

# THE ANALYST

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

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AN additional Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, June 2nd, 1926, the President, Mr. E. Richards Bolton, F.I.C., being in the chair.

A certificate was read for the first time in favour of Mr. Stafford Aston, F.I.C.

Certificates were read for the second time in favour of Messrs. Francis Harrold Banfield, M.Sc., Ph.D., A.I.C., and Albert Lester Williams, A.I.C.

The following were elected Members of the Society:—Messrs. Arthur Barraclough, B.Sc., A.I.C., George Gordon Elkington, Kenneth Massy Griffin, M.Sc., A.I.C., Herbert Firth, A.I.C., and Thomas Pickerill, B.Sc.

A paper was read by Mr. A. Lucas, O.B.E., F.I.C., on "Problems in connection with Ancient Egyptian Materials," which was followed by discussion.

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### The Determination of Copper in Foodstuffs.

BY L. H. LAMPITT, D.Sc., F.I.C., E. B. HUGHES, M.Sc., F.I.C.,  
P. BILHAM, B.Sc., A.I.C., and C. H. F. FULLER, B.Sc., A.I.C.

*(Read at the Meeting, February 3, 1926.)*

EXAMINATION of chemical literature shows that during the last few years a large number of methods have been described for the detection and determination of copper.

In a survey of these methods, in order to find one which, applied to foodstuffs, would give reliable results, many have been examined, and two methods developed which are considered by the authors to be suitable to the object in view.

## I. COLORIMETRIC METHODS.

Thomas and Carpentier (*Compt. rend.*, 1921, **173**, 1082) give a very sensitive reaction for copper, using the Kastle Mayer reagent, which is made by decolorising a 2 per cent. solution of phenolphthalein in 20 per cent. potassium hydroxide by means of zinc dust. A few drops of this reagent are added to a neutral solution containing copper, together with a few drops of hydrogen peroxide, whereby the brilliant red colour of the phenolphthalein is at once restored. This reaction is extremely sensitive, and it is claimed that it is possible to detect 1 part of copper in 100 million parts of water. The colour produced by amounts of copper from 0.01–0.10 mgrm. in 50 c.c. was so intense as to render the method impracticable for our work.

The same objection applies to the reaction of guaiacum resin with dilute copper solutions (Colwell, *Chem. Abstr.*, 1911, **5**, 913). The blue colour produced is so intense that only very small amounts of copper (less than 0.05 mgrm. of copper in 50 c.c. of solution) could be determined by its means.

A method devised by Denigès and Simonot (*J. Pharm. Chim.*, 1915, **8**, 186–7), depending on the violet colour of copper bromide in 30 per cent. sulphuric acid, was rejected chiefly owing to manipulative difficulties and the considerable variation in colour which followed even slight departure from the conditions of the test.

The method of Scott and Derby (described in *Standard Methods of Chemical Analysis*, Scott) based on the formation of a yellow colour when a solution of potassium ethyl xanthate is added to a solution containing a small amount of copper, has been in use in our laboratory for some time. The method is sensitive, but not excessively so, and can be used for amounts as low as 0.001 mgrm. of copper in 100 c.c. of solution. It has the disadvantage that it is exceedingly sensitive to variation in the  $P_H$  of the solution, and, in fact, we have found that on either side of neutrality it gives an opalescent solution due to precipitation of copper ethyl xanthate or possibly sulphur, thereby rendering the matching of the colour still more difficult than is even naturally the case with yellow solutions. This precipitation is quite common, and the causes of its occurrence are not easily ascertained; consequently the method was eventually discarded in favour of the ferrocyanide method.

**FERROCYANIDE METHOD.**—As carried out by us, the method is rapid in application, and covers a range from 0.07 to 0.40 mgrm. of copper with deviation of not more than 0.025 mgrm. At the extremes of this range the accuracy is least, the best results being obtained for amounts of copper in the neighbourhood of 0.35 mgrm. Amounts of copper in excess of 0.40 mgrm. (about 0.5 grain copper per pound of material, taking 5 grms.) give so much copper ferrocyanide that precipitation may set in while the colour is being matched, and therefore smaller quantities should be taken for a repetition of the determination.

The method is suitable for routine "sorting-out" tests; when greater accuracy is required the process described in Part II of this paper should be employed.

In the case of canned vegetables the whole contents are first emptied on to a hair sieve, the liquid allowed to drain off, and the solid portion reduced to a pulp in a large mortar. Other materials are sampled in the usual way. To 5 grms. of the material in a silica dish 2 c.c. of concentrated sulphuric acid are added, and the dish heated on the boiling water-bath until charring commences. It is then heated over a small flame until the excess of sulphuric acid has been removed, after which it is transferred to a muffle maintained at 650°–700° C. and heated until all carbon is burnt off. If the ash is not free from carbon, low values for copper will result. At the same time the muffle must not be too hot; if it exceeds a cherry red heat the ash may fuse into the silica dish, the determination become useless, and the dish unsuitable for further use for copper determinations. The ash is dissolved in 5 c.c. of 5 *N* hydrochloric acid, with the aid of heat, 20 c.c. of water added, followed by 7 c.c. of 5 *N* ammonia, and the alkaline solution filtered hot through a No. 41 Whatman paper, the filter washed once with hot water, the filtrate and washings being collected in a 100 c.c. beaker. The precipitate is dissolved off the filter paper into the silica dish with 5 c.c. of 5 *N* hydrochloric acid, the filter being washed through with about 20 c.c. of hot water. This acid solution is made alkaline by adding 7 c.c. of 5 *N* ammonia and then filtered into the 100 c.c. beaker containing the first alkaline filtrate. The combined filtrates are boiled until all free ammonia has been expelled, then cooled and transferred to a 100 c.c. Nessler cylinder, 1 gm. of ammonium acetate added, and the volume completed to the mark. Another 100 c.c. Nessler cylinder is filled with distilled water, to which 1 gm. of ammonium acetate and 3 grms. of ammonium chloride have been added. Two drops of a 3 per cent. solution of potassium ferrocyanide are added to each, the colour of the liquid in the first tube being matched by the addition of standard copper sulphate solution to the second tube. This standard copper solution is of such a strength that 1 c.c. = 0.0005 gm. of copper.

It is imperative to boil off all free ammonia from the combined filtrates. The resulting liquid then has a  $P_H$  of 4.0 to 5.0, but, as the optimum  $P_H$  for colour development is 7.0, ammonium acetate is added to give a buffered solution of this  $P_H$  value. Acid solutions cause a change towards yellow to occur, whilst, if the solution is alkaline, no red colour at all may be produced. (See Table I.)

#### THE EFFECT OF THE $P_H$ VALUE ON THE COPPER FERROCYANIDE COLOUR.

TABLE I.

Buffer solutions + 0.50 mgrm. of copper + 3 drops of potassium ferrocyanide.

$P_H$ 2	..	..	1.20 red + 0.80 yellow.
$P_H$ 4	..	..	1.55 red + 0.70 yellow.
$P_H$ 6	..	..	1.55 red + 0.40 yellow.
$P_H$ 8	..	..	1.15 red + 0.50 yellow.
$P_H$ 10	..	..	0.85 red + 0.50 yellow.

Table II shows that ammonium salts greatly increase the colour, giving a maximum at P<sub>H</sub> 7.

TABLE II.

Solutions containing ammonium salts + acid or alkali. 0.50 mgrm. of copper used in each case.

P <sub>H</sub> 3	..	..	1.65 red + 0.50 yellow.
P <sub>H</sub> 5	..	..	2.05 red + 0.55 yellow.
P <sub>H</sub> 6	..	..	2.10 red + 0.50 yellow.
P <sub>H</sub> 7	..	..	2.90 red + 0.80 yellow.
P <sub>H</sub> 8	..	..	Precipitation occurs.
P <sub>H</sub> 10	..	..	No colour produced.

## II. GRAVIMETRIC QUINOSOL METHOD.

The chief methods which have been suggested for the exact determination of copper in foodstuffs are the method of the A.O.A.C. and various electrolytic methods.

On applying the method of the A.O.A.C. some difficulties become apparent. Thus, the end-point in the titration with 0.01 *N* thiosulphate is not sharp, for, as the titration proceeds, the blue colour of the starch iodide complex changes slowly to red, then to a yellowish colour. Another disadvantage is that the method does not work well in the presence of tin salts, which are generally present in coppered canned vegetables. In general, the method is tedious and slow, and is not any more accurate than the quinosal method developed in these laboratories.

For the purpose of preventing the deposition of tin with copper, variations in electrolytic methods have been suggested, such as the addition of tartaric acid, hydrofluoric acid, or rendering the solution ammoniacal. These we have found to be unreliable, and, in consequence, we find it essential that electrolysis should be preceded by chemical separation of the copper, and for this purpose the following methods have been tried.

Fleming (*ANALYST*, 1924, 49, 275) gives a method for the detection of copper in which a solution of alkali thiocyanate and a few drops of a 1 per cent. solution of benzidine in alcohol are added to a little copper solution, giving rise to a deep blue coloration which, even with very small quantities of copper, rapidly changes to a precipitate and renders the reaction useless as a means of colorimetric determination.

It was thought, however, that this precipitation would provide an excellent means of separation of copper from other metals, and it was ascertained that metals, other than copper, remaining in solution after precipitation by ammonia in the presence of ammonium chloride, gave no reaction with the above reagents in neutral solution. Thus traces of tin escaping precipitation by ammonia do not cause any subsequent interference. A number of quantitative determinations of copper were made, and satisfactory results were obtained. It was noticed that if the copper precipitate was filtered off immediately and the filtrate allowed to stand, a further quantity of precipitate formed, but examination of this proved

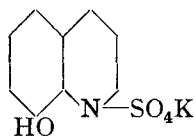
that it contained only a negligible quantity of copper. The method, however, was not so dependable as the quinosol method described later.

The well-known separation of copper as cuprous thiocyanate was also tried. The slightly acid copper solution was reduced with sodium bisulphite, and alkali thiocyanate added. The copper was completely precipitated as cuprous thiocyanate, but the precipitate was very fine and exceedingly difficult to filter off, and consequently this method was discarded. Finally, the quinosol method now to be described was selected as the most satisfactory.

**QUINOSOL METHOD.**—The copper can be determined gravimetrically, or the quinosol copper compound may be dissolved, and the copper determined electrolytically.

The reagent used to precipitate the copper is an antiseptic known as quinosol. Saul and Crawford (*ANALYST*, 1918, 43, 348) state that "This compound is understood to be the potassium salt of 8-hydroxy-quinoline-5-sulphonic acid." They observed that quinosol formed a voluminous precipitate with copper salts and suggested that this might afford a means of separation of copper.

Work carried out in these laboratories shows that copper forms a compound of definite composition with quinosol containing 18.55 per cent. of copper, corresponding to the replacement of two hydrogen atoms in one molecule of quinosol by one atom of copper. We find that quinosol is the double sulphate of potassium and 8-hydroxy-quinoline, as it gives the reactions for sulphates, and the percentage of  $\text{SO}_4$  radicle present in quinosol corresponds to the formula:—



Investigation showed that, with the exception of manganese, other metals remaining in solution after precipitation by ammonia did not interfere with the reaction. In the presence of manganese the quinosol separation must be followed by the electrolytic determination.

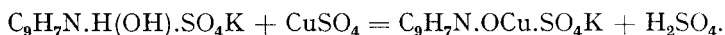
The sample is prepared as described in the previous section, but in this case 50 grms. are required for analysis. The destruction of such a bulk of material is most conveniently brought about by the action of nitric acid and sulphuric acid, as follows:—

Fifty grms. of the pulp are weighed into a 500 c.c. beaker and concentrated nitric acid (sp. gr. 1.42) added in the proportion of 6 c.c. to every gm. of *solids*, the whole being thoroughly agitated during the addition. Twenty c.c. of pure concentrated sulphuric acid (and a glass bead to prevent bumping) are placed in a Pyrex flask of 800 c.c. capacity clamped in a vertical position, and about 10 grms. of the nitric acid and vegetable mixture added, the flask being heated until the first vigorous action has ceased. After allowing the mixture to cool, a further amount is added, the flask again heated and the process repeated until all

the mixture has been treated. Care must be taken not to add too much mixture at any one time and to regulate the heating so that excessive frothing does not occur. All the mixture having been added, the flask is heated until all nitric acid and water have been driven off, when the reaction mixture will generally change from a pale yellow colour to black. A further addition of nitric acid is now made, and causes a clearing of the mixture. If, on further heating, the black colour reappears, the treatment with nitric acid is repeated until a colourless residue is obtained. The time required for complete destruction depends on the percentage of solids; for example, fruit pulps containing 10 to 15 per cent. of solids take about 1 hour. Substances containing much sugar or starch need special treatment as follows:—

Fifty grms. of the sample are so diluted with water as to reduce the vigour of the first reaction with nitric acid, but if, in spite of this precaution, frothing occurs, the diluted substance and the nitric acid are added alternately in small portions to the sulphuric acid in the Kjeldahl flask. In these special cases a longer time is required for complete destruction, 50 grms. of cocoa taking as long as eight hours. In all cases, in order finally to remove the excess of sulphuric acid, a current of air is blown through the Kjeldahl flask while the heating is continued, the sulphuric acid being quickly removed and the volume reduced to 2–3 c.c. in about 10 minutes.

After the destruction of organic matter the residual 2 c.c. of liquid is diluted to 50 c.c. with distilled water, a slight excess of ammonia added, the liquid filtered, and the precipitate washed. The precipitate is dissolved in a small amount of 5 *N* hydrochloric acid, reprecipitated with ammonia and filtered off, the two filtrates being combined and then boiled until the excess of ammonia has been driven off. Five c.c. of a 2 per cent. aqueous solution of quinosol are added to the hot solution, and a yellow flocculent precipitate separates almost immediately. The reaction follows the course:—



As the precipitate is soluble in acids, 2 c.c. of 0.05 *N* ammonia are added in order to neutralise the sulphuric acid liberated in the reaction. The mixture is allowed to digest on the water bath for half-an-hour, filtered through a weighed Gooch crucible, the precipitate washed with hot water, dried at 110° C. for 1 hour, cooled and weighed. The factor for the conversion of the weight of the compound to metallic copper is 0.1855, and to crystalline copper sulphate 0.7288.

The asbestos for the Gooch crucible should be of a quick filtering variety, and can be used a number of times if the copper quinosol compound is removed by treatment with strong nitric acid and subsequent washing with water. Crucibles made of Jena sintered glass have been used with success in this determination, the most suitable grade being G 3/5 – 7.

**ELECTROLYTIC METHOD FOLLOWING QUINOSOL SEPARATION.**—This method is a continuation of the quinosol process, and can be used as a confirmatory determination; it is also of use when the quinosol precipitate is very large due to

excessive amounts of copper, and is essential when manganese is present.

The quinosol precipitate is filtered off on a No. 41 Whatman filter paper and washed several times with hot water. The filter paper containing the precipitate is transferred to a 100 c.c. round-bottomed flask, 2 c.c. of concentrated sulphuric acid, and 10 c.c. of nitric acid are added, and the destruction of the organic nucleus is then carried out in a similar manner to the destruction of the original sample, except that, when clear, the mixture is heated until white fumes of  $\text{SO}_3$  are given off. The solution is then cooled, diluted to 50 c.c. with distilled water and electrolysed with a current density of 0.01 amperes per sq. cm. and a voltage of 2.5. With a current of 0.3 amps. passing through the cell amounts of copper up to 0.01 grm. are deposited completely in  $1\frac{1}{2}$  hours. The manipulations are as usually carried out for electrolytic determinations of copper. Manganese is converted into permanganate during electrolysis and remains in solution.

The accuracy of the results obtained depends chiefly on the degree of accuracy with which the cathode can be weighed, since the amount of copper obtained is necessarily small, being from 1 to 10 mgrms.

Tables III, IV and V give results obtained on fresh green peas to which known amounts of copper sulphate had been added.

TABLE III.  
FERROCYANIDE METHOD.

Amount of material used = 5 grms.

Copper added. Grains in 1 lb.	Copper found. Grains in 1 lb.	Error. Grains in 1 lb.
0.105	0.112	+ 0.007
0.105	0.126	+ 0.021
0.105	0.133	+ 0.028
0.158	0.175	+ 0.017
0.158	0.189	+ 0.031
0.210	0.231	+ 0.021
0.210	0.245	+ 0.035
0.263	0.280	+ 0.017
0.315	0.336	+ 0.021
0.315	0.336	+ 0.021
0.368	0.364	- 0.004
0.368	0.364	- 0.004
0.368	0.368	0.000
0.420	0.420	0.000
0.431	0.448	+ 0.017
0.473	0.455	- 0.018
0.473	0.476	+ 0.003
0.473	0.476	+ 0.003
0.525	0.518	- 0.007
0.525	0.560	+ 0.035
0.578	0.560	- 0.018
0.578	0.560	- 0.018
0.578	0.578	0.000
0.630	0.595	- 0.035
0.630	0.647	+ 0.017

TABLE IV.

## GRAVIMETRIC QUINOSOL METHOD.

Amount of material used — 50 grms.

Copper added. Grains in 1 lb.	Copper found. Grains in 1 lb.	Error. Grains in 1 lb.
0.070	0.070	0.000
0.140	0.148	+ 0.008
0.154	0.148	+ 0.006
0.210	0.200	- 0.010
0.217	0.224	+ 0.007
0.245	0.237	- 0.008
0.259	0.265	+ 0.006
0.280	0.281	+ 0.001
0.308	0.309	+ 0.001
0.350	0.353	+ 0.003
0.350	0.353	+ 0.003
0.350	0.346	- 0.004
0.350	0.350	0.000
0.350	0.351	+ 0.001
0.350	0.346	- 0.004
0.350	0.351	+ 0.001
0.350	0.358	+ 0.008
0.448	0.442	- 0.006
0.511	0.518	+ 0.007
0.560	0.550	- 0.010
0.595	0.585	- 0.010
0.630	0.622	- 0.008
0.700	0.699	- 0.001

TABLE V.

## ELECTROLYTIC METHOD AFTER QUINOSOL SEPARATION.

Amount of material used = 100 grms.

Copper added. Grains in 1 lb.	Copper found. Grains in 1 lb.	Error. Grains in 1 lb.
0.088	0.084	- 0.004
0.088	0.084	- 0.004
0.113	0.140	+ 0.007
0.175	0.182	+ 0.007
0.175	0.161	- 0.014
0.350	0.343	- 0.007
0.350	0.350	0.000
0.350	0.343	- 0.007
0.700	0.672	- 0.028

We wish to acknowledge with thanks the permission of Messrs. J. Lyons & Co., Ltd., to publish these results.



## DISCUSSION.

The PRESIDENT congratulated the authors on having made a thorough investigation of the existing methods for determining copper, and also on having worked up a suggestion made some time previously in *THE ANALYST*. He was interested to learn that copper formed a definite compound with quinosol and that definite results could be obtained.

Mr. A. CHASTON CHAPMAN suggested that instead of weighing the cathode it might be preferable to dissolve the copper, wash into a thin porcelain crucible, ignite and weigh as oxide.

Dr. B. S. EVANS asked what precautions were taken to ensure the complete removal of ammonia; and was there any objection to direct electrolysis. In the case of large amounts of copper he had always found that nitric acid was necessary to produce a coherent deposit; was it also necessary in the case of small amounts?

Mr. FULLER, replying, stated that litmus paper was used for testing when the ammonia had been driven off. As an extra precaution, boiling was continued for ten minutes after the litmus paper ceased to be affected.

Mr. BILHAM thought that the washing of the deposit into a thin porcelain crucible, though it had not been tried, would lead to greater accuracy, as the weight of the cathode was comparatively high. The objection to direct electrolysis in the case of small amounts of copper was that tin was also deposited, though when copper was present in large quantities some success had been obtained by this method. A previous removal of the tin ensured a clean, bright deposit. Nitric acid had not been found necessary.

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## A Test for Chinese Wood (Tung) Oil.

BY E. R. BOLTON, F.I.C., AND K. A. WILLIAMS, B.Sc., A.I.C.

(Read at the Meeting, April 7, 1926.)

COMMERCIAL Chinese wood oil (Chinese tung oil) is obtained from the seeds of *Aleurites Fordii*, or *Aleurites montana*, the former being the chief source of Hankow oil. Chinese wood oil must be clearly distinguished from Japanese wood oil (Japanese tung oil), which has distinctly different properties, and which is obtained from a different seed, namely, *Aleurites cordata*.

When either of the terms "wood oil" or "tung oil" is used commercially without further qualification, the Chinese variety is implied, and the Japanese variety, which is not suitable for the same purposes, cannot be substituted.

Tung oil yields analytical "constants" sufficiently different from oils likely to be used as adulterants to render the detection of appreciable quantities of an adulterant fairly simple. Nevertheless, the presence of certain oils to the extent of about 5 per cent. is difficult to detect with certainty. The question of

the adulteration of this oil has been dealt with by A. Chaston Chapman in this journal (*ANALYST*, 1912, **37**, 543).

The test now proposed has for its aim the separation, by solvent extraction, of the adulterating oil from the mass obtained on polymerising the oil by heat. Such separation has been attempted on previous occasions by others, but seems to have failed, owing to incomplete polymerisation of the tung oil, due to the nature of the method used for effecting polymerisation.

Chapman (*loc. cit.*) has already expressed the opinion that Worstall's polymerisation test, when carried out in the manner originally described, is unsatisfactory, in which opinion the present authors concur. It has been found, however, that the following modification of Worstall's test gives a satisfactory and evenly-polymerised mass.

**MODIFICATION OF WORSTALL'S TEST.**—One hundred and fifty grms. of the oil, contained in a stout aluminium beaker, exactly 3 inches in diameter and approximately 4 inches in height, are heated by means of a Bunsen burner so as to reach a temperature of 285° C. in approximately 4 minutes, the oil being vigorously stirred by means of the thermometer during the operation.

As soon as the temperature of the oil has reached 285° C. a stop-watch is started, and the temperature of the oil is thereafter maintained as nearly as possible at 285° C., the stirring being continued all the time. The time is noted when polymerisation suddenly sets in, as is indicated by the failure of the oil to drop from the thermometer when the latter is raised from the bath. Genuine tung oils reach the stage described after less than 8 minutes' heating at 285° C.

If a long-stemmed thermometer be used, a *stem correction* must be applied. A variation of 3° C. from standard temperature throughout the polymerisation will cause a difference of as much as one minute in the time of polymerisation with some specimens of tung oil.

A genuine tung oil of good merchantable quality produces a dry, firm gel having a pale yellow colour and a characteristic appearance and texture.

**EXTENSION OF THE MODIFICATION.**—The authors have extended this modification of Worstall's test as follows:—A portion of approximately 2 grms. is taken from the centre of the polymerised mass and weighed into a mortar to which are added about 3 grms. of dry "silver" sand and 2 ml. of petroleum spirit. The mixture contained in the mortar is now carefully incorporated with a pestle and ground until the petroleum spirit has, for the most part, evaporated. The bulk of the mixture is now transferred to an extractor, the mortar thoroughly washed with petroleum spirit into the extractor, and the extraction carried on in the usual manner. In these circumstances tung oils are found to give an extract of 28 per cent., with a variation not exceeding 2 per cent. on either side.

A large number of different tung oils have been tested in this manner, with the result that in no case did any authentic sample give more than 30 per cent. of extract, provided that the polymerisation had been carried out at a temperature

above 275° C. The fact that polymerisation is not completed, by the method proposed, at lower temperatures is shown by the following table:—

Temperature. °C.	Time for polymerisation. Minutes.	Extract. Per Cent.
310	3·10	28·35
285	7·25	28·25
268	13·50	42·20
250	27·75	58·10

RESULTS WITH ADULTERATED OILS.—In the case of adulterated oils the whole of the adulterant is obtained in the extract, together with a small proportion of unpolymerised tung oil, except in the case of tung oil adulterated with linseed oil, which yields after polymerisation approximately half the weight of the adulterant in the extract; this is exemplified by the following table:—

Foreign oil. Per Cent.	Tung oil. Per Cent.	Time for polymerisation. Minutes.	Extract. Per Cent.	Theoretical* extract. Per Cent.
Semi-drying oil (soya)				
0	100	7·5	29·4	29·4
5	95	8·0	33·4	33·1
10	90	9·0	37·4	36·6
20	80	14·0	45·0	43·5
33	67	20·0	55·5	53·0
50	50	57·0	68·5	64·6
67	33	400·0	79·4	77·0
Tung oil acids				
10·5	89·5	10·0	38·1	37·0
Linseed oil				
0	100	7·5	29·0	29·0
5	95	8·0	31·4	33·0
10	90	8·5	33·1	36·6
50	50	45·0	48·4	64·6

As shown in the fourth and fifth columns of the above table, the free fatty acids of tung oil do not polymerise; consequently, when these are present in any quantity over 2 per cent., allowance must be made in computing the amount of an adulterant (*cf.* Jameson, *ANALYST*, 1920, **45**, 328).

The proportion of adulterant present may be calculated from the following formulae:—

If the adulterant is not linseed oil or drying oil of high iodine value:

$$\text{Foreign oil per cent.} = (\text{extract per cent.} - 30\cdot0) \times 1\cdot33.$$

If the adulterant is linseed oil:

$$\text{Foreign oil per cent.} = (\text{extract per cent.} - 30\cdot0) \times 2\cdot70.$$

\* The figures in the last column are calculated on the assumption that the tung oil present is polymerised to the same extent as pure tung oil would be, and that none of the foreign oil in the mixture is polymerised or rendered insoluble in petroleum spirit.

By means of the test now proposed, in conjunction with the refractive index of the original oil, it can readily be decided whether the adulterant consists of linseed oil or not, and, in most cases, a clear idea of the nature of the adulterant is given.

The commercial value of tung oil presumably bears a direct relationship to the amount of polymerisable matter it contains, and, consequently, a test which measures this main constituent and separates non-polymerisable matters must surely give a better commercial valuation of the oil than any consideration of "constants" or "variables."

#### DISCUSSION.

Mr. E. M. HAWKINS, Chairman, asked whether the characteristics of the extract from polymerised tung oil were sufficiently constant to enable them to be used as a reliable test for the oil.

Mr. M. S. SALAMON put two questions: (1) Was there any considerable difference in the refractive index of the extracts from pure and adulterated tung oil? and (2) Had methylated ether been tried for extraction instead of petroleum spirit?

Dr. H. E. COX asked whether any difference was noticeable in the extracts from Chinese and Japanese wood oils and from North and South Chinese oils.

Mr. K. A. WILLIAMS, replying, said that the nature of the extracted matter had not been investigated in any great detail. The refractive index was fairly constant, varying between 1.49 and 1.50 at 25° C., but great care was desirable in the drying, since oxidation was liable to mask the presence of small amounts of adulterants. Methylated ether, petroleum spirit and a mixture of the two all gave the same figures, and the polymerised mass, after extraction by one solvent, remained quite insoluble in another. The only sample of (presumed) Japanese wood oil he had dealt with gave an extract of 51 per cent., as against 28-30 per cent. from Chinese wood oil. There was no difference between North and South Chinese oils; both came within the usual variations, never falling below 26 per cent., and never rising above 30 per cent.

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## Errors of Judgment in Chemical Analysis.

(PRELIMINARY NOTE).

BY J. F. TOCHER, D.Sc., F.I.C.

(*Read at the Meeting, April 7, 1926.*)

VARIATIONS IN PERSONAL JUDGMENT.—In the early part of the nineteenth century Bessel discovered the existence of variations in the judgments of two observers in their records of astronomical observations. Since that time astronomers have discussed the errors which such variations in personal judgment may introduce and also the proper methods of correction for them. In 1896, Professor Karl Pearson, by the application of the calculus of correlation, showed the extent to which the personal judgments of two observers were related to each other.

CHARACTER OF THE VARIATIONS.—In 1901, in a communication to the Royal Society ("Errors of Judgment," *Trans. Roy. Soc.*, 1901, 198, 253 *et seq.*), he showed that, in physical experiments, the individual and successive observations were not randomly distributed round the mean value. The view which had been hitherto held was that these observations were randomly distributed. An important result obtained by him in 1901 was that mean values of the personal judgment of an observer were of an irregular periodic character with respect to time. This result is at variance with the assumptions usually (and the author thinks erroneously) made that, for an observer in normal health, the personal equation in any one type of observation will remain sensibly constant for short periods of time, and that variations in personal judgment are due to accidental errors, and may be taken as randomly distributed in accordance with the law of frequency described by the normal or error curve. Recent work by Egon S. Pearson (*Biometrika*, 1922, 14, 23-102) has shown the reality of a secular movement for each observer. Not only is there a secular movement for each observer, when observations are made day after day, but there are also characteristic variations within a single series of observations made in one day. These variations are described as a sessional movement.

STUDY OF VARIATION IN CHEMICAL WORK.—It occurred to the author, in studying the work of K. and E. S. Pearson, to make a preliminary study of the nature of the variations of the results of determinations in chemical work, *such as might be carried out any day in an analyst's laboratory*, in the hope that a co-operative investigation might be undertaken by a number of analysts. The conditions affecting each series would be considered and an adequately large number of experiments planned for each series. In the case of burettes the error, if any, in each burette should be known. Unless this is taken into account, the personal judgment of the observer would be obscured by a fundamental error of measurement. Three series of preliminary observations were carried out—two subsidiary series, (1) weighings of a sovereign by students, to illustrate the effect of want of sufficient experience, skill and adequate training, and (2) weighings of a piece of lead by skilled workers; and the main series (3) determinations of the concentration of approximately 0.5 *N* sodium hydroxide solution, to illustrate the variations in volumetric work by a skilled worker.

PRACTICAL VALUE OF THE STUDY.—The practical value for the analyst of a study of the variations in chemical determinations is obvious. With a large series of observations of the strength of the bulk of a fluid used in volumetric work, one can estimate the range of the variations in the personal judgment of the observer. It will be evident that personal judgment occurs in determining 0.01 c.c. from a burette graduated in tenths or twentieths of a c.c. and in determining tenths of a mgrm. in ordinary weighings. Many of the other ordinary analytical operations are affected by the personal judgment of the observer. A study of personal judgment has a further practical value when samples of substances of not quite constant composition are analysed. It is known—to take one simple

example—that successive samples even of well mixed compound fertilisers vary in the actual proportions of their constituents. Thus different analysts may get results significantly different, not necessarily because of any variation in personal judgment, but also on account of the variation in the composition of the samples sent to different analysts. If variation in the personal judgment of an observer from a large series of determinations (given approximately by the probable error) is known, it can be eliminated from the result, and the residual deviations, if any, would indicate the extent of the natural variation in the composition of the article.

VARIATIONS IN WEIGHT DETERMINATIONS AND IN TITRATION RESULTS.—In series (1) the mean weight found was 7.98356 grms., with a standard deviation of 2.19 mgrms., a relatively large variability. The values found were not symmetrically distributed round the mean, and even numbers were more frequent than odd numbers. In other words, the students *selected* even numbers. In series (2) the weight of the piece of lead varied from 1.0010 to 1.0013 grms. according to the judgment of the observers, and there was no apparent tendency to record even numbers. In series (3) an approximately 0.5 *N* sodium hydroxide solution was selected for experiment. The strength, as determined for laboratory work, was such that 21.25 c.c. of the alkali solution were required for neutralisation by 10 c.c. of *N* sulphuric acid. The skilled observer then made over a dozen determinations each day, taking different volumes of *N* sulphuric acid solution at random each day at the same temperature. The volume of *N* sulphuric acid taken varied from about 4 to about 19 c.c. Methyl red solution (0.05 gm. in 500 c.c. of alcohol + 500 c.c. of distilled water, neutralised), was used as an indicator, and the varying volume of acid solution was made up with distilled water, so that the final volume remained constant for each experiment. The determinations were continued for five days, and altogether 87 determinations were made.

The determination of the strength of the sodium hydroxide solution varied from 0.4705 *N* to 0.4719 *N*, with a mean value of 0.47081 *N*. This range of variation can be seen to be due to several factors, namely, (1) the care of the observer in accurately measuring the varying volume of sulphuric acid (burette graduated in 1/20th c.c.) and the volume of solution used (burette graduated in 1/10th c.c.); (2) light conditions and other environmental factors affecting the observer; and (3) possibly the slightly varying volume of indicator used. The results are not comparable with results obtained by using equal volumes of acid.

The effect of taking *varying* quantities of the normal acid shows that it is necessary to allow for a longer interval of time for the draining of the burette for larger volumes when compared with the time taken for smaller volumes (Stott, *Trans. Soc. Glass Tech.*, 7, 125). For volumes up to about 10 c.c. the strength of the sodium hydroxide solution was found to be practically the same for each volume taken. With larger volumes than 10 c.c. the result tended to be lower than the average value.

A less variable result was obtained by taking precisely 10 c.c. of acid and noting the number of c.c. of soda required. The mean was at 21.25 + 0.0022, indicating a possible range of means in a large series from 21.2434 to 21.2566. The standard

deviation was 0.0188 c.c., or less than one half the variability of the long series with varying volumes of acid.

**PSYCHOLOGICAL FACTORS:**—The following statistical discussion deals with the long series of 87 determinations with varying volumes of acid. The secular movement can be seen by comparing the deviations from the mean results for each day. The mean value was at 21.223 c.c., and the movement was periodic round this value for the five days' period. An important psychological factor was brought out when the mean values of the first, the second, . . .  $n$ th observation for each day were successively determined and studied. We then got the mean values of a succession of observations for a forenoon. As already stated, variation in a series of this kind is spoken of as a sessional movement. The variation was clearly irregular, but periodic in character, and ran from 0.012 c.c. below the general mean for the first determination to a positive value of 0.026 c.c. for the thirteenth determination at the end of the forenoon. It is the nature of the variations and not their magnitude which is of scientific interest.

The magnitude of the difference between the mean  $n$ th and the mean  $(n + 1)$ th determination was greatest for the first two determinations.

Of interest also was the mean difference of the  $n$ th +  $(n + 1)$ th determination, expressed as a deviation from the general mean. These mean differences showed very clearly the irregular and periodic character of the sessional movement throughout the forenoon.

**DIRECTION OF FURTHER WORK REQUIRED.**—The foregoing observations, suggested by Pearson's experimental work, are of quite a preliminary character, and were undertaken merely to attract attention to the subject. It is clear that a series of experiments—more numerous and properly conditioned—is required in order to show definitely the nature of the variations in personal judgment in chemical work. The effect, for example, of using different volumes of acid with *proper delivery times* should be contrasted with the use of equal volumes of acid in the determinations, and similarly for other volumetric determinations. Varying volumes of methyl red or other indicator should also be used to show the effect of variations in the quantity of indicator taken. Environmental factors would also require to be taken into consideration in any series intended to form the basis of measurement of variations of one observer, and of many observers. Further problems are (1) the extent of the correlation of judgments of two observers, (2) the mean values obtained from hour to hour and from day to day by a number of observers, and (3) the mean values obtained by a number of observers from day to day, where each worker makes a large number of observations.

#### DISCUSSION.

The PRESIDENT suggested that the tired worker was responsible for many of the author's results, and drew the conclusion that chemists ought not to work too hard. As to the suggestion that chemists all over the country should analyse identical samples and compare results, he foresaw the time when a whole army of sub-committees would be continually employed on making calculations and obtaining curves.

Sir ROBERT ROBERTSON lamented that chemists did not know enough about statistics, and the author's paper showed how much real information could be obtained from them. He regarded the curves with mixed feelings, but had been assured that the burettes, jets and methods of drainage were in accordance with the N.P.L. specifications. That raised the question as to whether the N.P.L. specifications were satisfactory.

Continuing, he remarked that results appeared to get less accurate as time went on. He mentioned that a piece of black paper was helpful in taking burette readings, and was informed that it had been used. The danger, he concluded, was that having accepted the author's figures, and having arrived at a probable error in experimental work, chemists might be inclined to sit down under them and cease to strive for greater accuracy.

Mr. E. M. HAWKINS remarked that the time of drainage would have to vary with the amount of liquid run out of the burette.

Dr. B. S. EVANS said that recent work had shown that if the rate of delivery was greater than 1 c.c. per second, the burette did not drain down within reasonable time; it might continue draining after 20 minutes. This introduced another possible factor of error.

Mr. THOS. TICKLE asked whether the last drop, which was equivalent to about  $1/20$  c.c., was included in the reading.

Mr. A. MORE pointed out that if a burette 50 cm. long was allowed only 70 seconds to drain it did not satisfy the N.P.L. requirements. He asked whether the two standard solutions had been compared at the same temperature. If the liquids were not always kept in bottles of the same size under the same conditions of temperature, and containing the same amount of liquid, the rate at which the temperature of the liquid followed changes in air temperature would vary, and, in consequence, the actual temperature of the two liquids would seldom be the same. He had found, in the delicate titration of sea water for chlorine, that differences of temperature of the liquid due to storage of samples over night in bottles of different sizes, although otherwise in identical surroundings, were sufficient to vitiate the results. The differences between morning and afternoon results quoted by Dr. Tocher might be largely due to this avoidable cause.

Mr. HINTON pointed out that if a burette was to be used for sulphuric acid it should be calibrated with sulphuric acid.

Mr. M. S. SALAMON asked if the burette was filled by each worker or by some automatic arrangement.

The PRESIDENT concluded that the term "personal error" was very indefinite. It involved errors of observation, which were strictly personal, and errors of manipulation, which were mechanical. There were also errors involved in the completion of chemical reactions, and their effect on indicators. He would like, in effect, to know exactly what constituted the personal error.

Mr. WILLIAM PARTRIDGE noted that the standard had been taken as either the mean of a number of readings or a weight by one man, and that variations had been based on these. He contended that the mean line was not necessarily a true one; and it was quite possible that the first or second readings might be correct. The results were based on human judgment, which varied from one man to another. Who was the most accurate person selected to take readings?

Mr. G. RUDD THOMPSON said that the author had tried to reduce the personal error to a mathematical formula; but how did he know that the burette was not subject to the same errors as had been recorded in the readings? If one man calibrated and another titrated two possible distinct errors were introduced into the final reading.

Mr. F. W. F. ARNAUD contended that reading a burette to three decimal places involved unwarranted accuracy.



Dr. TOCHER, in reply, said that no one could know accurately the strength of any solution from two determinations. Workers did not know the true strength of any solution. They knew only their own results and what deductions could be drawn from them. The argument about tired workers was merely a surmise. Every worker was more or less a tired worker. There was no doubt that the time of drainage would have to vary with the amount of liquid taken. The drainage time had been fully worked out in the National Physical Laboratory and elsewhere. No titration experiments had been conducted by junior workers. The experiments had been made only by skilled workers, except in the case of weighing of a sovereign. These weighings had been done by students. The object of the experiments was to find the variability of the determinations by a skilled worker. In answer to Mr. Partridge, Dr. Tocher said that the mean value of all the observations made under the same conditions was the best approximation to the true value. The true value was unknown and remained unknown. The accuracy of observers varied from person to person, and the most accurate observer could not be discovered except by putting analysts to the test. Each analyst could be asked to conduct a series of observations, and the person with the smallest probable error would be the most accurate observer, but the most accurate observer could not be found *a priori*. He was sorry to say there was a tendency to judge all these problems *a priori* and not from the results of observations. In answer to Mr. Rudd Thompson, Dr. Tocher said that the burette used was the same burette throughout, and, as the graduation of the burette did not change during the course of the observations, the variations must be due to the judgment of the observer. As a matter of fact, the burette was a carefully calibrated and standardised burette. In answer to Mr. Arnaud, Dr. Tocher said it was possible, but not probable, that the variations in the first two readings were peculiar to the observer, but that had to be established by a series of experiments made by other observers.

In answer to Mr. More, he said that the delivery time, excluding the time of drainage, was approximately 70 seconds for the burette. It was quite true such a burette required a longer time for drainage than a burette, the delivery time of which ranged from two to three minutes. Experiments were now being conducted with burettes with a much longer period of delivery time. In reply to the President, Dr. Tocher said that personal error was the error due to the observer alone. In the case of titration experiments, the personal error would be determined from the variations in determining the strength of a solution with a properly standardised burette with a long delivery time and time allowed for drainage, the acid solution being accurately ascertained, the temperature and other factors being, as far as possible, the same for each determination. The personal error was the sum of many errors due alone to the individuality of the observer. Two or three determinations were insufficient to ascertain the strength of a solution with a high degree of accuracy. A few hundred determinations were necessary in order to determine the particular form of frequency distribution and the range of the variations. The frequency distribution found was not necessarily a symmetrical or normal distribution, but was most probably skew, due to the judgment of the observer, as had been found in other experimental work.

As a result of these observations there was no doubt in Dr. Tocher's mind as to the reality of a sessional movement during the day in titration experiments and also as to the reality of a secular movement from day to day. Both movements were irregularly periodic in character. If a number of skilled men made a series of determinations of the strength of the same fluid over a long period of time, the probable error of the determination could be accurately found. The nature of the mean sessional and mean secular movements would also be discovered.

## Applicability of the Mydriatic Test to the Detection of Datura in Decomposed Viscera.

BY D. N. CHATTERJI, B.A., B.Sc., A.I.C.

POISONING by datura is of common occurrence in India. The drug is seldom administered, however, for a homicidal purpose. Its use is mainly restricted to the stupefaction of the victim so as to facilitate robbery or other crime. Hence the quantity of the poison administered is generally below its lethal dose. But at times the dose accidentally exceeds this limit, and death results.

If, in a medico-legal investigation of such a case, datura seeds or their fragments are discovered in the stomach contents, they are readily identified. Otherwise the alkaloidal principle of datura has to be isolated and identified. In most of these cases the residue obtained from a Stas-Otto extract is so small that it does not admit of the purification necessary for the successful application of chemical tests in addition to the mydriatic test, which, being a very delicate and reliable one, is always made. It has been found to respond, even when the chemical tests have failed. But in the case of decomposed viscera reliance on the mydriatic test alone for the detection of atropine is open to objection, inasmuch as certain products of decomposition have also been known to produce mydriasis. In such cases, whenever possible, Vitali's test would be the most suitable supplementary test in preference to others if not more than one can be performed, as not only is the test a very delicate one, but also it is said that the only putrid product which has been found to react with it failed to produce mydriatic action (see *Medical Jurisprudence, Forensic Medicine and Toxicology*, by Withaus and Becker, second edition, Vol. IV, p. 893).

During the course of work in this laboratory within recent years, viscera in more or less highly decomposed condition were extracted in 55 cases by the Stas-Otto method, and the residue examined, with the following results:—

(a) Number of cases in which mydriasis was observed and the presence of atropine was confirmed by Vitali's test	.. .. .	3
(b) Number of cases in which mydriasis was observed, but the Vitali's or other tests failed to react	.. .. .	2
(c) Number of cases in which mydriasis was observed, but the quantity was not sufficient for other tests	.. .. .	1
(d) Number of cases in which no mydriasis occurred	.. .. .	49

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Of the two cases under (b), death in one occurred under circumstances which, as elucidated by police enquiry, would raise the suspicion that the deceased person

was a victim of datura poisoning. The other case related to an unknown man whose viscera were sent for analysis, together with those of another, also in decomposed condition, who died apparently under the same circumstances as the first man, and in whose case the presence of atropine was confirmed by Vitali's test, in addition to the mydriatic test. The only case, therefore, in which there was no other direct or indirect evidence of datura poisoning than the fact that mydriasis was obtained from the Stas-Otto extract of the viscera, was the one noted under (c).

It would thus appear that the occurrence in decomposed viscera of a putrid product capable of producing mydriasis is a rare event, and that the evidence based on the mydriatic test alone is of sufficient significance as an indication of the presence of atropine, particularly when other evidence, *e.g.* the history and symptoms of the case, also points to the administration of the same poison.

It is also of interest to note from the cases recorded above that atropine is not always destroyed beyond possibility of detection during the decomposition of cadaveric remains.

GOVERNMENT LABORATORY, AGRA, INDIA.

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## Notes.

*The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.*

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### METHOD FOR THE COMBINED DETERMINATION OF OXYGEN ABSORBED AND ALBUMINOID AMMONIA IN SEWAGES AND EFFLUENTS.

THE author has found that an alkaline solution of potassium permanganate may be used for the determination of the oxygen-absorbing powers of these liquids and that the results are concordant and in closer agreement with the natural absorption than those obtained by the acid method.

This method has the additional advantages of giving a definite end-point in the albuminoid ammonia determination and absolute correlation between these two most important tests.

*Process.*—Distil off free ammonia as usual, leaving a volume of approximately 250 c.c. Add 25 c.c. of 20 per cent. sodium hydroxide solution and usually 20 c.c. of N/8 potassium permanganate solution. Heat under reflux for 30 minutes, cool, and make up to 500 c.c. Remove two separate portions of 50 c.c. each, acidify, add potassium iodide, and titrate with N/80 sodium thiosulphate solution. Each result gives the oxygen absorbed by one-tenth of the original volume of sample taken, and is 4 times the result for 4 hours at 80° F.

Return the remaining 400 c.c. to the flask, distil off ammonia and Nesslerise. This gives the albuminoid ammonia from 4/5 of the volume of sample taken, and is slightly greater than the ordinary Wanklyn value.

All reagents used should be free from albuminoid ammonia, and blank determinations should be made.

J. W. HAIGH JOHNSON.

WAKEFIELD.

## THE DETECTION OF APPLE-PULP IN JAM.

THE detection of apple-pulp in jam by the direct microscopical examination of a morsel pressed out between microscope slide and cover-glass, with or without previous treatment with iodine solution, sometimes fails in its purpose altogether, for the reason that the small quantity examined contains no apple cells.

The following process allows much greater certainty over negative findings, because cells with apple characters appear in the final preparation with from five to thirty times the frequency they do in direct examination.

Ten grms. of the jam are mixed with 100 c.c., or so, of warm water (a temperature of 60° or 70° C. does not affect the characters of important cells), but care must be taken not to break up any whole fruit present by mixing, since this would correspondingly impoverish the final sediment in apple cells. The liquor is strained through wire-gauze (a strainer with a mesh of 20 is suitable) either into a centrifuge tube with a capacity of about 15 c.c. or into a urine-sedimenting cylinder, and is then centrifuged or left to settle. A minute of centrifuging or two hours of sedimentation suffices to give a deposit much richer in apple cells than was the original jam, and these cells retain any iodine-reacting character they showed in the jam.

Centrifuging is preferable to sedimentation, as, the sediment being more compact, it allows an ample number of cells to be placed at one time on the slide. Moreover, not all the apple cells fall by gravitation in two hours, and after the first collection has settled (which takes from forty-five minutes to two hours), the top liquor may be decanted and left overnight for the lighter apple cells to settle.

Any iodine-reacting character possessed by the apple-cells at the time of manufacture persists in jam for a long while. The test mentioned above gave excellent iodine tints in the case of a jam bought thirty-nine months previously.

WILLIAM PARTRIDGE.

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## Notes from the Reports of Public Analysts.

*The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of interest to the Society. Notes made from such reports would be submitted to the Publication Committee.*

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### CITY OF BIRMINGHAM.

#### REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1926.

Of the 1491 samples examined, 1311 were analysed under the Sale of Food and Drugs Acts, 1274 being bought informally (31 adulterated) and 37 formally (7 adulterated). Five samples of apples were tested owing to consumers attributing internal pains to arsenic in the apples, but the minute quantities detected on the skin of the apples did not justify the allegation.

MILK.—Twenty-eight formal samples (4 adulterated) and 740 informal samples (20 adulterated) were examined.

To test the variation of the solids-not-fat of a herd of cows from day to day, samples were taken at one of the railway stations from milk consigned by a farmer who had 22 cows.

Samples of the two "meals" were taken on 11 consecutive days, and the solids-not-fat only varied from 8.7 to 8.9 per cent. On three days there was a fall of snow, but on the other days the temperature was comparatively mild. The percentage of fat showed more variation, but as the farmer subsequently stated that "cows with calves are sometimes milked before the calves are put on them, and sometimes after," the variation is not surprising.

CAKE.—Fourteen informal samples of cake were tested for boric acid, and four samples of "Genoa cake" which contained from 7 to 9 grains of boric acid per lb. were reported as adulterated.

SCOTCH WHISKY.—Nine samples did not exceed the limit of 35° under proof. Three samples from one vendor were adulterated with water, an informal sample to the extent of 2 per cent., and a second informal sample and a formal sample to the extent of 5 per cent., being 38.5° U.P. The vendor, who attributed the loss in strength to evaporation, was fined £2. Experiments were therefore made to ascertain the rate of loss of strength in particular conditions. The first experiment was to determine the rate of evaporation in a bottle which was left uncorked. A quantity of  $\frac{3}{4}$  pint of whisky was put in a spirit bottle, which was left *uncorked* for 22 days. During that period the spirit strength altered from 31.4° U.P. to 32.4° U.P., while about  $\frac{1}{2}$  oz. of the spirit had evaporated. The air temperature during the experiment varied from about 50° to 70° F.

In the next experiment  $\frac{1}{4}$  pint of whisky was put in a  $\frac{1}{2}$  pint drinking glass and left *uncovered* for six hours. The strength of the spirit altered from 31.2° U.P. to 32.3° U.P., or a loss of 1.1° of proof spirit. The air temperature during the experiment was 60° to 70° F. The next morning the strength had fallen to 35.3° U.P., showing a loss of 4.1° of proof spirit in 24 hours. About  $\frac{1}{4}$  oz. of the liquid had evaporated.

These experiments show that to produce an appreciable loss of spirit strength there must be very gross carelessness in keeping the whisky, and that under reasonable conditions evaporation will not account for a deficiency of 3.5°, which corresponds to about 5 per cent. of excess water.

J. F. LIVERSEEGE.

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## COUNTY OF KENT.

### REPORT OF THE COUNTY ANALYST FOR THE FOURTH QUARTER, 1925.

THE total number of samples of food and drugs examined during the quarter was 898, of which 20 (2.2 per cent.) were adulterated. All the 18 samples of drugs examined were genuine. There were also examined 2904 samples of milk taken from single cows and herds, to ascertain the quality of the milk yielded.

MILK.—Of the 387 formal samples, 11 were adulterated. A marked improvement was shown in the quality of milk sampled on Sundays. Only 4 of the 164 Sunday samples were adulterated and 6 of inferior quality, but one sample contained 22.7 per cent. of added water. During the year 443 samples were taken on Sundays (4.7 per cent. adulterated), whilst in 1924 the percentage of adulterated Sunday samples was 7.

Twenty-six samples of Grade A milk were examined. None showed any evidence of added water, but in two instances there were deficiencies of fat, and one sample contained only 3.0 per cent. of fat. The average amount of fat in these Grade A milks was 3.53 per cent., whereas the average amount found in the ordinary milks during the quarter was 3.85 per cent.

ARSENIC IN APPLES.—Three samples of imported apples were examined, and one of these (Jonathans) was found to contain 1/33rd of a grain of arsenic per lb. The vendor, on being notified of the result, at once undertook to withdraw his stock of these apples from sale.

SAGO.—A sample bought as sago proved to be tapioca, and was therefore reported to be adulterated. Some vendors appear to prefer to sell tapioca when sago is asked for, owing to its having a whiter and cleaner appearance.

F. W. F. ARNAUD.

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## Legal Notes.

*Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.*

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### MEANING OF THE WORDS "EXPOSED FOR SALE."

ON May 19th a Paddington tradesman was summoned at Marylebone Police Court for exposing margarine for sale without attaching to each parcel a label in such a manner as to be clearly visible, as required by the Margarine Act.

Evidence was given by an inspector that he was supplied with  $\frac{1}{4}$  lb. of margarine from a box on a shelf behind some jars. The parcel itself was properly marked, but the bulk was not labelled with letters  $1\frac{1}{2}$  inch in size in accordance with the Act.

The defendant stated that the box was labelled "margarine," and, so far as he knew, it was marked as required by the Act. No one standing in front of the counter could see the margarine until the jars were removed.

The Magistrate (Mr. Bingley) observed that "exposed for sale" meant that it was in the shop for sale, but the solicitor for the defence contended that the meaning did not go so far as that. He submitted that the prosecution could not succeed in view of the decision of the High Court in the case of *Crane v. Lawrence*, which held that "exposed for sale" meant exposed in the shop to the view of the purchaser. In that case the purchaser had asked for margarine, and had been served from a parcel then in the shop, unlabelled, but placed behind a screen so as not to be visible. The Court had found that this was not "exposed" within the meaning of the Act.

The Magistrate (after reading the case) said that he was surprised at the decision. He would have thought that anything in a man's shop was necessarily exposed for sale. In view of the High Court decision he dismissed the summons, but refused costs to the defendant, since, but for that decision, he would have been against him.

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### EXCESS WATER IN BUTTER AND A LABEL WARRANTY.

ON May 24th a shopkeeper was summoned at Slane, Co. Meath, for the sale of butter which, on analysis, had been found to contain 20.01 per cent. of water.

The defendant stated that she had bought the butter from a wholesale firm, who had guaranteed it to be pure, and that she had not tampered with it. It was New Zealand creamery butter, and a warranty as to purity was wrapped round it.

The Justice said that the wrapper produced was a warranty as to purity, but was it a warranty as to the percentage of water? In two cases referred to by the prosecution there had been negotiation or question of warranty other than the label. In his opinion, all the label guaranteed was that the article was pure butter, not margarine, nor a mixture of butter and margarine. He thought that the wholesale firm would be perfectly entitled to put that on the label, provided that the butter did not contain margarine or any other foreign substance.

There was, however, an offence when there was an excess of water in the butter, because the purchaser was not getting what he bargained for. He was satisfied that the defendant had not tampered with the butter, and imposed a small fine of 5s. and costs. This would put on the wholesale firm the onus of seeing that butter in future did not contain excess water.

The solicitor for the wholesale firm stated that they had bought this butter in the London market with a special warranty against excess water. It was Australian butter, and had passed the Australian Government tests, which were very severe.

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## Government of the United Provinces of Agra and Oudh and of the Central Provinces.

### ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1925.

ACCORDING to the Report of the Chemical Examiner (Mr. D. N. Chatterji) the total number of medico-legal and chemical cases investigated was 1922, involving the examination of 3851 articles. Of the 1068 medico-legal cases, 394 were for suspected human poisoning, 47 for cattle poisoning, and 616 were blood-stain cases. There were also 854 analyses made of water and miscellaneous articles.

COCAINE.—The number of substances examined for cocaine was 563, as against 820 in 1924. Pure cocaine was found in 44 samples, and impure cocaine (traces of dirt or other impurities) in 306 samples, whilst 163 samples consisted of cocaine in admixture with other substances (antipyrin, benzoic acid, etc.). Since the close of the war there was, until 1925, a steady increase in the number of cocaine samples submitted for examination, but there was a fall in the quality of the drug, only a small percentage of the samples consisting of pure cocaine.

MEDICO-LEGAL CASES.—Details are given of a number of cases presenting points of special interest.

In a case from Shahjahanpur a pill intended for poisoning cattle was found to contain opium—a drug not commonly used for this purpose.

In a Moradabad case a man died with symptoms of irritant poisoning. No definite indications of poisoning were detected on *post-mortem* examination, but the appearances suggested double pneumonia. Analysis of the viscera, however, showed the presence of a fair amount of arsenic. A similar case occurred in 1924, in which there was no *post-mortem* indication of poisoning, although arsenic was present in the viscera.

Fatal cases of cocaine poisoning are of rare occurrence, but one was reported from Bareilly, where a young woman died after taking an excess of the drug. The symptoms were discomfort, thirst, and confused speech, followed by unconsciousness after 2 hours, and death in about 3 to 4 hours. Cocaine was identified in the contents of the stomach.

In a case from Jaunpaur a man was taken ill after smoking "ganja," the symptoms suggesting datura poisoning. He was sent to the hospital and ultimately recovered. A mydriatic alkaloid was extracted from the vomit.

Some myriapoda, locally known as "Gar-gualan," were sent to the laboratory from Basti, where it is believed that they act as an irritant poison if administered internally, and are consequently used for poisoning cattle. Another curious property attributed to them is that the smoke emitted from them on burning will produce impotency in animals exposed to the fumes. Centipedes are known to have poison glands, and millipedes, which are said to be harmless to man, have special glands known as "stink glands," which secrete a peculiarly offensive fluid, in which prussic acid is said to have been detected. In the specimens submitted for examination no poisonous substance could be detected. They were identified by the Imperial Entomologist as belonging to a class closely related to the *Diplopoda*, *Phylum arthropoda*, and probably of the genus *Spirobolus*.

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## Department of Scientific and Industrial Research.

### FOOD INVESTIGATION BOARD.

#### Special Report No. 25.

#### THE HANDLING AND TRANSPORT OF FISH.\*

IN Great Britain the average temperature of the fish landed, including that from the long distance trawlers, was found to be 36·8° F., and occasionally with large fish up to 46·4° F., when plenty of ice had been used on the fish. The fish after landing lies on the quays for an average of 5 hours, with an average of 7 hours before icing. An average fish of 2 lbs. takes about 60 minutes, under the conditions obtaining, to reach air temperature right through. The fish are packed in boxes with crushed ice between the layers, about 20 to 25 per cent. of the fish weight of ice being allowed. Thus the fish near the sides of the boxes receive little cooling, and the subsequent forcing down of the lid is very liable to cause damage, and possibly accounts for the slight putrefaction sometimes observable even when plenty of ice is present.

Fish travels by train in various types of vans, but almost invariably these merely serve as protection from weather, and do not cool the fish in any way (as found from temperature records). The freight of ice in fast train traffic is high, although it is not charged for on goods trains.

The average temperature curve for fish during time on quay, in transit and in market, shows a peak during the 9th to 10th hours, which may reach 80° F. or more according to the air temperature. The high temperature period lasts long enough for the fish tissues to become flooded with bacteria, and subsequent lowering of the temperature will only diminish their activity and not their number, and intense activity will at once be resumed on subsequent rise of temperature. To preserve fish it is essential to keep the temperature consistently low.

In France conditions are more satisfactory, inasmuch as the interval between landing of the fish and packing only averages 1½ to 2½ hours, and packing aims at exclusion of air from the fish, prevention of direct contact between the ice

\* By E. Griffiths and C. Heron. Obtainable at Adastral House, Kingsway, W.C.2.  
Price 9d. net.



and the fish, and prevention of damage by crushing down of the box lids on the fish. Also, transit is by means of specially insulated vans, some having ice in special compartments at their ends. A difference of 20 to 25° F. was found during the summer months between the outside atmospheric temperature and the inside temperature of these wagons when reasonably filled. In an ordinary fish van in the United Kingdom such a difference is never reached, and any difference there is involves a very large expenditure of ice.

D. G. H.

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## Ministry of Health.

### POSTPONEMENT OF FOOD PRESERVATIVES REGULATIONS.

THE Minister of Health has written to the London Provision Exchange stating that, in consequence of representations which have been made to him, he has decided to postpone the operation of the Public Health (Preservatives in Food) Regulations, 1925, so far as they relate to bacon and hams, for a period of six months, *i.e.* until July 1, 1927. In making this concession the Minister has stated that he cannot contemplate any further postponement of the Regulations, and that he cannot entertain any suggestion that the presence of boron compounds shall be permitted in bacon and ham imported or sold in this country after the date mentioned.

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### ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

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## Food and Drugs Analysis.

**Behaviour of Different Starches towards Dyestuffs and Iodine. J. Hübner and K. Venkataraman.** (*J. Soc. Dyers and Col.*, 1926, 42, 110-121.)—All starches absorb larger amounts of basic than of acid or substantive dyestuffs from aqueous solutions at the ordinary temperature. Most basic dyestuff is absorbed by rice starch, which is followed in order by the starches of maize, potato, tapioca, wheat and sago; in some cases maize and potato, and also tapioca and wheat change places. The depth of the colour of the dyed starches does not always correspond with the actual amount of dyestuff absorbed. Thus, rice starch absorbs more methylene blue, but is dyed a lighter shade, than the other starches; this phenomenon is not due solely to the greater whiteness of the rice starch. With the acid dyestuffs and the direct dyeing cotton dyestuffs no regularity in behaviour is observable. Although a part of the dyestuff absorbed by starch is removable by washing with water, the shades remain strong, and are thus comparatively fast to water. Starch absorbs only minute proportions of the dyestuffs, but is capable of exhausting the solution of a basic dyestuff. Since, with the exception of sago starch, gelatinised starches absorb less dyestuffs than the

corresponding original starches, the particles of the former are apparently the coarser. Cupric salts, but not ferrous ammonium sulphate or ferric alum, are absorbed by starch. Tannic acid also is absorbed, the amount taken up decreasing in the order: wheat, maize, tapioca, rice, potato, sago.

*Inulin*.—Inulin absorbs methylene blue to some extent, but not acid dyestuffs. The direct dyeing cotton dyestuffs are steadily absorbed by inulin until their solutions become exhausted. When a solution of Congo red or diamine black is thus exhausted, the resulting solid product consists of a mixture of a white or pale-coloured substance containing the bulk of the inulin, with a small proportion of a far more deeply coloured substance.

T. H. P.

#### Determination of Reducing Sugars by means of Fehling's Solution.

**H. L. Hind.** (*J. Inst. Brew.*, 1926, 32, 208.)—Dianol green, proposed as internal indicator in the titration of reducing sugars by Fehling's solution (Mann, *Chem. & Ind.*, 1926, 45, 187) has an advantage over the methylene blue of Lane and Eynon (*ANALYST*, 1923, 48, 220) in not being re-oxidised, but the colour change in the red liquid containing cuprous oxide is not so sharp, and particularly difficult to ascertain in artificial light.

D. G. H.

#### The Clearing of Sugar Solutions (Wines) by Mercuric Salts. L.

**Semichon and Flanzky.** (*Ann. Falsif.*, 1926, 19, 208–226.)—By the use of acid sulphate of mercury as precipitating agent complete decolorisation and absolute clearness of the liquid treated may be obtained, and the nature and quantity of the sugars present are left unaltered. A large proportion of any gum or pectin present is removed, which is not the case when lead salts and charcoal are used. The mercuric reagent is prepared by mixing 250 c.c. of water and 50 c.c. of sulphuric acid (sp. gr., 1.710) and at once adding, little by little, and with continuous shaking, 60 grms. of finely powdered mercuric oxide (yellow or red). The last portions of oxide should be ground with a little of the liquid. After standing overnight, impurities are filtered off. Any white crystalline deposit of neutral sulphate formed on keeping may be neglected. In the case of liquids difficult to decolorise 6 c.c. of the mercuric reagent are added to 100 c.c. of liquid, and the whole made up to 110 c.c. A violet gelatinous precipitate is formed with red wines, and a brown precipitate with white wines. After shaking at intervals for 10 to 15 minutes, and after the appearance of a colourless supernatant liquid, the mixture is filtered, and a current of hydrogen sulphide slowly bubbled through the filtrate. This is stopped for red liquids when the precipitate becomes homogeneous and grey and the froth has disappeared, and for yellow liquids in the same way when the orange colour changes to brown. Under these conditions all excess of mercury is removed, and there is no excess of hydrogen sulphide. For easily decolorised liquids only 3 to 4 c.c. of reagent are used, and for fresh wort 4 to 5 c.c., and contact is allowed for 20 minutes.

D. G. H.

#### Influence of Sugar on the Determination of Ammonia in Grape Must.

**J. Ventre and E. Bouffard.** (*Compt. rend.*, 1926, 182, 784–786.)—Determinations of known amounts of ammonia have been carried out by the methods of Duclaux,

Laborde, and Müntz in the presence of varying quantities of different sugars. In the case of invert sugar the amounts of ammonia found decrease with an increase in concentration of the sugar. In the presence of 30 per cent. of invert sugar, the three methods yield results indicating 78.5, 46.0, and 96.7 per cent. of the theoretical quantities of ammonia, respectively. For 24 per cent. of laevulose the corresponding figures are 78.0, 48.5, and 93.1 per cent.; for dextrose the errors are less marked, and for sucrose they are almost negligible. In all cases Müntz's method, in which the distillation is carried to dryness and the ammonia collected *in vacuo*, gave the most satisfactory results. The errors noted are probably the sum of the errors due to the individual sugars present.

J. G.

**Influence of Sugar on the Determination of Ammonia in Grape Must.** J. Ventre and E. Bouffard. (*Ann. Falsif.*, 1926, 19, 226-230.)—If the ammonia from the must is displaced by magnesia and collected in the distillate, a marked retention of ammonia may occur in the presence of reducing sugars. Nitrogenous compounds undecomposed by strong bases and similar to the glucosines of Tanret are probably formed. (See preceding abstract.)

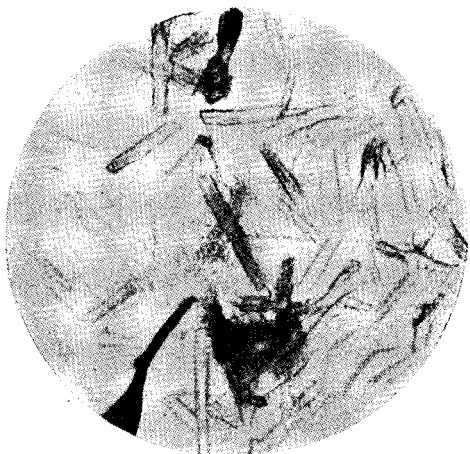
D. G. H.

**Behaviour of Gelatin towards Colouring Matters in Wines.** A. Kickton and F. Mayer. (*Z. Unters. Lebensm.*, 1926, 51, 132-137.)—The detection of colouring matters in wine by means of strips of filter-paper soaked in gelatin, dried, and suspended in the sample, is compared with other tests available for this purpose. Experiments were made on a large number of wines of different varieties, on aqueous solutions of coal-tar dyes, and on wines to which these dyes had been added. The dyes were subsequently dissolved out and tested with ammonia, and the colours obtained shown to be intermediate between those natural to the wine, and those due to the added dye. The method is not wholly to be recommended, the official wool test being preferred, supplemented by the cotton test and chemical investigation of the dyes. The lead acetate and mercuric oxide methods are limited in application, though extraction of the colour from the ammoniacal wine with amyl alcohol also gives positive results.

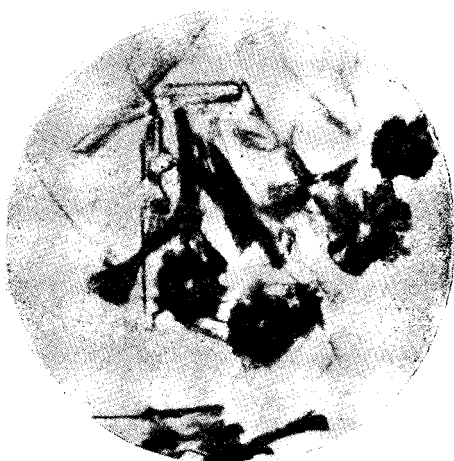
J. G.

**Identification of  $\alpha$ -Palmitodistearin in presence of  $\beta$ -Palmitodistearin.** F. J. F. Muschter and G. Visser. (*Chem. Weekbl.*, 1926, 23, 250-252.)—Bömer's method (*ANALYST*, 1913, 38, 204, 214; 1914, 39, 84, 171) of detecting beef or mutton fat in lard is based upon the fact that the distinctive glyceride of lard,  $\alpha$ -palmito-distearin melts at a temperature differing by 5° C. from its separated fatty acids, whereas in the case of  $\beta$ -palmitodistearin, the distinctive glyceride of beef and mutton fats, the corresponding difference is only 0.1° C. Bömer's test (according to which the crystals obtained from pure lard in a specified manner, so that they melt between 61° and 65° C., should show a value of not less than 71° C. when the m.pt. of the glycerides is added to twice the difference between that m.pt. and the m.pt. of their liberated fatty acids) is here shown to be untrustworthy. Only the microscopical identification of the isomeric modifications can be accepted as definite proof of the adulteration of lard with beef or mutton fat.

To obtain well-formed crystals, 1 part of the fat is first crystallised from 2 parts of ether, and the deposit recrystallised from ether containing about 2 per cent. of



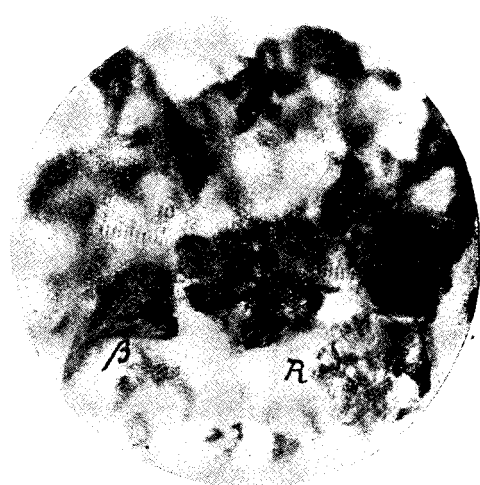
(1) Crystals of  $\alpha$ -palmitodistearin  $\times 100$ .



(2) Crystals of  $\alpha$ -palmitodistearin, showing rosette groups.



(3) Crystals of  $\beta$ -palmitodistearin.



(4) Rosette forms of  $\alpha$ -crystals in presence of  $\beta$ -crystals.

absolute alcohol (1 part of fat in 5 to 6 parts of solvent). The crystallisation should be made as rapidly as possible (*i.e.* with vigorous stirring at  $10^{\circ}$ – $15^{\circ}$  C.), and after each crystallisation the deposit should be washed with 1 to 2 c.c. of the solvent. It is advantageous to stain the crystals with the Giemsa-Romaowsky stain (azure-eosin, as used in bacteriology); this makes them suitable for microphotography on Agfa-chromo-isolar plates, with yellow screen. As thus crystallised, the  $\alpha$ -crystals show well-defined chisel-shaped forms with occasional rosette

groupings, whilst the  $\beta$ -crystals show small fan-like groups. Occasionally, at first sight, a group may appear to consist of  $\beta$ -crystals, which, when more highly magnified, will prove to be  $\alpha$ -crystals.

**Natural and Caffeine-free Coffees.** J. Pritzker and R. Jungkunz. (*Z. Unters. Lebensm.*, 1926, 51, 97-114.)—In the determination of moisture in coffee, concordant results are obtained with the whole or ground beans, by using the usual steam-oven method or that of the authors, in which the water is distilled over in xylene and determined in the distillate. The water extract is determined from the specific gravity of a 5 per cent. infusion of the ground coffee, or from a direct determination of the soluble solids. For the determination of caffeine, Fendler and Stuber's method is modified, thorough extraction being ensured by boiling the ground coffee under a reflux condenser with chloroform and ammonia. The acidity is determined by direct titration of the water extract, a spotting-tile being used; it is higher in the roasted than in the raw coffee, though it decreases progressively if the coffee is more heavily roasted. The percentage lost during roasting runs parallel with the increase in percentage extract produced. No substantial difference exists between the analyses of ordinary and of commercial caffeine-free coffee, apart from a slight decrease in extract in the latter case. Data obtained from samples on which attempts were made to remove caffeine before roasting were similar, on the whole, to the normal values. A slight decrease in extract is almost completely accounted for by the solids dissolved in the condensed water from the steam used in the process. For removing caffeine the action of boiling water followed by chloroform or ammonia is more effective than treatment with benzene or steam, or both, for various periods. The lowest recorded value is 0.03 per cent. of caffeine, produced as a result of prolonged treatment with 1 per cent. ammonia. Of the roasted natural coffees analysed from various localities, those from Novo Redondo and Mozambique contained the greatest and least amounts of caffeine (2.43 and 0.72 per cent.) respectively. The moisture-content of 3 per cent. for roasted coffees stipulated by some authorities is considered too low, about 7 to 8 per cent. being suggested. The minimum value of 20 per cent. for the water extract is approved. J. G.

**The Alkaloids of *Ceanothus Americanus*.** A. H. Clark. (*Amer. J. Pharm.*, 1926, 98, 147-156.)—*Ceanothus americanus* (Jersey or New Jersey tea, red root, wild snowball) belongs to the *Rhamnaceæ*, and infusions of the entire plant are used for their astringent properties. Recently it has been shown that the plant has a marked power to reduce blood pressure. Examination of the drug (bark of the root) has shown it to contain a complex mixture of alkaloids. One crystalline alkaloid (m.pt. 255° C.) was isolated, almost snow white, less bitter than the remaining amorphous mixture of alkaloids, almost insoluble in water and much less soluble in alcohol than the amorphous alkaloids. The solubility in alcohol of all the different products obtained from the alkaloid appeared to decrease with increase in m.pt. Solutions in hydrochloric acid (1:1000, 1:2500 and a "stronger" solution) of the amorphous mixture and of the crystalline alkaloid

were treated with various reagents, and the precipitates examined microscopically. The precipitates were amorphous with iodine in potassium iodide (Wagner's reagent), potassium mercuric iodide (Mayer), potassium cadmium iodide (Marme), zinc chloriodide, phosphomolybdic acid (Sonnenschein), phosphotungstic acid (Schleibler), silicotungstic acid, tannic acid (in strong solutions), mercuric chloride (in strong solutions), mercuric nitrate (Millon), platinum chloride, potassium ferrocyanide and ferricyanide (in acetic acid solutions only), and potassium permanganate (precipitates then reduce the manganese). With potassium bismuth iodide (Dragendorff) brick red crystals are formed with the crystalline product, and with picric acid (Hager) and gold chloride the precipitate from the crystalline alkaloid is also crystalline.

D. G. H.

**American Wormseed Oil. A. Hogstad, Junr.** (*Amer. J. Pharm.*, 1926, **98**, 188-204.)—An investigation of the "Western" American wormseed plant over two seasons from the seedling stage to final maturation showed that the essential oil is secreted by the glandular hairs, for the most part situated on the upper half of the ovary, but also found on the younger stems and the leaves, though practically absent from the woody portions of the plant. The oil was obtained by distillation of the fresh herb, which probably accounts for the fact that a standard oil was not obtained. In no case did the oils from the 1924 planting comply with the requirement of the U.S.P.IX. Only a trace of oil was obtained from non-flowering plants, more oil very low in ascaridole content from plants in the early flowering stage, and the greatest oil yield (still low in ascaridole) from plants at the pollination stage. If the herb is air-dried before distillation, the yield of ascaridole is greater. (It should be noted that ascaridole has not been definitely shown to be the active anthelmintic compound of *Oleum chenopodii*.) Most of the oil comes over in the first 5 to 10 minutes of a 35 minutes' distillation run. Characteristics of certain of the oils produced were as follows:—

	Sp. gr. at 25° C.	Ascaridole Per Cent.	$n_D^{20}$	Optical rotation.	Solubility in 70 per cent. alcohol.
7A. Partly matured					
herb	0.8552	12	1.4760	- 11.548°	insol. 1:8 to 1:15
9A.     "     "	0.8974	26	1.4750	- 15.124°	"     "     "
13A. Fairly well					
matured herb	0.9470	56	1.4735	- 13.518°	"     "     "
15A. Mature herb	0.9302	44	1.4743	- 15.065°	"     "     "
16A.     "     "	0.9536	57	1.4740	- 8.273°	sol. 1:15; insol. 1:8
21A.     "     "	0.9559	62	1.4735	- 15.373°	insol. 1:8 to 1:15

D. G. H.

**Aseptosol: A New Antiseptic Phenol from Betel Leaves. J. McLang.** (*Chem. Trade J.*, 1926, **78**, 560.)—The essential oil obtained from the leaves of *Chavica betle* contains as one of its constituents a phenol to which the name of "aseptosol" has been given. The pure phenol melts at 15.8° C. and solidifies at 15.2° C. Its b.pt. is 230°-231° C. (at 750 mm. pressure), and its sp. gr. is 1.0203

at 15° C. and 1.0175 at 20° C. It is nearly colourless, and has an odour somewhat resembling that of phenol. It is much more stable, and has much greater bactericidal power than the chavicol mixture of which it forms part. It yields alkali salts which crystallise well. Unlike the allied product, eugenol, it does not resinify. It is the most active ingredient of the juice of the betel leaves, which have long been chewed by the natives of the East Indies to whiten and preserve the teeth.

**Analysis of Sodium Bicarbonate. Isnard.** (*Ann. Chim. Anal.*, 1926, 8, 103–105.)—The method of the French Codex for detecting neutral carbonate in sodium bicarbonate, which consists in determining the residue (0.63 gm.) left on igniting 1 gm. of the pure salt (also in the absence of coloration when the salt is ground up with an equal weight of calomel), is shown to be untrustworthy. Measurement of the volume of carbon dioxide evolved on heating sodium bicarbonate (Belgian, Italian and American Pharmacopoeias) will give a reliable indication of the proportion of neutral salt present, and for a quantitative test it is recommended to determine the excess of sodium hydroxide left after addition of the theoretical quantity for neutralisation of the active carbonic acid. The total alkali may then be determined by titration in the presence of methyl orange. Sodium carbonate formed from the salt in the presence of moisture contained water corresponding to about 3H<sub>2</sub>O, and not 5H<sub>2</sub>O, as stated by certain authors.

D. G. H.

## Biochemical, Bacteriological, etc.

**Argon in Blood. L. Hackspill, A. P. Rollet and M. Nicloux.** (*Compt. Rend.*, 1926, 182, 719–721.)—Quantities of nitrogen and argon have been detected in defibrinated ox blood in amounts corresponding to their solubility coefficients and to their partial-pressures in air. A dried clot of blood evolves no trace of argon when burnt in the presence of copper oxide, so that no support is lent to the theory of Pictet, Scherrer and Helfer (*Helv. Chim. Acta.*, 1925, 8, 537) that this gas is the product of the radioactive disintegration of potassium. J. G.

**Determination of Uric Acid in Blood. H. Brown.** (*J. Biol. Chem.*, 1926, 68, 123–133.)—A direct method for the determination of uric acid in blood is described which has the following advantages over previous direct methods: (a) The technique is simplified because the uric acid reaction takes place at room temperature and thus eliminates heating in the water bath. (b) Turbidity formation is greatly delayed, making possible the simultaneous analyses of a large number of bloods. (c) Results are obtained which are nearer those of the Folin-Wu technique and, therefore, its use does not necessitate a new conception of higher "normal" uric acid values. A standard solution is made from the stable stock lithium urate solution preserved with formaldehyde, as recommended by Folin (*J. Biol. Chem.*, 1922, 54, 153). In a 500 c.c. volumetric flask 2.5 c.c. of the stock are diluted to 400 c.c. with water, 1 c.c. of formalin and 10 c.c. of 0.66 N sulphuric acid are added and the solution is diluted to the mark. This will keep at least

8 weeks; 5 c.c. of it are equivalent to 0.025 mgrm. of uric acid and the hydrogen ion concentration corresponds closely to that of a properly made tungstic acid filtrate. The method is as follows:—Ten c.c. of tungstic acid blood filtrate are transferred to a 100 c.c. Erlenmeyer flask and 5 c.c. of distilled water added. To two other flasks are added, respectively, 5 and 10 c.c. of the diluted uric acid standard, and the volumes made up to 15 c.c. with water. To each flask are then added (from a burette) 5 c.c. of a 5 per cent. sodium cyanide solution and 0.5 c.c. of the reagent (phosphotungstic acid of Folin and Wu; *J. Biol. Chem.*, 1919, 38, 98), and the contents of each flask are mixed. After 20 minutes' standing at room temperature the usual colorimetric comparisons are made. The above standards are good for uric acid values up to about 6.5 mgrms. per 100 c.c. of blood. Other standards may be prepared for higher values. Tables show comparisons of results obtained by this method with those obtained by the Folin-Wu and Benedict methods.

P. H. P.

**Biological Value of the Nitrogen of Mixtures of Patent White Flour and Animal Foods.** H. H. Mitchell and G. G. Carman. (*J. Biol. Chem.*, 1926, 68, 183–215.)—The total nitrogen content of a food, rather than its total protein content, is the better starting point in its biological evaluation as a source of nitrogenous compounds in anabolism. Experiments have been made to determine the biological value of the nitrogen of animal food alone, of white flour alone, and of a mixture of the two, always in the proportion of one part of nitrogen from the animal food to 2 parts of nitrogen from white flour. Tests were made on rats. The average biological value of the nitrogen of white flour is 52, of whole egg 94, of egg albumin 83, of milk 85, of veal 62, and of beef 69. The varying content of connective tissue in different cuts of the same kind of meat appears to modify the biological value of their nitrogen, the greater the proportion of the connective tissue, the smaller being the biological value. Mixtures of flour and egg nitrogen (2:1) have an average biological value of 75. With no supplementary relation between them the expected value would be 66; therefore the difference between 66 and 75 may be taken as a measure of the supplementary effect. The supplementary effects of the other mixtures are given, and comparing white flour and whole egg, egg albumin, milk, beef, or veal, the relation is greatest between white flour and beef, and least between white flour and egg albumin. The excretion of faecal nitrogen per grm. of food consumed and of urinary nitrogen per 100 grms. of body weight by the rat is nearly the same on a ration containing from 0.6 to 0.75 per cent. of whole egg nitrogen as on a nitrogen-free ration; hence it is proposed to substitute this low egg-nitrogen ration for a nitrogen-free ration in the standardisation of rats in these protein studies. The rat rapidly adjusts its excretion of urinary nitrogen to a change in ration.

P. H. P.

**Rapid Preparation of Mono-molybdophosphotungstic Acid as a Reagent for Polyphenols and Vitamins.** N. Bezssonoff. (*Comptes Rend.*, 1926, 20, 1223–1224.)—A solution of 74 grms. of sodium tungstate, 8 grms. of phosphomolybdic acid and 10 c.c. of ortho-phosphoric acid (sp. gr. 1.75) is treated,



drop by drop, at 45° C. with 85 c.c. of dilute sulphuric acid (125 c.c. of strong acid diluted to 250 c.c. at 15° C.). After standing for 3 hours crystallisation is complete, and the crystals are collected on a filter and washed with 50 c.c. of 15 per cent. (by vol.) sulphuric acid, about 60 grms. of crystals being thus obtained. These are dissolved in 100 c.c. of redistilled water at 45° C., precipitated by 35 c.c. of 50 per cent. (by vol.) sulphuric acid, and washed with 15 per cent. acid. On adding a few drops of the strong aqueous solution of the crystals to 2 to 3 c.c. of a 1:1000 solution of pyrogallol a yellow-brown colour should be produced, lasting at least 2 hours. The reagent is prepared by rapidly drying 15 grms. of crystals on filter paper and dissolving them in 100 c.c. of 5 per cent. (by vol.) sulphuric acid; it may be kept for 2 months in a yellow flask closed by a rubber stopper (*cf.* ANALYST, 1921, 46, 462).

D. G. H.

**Vitamins in Heat-Sterilised Food.** C. M. Dugdale and R. J. Munro. (*J. Soc. Chem. Ind.*, 1926, 45, 135-140.)—Finely minced meat foods were adequately sterilised in 85 grm. pots with a total heating of 110° C. for 40 minutes, and soups in 10 oz. cans at 115° C. for 60 minutes, and given to rats as supplementary to vitamin-free basal diets after the rats had ceased to grow and had begun to lose weight. The results obtained indicate that lean meat and its normally associated fat have a much higher value in vitamins *A* and *B* than has been acknowledged hitherto, a daily ration of 3 grms. of minced meat and less than 10 grms. of soup being sufficient to establish normal growth for a rat; also that commercial sterilisation appears to have little effect on these two vitamins. Vitamin *A* was adequately supplied by 3 c.c. of milk daily, but vitamin *B* required more than 15 c.c.; and 2 grms. and 4 grms. respectively of fresh cabbage leaves were inadequate to supply vitamins *A* and *B*.

D. G. H.

**Variations in Fat-Soluble Vitamin Content of Eggs preserved by different Methods.** I. A. Manville. (*Amer. J. Hyg.*, 1926, 6, 238-253.)—A study is given of the quantitative changes in the fat-soluble vitamin of eggs that had been preserved in water glass, in cold storage, and of yolks that had been frozen. Experiments were made on rats, and growth, freedom from infection and reproductive ability were taken as standards by which to judge the value of the egg yolk inclusions in the diets. Since, however, a reproductive disturbance occurred before growth failure or infection, this was considered the deciding factor. Charts show the results. Three lots of fresh eggs were gathered from the same source at the same time of year. One lot was placed in cold storage for one year; another was placed in water-glass for 18 months, and the third lot was used to establish standards by which the first two could be compared. The ethereal extract of the yolks was given in amounts ranging from 0.25 per cent. to 5 per cent. It was found that cold storage eggs lose not less than 75 per cent. of their vitamin value, water-glass eggs 50 per cent., and frozen eggs something less than 50 per cent. The low temperatures at which these frozen eggs were kept (0°-10° F.) and the fact that they were sealed in air-tight containers, indicate a method of storage which exposes the vitamin studied to the least amount of destruction.

Rats were maintained in a fairly normal condition by as low an amount of egg oil as 18 mgrms. per day; probably this could be reduced further. By feeding rats on graduated amounts of egg oil (fat-soluble vitamin), it was found that there is an optimal level at which this vitamin can be given, and that apparently as much harm results from an excess as from a partial or complete lack of it. Spring eggs contain more vitamin than winter eggs, and hot-house vegetables (lettuce) have less value than vegetables which have been grown in the field. P. H. P.

**Quantitative Study of Storage of Vitamin A.** H. C. Sherman and M. L. Cammack. (*J. Biol. Chem.*, 1926, 68, 69-74.)—A further study has been made of the extent to which vitamin A can be stored in the body, and the times and conditions of feeding necessary to induce maximum storage in experimental animals of different ages. Survival periods of rats of known age, pedigree and previous nutritional history, when placed upon diet devoid of vitamin A, but fully adequate otherwise, were taken as measures of the relative stores of vitamin A which the body had accumulated. The richer the diet in this vitamin the greater is the amount stored in the body. Rats of the same age, but with different dietary history, survive the withdrawal of vitamin A from their foods in accordance with the richness of their previous diet in this vitamin; but the increase in the survival period is not arithmetically proportional to the increase in the level of vitamin A intake. The addition of cod-liver oil to an already good diet quickly and largely increased the bodily store of the vitamin, but the animal only gradually completes the process of acquiring the maximum quantity the body can store. Feeding with a normal diet enriched by the addition of 4 per cent. of cod-liver oil for 1 week just previous to the transfer of the animals to a diet devoid of vitamin A caused prolongation of life, and the longer the feeding period (*e.g.* 8 weeks) the longer the survival period, but again the proportion was not arithmetical. Attainment of the maximum store of vitamin A is apparently a process of gradual accumulation which is relatively rapid in its earlier stages and becomes slower as the maximum is approached. A rapid storage of the entire maximum amount is apparently not possible. Rats of 6 months showed the highest results when opportunities for storage had been equal, but, given different opportunities for storage, it is possible for a 2 months old rat to obtain a reserve as great as that in a 6 months old animal of the same inheritance, but of less fortunate dietary history.

P. H. P.

**Observations on the Extraction of Vitamin B from Wheat Germ.** E. V. McCollum and H. D. Kruse. (*Amer. J. Hyg.*, 1926, 6, 197-200.)—Attempts have been made to find a method for the selective extraction of vitamin B from natural foods with minimum contamination with other substances. Extracts of wheat germ have been prepared, by the use of 95 per cent. alcohol containing 1 per cent. of an acid, with a view to finding whether the solubility of the vitamin in the form of a salt would be greater in alcohol than is that of the vitamin itself. The extracts were tested on young rats. Citric and acetic acids had no solvent effect, and phosphoric, hydrochloric and sulphuric acids only a very slight one.

Nitric, lactic and benzoic acids, in alcohol, extracted more vitamin *B* than did alcohol itself. Owing to the benzene nucleus in benzoic acid and the hydroxyl group in lactic acid seeming to favour the formation of salts of the vitamin, solutions of tannic and gallic acids in alcohol were tested as solvents for the vitamin, and these gave excellent results. Evidence given shows that most of the vitamin *B* which is extractable by alcohol and gallic acid from wheat germ is removed within a relatively short time. Alcohol containing those acids which give a good extraction of the vitamin, produces extracts of a decidedly simpler character than one yielded by any extraction methods hitherto described. The possibility was also tested of forming alcohol-soluble compounds of certain double salts of which the vitamin might be one component. Of the inorganic salts used, zinc and cadmium chlorides yielded slightly active extracts, but the others gave negative results.

P. H. P.

**Forms of Lactic Acid Produced by Pure and Mixed Cultures of Bacteria.** C. S. Pederson, W. H. Peterson and E. B. Fred. (*J. Biol. Chem.*, 1926, 68, 151-164.)—The production of the two enantiomorphs of lactic acid by biological agents is an example of the relation between stereoisomerism and biological activity. Experiments are described which show that in pure cultures bacteria may produce dextro- or laevo-lactic acid almost exclusively. When grown in mixed cultures with an organism which does not produce lactic acid (in this case the acetone butyl alcohol organism) large quantities of the opposite enantiomorph may be produced. It is possible that both forms of acid are produced by all lactic acid bacteria. In some cases the production of the two forms is nearly equal, whilst in other cases the point of equilibrium is near 100 per cent. production of one of the enantiomorphs. The solubility of the three zinc lactates has been determined. In a mixture of two zinc lactates the solubility of each component is influenced by the quantity which is present of the other component. A separation of inactive and active zinc lactates is best effected at or above 35° C., since above 25° C. the solubility of the active salts increases decidedly with an increase in temperature. The active salts, especially those of the dextro acid, have a tendency to form supersaturated solutions. Data are given which show that a sharp separation of the active and inactive types would involve an extended series of crystallisations.

P. H. P.

## Toxicological and Forensic.

**Relative Toxicity of the Lupine Alkaloids.** J. F. Couch. (*J. Agric. Res.*, 1926, 32, 51-67.)—The alkaloids were obtained from specially grown and identified species of lupins. Lupanine was prepared from *Lupinus angustifolius* and *L. polyphyllus*; hydroxylupinine and *d*-lupinine from *L. polyphyllus*; and spathulatine from *L. spathulatus*, but the U.S.P. sparteine was used on account of the difficulty of completely separating it from lupinine. Toxicity was determined on guinea-pigs of standard weight, and the symptoms of poisoning were

similar for each alkaloid except sparteine. Death was always due to asphyxia following depression and general paralysis, but with sparteine, tremors and spasms were always present in fatal cases. The most toxic of the alkaloids examined was *d*-lupinine, with a minimum lethal dose of 22 mgrms. per kilo.; sparteine was about 5 per cent. less toxic. The toxicity of lupinine was 85 per cent. that of *d*-lupinine, whilst spathulatine was about 70 per cent., and hydroxylupinine only 10 per cent. as toxic as *d*-lupinine. The minimum lethal dose by mouth was ten times that for subcutaneous injection. In the case of sparteine and hydroxylupinine the minimum lethal dose by subcutaneous injection was nearly twice that by intraperitoneal administration.

D. G. H.

**Poisoning by Manganese Compounds. H. Handovsky and others.** (*Arch. exp. Path. Pharm.*, 1926, **110**, 265; *Brit. Chem. Abstr.*, A, 1926, 320.)—Acute poisoning occurs only when the concentration of manganese in the blood suddenly becomes very high, and it is accompanied by nervous disturbances. In chronic poisoning this high concentration is not reached, nervous symptoms are not observed, the liver is chiefly attacked, and death occurs usually with smaller amounts than in acute poisoning, the lethal dose for the former being 40 mgrms. per kilo, and for the latter 50 mgrms. per kilo. In the chronic condition manganese citrate is more poisonous than the chloride. About 50 per cent. of the manganese is excreted in the faeces, and some is found in bone, bile, pus, ascitic fluid, spleen, brain and liver, only a little in the lungs and a trace in the urine. Manganese is only found in muscle after injection of the chloride and not after injection of complex organic salts.

R. F. I.

## Water Analysis.

**Chlorinated Drinking Water and its Use in the Preparation of Canned Foods. H. Serger.** (*Z. Unters. Lebensm.*, 1926, **51**, 125–132.)—Experiments have been carried out with the object of detecting any ill-effects caused by the use for cooking purposes of water sterilised by chlorination. Samples of water containing from 0.1 to 1.0 grm. of chlorine per cb. m. were used in the preparation of asparagus, beans and carrots, and the various physical properties (*e.g.* taste, colour, appearance, reaction, etc.) of the products noted. In no case did these differ markedly from those of the controls, nor was free chlorine detectable. The starch-iodide test for free chlorine fails at concentrations of less than 0.05 mgrm. per litre. If, however, the method of Le Roy (*Compt. Rend.*, 1916, **162**, 327) is used, or, if the whole of the water is frozen, the ice-block split, and the starch-iodide test applied on the middle of the inner surface, 0.0005 mgrm. of active chlorine per litre may be detected.

J. G.

**Determination of Dissolved Oxygen in Effluents. E. R. Trotman.** (*J. Soc. Chem. Ind.*, 1926, **45**, 110T.)—Winkler's method presents two difficulties, *viz.*, closing the filled apparatus and the admission of air when adding the hydrochloric acid. These are overcome as follows:—A wide-mouthed bottle (260 c.c.)

is fitted with a rubber bung, through which are inserted a side-tube with a glass tap and a small tap-funnel drawn out to reach to the bottom of the bottle. The bottle is marked at a point on the neck, about 10 c.c. below the bung, and the capacity to this mark ascertained. To make the determination, 10 c.c. of petroleum oil are poured into the apparatus, which is then almost filled with the sample, the bung inserted, and the contents of the bottle brought up to the mark by adding more of the sample through the side-tube. One c.c. of saturated manganese chloride solution is added and washed down with petroleum oil, and then 1 c.c. of a solution containing 33 per cent. of sodium hydroxide and 10 per cent. of potassium iodide. The taps are closed, and the contents well mixed. Five c.c. of concentrated hydrochloric acid are now added through the funnel and the liberated iodine titrated with 0.01 *N* sodium thiosulphate solution. The addition of the solutions displaces the same volume of the petroleum. R. F. I.

## Agricultural Analysis, etc.

**The Colour of Red Formations.** G. E. Dorsey. (*J. Geol.*, 1926 (2); *Nature*, 1926, 117, 703.)—It is shown that rocks which are not red frequently contain more iron, and even more ferric oxide, than do the red beds. The red colour is due not merely to oxidation (which is widespread), but also to dehydration. Favourable conditions for the production of the red hydroxide (turgite) and the red oxide (haematite) occur in warm, moist climates, and not, as has previously been asserted, in deserts or semi-arid regions. Ferric hydroxide turns red spontaneously by dehydration, even under water, if given sufficient time. In the tropical belts heat favours dehydration, and the heavy growth of vegetation keeps the soil from being rapidly removed. Most sediments are carried to the seas, and there, exposed to the reducing action of marine organisms, they lose any red colour they originally possessed. But red detritus is able to retain its colour if it comes to rest upon the continents where no widespread reduction is in progress. Occasionally, as at the mouth of the Amazon, fresh water and red detritus are sufficiently abundant to force the true marine conditions further from the shore.

## Organic Analysis.

**Determination of Total Solids. A New Micro Method.** A. C. Rottinge. (*Oesterr. Chem. Ztg.*, 1926, 29, 1-4; *British Chem. Abstr.*, 1926, B210.)—Five to 10 drops of any solution containing from 5 to 60 per cent. of extract are dropped on a roll of filter paper (0.45 mm. thick) contained in a weighing bottle, previously and subsequently brought to constant weight by heating in a hard glass boiling tube closed with a rubber stopper through which is passed a calcium chloride tube terminating in a capillary stopcock, so that the whole may be immersed in a boiling water bath for 30 minutes, evacuated to 20 mm., left in the bath another 30 minutes, cooled and weighed. A series of weighing bottles may be treated in the same boiling tube. Apart from traces of sucrose, which may give rise to an

error (less than 0.2 per cent.) due to inversion, the greatest error of the method is 0.2 per cent., but the temperature must be maintained between 90 and 110° C.

D. G. H.

#### **New Micro Method for Determining Carbon in Organic Compounds.**

**H. L. Lochte.** (*J. Amer. Chem. Soc.*, 1926, 48, 1301-1305.)—The method previously described (*ANALYST*, 1925, 50, 198) is modified to serve as a micro method. Use is made of a Monel metal bomb of dimensions 180 × 30 mm. and of similar structure to the Parr oxygen bomb. A 30 mm. Pyrex test-tube of suitable length, which slides into the bomb as a temporary lining, is used subsequently as titration vessel; this procedure obviates rinsing, but prevents vigorous shaking and leaves the metal exposed to any corrosive gases formed. Nitrogen and sulphur do not interfere with the use of the method and the metal does not corrode unless compounds with more than small proportions of halogens have to be analysed. If carbon is the only element to be determined, 10 c.c. of saturated barium hydroxide solution are introduced into the test-tube, and, with a chlorine-free solid, a pellet of the substance weighing 0.01 to 0.03 gm. is placed in the cup, and the usual ignition wire adjusted. The ignition is effected as in the macro method. The bomb is rotated for 30 minutes in a shaking apparatus set at such an angle that about 75 per cent. of the inner surface of the test-tube is exposed to the absorbing liquid when the speed is about 100 revs. per minute. The excess of alkali in the tube is neutralised by approximately 0.5 *N* hydrochloric acid, the final phenolphthalein end-point being then attained by means of 0.2 *N* acid. From 2 to 7 c.c. of this acid beyond that required to react with all carbonate present are then added in presence of methyl orange, and, when all specks of carbonate have disappeared the excess of acid used is determined by titration with 0.1 *N* barium hydroxide solution. It is advisable always, and necessary with less than 0.005 gm. of carbon, to obtain the exact end-point with methyl orange by matching a standard colour, such as that of methyl orange, in a sodium acetate and acetic acid buffer solution or, more conveniently, that of a mixture of ferric chloride and cobalt nitrate, as recommended by Kolthoff. Lindner's procedure, with only phenolphthalein as indicator, involves boiling the solution under a reflux air condenser for 30 minutes, but gives a sharper end-point.

No satisfactory method has yet been devised of applying this method to liquids with b.pt. below 100° C., but with a less volatile liquid, a drop from a small pycnometer may be placed on a weighed pellet of an igniter such as benzoic acid in the platinum foil cup and ignited as soon as possible.

T. H. P.

#### **Fractional Extraction of Liquid Fatty Acids of Linseed Oil.** G. Agde.

(*J. pr. Chem.*, 1926, 112, 37; *Brit. Chem. Abstr.*, A, 1926, 269.)—The contention of Erdmann that linolic acid can be isolated by the fractional extraction with alcohol of the basic zinc salts of the liquid fatty acids is not confirmed. Although the later fractions give products having the iodine value of  $\alpha$ -linolic acid, these are really mixtures of linolenic, linolic and oleic acids. The mixed salts are normal, not basic. The investigation shows that a separation of the liquid acids cannot be based on the fractional extraction of their zinc salts.

R. F. I.

**Seed and Oil of *Johannesia Princeps*. G. Etzel and C. G. King.** (*J. Amer. Chem. Soc.*, 1926, 48, 1369-1372.)—The air-dried, shell-free seeds of *Johannesia princeps* yielded, on pressing under 200 atmos., 26.6 per cent., or, on extraction with ether, 55.7 per cent. of a pale, yellowish-green, semi-drying oil,  $d$  0.9257 at 15.5° C., and 0.9229 at 20° C.,  $n$  1.4770 at 15° C. and 1.4750 at 20° C., iodine value (Hanus) 115.7, ester value 186.7, acid value 5.4, acetyl value 8.7, Reichert-Meissert value 1.2, Polenske value 0.345, unsaponifiable matter 1.17. The fatty acids contained 7.79 per cent. of saturated acids, 27.9 per cent. of linolic acid, and 52.24 per cent. of oleic acid. The percentage composition of the original seed was: Oil, 56.89; moisture, 2.21; ash, 5.20; crude fibre, 2.09; protein, 27.08; carbohydrates (by difference), 6.56; phytin (included in ash and carbohydrates), 5.70.

T. H. P.

**Crystalline Salts of Abietic Acid. Determination of Abietic Acid. G. Dupont, L. Desalbres and A. Bernette.** (*Bull. Soc. Chim.*, 1926, 39, 488-495.)—Crystalline hydrogen sodium abietate may be prepared from an alcoholic solution of abietic acid by the addition of a quarter of the quantity of sodium hydroxide required for neutralisation. The acicular crystals, which separate on standing, melt at 170-175° C., are slightly soluble in water and most organic solvents, and soluble in boiling alcohol. Analysis shows the salt to consist of 3 molecules of abietic acid and 1 of neutral sodium abietate. The formation of this abietate may be used for determining the proportion of abietic acid in various resins and for isolating the acid. Alkali metals give well defined crystalline salts in the presence of excess of abietic acid, corresponding to a formula of  $3C_{20}H_{30}O_2$ ,  $C_{20}H_{29}O_2M$ . With ammonia and amines, salts are most readily formed in neutral solution. Lead gives a well defined crystalline salt, but the other heavy metals and the alkaline earth metals form amorphous or micro-crystalline precipitates.

D. G. H.

**Anti-knock Materials. W. H. Church, E. Mack and C. E. Boord.** (*Ind. Eng. Chem.*, 1926, 18, 334-340.)—A large number of compounds have been investigated as regards their action in suppressing or inducing detonation in internal combustion engines. In addition to lead tetraethyl and other compounds known previously, four compounds were found to have anti-knock properties, these compounds being nickel carbonyl, bismuth trialkyl and triaryl compounds, cadmium alkyl compounds, and titanium tetrachloride. There is no evidence that the valency of the element is essential in determining its antiknock properties; whilst lead tetrastearate is without effect, lead thioacetate (divalent) gives effective suppression. In view of inconsistent results obtained in investigations on the suppression of detonation in an open tube it is not justifiable to apply the observations to the study of the suppression of knock in a motor. The relative effectiveness of an anti-knock compound would appear to be governed by the following properties, the optimum conditions being placed in parentheses: 1. Volatility (b.pt. below 400° C.). 2. Amount of free metal liberated when heated in air (should be complete). 3. Decomposition temperature (between

200° and 300° C.). 4. Temperatures developed by oxidation of the metal (high compared with ignition temperature of the fuel). 5. Size of particles and rate of oxidation (size, colloidal, to favour rapid oxidation).  
W. P. S.

**Test for Mercerisation. R. W. Kinkead.** (*J. Text. Inst.*, 1926, 17, T213.)—A small cutting of the material is stained for a few minutes in a cold solution (0.001 per cent.) of methylene blue containing 0.5 per cent. of sodium carbonate. It is then rinsed and placed in a test-tube with about 10 c.c. of a 3 per cent. solution of sodium carbonate and 4 drops of iodine solution (1 gm. per 100 c.c. of 20 per cent. potassium iodide solution). The solution is heated rapidly to boiling, poured off, and immediately replaced with cold sodium carbonate solution. Mercerised material becomes reddish-purple; unmercerised remains blue. The iodine is necessary to oxidise any reducing substances present in the material which would reduce the methylene blue to the colourless leuco-compound. The test is quite reliable, with certain precautions in the case of linen mercerised by the usual process (*i.e.* treated with a sodium hydroxide solution not weaker than 40° Tw.). The test has been applied to linen cloths mercerised in the laboratory and also under factory conditions, under tension and without tension. Certain finishing materials interfere, *e.g.* starch should be removed by boiling for 10 minutes with 3 per cent. sodium carbonate solution. Tendering by boiling for 1 hour with sulphuric acid (1.6 grms. per litre) does not invalidate the test. Damask treated with bleaching powder and washed free from active chlorine and acid does not respond. Mercerised linen cloths dyed with vat and direct dyes give positive results. Direct-dyed cloths should first be stripped with hydrosulphite or titanous chloride. The effect of mercerisation with mineral acids or calcium thiocyanate on the test is also described. By also using Hübner's iodine test, which is satisfactory for acid-mercerised goods, an indication can be obtained as to the mode of mercerisation employed.  
R. F. I.

## Inorganic Analysis.

### Determination of Small Quantities of Hydrogen in Gaseous Mixtures.

**P. Lebeau and P. Marmasse.** (*Compt. Rend.*, 1926, 182, 1086–1087.)—The procedure previously described for the analysis of a gaseous mixture (*Compt. Rend.*, 1913, 156, 144, 325, 557; *Ann. Chim. Phys.*, 1917, 8, 221) gives a residue containing methane, hydrogen, nitrogen, rare gases, oxygen and carbon monoxide. When such a mixture is passed into an apparatus containing silica gel previously freed from gas at 150° C. in a vacuum and cooled to about –190° C. by liquid air, the pressures of the nitrogen, methane, carbon monoxide, oxygen and argon are so small that they may be neglected, the respective amounts of the first four of these gases which would be entrained by the passage of 1 litre of hydrogen being 0.01, 0.0005, 0.001, and 0.008 c.c. The gases which are not fixed by silica gel under these conditions are hydrogen and helium; neon has not been investigated. With gaseous mixtures of known composition and including a small proportion of



hydrogen the method yielded accurate results, and the absence of even traces of hydrogen in marsh gas and other natural gas has been demonstrated with its aid.

T. H. P.

**Gravimetric Determination of Copper as Cuprous Iodide.** I. M. Kolthoff and H. A. Kuylman. (*Chem. Weekbl.*, 1926, 23, 185-186.)—Winkler's method of determining copper by precipitation with iodine as cuprous iodide (*Z. anal. Chem.*, 1923, 63, 324) gives good results, even with a strongly acid solution of the cupric salt, provided that, after the precipitation and boiling, the liquid is allowed to cool in a flask through which is passed a current of carbon dioxide. In the presence of air oxidation of the iodide takes place and some of the cuprous iodide is dissolved. Otherwise it is only slightly soluble (1.5 mgrms. per litre at the ordinary temperature). The precipitate is collected on a Jena sintered glass filter, washed with about 150 c.c. of cold water, and then with a few c.c. of alcohol, and dried to constant weight at 130° C. Accurate results are thus obtained, even in the presence of large quantities of ferric salt, so that the method should be applicable to the determination of copper in pyrites.

**Detection of Cadmium in presence of Copper.** R. Meurice. (*Ann. Chim. Anal.*, 1926, 8, 130-131.)—A small quantity of the solution is treated in a test tube with 1 c.c. of a 1 per cent. solution of brucine sulphate, then with potassium bromide; in presence of cadmium an abundant white precipitate of cadmium brucine bromide is formed, insoluble in moderately strong sulphuric acid. Copper gives no precipitate under the same conditions. The reaction also differentiates bromides from chlorides, as the latter give no precipitate with cadmium and brucine salt.

W. R. S.

**Determination of Thallium.** F. Mach and W. Lepper. (*Z. anal. Chem.*, 1926, 68, 36-45.)—Certain methods were examined critically. The precipitation as chromate in slightly ammoniacal solution, and washing of the precipitate with 1 per cent. potassium chromate solution followed by 80 per cent. acetone, is a reliable method. Precipitation as iodide, either in ammoniacal or in acetic solution, gave negative errors, e.g. - 0.0041 with 0.5156, - 0.0020 with 0.1364, and - 0.0009 with 0.0337 gm.  $Tl_2SO_4$ . Browning and Palmer's method (precipitation with potassium ferricyanide and hydroxide, and weighing of the precipitated thallic hydroxide dried at 200° C.) gave the best results. Thallium can be determined accurately as chromate in presence of arsenic acid; for the separation from lead, the lead is precipitated as sulphate.

W. R. S.

**Volumetric Determination of Chromium.** B. Reinitzer and P. Conrath. (*Z. anal. Chem.*, 1926, 68, 81-114.)—In presence of an excess of sodium acetate chromic salts are converted quantitatively into chromate by addition of permanganate to the boiling solution, chlorides not interfering. Addition of barium chloride or nitrate previous to titration facilitates recognition of the end-point, as barium chromate is precipitated and the solution decolorised. The permanganate solution may be standardised against iron or sodium oxalate, as the

reaction proceeds stoichiometrically:  $\text{Cr}_2\text{O}_3 + \text{Mn}_2\text{O}_7 = 2\text{CrO}_3 + 2\text{MnO}_2$ . In the determination of chromium in ferrochrome, iron does not interfere if the chromium content is higher than 5 per cent.; the iron can be precipitated as basic acetate, leaving a colourless solution. With lower chromium contents, as well as in presence of cobalt, nickel, and manganese, the alloy is dissolved in hydrochloric acid, the solution almost neutralised with sodium carbonate, and a small excess of precipitated barium carbonate emulsion added. A vigorous current of carbon dioxide is passed through the solution for 15 minutes, when the precipitation of the chromium is complete. The precipitate is filtered off on porous glass or porcelain and dissolved in dilute nitric acid; a little ferrous salt (which need not be removed quantitatively by washing) is oxidised by boiling. An aliquot part of the solution is nearly neutralised with sodium carbonate, treated with barium nitrate and excess of sodium acetate, boiled, and titrated with permanganate. W. R. S.

**Co-Precipitation of Magnesium with Aluminium Precipitates.** A. Lassieur. (*Ann. Chim. anal.*, 1926, 8, 97-98.)—If aluminium is precipitated quantitatively from solutions containing even large proportions of magnesium in the presence of only the necessary quantity of ammonia (*i.e.* a solution of  $P_{\text{H}} = 7$ ) aluminium alone is precipitated, but with marked excess of ammonia magnesium is carried down if more than 0.05 gm. per litre is present. The presence of salts of ammonia in relatively large proportions prevents this mechanical precipitation. D. G. H.

**Determination of Small Amounts of Potassium.** M. Delaville and P. Carrier. (*Compt. Rend.*, 1926, 182, 701-703.)—A measured quantity of solution containing the potassium is allowed to react with cobaltic nitrite reagent for 30 minutes, and the whole then centrifuged for 10 minutes. The precipitate of potassium cobaltinitrite is washed by decantation till the wash-water is colourless, and dissolved in 2 c.c. of hydrochloric acid, neutralised with ammonia, and a 4 per cent. solution of nitroso- $\beta$ -naphthol added. The precipitated cobalto-nitroso-naphthol is filtered off and heated in a Pregl micro-furnace. The amount of cobalt in the resulting oxide is then determined by a method analogous to that used by Fontés and Thivolle (*ANALYST*, 1923, 48, 511) for iron. The oxide is reduced in a current of pure hydrogen below 600° C., treated with the phosphomolybdic acid reagent, and titrated with potassium permanganate solution till the blue colour (due to  $\text{MoO}_2$ ) disappears. For quantities of potassium varying from 0.139 to 1.053 mgrm. the maximum recorded error is 2.1 per cent. J. G.

**Volumetric Determination of Potassium.** R. Meurice. (*Ann. Chim. Anal.*, 1926, 8, 129-130.)—The neutral solution, containing about 1 gm. of potassium chloride, is treated with excess of sodium hydrogen tartrate, so as to yield 0.045 to 0.05 *N* acidity. An equal volume of methyl alcohol (97 per cent.) is added to the liquid, which is kept for an hour in running water at 12° C. Filtration and washing with methyl alcohol (1:1 water) are carried out at 20° C. The precipitate is dissolved in a known excess of sodium hydroxide solution, which

is titrated back with standard acid in presence of phenolphthalein. The accuracy is stated to be within 1 per cent.; filtration and washing of the precipitate should be carried out with despatch. W. R. S.

**Separation and Determination of Tellurium. A. Brukl and W. Maxymowicz.** (*Z. anal. Chem.*, 1926, **68**, 14-22.)—Tellurium forms a very unstable sulphide soluble in alkali sulphides, and the solution gives a precipitate of tellurium by the action of a sulphite:  $\text{Na}_2\text{TeS}_4 + 3\text{Na}_2\text{SO}_3 = 3\text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{S} + \text{Te}$ . Tellurium may be determined as follows by the application of this reaction:—The acid solution is made slightly ammoniacal, warmed, and treated with yellow ammonium sulphide until the precipitate has re-dissolved. The solution is then boiled for 10 to 20 minutes with 20 to 25 c.c. of a saturated solution of sodium sulphite; when the yellow colour of the solution has been discharged, black tellurium is precipitated, which flocculates as the boiling proceeds. The liquid is then diluted to 200 to 300 c.c. and boiled with a little more sulphite, as a test for quantitative precipitation. If small, the precipitate should be left to settle for some hours. It is collected in a Gooch crucible, washed with hot water, alcohol, and ether, and dried at 100° C. As the precipitate is liable to oxidise, the drying is best carried out in a current of nitrogen.

The above method leads to improved processes for the separation from metals of the hydrogen sulphide group: (1) *From lead*:—The solution is evaporated with sulphuric acid until it fumes, cooled, diluted, heated to boiling, and left to stand for some time. The lead sulphate is collected and washed as usual; the filtrate is treated with ammonium hydroxide and sulphide and boiled, when a very small quantity of lead sulphide collects. This is filtered off and converted into sulphate; the filtrate is treated with sodium sulphite for tellurium. (2) *From bismuth*:—The solution is treated with sodium carbonate until a slight precipitate forms, and boiled with potassium bromide and bromate (*ANALYST*, 1926, **51**, 161). The oxybromide is filtered off and converted into bismuth phosphate; the tellurium is recovered from the filtrate as before. (3) *From mercury*:—The solution is made alkaline with sodium hydroxide, and enough sodium sulphide is added to re-dissolve the precipitate. An excess of ammonium chloride is added, and the solution well boiled. The precipitated mercuric sulphide is collected and washed with colourless ammonium sulphide, then water; the filtrate is precipitated with sodium sulphite. (4) *From copper*:—The precipitated sulphides are stirred up with a little yellow ammonium sulphide and 100 c.c. of water; in the case of a solution, ammonium hydroxide and polysulphide are added in slight excess. In either case the precipitate is dissolved with potassium cyanide, and the solution boiled. If a fair amount of tellurium is present, it begins to separate at this stage. The liquid is gently boiled, with addition of 10 to 15 c.c. of saturated sulphite solution, for 10 to 20 minutes, then diluted to 200 or 300 c.c., and a little more cyanide is added before cooling; this re-dissolves any copper sulphide. For minute quantities of tellurium, filtration should be delayed for some hours until the precipitate has settled. (5) *From gold*:—The separation is the same as for

copper. The filtrate from the tellurium is evaporated almost to dryness with sulphuric acid for the recovery of the gold. (6) *From selenium*:—The treatment with sulphite causes precipitation of selenium, which is, however, kept in solution by suitable addition of cyanide. The ammonium sulphide solution of the two elements is decolorised with cyanide, boiled, and treated with 10 to 20 c.c. of the sulphite solution. Boiling is interrupted when the tellurium precipitate has coagulated completely. The recovery of the selenium from the filtrate is not quite quantitative. Test separations show satisfactory results. W. R. S.

**Analysis of Bifluorides.** E. C. Roper and E. B. R. Prideaux. (*J. Soc. Chem. Ind.*, 1926, 45, 109T.)—*Potassium bifluoride*.—In the volumetric titration with sodium hydroxide and phenolphthalein an uncertain end-point is caused by the presence of silicofluoride. This may arise from the alkali, or be present in the bifluoride. The beakers used should be coated with ceresin wax. A commercial sample analysed by this method showed 26.8 and 27.2 per cent. of hydrofluoric acid. By heating this fluoride to just below a red heat in a special apparatus 88–89 per cent. of the hydrofluoric acid can be volatilised. The apparatus consists of a copper combustion tube ( $\frac{1}{2}$  inch internal diameter) containing a platinum boat. Air, dried by phosphorus pentoxide, is led through the tube, which is provided with a conical platinum stopper bearing a platinum tube bent at right angles and dipping into a known volume of pure standard alkali. The residue in the boat is weighed and also titrated. The loss of weight of this particular sample was 23.84 per cent. The hydrofluoric acid absorbed by the alkali was 24.44 per cent., and that found in the residue 2.58 per cent.

*Sodium bifluoride*.—The loss on ignition just below a red heat (hydrofluoric acid and moisture) was 30.6 and 31.0 per cent. Direct titration gave 29.9 per cent. of hydrofluoric acid. Sodium is determined as sulphate after ignition with sulphuric acid, and the fluorine as calcium fluoride. Percentage results on this sample were as follows:—

	HF.	NaF.	H <sub>2</sub> O.	Na.	F.
Commercial ..	29.9	68.06	2.04 (by diff.)	37.32	59.2
Theoretical ..	32.27	67.73	—	37.11	61.28

The deficit in hydrogen fluoride is rather greater than would be expected from the surplus of sodium fluoride. R. F. I.

**Determination of Chlorates and Perchlorates.** K. Scharrer. (*Chem. Ztg.*, 1926, 50, 274.)—From 5 to 10 grms. of a mixture containing pure sodium nitrate and less than 10 per cent. of potassium chlorate are fused over a low flame in a covered nickel crucible. According to the amount of chlorate present, from 5 to 10 grms. of copper powder are added carefully in small portions, care being taken to avoid too great an excess and too high a temperature. The melt is raised to a dull glow, cooled, extracted with warm water, filtered, and the chlorides in the filtrate determined. In the case of perchlorates the reduction takes 1 to 2 hours. The maximum errors recorded for potassium chlorate and perchlorate

respectively are 0.06 and 0.1 per cent., the amounts taken being from 0.047 to 0.987 gm., and from 0.052 to 0.683 gm. Copper powder may be prepared by the reduction of finely ground copper oxide with methyl alcohol vapour at red heat.

J. G.

**Determination of Perchloric Acid.** O. Loebich. (*Z. anal. Chem.*, 1926, 68, 34–36.)—The aqueous solution, containing about 0.1 gm. of perchlorate ion in 60 c.c., is acidified with 1 c.c. of 2 *N* sulphuric acid, heated to incipient boiling, and treated with 10 c.c. of a solution of 10 grms. of nitron and 5 c.c. of glacial acetic acid in 85 c.c. of water. After 2 to 3 hours' standing in an ice cupboard the crystalline nitron perchlorate is collected in a porous glass crucible (G5–7 Jena) and washed with 10 c.c. of ice-water in 6 to 7 portions with very gentle suction. Each washing should be given 5 seconds' suction. The precipitate is weighed after being dried at 110° C. The magnitude of the error is given at 0.25 per cent.

W. R. S.

**Preparation of Starch Solution for Use in Iodimetric Titrations.** C. L. Alsborg, E. P. Griffing and J. Field. (*J. Amer. Chem. Soc.*, 1926, 48, 1299–1300.)—The following procedure yields a 0.1 to 0.5 per cent. starch solution which shows little or no Tyndall effect and remains clear for months, retrogradation being extremely slow. Dry starch is ground in an ordinary pebble mill until most of the granules appear cracked or frayed under the microscope, and, in glycerol or cedar-wood oil, fail to show the black cross when viewed under the polarising microscope. This grinding may occupy many hours, but a single operation gives sufficient starch to last many years. About 2 parts of the ground material is sifted slowly into 100 parts of distilled water kept stirred mechanically for about an hour. The liquid is centrifuged at about 2000 revs. per min. for 30 to 60 minutes, and the supernatant liquid then decanted and stored under a layer of toluene. Wheat starch gives a water-clear solution, but the solution obtained from potato starch exhibits opalescence, which may be removed by repeated filtration by suction through kieselguhr.

T. H. P.

## Physical Methods, Apparatus, etc.

**Photometric Method of Measuring the Covering Power of Paints.** H. D. Bruce. (*Technologic Papers, U.S. Bureau of Standards*, 1926, 20, 173–190.)—This method is based on the reduction produced in the contrast between black and white surfaces by superposition of a thin coat of paint; with equally thick coats this reduction in contrast becomes more marked as the covering power of the paint increases. The background for the paint consists of an opaque glass disc 10 inches in diameter, one half being as truly white and the other as truly black as possible. The halves are cemented together on a glass backing with litharge-glycerin cement and then ground to a flat, semi-polished surface with optical emery. The plate is clamped to a vertical spindle and, after 20 to 30 c.c. of paint, previously passed through a 200-mesh sieve, have been poured on to the

centre, is rotated so that the excess of paint is thrown off and a film tapering from a small peak at the centre to a minimum at the edge remains. The dry disc is lighted uniformly by means of a lighting box, and the relative brightnesses of the two halves measured by means of Martens' photometer; the thickness of the film at any point is measured by means of an Ames' dial.

If the contrast ratio, which is the ratio between the brightness of the black half of the painted disc and the brightness of the white half, is denoted by  $y$ , and the thickness of the film by  $x$ , the formula  $y = x^2/(x^2 + c)$  expresses the experimental results except for such low thicknesses as cannot be measured. For two uniformly illuminated fields to be distinguished, the duller should not be more than 98 per cent. as bright as the other, and the covering power of a paint may conveniently be derived from that thickness of dry film which makes the black half of the disc 98 per cent. as bright as the white half. If  $b$  is the measured contrast ratio for the film thickness  $a$ , then the covering thickness of the paint is given by the expression  $7a \sqrt{\frac{1}{b} - 1}$ , and the covering power in square feet covered per gallon of paint may be calculated from the formula,

$$\frac{0.4075 (100 - \text{percentage of volatile thinner in the paint})}{\text{Covering thickness in mm.}}$$

T. H. P.

## References to Scientific Articles not Abstracted.

THE ELEMENT OF ATOMIC NUMBER 61; ILLINIUM. By J. A. Harris, L. F. Yntema and B. S. Hopkins. *Nature*, 1926, **117**, 792 (June 5).

The rare earth element, illinium, isolated from residues from monazite sand after extraction of thorium and part of the cerum—Separated from neodymium by fractional crystallisation of the bromates—Absorption spectrum masked by those of neodymium and samarium—Illinium identified by X-ray analysis.

SOME ASPECTS OF THE NEW REGULATIONS ON FOOD PRESERVATIVES. By C. A. Mitchell. *Medico-Legal Society*, April 18, 1926 (to be published in the *Trans. Medico-Legal Soc.*).

Comparison of Reports of Departmental Committees of 1901 and 1924—Comparison of Draft and Final Regulations—Inconsistencies in the New Regulations—Modifications required—Need of standard methods of analysis—Regulations should have statutory force.

ODOURS AND THE SENSE OF SMELL. By J. H. Kenneth. *Nature*, 1926, **117**, 591 (April 24).

Morphological, psycho-physiological and physico-chemical aspects—Nature of olfactory stimulation—Measurement of olfactory acuity—Investigation of olfactory reflexes and odour preferences—Phenomena connected with odorous particles—Bibliography.

THE PERCEPTION OF ODOUR. By H. Nicol. *Perf. and Ess. Oil Rec.*, 1926, **17**, 176 (May).

A "molecular" theory of smell—Simultaneous bombardment of olfactory nerve endings by numerous particles—Radiograph of nasal sinuses.

References: Berthelot, *Ann. Chim. Phys.*, 1901, **22**, 460; *Compt. Rend.*, 1904, **138**, 1249; Heyninx, *Essai d'Olfactique Physiologique*, 1919, p. 249; Grijns, *Arch. Néerl. Physiol.*, 1919, **3**, 377; F. A. Hampton, "The Scent of Flowers"; A. L. Turner, "Accessory Sinuses of the Nose," 1901.

POLLUTED ATMOSPHERE A FACTOR IN THE DETERIORATION OF BOOKBINDING LEATHER. By F. P. Veitch, R. W. Frey and L. R. Leinbach (Leather and Paper Lab., Bureau of Chemistry, U.S. Dept. Agric.). *J. Amer. Leather Chem. Assoc.*, 1926, **21**, 156–176.

Outline of previous investigations (References)—Effects of light and air—Absorption of sulphurous and acid impurities from air—Analyses of old leather bindings—Methods of preventing absorption—Neutralisation of harmful impurities as absorbed.

## Reviews.

THE B.D.H. BOOK OF STANDARDS. Pp. 109 and index. Published by the British Drug Houses, Ltd.

This little book is the outcome of the "List of Reagents for Analytical Purposes," originally prepared by a Special Committee of the Institute of Chemistry and the Society of Public Analysts at the beginning of the late war.

Its object is to indicate the requirements, as regards purity and strength, of reagents intended for analytical work, and to ascertain how far they are obtainable in this country.

The original list has been long out of print, and, the war being over, the Council of the Institute of Chemistry decided that an undertaking of this sort no longer came within its normal functions. In view of this, the British Drug Houses, who all along have been interested in the matter on the commercial side, have, with the consent of the Institute and of this Society, reissued and extended the list.

The number of substances dealt with has been nearly doubled, and the requirements, both as to comprehensiveness and stringency, have much increased. In addition to this, important improvements have been made in the original monographs, among the chief being the substitution of the simpler Gutzeit process for arsenic for that of the Marsh-Berzelius method, and the introduction, in a large number of cases, of specified limits of purity; and, coupled with these, quantitative methods of estimation.

No less than seventy new substances have been dealt with, including some of the most commonly used reagents which have hitherto been overlooked, such as Ammonia solution, Barium thiosulphate, Formaldehyde, Glycerin, Dimethylglyoxime and Petroleum spirit.

This little publication, moreover, embodies much fresh experimental work, as well as a mass of information gleaned from the experience of the post-war years.

It is excellently printed, the directions are clear, concise and to the point, and, from its obvious utility, it should certainly find a place in every analytical laboratory.

C. H. CRIBB.

A DICTIONARY OF APPLIED CHEMISTRY. By SIR EDWARD THORPE, C.B., LL.D., F.R.S. Vol. VI (S-acid to Tetryl). London: Longmans, Green & Co. Price 60s.

Owing to the lamented death of Sir Edward Thorpe, the final revision of this and the concluding volume of the Dictionary has been carried out by Dr. Forster Morley, and, while complimenting Dr. Morley on having brought Vol. VI through the press, all chemists will share the deep regret of the reviewer that Sir Edward Thorpe did not live to see the completion of the final volumes of this edition of his work.

The first impression which the reader obtains on referring to the present work is one of the enormous volume of precise knowledge which is now at the disposal of chemists; thus, in Volume VI over six hundred pages are devoted to subjects falling under the letter S, and the subject matter is mainly in a condensed form. To review such a work is not easy, and the writer proposes to deal in a general manner with only a few of the more important articles.

Sulphuric Acid is treated very thoroughly by Dr. Auden, who obviously has an intimate acquaintance with the methods in use for the manufacture of the acid by the chamber and contact process. In addition to the detailed descriptions of the manufacturing process, the theoretical side of the subject receives due consideration. An interesting feature in this volume is the article on Smoke Prevention by Professor Braime, who discusses the atmospheric conditions in our large towns, due to the use of bituminous coal as a fuel in the domestic grate and in industry. Emphasis is laid on the impossibility of avoiding the discharge of smoke into the atmosphere when bituminous coal is burned in the domestic grate, owing to the distillation of the tarry decomposition products during and after replenishing, the ignition temperature of the vapours not being reached. Analyses are given of various samples of soot and of atmospheric suspended matter, and the injurious effects on the national health due to smoke pollution are pointed out. In conclusion, a summary is given of the Newton Committee Report.

In view of the great industrial importance of sodium salts the section on Sodium is necessarily very long. Mr. Baker, of the Kastner-Kellner Alkali Company, writes an admirable account of the properties and manufacture of the element and its principal compounds, and has succeeded in making the subject matter interesting without the sacrifice of scientific accuracy, an achievement of no mean order. The author's success would appear to be largely due to his adoption of a chronological sequence in tracing the development of the industry from its inception, and Mr. Baker is to be congratulated on having produced an altogether excellent article.



Sir Daniel Hall writes the article on Soils, which is divided into two sections, the first dealing with the classification, composition and analysis, whilst the second part is devoted to the micro-organisms present in the soil. The whole article occupies a space of only ten pages, and in this compass it is naturally impossible to give more than a very brief outline of this very complex subject.

The name of the author is a sufficient guarantee of the excellence of the subject matter, but probably many will share the opinion of the reviewer that more space might have been devoted to this, the oldest and perhaps the most important branch of applied chemistry. In the volume under consideration many subjects of minor relative importance are discussed at considerable length, and it is felt that this lack of balance may be thought an imperfection in a book which is in daily use by workers in all branches of chemistry.

In the article on Spectroscopy, Professor Baly contributes a concise account of the construction and use of the modern spectrometer. Descriptions are given of laboratory methods for obtaining and examining flame, arc, gas and absorption spectra, and the application of spectroscopic methods to analysis is discussed.

The description of the work of Hartley and others on the quantitative analysis of alloys by means of the spectroscope will be of special interest to analytical chemists. A closely reasoned resumé is given of the large amount of work which has been done during the last twenty years with the object of correlating observed absorption spectra and chemical constitution. The author finally rejects in unequivocal terms any theory advanced to explain absorption spectra of solutions of organic compounds by means of space formulae, and in place of such formulae explains the observed phenomena in terms of a molecular phase hypothesis based on the quantum theory.

Sugar is treated in this volume in two sections. The first section, written by Mr. Heriot, of Glasgow, consists of detailed descriptions of the most modern machinery used for extracting sugar from the cane and beet respectively, followed by an account of the methods used to-day for the preparation of the various types of refined sugar manufactured. The second section deals with the analysis of cane sugar and other carbohydrates, and is contributed by Professor Ling and Dr. Nanji. The authors give a very good selection of modern and reliable methods which have been found to give accurate results in their hands, and the more recent iodimetric methods for the determination of aldoses are described. A good account is given of the determination of sugar in the blood, followed by descriptions of the preparation, properties and standardisation of insulin.

The article on Synthetic Drugs is revised by Professor Barger, and in the space of thirty-three pages an excellent summary is given of the present state of our knowledge of the relation between chemical constitution and physiological action, whilst an account is given of the specific action of the more important synthetic drugs.

In discussing the relation between structure and physiological action mention is made of Ehrlich's ingenious theory of the dependence of selective action of a given nucleus upon the presence of combined "anchoring" groups. An outline

is given of the influence of the amino, alkyl, hydroxyl and carbonyl groups and of halogen atoms in developing or diminishing toxicity, followed by a description of the more important drugs classified, in accordance with their medicinal action, under the headings of anaesthetics, therapeutic dyes, organic arsenicals and other specifics for parasitic infections, cathartics, and glandular organs and their extracts. Of especial interest is the excellent summary of the work of Ehrlich in searching for specifics for parasitic infections, leading to the synthesis of salvarsan. Mention is made of the synthesis of "205 Bayer" and of its successful action in the treatment of the terrible scourge of sleeping sickness, but unfortunately the constitution of this drug is, up to the present, known only to the manufacturers.

The high standard of excellence of the printing and binding noted in the previous volumes is maintained in volume VI, and the publication as a whole constitutes a library in itself which few chemists would willingly be without.

GEO. R. THOMPSON.

ADDENDUM.—The section on Tannins, which has been revised by Professor Perkin, gives an admirable outline of the researches which have been made since the last edition to elucidate the constitution of these compounds and their derivatives. It includes recent work, such as the colorimetric methods of determining tannins and Miss Price's modification of the gold beater's skin test, and has a reference to the discovery of tannins free from glucose. It should be mentioned, however, that the statement (p. 656) that Nierenstein "now concludes that glucose is an essential constituent of tannin," while doubtless correct in 1914 (the date of the reference given) is not in accordance with Dr. Nierenstein's more recently published views on this question.—EDITOR.

INTRODUCTION TO THE STUDY OF ORGANIC CHEMISTRY. By JOHN WADE, D.Sc. (Lond.). Revised and enlarged by HENRY STEPHEN, O.B.E., D.Sc. Pp. xx. + 646. London: George Allen & Unwin. Price 8s. 6d. net.

Dr. Stephen is to be congratulated on the excellent way in which he has revised and enlarged the well-known work of the late Dr. Wade, without in any way obscuring the almost ideal teaching plan upon which it is based. A new chapter on pyrone, chromone and xanthone has been added. For the sake of those unfamiliar with previous editions it will, perhaps, not be out of place to give a brief outline of the book.

It is divided into three main parts, each of which is further subdivided into sections containing several chapters. At suitable points synoptic charts are interposed. These should be a real help to the student in mastering the overwhelming mass of detail which characterises organic chemistry.

Part I opens in a very simple way, namely, with the preparation of pure alcohol. From this the reader is led, through the study of the properties of this substance, to a consideration of such operations as combustions, molecular weight determinations, etc. Derivatives of alcohol are then studied, and by almost imperceptible stages the question of molecular structure is introduced, and near

the end of Part I the hydrocarbons are considered as a basis for classification. This section lays the foundations of organic chemistry, and thus prepares the way for the systematic study of the two great divisions of the subject which are discussed in Parts II and III.

Part II is devoted to a very exhaustive treatment of complex aliphatic compounds. An extremely large range of substances is dealt with, and it is very difficult to find anything of real importance which is not mentioned.

Part III treats of aromatic and cyclic compounds. Here, again, the mass of fact presented in so brief a space is little short of astounding.

The book closes with a scheme of practical work and excellent subject and author indexes.

On reading through the book one cannot help being struck by the vast amount of detail which it contains, but which nevertheless is presented in such a way that the main outlines of the subject are in no way obscured. The reviewer has found only one misstatement of fact, namely, on p. 172, where it is stated that linoleic acid,  $C_{17}H_{31}COOH$ , is the active constituent of linseed and other drying oils.

The chief merit of this volume lies in the scheme of practical work which runs parallel with the text. Very precise instructions are given for making illustrative experiments. If these are worked through, in conjunction with lectures and reading, very good results should accrue. From the teaching point of view, *Wade's Organic Chemistry* is far ahead of the dictionary type of text-book, and is well worth the consideration of those engaged in teaching "pure" organic chemistry.

HAROLD TOMS.

METHODEN DER BAKTERIOLOGISCHEN UNTERSUCHUNG VON NÄHRUNGSMITTELN.

By WALTER GAETGENS. Pp. 506. 10 ins.  $\times$  7 ins. 17 illustrations.  
Berlin: Urban & Schwartzburg.

This volume appears as instalment No. 172 of Dr. Emil Abderhalden's *Handbuch der Biologischen Arbeitsmethoden*, being classified under Abt. IV, *Angewandte Chemische und Physikalische Methoden* as Vol. VI of Part VIII. In the introduction the author states that his intention has been to afford guidance in the demonstration and identification of the more important saprophytic and pathogenic bacteria, the latter not being limited to those which have hitherto been easily identified, but including also such pathogenic organisms as might conceivably occur in foods and give rise to infectious diseases in animals and human beings.

Owing to the wideness of the field covered and the wealth of detail given, descriptions of laboratory technique have been omitted except in a few special cases, such as the operations connected with sampling, which are most carefully described under several headings. Similar considerations, no doubt, account for the fact that, though the book appears to have been published in 1925, one finds hardly any footnote references to work dated later than 1922, the introduction being dated January 1923. For any regrets on this score, however, the reader will be compensated by the conscientious and thorough manner in which the author has performed his task.

About two hundred pages are devoted to descriptions of the morphology, culture, etc., of a very comprehensive list of micro-organisms, pathogenic or otherwise, which have to be considered in connection with meat. To all engaged on public health work, this section should prove most useful for purposes of reference. The section on fish is mainly concerned with the organisms causing specific diseases of fish; it would also have been interesting to find mention of the moulds which have been known to grow on the surface of salted cod.

The section on milk is mainly of value for its descriptions of pathogenic organisms, though exception might be taken to the rather positive statements that *Streptococcus mastitidis* may easily be distinguished morphologically from its harmless congeners in mixed milk. In connection with the lactic acid bacteria it is really unfortunate that one has to look in vain for even so much as a footnote reference to Orla Jensen's important work on this group which appeared in 1919, whilst some seven pages are given up to Löhnis's classification of 1907. Similarly, the section on beet juice might well have contained some reference to Orla Jensen's work on the so-called "Beta" bacteria. Under the heading of butter aroma bacteria there is no mention of Hammer's interesting work published in America in 1920. As the bacteriology of such articles as mustard, tea, coffee and cocoa receives attention, it would have been interesting to find mention of the organisms which manage to pick up an existence on the surface of damp salt.

Under the heading of *coli* bacteria in connection with the examination of water the interesting question as to the distinction between the types which render water liable to suspicion by their presence, and the types whose presence has little or no significance, hardly receives adequate attention. No mention is made of McConkey's media, or of many of the methods commonly used in this country for the examination of the strains of *B. coli* found in water. The book concludes with a useful series of recipes for stains, nutrient media, etc., which, however, are all innocent of any references to hydrogen ion concentration.

One cannot but feel that the book would have gained much if greater attention had been given to the more important work of foreign investigators, though, on the whole, it must certainly be regarded as a worthy member of the monumental series to which it belongs. A table of contents leads a precarious existence on the inside and back of the paper cover; there is no index, but as the paging of the book starts at 1303, it is to be presumed that the deficiency will be remedied in a later instalment of the series; this is rather an unsatisfactory state of affairs, however, for purchasers of individual volumes.

PAUL S. ARUP.

A PRACTICAL HANDBOOK OF RAT DESTRUCTION. By C. L. CLAREMONT, B.Sc., F.I.C. Pp. 186. London: John Hart.

Officers of local authorities who have to administer the Rats and Mice (Destruction) Act, 1919, and occupiers of rat-ridden premises, will welcome this book, for the author, in his capacity of Research Chemist in charge of the Rat

Research Department of the Ministry of Agriculture, has had every opportunity of investigating the problem of rat destruction.

Official chemists, especially in agricultural areas, are frequently consulted as to efficient rat poisons; hence, the appendix (Formulae of Baits) in conjunction with Chapters III and IV of the handbook, describing methods of preparing the baits, should be of very great use to them.

The introduction, in which figures are quoted showing the material damage caused by rats, and Chapter VI, which indicates the various diseases caused by them, show clearly the importance of the subject of the handbook. Other chapters deal with rats and their habits, co-operation in rat destruction, and a most useful discussion of the Act.

The book is written in a simple style, which should make it acceptable also to the general public, and it has several illustrations and figures which add to the interest of the text. The Appendix gives twelve formulae of poisons which have been successfully tried upon rats by the author, and these alone make the book of great value.

F. W. SMITH.

VOLATILE SOLVENTS AND THINNERS. By NOEL HEATON, B.Sc. Pp. viii. + 148. London: Ernest Benn, Ltd., 1925. Price 15s. net.

This book is one of the series of monographs on Oil and Colour Chemistry edited by Dr. R. S. Morrell, and it deals with those organic liquids which can be distilled without decomposition, which are capable of complete evaporation at atmospheric temperature, and which have a pronounced solvent action on oils, fats, waxes and similar substances without alteration of their chemical composition. The less volatile compounds used as plasticisers and the vegetable fixed oils are thus excluded from the scope of the book.

The information contained in the book is remarkably full and accurate, and, although most of it has inevitably been published elsewhere, it will be found that the author has collected it together with an unusual degree of skill and discretion, with the result that the matter in the book is not only generally accurate and reliable, but is also presented in a clear and readable style, too often lacking in technical literature of this kind. The reader also has the benefit of a large amount of first-hand knowledge gained by the author during his extensive experience with solvents. The author's own views, in fact, will be found to be distinguished by a pleasing soundness and sanity of outlook which add greatly to the value of this excellent work.

With regard to the analysis of solvents, detailed descriptions of apparatus and methods are excluded, but the most important tests for purity, as well as the chief physical properties, are indicated with sufficient detail to be of real value, and references are given so that further details can be consulted. The B.E.S.A. standard polymerisation test for turpentine is given *verbatim*, but the description is somewhat difficult to follow in the absence of a diagram of the apparatus.

The first chapter deals with petroleum hydrocarbons, and gives a remarkably good account of "white spirit," though there is an error on p. 22, fourth line from

bottom, where "lower specific gravity" is written instead of "higher specific gravity." Considerable stress is rightly laid on the variations of the properties of white spirit derived from different sources of petroleum "crude"; no mention is made of Trinidad white spirit which is noteworthy for its high specific gravity of about 0.81 as compared with those given in the book, ranging from 0.765 for American to 0.795 for Borneo. The author states that he has been unable to trace the origin of the name "ligroin," and it would certainly be of historic interest if some light could be thrown on this peculiar freak of nomenclature. All chemists will probably cordially agree with him in wishing for the abolition of the word "benzine," and its replacement by "petroleum spirit," followed by an indication of the distillation range.

Succeeding chapters deal with coal-tar hydrocarbons; the turpentine group; the alcohol group; ketones and ethers; esters; hydrocarbon chlorides; and carbon bisulphide. All are excellent, so that it is difficult to single out any one section for special mention, but the section dealing with butyl alcohol particularly impressed the reviewer by its fullness and accuracy. In the chapter dealing with the halogen compounds some mention might have been made of glycolchlorhydrin as a possible non-inflammable, non-toxic solvent for cellulose esters. It is in connection with cellulose esters that the one serious criticism of the book must be made. Almost throughout, cellulose is written where nitrocellulose or acetyl-cellulose is intended—a serious blemish in a scientific work. The book concludes with a chapter on general observations and an appendix giving the chief chemical and physical data of the solvents dealt with in the book.

The price of the book is somewhat high in proportion to its size, particularly as it is defaced by three pages of advertisements at the end. The author is to be congratulated on having written a book which will be found indispensable, not only to those engaged in oil and colour chemistry, but also to all chemists concerned with industrial solvents.

PERCY MAY.

ORGANIC SYNTHESSES. Vol. V. CARL SHIPP MARVEL, Editor in chief. Pp. 110.  
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Volume V. of Organic Syntheses shows some increase over former volumes in the number of preparations and also in that of the contributors. The general character of this series is now well known, and therefore needs no description. A new feature is the introduction of two preparations which are not syntheses, *viz.* those of *l*-cystine from hair and *d*-glutamic acid from wheat-flour; the editors hope that other similar preparations will appear in future volumes. A second method of obtaining ethyl oxalate is described, and among the remaining thirty syntheses may be noted adipic and glutamic acids, isatin, nitro-urea, and derivatives of pinacol and cyclohexanol. As in Vol. IV. a number of the preparations are on a comparatively small scale.

A. F. KITCHING.