of the unadulterated oil. The oil was first analysed to prove its purity. The figures obtained agreed fairly with the calculated ones.

Experiments were then made on mixtures of citral and limonene of known composition. The citral used was a pure citral from lemon-grass oil, optically inactive, made by Kahlbaum; the limonene was obtained from genuine oil of lemon, and had a specific rotation of $+66^\circ$ at 20° C. The figures obtained are worth giving in detail :

Quantity of Limonene used.	Quantity of Citral added.	$[\alpha]_D$ at 20° C. of the Mixture.	$[\alpha]_D$ at 20° C. of the Terpene obtained by Treatment with Potassium Bisulphite.	Difference.	Quantity of Citral.	
					Found Per Cent.	Calculated Per Cent.
19.8	0.2	$+65^\circ 28'$	$+66^\circ 0'$	$+0^\circ 72'$	1.10	1.00
19.6	0.4	$+64^\circ 70'$	$+66^\circ 0'$	$+1^\circ 30'$	1.97	2.00
19.4	0.6	$+64^\circ 0'$	$+66^\circ 0'$	$+2^\circ 0'$	3.04	3.00
19.2	0.8	$+63^\circ 30'$	$+66^\circ 0'$	$+2^\circ 70'$	4.10	4.00
19.0	1.0	$+62^\circ 70'$	$+66^\circ 0'$	$+3^\circ 30'$	5.00	5.00
18.8	1.2	$+62^\circ 0'$	$+66^\circ 0'$	$+4^\circ 0'$	6.07	6.00
18.6	1.4	$+61^\circ 30'$	$+66^\circ 0'$	$+4^\circ 70'$	7.13	7.00
18.4	1.6	$+60^\circ 70'$	$+66^\circ 0'$	$+5^\circ 30'$	8.04	8.00
18.2	1.8	$+60^\circ 0'$	$+66^\circ 0'$	$+6^\circ 0'$	9.10	9.00
18.0	2.0	$+59^\circ 30'$	$+66^\circ 0'$	$+6^\circ 70'$	10.16	10.00

Finally, observations were made on a terpene-free "concentrate," for which the author wishes to thank Messrs. Santi de Pasquale. This gave the following figures :

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Specific rotation at 15° C.	9·20°
Specific gravity	0·8975
Quantity of ester (as geranyl acetate)	19·55 per cent.
Refractive index at 15° C. (Zeiss refractometer) ...	89

The process detailed above was then applied, and a difference in specific rotation of $-13\cdot1^\circ$ was obtained. Knowing the quantity of geraniol present from the first analysis, the quantity of citral could be calculated, and was 58·49 per cent. by volume, or 65·72 per cent. by weight.

The author is pursuing investigations of other terpene-free concentrates, in order to establish the ordinary amount of aldehyde therein. E. K. H.

A Reaction of Laurel Oil. Monpurgo. (*Giorn. di Farm. di Trieste*, 1905, 353; *Ann. de Chim. anal.*, 1905, x., 327.)—Laurel oil is stated to be frequently adulterated. The pure oil, when shaken with twice its volume of alcohol and filtered, yields a green filtrate the colour of which is not modified by the addition of ammonia, but is changed to yellowish-green by hydrochloric acid. The iodine value ranges from 66 to 78, the saponification value from 197 to 210, and the melting-point from 32° to 36° C. When the oil is heated with twice its volume of alcohol and the liquid cooled slowly the white mass that separates appears amorphous under the microscope. When several drops of an ethereal solution of the oil are thrown into absolute alcohol the mixture remains clear in the case of a pure product. C. A. M.

Note on the Analysis of the Compound Tincture of Camphor (Paregoric). F. C. J. Bird. (*Pharm. Journ.*, 1905, lxxv., 154.)—As no analytical method is described or suggested in the British Pharmacopœia for determining the strength in morphine of a sample of this tincture, the official process for tincture of opium might be considered as applicable. However, to work with the equivalent of the official quantity of 80 c.c. of tincture of opium, it is necessary to employ no less than 1,300 c.c. of compound tincture of camphor. Fair results may be obtained by taking only 250 c.c., but with smaller quantities than this the amount of morphine found is too low. If only 10 c.c. of the sample be assayed, the alkaloid may be missed altogether.

The following process answers well with as little as 2·5 c.c. of the tincture, although 10 c.c. is recommended as the most suitable quantity: 10 c.c. of the sample are evaporated to dryness on a water-bath, the residue is taken up with dilute alcohol and a minute drop of acetic acid, again evaporated, and finally dissolved in 2 c.c. of water. The solution is poured through a filter, the filter is washed, and the filtrate and washings extracted three times with hot amyl alcohol, after adding a little potassium carbonate. The united extracts are evaporated to dryness. The residue is then dissolved in a little dilute hydrochloric acid, filtered through a small filter containing charcoal, and washed. The clear solution is now rendered alkaline by the addition of a little powdered ammonium carbonate, and extracted three times with hot amyl alcohol. The mixed extracts should measure about 8 c.c., and are evaporated to dryness. The usual reactions may be applied to portions of a solution

of this final residue, and the colorations obtained compared with those yielded from 10 c.c. of a sample of compound tincture of camphor of known strength.

W. P. S.

The So-called "Manipulated" Opiums. P. Guigues. (*Journ. Pharm. Chim.*, 1905, xxii., 103-107.)—According to the author, Smyrna opium normally contains from 12 to 14 per cent. of morphine, though in some cases, owing to part of the pericarp being removed with the coagulated latex, it sometimes contains less. Such natural, though inferior, products, are exported to Germany, England, and the United States, where the Pharmacopœias require opium to contain about 10 per cent. of morphine. But, with this exception, it is stated that all opiums containing a low percentage of morphine are products "manipulated" in Smyrna for French and Italian consumption; the amount being reduced to 10 per cent. for France and to 6 per cent. for Italy. The author has received samples and details of the method of preparation from Smyrna dealers. The fresh opium is converted into paste and mixed with apricot pulp or similar products, so as to reduce the proportion of morphine to the required extent, after which the mass is divided into small cakes, which are wrapped round with the fruits of a species of rumex. The analysis of three samples gave the following results:

Sold as—	Water. Per Cent.	Ash. Per Cent.	Aqueous Extract. Per Cent.	Morphine. Per Cent.	Narcotine. Per Cent.
No. 1. Opium, superior quality	11·45	4·10	46·48	11·18	1·65
No. 2. „ average quality	12·12	3·60	55·98	nil.	2·37
No. 3. „ inferior quality	10·30	6·15	29·78	1·9	1·29

All the results were calculated on the dry substance. The extract of No. 1 and No. 2 had the normal red-brown colour, while that of No. 3, which swelled up into a gelatinous mass, was brownish-yellow. No. 1 was forwarded as a genuine opium, whilst No. 2 was stated to have been mixed with pulp, and No. 3 with coagulated white of egg. The amount of reducing sugars (as dextrose) in No. 2 was 10·25 per cent., while No. 1 gave 8·6 per cent. and No. 3 2·85 per cent. Hence, assuming that No. 1 was really a pure product, the amount of reducing sugars is not conclusive of adulteration. Sample No. 3 contained a large amount of nitrogen (*cf.* ANALYST, xxx., 310).

C. A. M.

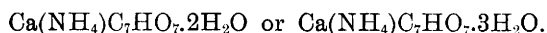
The Determination of Morphine in Opium. L. Valenti. (*Giorn. di Farm. di Trieste*, 1905, 289; *Ann. de Chim. anal.*, 1905, x., 326.)—From the results of comparative determinations by different methods the author recommends that of Fluckiger (precipitation from a solution in ether-alcohol). The only drawback is the solubility of the morphine in the solvent. This amounts to 0·118 gram per 100 c.c., and ought to be added to the weight of morphine found.

C. A. M.

Meconic Acid in the United States Pharmacopœia, 1890, Assay of Opium and Certain Meconates. Edward Mallinckrodt, jun., and Edward A. Dunlap. (*Journ. Amer. Chem. Soc.*, 1905, xxvii., 946.)—In making an assay of opium by the United States Pharmacopœia (1890), process, in which the morphine is

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precipitated from the aqueous extract by dilute ammonia after the addition of some alcohol and ether, the formation of a layer of white or yellowish-white substance adhering to the bottom of the flask is frequently noticed. The authors have analysed both this scale and a similar substance artificially prepared, and conclude it to be an ammonium calcium meconate of the formula :



The chief importance of this salt lies in the fact that it consumes an amount of acid equivalent to one-quarter of the same weight of morphine, and hence its presence vitiates the subsequent titration of the morphine with acid. The same, or a similar salt, appears to have been noticed, but not analysed, by Robiquet in 1833 (*Ann. Chem.*, v., 82).

A. G. L.

Adulterated Saccharin. R. Krzizan. (*Zeit. Untersuch. Nahr.-Genussmittel*, 1905, x., 245-247.)—Five samples of saccharin tablets examined were found to consist almost entirely of plaster of Paris. Only traces of saccharin were present, and this had evidently been dusted over the surface of the tablets. A sixth sample also consisted mainly of plaster of Paris (about 92 per cent.), the amount of saccharin present being 1.63 per cent.; the remainder consisted of calcium phosphate, calcium carbonate, and sodium hydrogen carbonate.

W. P. S.

A Method of Determining Pyramidon. A. Astruc and G. Pégurier. (*Ann. de Chim. anal.*, 1905, x., 302, 303.)—The method is based upon the fact that pyramidon, like antipyrin, combines with picric acid (1 molecule : 1 molecule) to form an insoluble compound, and that the excess of picric acid can then be titrated in the way devised by Lemaire. In making an estimation 0.231 gram of the sample (molecular weight of pure pyramidon = 231) is dissolved in 10 c.c. of water, and the solution mixed with 40 c.c. of $\frac{N}{20}$ picric acid solution (11.45 grams per litre). The mixture is shaken for some minutes to promote the formation of the compound, and then filtered, and the excess of picric acid determined in 25 c.c. of the filtrate by titration with $\frac{N}{10}$ potassium hydroxide, with phenolphthalein as indicator. Four times the number of c.c. of alkali used, deducted from the original 40 c.c. (of picric acid) and multiplied by five, gives the percentage of pure pyramidon in the sample.

C. A. M.

The Determination of Iron in Ferrum Redactum. A. Christensen. (*Zeit. anal. Chem.*, 1905, xlv., 535-540.)—The method of determining the metallic iron in the *ferrum redactum* of the German Pharmacopœia consists in dissolving the metal by means of iodine in potassium iodide, but the author regards this as inferior to Wilner's method (digestion with mercuric chloride), though that too is shown to be liable to give erroneous results. The method in which ferric chloride is used ($\text{Fe} + 2\text{FeCl}_3 = 3\text{FeCl}_2$) and the insoluble residue of iron oxide weighed has long been abandoned as unreliable, since part of the oxide may also pass into solution as a basic salt. Good results, however, can be obtained by titrating the resulting solution, and taking care that the ferric chloride reagent is absolutely free from acid.

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It can be prepared by dissolving the anhydrous ferric chloride little by little with constant stirring in cold water. Even if a slight black insoluble residue be left, its amount can be determined once for all, and deducted in subsequent determinations. A weighed quantity (about 0.5 gram) of the *ferrum redactum* is placed in a 100-c.c. flask, from which the air has been expelled by carbon dioxide, 50 c.c. of the ferric chloride solution introduced, and the whole shaken at intervals for fifteen to twenty minutes, while the flask is either kept closed or a continuous current of carbon dioxide passed through it. The liquid is then made up to the mark with boiled water, well shaken, and allowed to stand overnight, after which 10 to 20 c.c. are withdrawn, added to 50 c.c. of 10 per cent. sulphuric acid (previously boiled and cooled in a current of carbon dioxide), and titrated with $\frac{N}{10}$ potassium permanganate solution. The tabulated results obtained by this method are closely concordant, and agree well with those calculated from the amount of hydrogen evolved on treating the substance with dilute sulphuric acid.

C. A. M.