THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Obituary

CHARLES THOMAS KINGZETT

To most of our members Kingzett had become little more than a name, but in his early days he took a prominent part in the organisation of the profession of chemistry, being one of the original members of the Institute of Chemistry when it was founded in 1877.

He was born in 1852 at Oxford, was educated there, studying chemistry under Sir Benjamin Brodie, and began his professional career as assistant to Madan at the University Laboratory. Afterwards, for a short time, he was science master in a school, but in 1870 abandoned teaching in favour of technical chemistry, becoming chemist to the Liverpool Soda Works. Soon afterwards he went as research assistant to Thudichum, with whom he remained for some years, until, in 1877, he started a consulting practice in partnership with Dr. B. H. Paul.

An investigation of the antiseptic properties of conifer essential oils had a commercial result in the establishment of the Sanitas Company, Ltd., of which Kingzett was first chemist and technical manager and afterwards chairman.

He was one of the oldest surviving members of our Society, which he joined in 1881, becoming Vice-President in 1885. Several papers were contributed by him to early issues of THE ANALYST, including "Analyses of Asphalte Pavements" (1882, **7**, 4) and "The Estimation of Hydrogen Peroxide" (1888, **13**, 62), and his last communication, on "The Absorption of Oxygen by Phosphorus," was published last year (ANALYST, 1934, **59**, 816).

Of recent years Kingzett's name became familiar to the general public by the publication of successive editions of his *Chemical Encyclopaedia*, the fifth edition of which appeared in 1932, and was reviewed in our journal (ANALYST, 1932, **57**, 809). This last edition showed that the author had kept a receptive mind to modern advances in chemical theory. Another semi-popular book was a collection of essays, first published in 1880 under the title of "Nature's Hygiene"; it ran through several editions, the fourth of which was reviewed in 1898 (ANALYST, **23**, 191).

Kingzett died on July 29th at his home at West Byfleet, and the Society was represented at his funeral by Mr. R. L. Collett. EDITOR

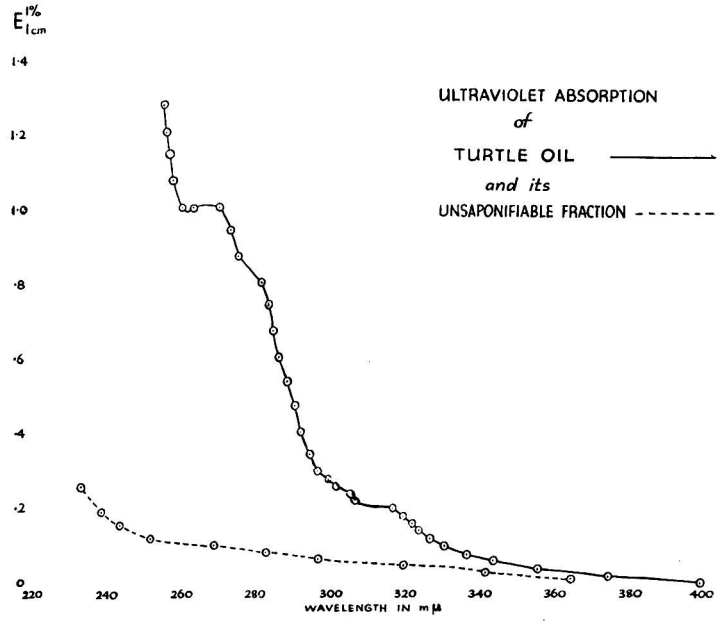
The Physical and Chemical Characteristics of Turtle Oil

BY WALTER LEE, A.I.C.

(Work done under the Society's Analytical Investigation Scheme)

INTRODUCTORY.—In the *Pharmaceutical Journal* (1934, **132**, 592) attention is drawn to the recent use of turtle oil in cosmetic preparations. It is claimed that the oil is very easily absorbed by the skin, and that, although some skins react to it unfavourably, as its action is supposed to be markedly astringent, it could form the basis of an ideal "skin-food." The women of Indian tribes in Mexico, who use turtle oil extensively for this purpose, are notably free from wrinkles, even the older women. Its use for this purpose has, however, been restricted in the past by the very objectionable odour of the crude oil, but refined oils have recently been placed on the market for use in cosmetics, and these have only a faint odour easily masked by appropriate perfuming. The refined products vary from light yellow semi-fluid oils to golden-yellow oils of butter-like consistence.

SOURCES AND VARIETIES.—Most of the commercial oil is obtained from the muscles and genital glands of the giant sea-turtle, the turtles used being from 250 to 700 years of age and weighing from 300 lbs. There are several varieties



of the oil on sale in England, but only one has any real market, and most of the experimental work here described was done on this type of oil. A specially "processed" and deodorised oil is also on sale, but principally in South Africa. This is very light in colour, whereas an Egyptian oil, which has a greater sale in

this country and is supposed to be obtained from the liver and glands, is of a much deeper yellow colour. I have been unable to discover the habitat of the turtles from which the Egyptian oil is obtained, but it is known to be different from that of the oil mainly used in this work; this oil comes from an isolated district on the west coast of Africa.

EXPERIMENTAL.—Four separate pounds of the refined West African oil, as purchased, were mixed in a dry container. The product was solid at ordinary room temperature and light yellow, had a mild but quite distinct odour, and melted to a golden-yellow oil. It bleached on exposure to light.

The following values were determined on the filtered oil:

Melting-point (incipient fusion)	24·6° C.
,, (final fusion)	25·6° C.
Solidifying-point	22·5° C.
Titre	25·5° C.
Sp.gr. at 40°/40° C.	0·9112
Refractive index, n_D^{40}	1·4599
Saponification value	209
Unsaponifiable matter (S.P.A. method)	0·6 per cent.
Iodine value of the unsaponifiable matter (Bolton and Williams method)	92·5
Iodine value	64·6
Acid value	2·0
Percentage of insoluble bromides on the free acids (Gemmel's method)	5·0
Melting-point of the bromides .. .. darken above	200° C.
Reichert–Meissl value	0·2
Polenske value	1·7
Kirschner value	0·06
Acetyl value	3·5

Small quantities of the three varieties of oil mentioned (6–10 g.) were obtained, and these gave the following values:

Type of oil	n_D^{40}	Iodine value	Saponification value	Unsaponifiable matter (petroleum spirit extraction) Per Cent.
(1) Specially "processed" and deodorised oil	1·4599	66·6	214·0	0·44
(2) Egyptian oil	1·4585	57·2	213·5	0·30
(3) African oil (same source as that of main bulk) ..	1·4599	67·8	209·0	0·43

The Egyptian oil has, therefore, a lower state of unsaturation and a lower content of unsaponifiable matter.

The oil was stated to be particularly rich in vitamins, and this was supposed to be one of the contributory factors towards its astringent action. Dr. Lester Smith has measured the ultra-violet absorption spectrum, using a Spekker photometer and a Hilger E2 spectrograph. The oil was examined in ethereal solution at concentrations of 5 per cent. and 1·5 per cent. in a 1-cm. cell. The intensities of absorption, expressed as $E_{1\,cm.}^{1\,\%}$, are shown in Fig. 1. A sample of the oil was saponified by boiling for a few minutes with alcoholic potash,

and the unsaponifiable matter was exhaustively extracted with ether. The solution was made up to a strength corresponding with a 5·83 per cent. solution of the original oil, and the absorption spectrum of this solution was measured in a 1-cm. cell. The absorptions, calculated to $E^{1\%}_{1\,cm.}$, are shown in the same figure (the concentration is that of the equivalent amount of oil, not that of the unsaponifiable fraction itself).

It is clear, from inspection of the two curves, that the bulk of the absorption of the turtle oil is due to the glyceride fraction, since the absorption is so greatly diminished when the unsaponifiable fraction freed from glycerides is examined. The very low intensity of absorption of the unsaponifiable fraction and the absence of any inflections in the curve indicate that no significant amounts of vitamin *A*, ergosterol or other pro-vitamin *D* are present, and also point to the absence of vitamin *E*.

COLOUR TESTS.—The sulphuric acid liver-oil test was completely masked, although as this variety of oil is not supposed to be a liver oil, no positive result was expected. Halphen's cottonseed oil test, the furfural sesamé oil test, and, in view of the close resemblance of some of the values to those of lard, crystallisation from ether were all tried. In no case did any characteristic colour or form develop.

REMARKS.—Several analyses of turtle oil are recorded by Lewkowitsch (*Technology of Oils, Fats and Waxes*, 6th Ed., Vol. II, p. 475), and the figures were compared with those obtained with the refined oil. As was to be expected, appreciable differences were found in all those figures that might conceivably be altered by modern refining processes. The following table illustrates this:

Observers	Zdarek	Sage	Tsujimoto	Lee
Sp.gr.	0·9198 at 42·5° C.	0·9192 at 25° C.	0·9335 at 15° C.	0·9112 at 40° C.
Solidifying-point	10–0	19–18	—	22·5
Melting-point	23–27	24–25	—	24·6–25·6
Saponification value	209	211·3	193·8	209
Iodine value	112	111	127·4	64·6
Reichert–Meissl value	4·6	4·8	—	0·2
Refractive index	1·4677 at 30° C.	1·4665 at 50° C.	1·4769 at 20° C.	1·4599 at 40° C.
Insoluble bromide value, per cent.	29·45	—	—	5·0
Titre	28·2	—	—	25·5

It will be seen that the iodine value of the refined oil is about half that of the crude oil, whilst the insoluble bromide value, as might be expected from the greater saturation indicated by the iodine value, is also very much less. An insoluble bromide value of only 3·53 per cent. has, however, been obtained by Tsujimoto with snapping turtle oil. In that case the proportion of bromine in the bromo-acids did not correspond with the amount required for clupanodonic acid. The m.p. of the insoluble bromides from the oil I have examined shows that turtle oil is normal in this respect, which would not have been expected if the results obtained by Tsujimoto with snapping turtle oil had applied to this oil. Further features of the oil are:—(*a*) Its low content of unsaponifiable matter, (*b*) a Bolton–Williams figure falling within the range (90 to 96) given for this type of oil, and

(*c*) a very low vitamin-content. It is also interesting to note that the unsaponifiable matter extracted by the S.P.A. method was regularly 0·1 to 0·15 per cent. higher than that obtained by a petroleum spirit extraction. Lastly, the refined oil has lost one of its characteristic features in having an almost negligible Reichert–Meissl value, against a value of nearly 5 given by the crude oil.

I wish to record my indebtedness to Mr. Manley for facilities for doing this work, to Mr. Houlbrooke for advice, and to Dr. Smith for the measurement and interpretation of the ultra-violet absorption spectrum.

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The Determination of Diacetyl and Acetyl Methyl Carbinol

BY C. R. BARNICOAT, M.Sc., A.I.C.

VARIOUS workers have determined diacetyl in butter, and, as the samples have been derived from different sources and the methods of analysis are not identical, it was not to be expected that the results would be uniform. The higher amounts are from highly flavoured butters, and there are wide variations in figures reported: 2 to 4 p.p.m. (van Niel *et al.*)[1]; 0·05 to 0·35 p.p.m. (Schmalfuss and Barthmeyer)[2]; 0·05 to 0·5 p.p.m. (Davies)[3]; and 3 p.p.m. (Testoni and Ciusa).[4]

The published methods for determining diacetyl and its precursor (hereinafter referred to as "carbinol") are all based on (*a*) separation of the diacetyl by distillation, and (*b*) precipitation of the diacetyl in the distillate as nickel dimethylglyoxime. Schmalfuss and Barthmeyer[5] and Michaelian, Farmer and Hammer[6] recommend the oxidation of the carbinol to diacetyl by means of ferric chloride, and the determination of this diacetyl with that already present in the sample. Another portion is distilled in an inert atmosphere of carbon dioxide for determination of the actual diacetyl-content. Davies[3] uses oleic acid as oxidising agent, and claims accurate yields (±3 per cent.) for small quantities of diacetyl obtained from butter. In general, the term "diacetyl" is loosely applied in the literature to both diacetyl and diacetyl plus carbinol. As none of the published methods so far examined gave satisfactory results, detailed experiments were made, and a modification was devised which gives consistent results, although with quantities ranging from 0·1 to 10 mg. they still tend to be slightly low.

EXPERIMENTAL

I. CONDITIONS AFFECTING THE COMPLETENESS OF PRECIPITATION OF DIACETYL AS NICKEL DIMETHYLGLYOXIME.—Most workers have followed van Niel's technique,[7] in which the dilute diacetyl solution is heated with the appropriate reagents for 1 hour at 80 to 90° C., and then cooled and allowed to stand for 24 hours before filtering and weighing. The experimental losses recorded by van Niel

are, however, of the order of the actual amounts of precipitate commonly found from 1 kg. of butter. It was further observed that the residual filtrates deposited more precipitate when further heated. The conditions governing complete precipitation were therefore studied. Polak's "50 per cent. Diacetyl" (50·2 per cent. by actual determination) was freshly diluted when required as a standard; it is more stable than the pure chemical.

(i) *Reagents.*—A satisfactory mixture is: 4 ml. of 20 per cent. (w/v) hydroxylamine hydrochloride; 4 ml. of 20 per cent. sodium acetate solution; 2 ml. of 5 per cent. nickel chloride solution (free from cobalt and iron). Actually, a reagent of this composition recovered from previous determinations is preferable, particularly for the determination of the smaller amounts (see Part V).

(ii) *The Effect of the Period of Heating.*—(*a*) In experiments in which van Niel's conditions were followed (1 hour at 80 to 90° C. and 24 hours' standing) the following results were obtained:

Diacetyl taken mg.	Equivalent to nickel dimethyl-glyoxime mg.	Nickel dimethyl-glyoxime found mg.	Number of determinations	Error	
				mg.	Per Cent.
0·20	0·34	0·30	2	0·04	−11*
2·00	3·4	3·0–3·1	7	0·3 to 0·4	−10
4·00	6·7	6·1	2	0·6	−9

* Determined colorimetrically by the method described later.

The incomplete precipitation was confirmed by the fact that, after further heating and cooling of the filtrates, the red nickel compound appeared.

(*b*) Experiments were then made with dimethylglyoxime (0·5 to 2·0 mg.) and the usual reagents. Precipitation was found to be complete, even after momentary heating to 90° C.

(*c*) The heating period for the actual diacetyl determination was extended to several hours on the hot-plate at 80 to 90° C. (during which it was allowed to evaporate), followed by overnight heating in a water-oven at 70 to 80° C. Within a small experimental error, which was inconsistent, the results were accurate, and, on evaporation of the mixed filtrates, only negligible amounts of the red nickel compound were detected. The results were as follows:

Diacetyl taken mg.	Equivalent to nickel dimethyl-glyoxime mg.	Nickel dimethyl-glyoxime found mg.	Number of determinations	Error	
				mg.	Per Cent.
0·20	0·34	0·34	2	nil	—*
0·40	0·7	0·6–0·7	2	nil—0·1	−7
0·70	1·2	1·2	1	nil	—
1·00	1·7	1·6–1·7	6	nil—0·1	−3
2·00	3·4	3·4–3·5	4	nil—0·1	+2
5·00	8·4	8·5–8·7	2	+0·1–0·3	+2
10·00	16·8	16·9–17·2	3	+0·1–0·4	+2

* Determined colorimetrically by the method described later.

The conversion of diacetyl into the nickel salt of dimethylglyoxime takes place in the following stages:

(1) $CH_3.CO.CO.CH_3 + H_2NOH \rightarrow CH_3.C(:NOH).CO.CH_3 + H_2O$ (monoxime).

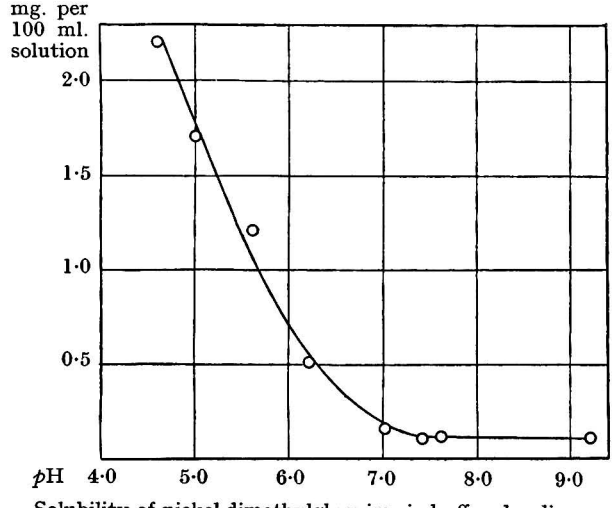
(2) $CH_3.C(:NOH).CO.CH_3 + H_2NOH \rightarrow CH_3.C(:NOH).C(:NOH).CH_3 + H_2O$ dioxime (dimethylglyoxime).

(3) $2CH_3.C(:NOH).C(:NOH).CH_3 + NiCl_2 \rightarrow [CH_3.C(:NOH).C:(NO).CH_3]_2Ni + 2HCl$. Nickel diacetyldioxime (dimethylglyoxime).

Judging by the rapid disappearance of the odour of diacetyl when it is added in dilute solution to the hydroxylamine-nickel reagent, reaction (i) is rapid, whilst reaction (iii) is rapid when the solution is heated. It is therefore apparent that reaction (ii) is slow (being "non-ionic"), and requires prolonged heating for its completion, owing probably to steric hindrance at the vicinal carbonyl oxygen atoms when the combination with the second hydroxylamine molecule to form the dioxime takes place.

(iii) *The Effect of pH of Solution.*—The solubility of nickel dimethylglyoxime (previously dried at 110° C.) in dilute buffered sodium acetate solution is given in the following graph:

The reagent becomes acid on heating, and appreciable losses may occur unless ammonia is added to the solution after cooling, until the odour persists and the reaction is slightly alkaline to litmus paper. If ammonia is added before the original solution is heated, precipitation of nickel salts is likely to occur, leading to high results in the determination.



Solubility of nickel dimethylglyoxime in buffered sodium acetate (8 per cent.) solution

(iv) *The Period of Standing.*—Slight losses occur unless the nickel compound is given adequate time to crystallise after cooling and neutralisation of the solution, particularly when minute amounts are being determined. Three days appear to be sufficient, but it is safer to allow a considerably longer period of standing.

(v) *The Effect of Volume of Solution.*—In large volumes of solution (50 to 100 ml.) the losses slightly exceed the solubility losses, as shown in the graph,

which is probably due to the incomplete conversion of the monoxime into the dioxime at high dilutions. It is therefore preferable, particularly when determining traces by the colorimetric method, to evaporate the solution (at 80 to 90° C.) for some hours on a hot-plate to a volume of 10 ml., by which means one avoids (*a*) the precipitation of nickel salts on adding ammonia, which is likely to occur if an excess of ammonia is inadvertently added, and (*b*) solubility losses.

II. THE SEPARATION OF CARBINOL + DIACETYL ("TOTAL DIACETYL") FROM BUTTER BY DISTILLATION.—For the determination of "total diacetyl" the carbinol is oxidised during distillation to diacetyl, which is estimated together with that already present.

(i) *Apparatus and Method.*—Glassware with ground-glass joints is desirable, but may be replaced by stock apparatus with rubber bungs which have been roughened with sandpaper, treated with several coatings of "Durofix" adhesive (a cellulose preparation), and dried after each application in a water-oven. This coating only occasionally needs patching or renewal. A bolt-head round-bottomed flask is used for the distillation, and its capacity must be rather more than twice the total volume of the butter and oxidising solution. The inlet tube from the steam-generator ends in a small bulb bored with several holes, by which means the entering jets of steam promote the mixing of the melted butter-fat with the underlying (oxidising) solution. The still-head is a wide glass tube with a bulb, and must be heavily lagged.

The underlying solution is $N/10$ with respect to sulphuric acid, and sufficient solid sodium chloride to saturate the solution and the butter serum is weighed into the flask after the butter sample. A 50-cm. Liebig condenser carries an adapter which *dips into the hydroxylamine-nickel reagent*, and the distillate is stirred into the reagent at short intervals. The condenser must be thoroughly washed into the test solution after each determination, and then cleaned with alcohol.

The distillation flask is surrounded by a calcium chloride brine-bath maintained at 110° to 115° C. during the distillation; at a higher temperature excessive amounts of fatty impurities are carried over. The distillation proceeds smoothly and is complete when about 70 ml. of distillate have been collected in about 40 minutes. Failure to follow these directions exactly results in incomplete recovery unless the distillation is unduly prolonged, and also in great difficulty through frothing and bumping.

(ii) *The Optimum Amount of Oxidising Agent.*—Known amounts of diacetyl were steam-distilled from 500 ml. of the "underlying" solution containing various amounts of 40 per cent. (w/v) ferric chloride solution. The following results were obtained:

	Ferric chloride solution added ml.	Ferric chloride in underlying solution. Per Cent.	Diacetyl added equivalent to nickel dimethyl-glyoxime mg.	Nickel dimethyl-glyoxime found mg.	Number of determinations
(*a*)	250	20	17·1	15·0–14·6	2
(*b*)	250	20	8·55	6·6	1
(*c*)	100	8	8·55	8·4	1
(*d*)	25	2	8·55	8·8	1
(*e*)	None	None	17·1	17·0	2
	Distilled from underlying solution + butter freed from diacetyl				
(*f*)	250	20	17·1	17·1	1
(*g*)	250	20	8·55	7·8	1

The higher concentrations of ferric chloride (*a*, *b* and *g*) have a destructive effect on the diacetyl, which is less marked when the layer of butter is present.

A sample of butter (previously held at −10° C. for 6 months and containing an average amount of diacetyl + carbinol) gave the following results:

800 g. of butter over 500 ml. underlying solution containing

Ferric chloride (40% w/v) ml.	Ferric chloride in underlying solution Per Cent.	Nickel dimethylglyoxime found mg.
nil (distillation in CO_2)	nil	nil
10	0·8	1·1
25	2·0	1·1
50	4·0	1·5
250	20·0	1·4

While it has just been shown that excessive amounts of ferric chloride tend to decompose the diacetyl (under these conditions of distillation), on the other hand sufficient must be present to ensure maximum conversion of the carbinol into diacetyl; hence the concentration adopted throughout has been 50 ml. of 40 per cent. solution per 500 ml. underlying mixture (*i.e.* 4 per cent. ferric chloride solution). It is possible that butan-2:3-diol—the precursor of acetylmethylcarbinol—is, if present, also converted into diacetyl in this process.

III. The Separation of Diacetyl from Butter by Distillation.—(i) *Apparatus and Method.*—As described in previous publications (Schmalfuss and Barthmeyer[5]; Michaelian, Farmer and Hammer[6]), this distillation is made in an atmosphere of carbon dioxide.

The apparatus is as previously described, except that an extra glass tube (i) projects about ½ inch through the treated rubber bung, and is tapered to a fairly fine jet. This is connected with a carbon dioxide generator, and the flask (containing the sample, sodium chloride, and *N*/5 sulphuric acid equal to one-fourth the volume of the butter taken) is flushed out with a strong stream of the gas for some minutes before the brine-bath, heated to about 115° C., is brought into place. As the butter melts, carbon dioxide is also introduced gently through the steam-inlet tube (ii), while the flow through (i) is gradually cut down. When frothing begins, the carbon dioxide is immediately cut off, and replaced by a strong current of steam, the effect of which is to cause the frothing to subside, although occasionally it may also be necessary to lower the brine-bath temporarily. The gas stream at (i) is cut down to a bubble or less per second, so as to maintain a slight outward pressure at the still-head and prevent diffusion of air into the flask.

(ii) *Results and Accuracy of the Determination.*—Two lots of butter, each 400 g., were steam-distilled over dilute acid for 2½ hours, and the final distillates were collected and found to be free from diacetyl. After cooling, 100 ml. of *N*/5 sulphuric acid and known amounts of diacetyl were added to each, 40 g. of sodium chloride were introduced, and the diacetyl was distilled, the flasks and

contents being well cooled after each test. The following results were obtained:

Diacetyl added, mg.:										
0·050	0·060	0·10	0·15	0·40	0·50	0·70	1·00	2·00	4·00	5·00
Equivalent to nickel dimethylglyoxime, mg.:										
—	—	—	—	—	0·85	1·2	1·7	3·4	6·7	8·4
Nickel dimethylglyoxime found, mg.:										
—	—	—	—	—	0·8	1·0	1·5	3·1	6·4	8·0
Equivalent to diacetyl, mg.:										
0·035*	0·060*	0·12*	0·14*	0·38*	0·5	0·6	0·9	1·85	3·85	4·8

* Estimated colorimetrically.

The results are slightly low. Even the very gentle passage of carbon dioxide during the distillation appears to carry off a portion of uncondensed diacetyl. This explanation is probably correct, because very low results are obtained when a strong current of carbon dioxide is used throughout the distillation (Schmalfuss and Barthmeyer)[5]. The losses from butter are probably less than from artificial mixtures; nevertheless, as this determination of actual diacetyl is the more important of the two methods, it is under further investigation.

IV. PURIFICATION AND WEIGHING OF THE PRECIPITATE.—Notwithstanding the precautions recommended in the foregoing sections, these tedious operations may be to no purpose, unless the following technique is applied when washing the precipitate.

(i) *Transference and Washing of Precipitates.*—In an actual determination the distillate and condenser rinsings contain considerable amounts of fatty impurities (*e.g.* 0·3 to 2·4 mg. in one series), and at the beginning of the work these unnoticed impurities caused unduly high and puzzling results. This difficulty may be overcome in the following way:—For the gravimetric determination small Gooch crucibles are satisfactory; the asbestos mat, prepared from fibre digested in concentrated hydrochloric acid, is thoroughly washed with water (at least 10 fillings), and the precipitate of the red nickel compound is transferred, with thorough washing, from the beaker. The beaker (which usually still contains adhering precipitate) and the crucible are dried for 2 hours at 110° C. After cooling, the beaker is washed out on to the crucible with 30 to 40 ml. of ether, which has been recently distilled over flake caustic soda and charcoal. The dehydrated nickel compound is quite insoluble in this neutral, peroxide-free ether, and the fatty impurities are removed. The beaker and crucible are replaced for a short time in the oven until free from ether, and, when cool, are again thoroughly washed with water to remove any traces of precipitate and reagent, a "policeman" being used if necessary. The crucible is finally dried for 2 to 3 hours at 110° C. and allowed to cool in a desiccator. The use of alcohol or hot water for washing the precipitate, as recommended by some workers, must be avoided, as the nickel compound is appreciably soluble in both.

(ii) *Weighing.*—The cooled crucible is allowed to stand for 1 hour in the balance-case before weighing. (No drying agent is present in the balance-case.) Concordant weighings, occasionally varying by 0·1 mg. are thus obtained. The

precipitate is dissolved by leaving the crucible half-filled with concentrated hydrochloric acid; the crucible is then thoroughly washed, dried at 110° C., and "conditioned" prior to being used again. It is practically impossible to avoid the inclusion of from 0·1 to 0·3 mg. of dust in the precipitate, leading to high results, unless an allowance is made by taking the tare weight of the crucible after that of the precipitate.

Calculations.

(i) Nickel dimethylglyoxime × 0·596 (*i.e.* 0·6 for small amounts) = *diacetyl.*

(ii) Nickel dimethylglyoxime × 0·610 = *acetylmethylcarbinol.* It is convenient to calculate this to diacetyl, instead.

(iii) The process of distillation with ferric chloride gives a precipitate equivalent to both acetylmethylcarbinol and diacetyl.

(iv) The process of distillation in carbon dioxide gives a precipitate equivalent to the actual flavouring substance, diacetyl.

(iii)—(iv) gives the flavourless precursor (carbinol) content.

V. A Colorimetric Method for the Determination of Traces of Nickel Dimethylglyoxime.—The amounts of diacetyl found in New Zealand butters have been minute, and mild-flavoured butters usually have a very low content of "total diacetyl" (carbinol + diacetyl).

The gravimetric determination of a few tenths of a milligram of precipitate is liable to involve a high percentage error, when the weighing is done on the usually four-place balance, and a colorimetric method suitable for amounts below 1 mg. of nickel dimethylglyoxime has therefore been devised.

The method outlined by Davies[3], in which the intensity of red colour given by the precipitate on the asbestos mat of a Gooch crucible is compared with the colours given by a standard series of precipitates, has not proved successful, owing to the facts that the precipitate comes down in both flocculent and crystalline form, the latter being of little colouring power, and that traces of precipitate are apt to be obscured under the particles of asbestos.

In the present method the nickel compound is dissolved in chloroform, and the resulting yellow solution is compared with standard solutions.

The colorimetric estimation of nickel dimethylglyoxime by dissolving it in chloroform and allowing the solvent to evaporate spontaneously, leaving a red stain which is compared with standards, was worked out by Bertrand and Macheboeuf.[8] It is not satisfactory for this work, because the amounts of precipitate are usually too large, and the evaporating solvent leaves a series of dark rings of precipitate interspersed with lighter areas.

(i) *Apparatus.*—As previously described.

(ii) *Method.*—When the precipitate is judged to be less than 1 mg. it is filtered by means of a King filter-stick,[9] and washed several times, and both beaker and filter-stick are dried for 2 hours in the oven at 100° C. When cold, the beaker is washed with 30 ml. of freshly-distilled ether, which is removed through the filter-stick, and the apparatus is again heated until the ether has evaporated. After cooling, the washing with water is repeated, the inner glass tube and rubber connector are removed from the filter-stick, and the outer tube (which carries the

asbestos and precipitate) and beaker are dried at 110° C. When nearly cold, 10 ml. of recently distilled neutral chloroform are added, and the beaker is covered with a watch-glass and warmed gently. When solution is complete, it may be necessary to filter the cooled solution (from asbestos fibres) through a plug of cotton wool into the small Nessler tube (specimen tubes with plane ends, selected so that the 10-ml. marks are of even height, are suitable for the purpose). The colours are compared in the usual way with standard solutions of nickel dimethylglyoxime in chloroform. The standard solution does not keep, particularly in the light, owing to the formation of acidic substances from the chloroform.

The solubility of the nickel compound is only 14·8 mg. per 100 ml. at 14° C., and concentrations higher than 1·0 mg. per 10 ml. are rather too dark for comparison. The faint yellow colour of the smaller amounts is not suitable for measurement in a tintometer or colorimeter.

It has since been found that tetrachloroethane is the only common solvent in which the nickel compound is more soluble than in chloroform (solubility in tetrachloroethane 28 mg. per 100 ml. at 16·5° C.).

Experiments with the Colorimetric Method.—With large volumes of solution and fresh reagents the results are slightly low. For example, in experiments in which 0·20 mg. of diacetyl were added, the following results were obtained:

	After 24 hrs. mg.	48 hrs. mg.	72 hrs. mg.	144 hrs. mg.
(*a*) 10 ml. of fresh reagents in 50 ml. total volume	0·15	0·16	0·14	0·17
(*b*) 10 ml. of fresh reagents in 10 ml. total volume	0·16	0·17	0·18	0·18

Another experiment, in which the precipitates were allowed to stand for 10 days before filtering, gave the following results:

Diacetyl added, in 10 ml. (mg.)	nil	0·05	0·10	0·20	0·40	0·60
,, found, in 10 ml. ,,	nil	0·025	0·068	0·15	0·32	rather dark for comparison, but about equal to standard.
,, loss, in 10 ml. ,,	—	0·025	0·032	0·05	0·08	

The losses are parallel with the amounts of precipitate and, strictly, are not solubility losses.

In order to compensate for the solubility, the mixed reagents were saturated with nickel dimethylglyoxime by boiling and allowing the precipitate to form in the usual way for 10 days before filtering. Determinations by means of this reagent in a series of tests similar to those described (0·05 mg. of diacetyl and upwards) gave results in which the standards were satisfactorily matched, although tending to be high.

Preparation of Reagent.—The following method of preparing the saturated reagent has now been adopted:*

The filtrates from a number of diacetyl determinations are concentrated to the original volume of reagent-solution (*i.e.* 10 ml. per determination), ammonia is

* The use of recovered reagent and evaporation to the 10-ml. mark on a hot-plate [*cf.* Part I(i)] are now followed in all determinations, and the risk of missing minute amounts is thereby avoided.

added, and the solution is allowed to stand for as long as possible before filtering from a minute quantity of impurity (in which only a trace of nickel dimethylglyoxime is usually detectable). Hydroxylamine hydrochloride is added to bring the solution back to its original strength, the hydroxylamine-content being conveniently found by the method given in the *B.D.H. Book of A.R. Standards.*

The results obtained by the use of this reagent are invariably a shade high, and control tests made on one lot of reagent gave:

Diacetyl added (mg.) ..	0·050	0·10	0·20	0·40	Blank, 10 ml. of reagent only.
„ found „ ..	0·055	0·111	0·22	0·425	—
Correction to be deducted (mg.)	0·005	0·01	0·02	0·03	<0·002

Control determinations should be carried out with each lot of reagent, as the corrections are of a different order for various recovered reagents. The ordinary "blank" determination is of no value. The actual results obtained (which are corrected) are given in Parts I and III (pp. 654, 658).

The presence of the dissolved nickel dimethylglyoxime seems to hasten the precipitation. In one experiment 0·20 mg. of diacetyl gave the following amounts of precipitate with the saturated reagent:

	24 hours	48 hours	72 hours	48 hours
Diacetyl found, mg. ..	0·20	0·18	0·20	0·20 (corrected)

Nevertheless, it is preferable to allow the solution to stand for several days before filtering.

By using this technique and smaller amounts of butter, this method could be adapted for control purposes of the "total diacetyl," and results of fair accuracy would be obtained within about 48 hours after distillation.

GENERAL REMARKS.—*The Effect of Diacetyl on the Oxidation of Butter-fat.*—Great emphasis is laid by some writers on the pro-oxidative effect of diacetyl on butter-fat and the vitamins. The work of King[10] is the only investigation, so far as I am aware, which deals with this point, and his lowest concentrations of diacetyl examined were 50 p.p.m., which scarcely affected his samples of butter-fat after 90 to 100 days in the dark at 22° C. As the diacetyl-content of butters of the highly-flavoured type never exceeds 4 p.p.m. (*loc. cit.*), it is not considered that diacetyl itself is responsible for the poorer keeping qualities of "ripened" cream butter.

The Effect of the Age of the Sample upon its Diacetyl-content.—Results obtained with butter made from slightly "ripened" cream were as follows:

	Carbinol + diacetyl p.p.m.
Butter A (3 months frozen storage)	1·0
Butter A (4 months further keeping at room temperature; quite tallowy)	0·6
Butter B (2 months frozen storage)—4 p.p.m. diacetyl added for experimental purposes	4·8
Butter B (6 months further keeping at room temperatures; very tallowy, bleached throughout and "cheesy"; inedible) ..	1·1

The loss is not as great as might be expected.

THE DETECTION OF ADDED DIACETYL IN BUTTER.—It has been stated (Davies[3]) that "the finding of a relatively high diacetyl-content in association with a low acidity of butter should be viewed with suspicion. . . ." As most butter factories in New Zealand, Australia and U.S.A. neutralise their cream before churning, it is difficult to see that either the acidity or *p*H value of the butter could be regarded as a reliable indication of the acidity developed before neutralisation, although there is an approximate relationship with the acidity at churning (F. H. McDowall, unpublished work). It is more likely that the ratio of the diacetyl to carbinol + diacetyl (which in New Zealand butters is low) would be of more value, unless both diacetyl and carbinol were added, in which case the problem of detecting such sophistication would appear to be insoluble, unless bacteriological determinations gave any guide as to whether a "starter" had been used in the cream from which the butter was churned.

In any case, it would seem that the problem of detecting added diacetyl in butter is likely to be difficult, particularly until more is known about the range of concentration to be expected in genuine butter obtained from numerous countries and manufactured under various conditions.

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The Determination of Moisture in Cereal Products by Distillation with Tetrachloroethane

By J. M. TUCKER, B.Sc., F.I.C., and T. E. BURKE, A.I.C.

(*Read at the Meeting of the North of England Section, February* 9, 1935)

Introduction.—The different types of moisture present in cereal products cause widely different results to be obtained by different methods of estimation. Snyder and Sullivan,[1,2] in a series of investigations into the moisture-content of flour by different methods, suggested three stages of drying, during which the following types of moisture are removed:—(1) Free; (2) adsorbed; (3) loosely chemically combined. Fisher[3] suggested similar stages, as the result of a study of the rate of drying of flour over sulphuric acid.

It appears that the drying of flour at 100° C. at normal pressures drives off the first, and part of the second, type. The third type is removed only at 120° C. to 130° C. at ordinary pressures, or at 100° C. under greatly reduced pressure. Interaction with calcium carbide leaves about 4·5 per cent. of non-reacting moisture, as compared with the vacuum-oven method at 100° C.[4]

Of the distillation methods, that of Duval[2] consists in distilling the water from high-boiling paraffin, and is a troublesome process. Immiscible solvents which distil with the water have been suggested, *e.g.* toluene, xylene, light petroleum (b.p. 104° C.), tetrachloroethane and mixtures of these. The lower-boiling liquids take hours to carry over all the water,[5] whilst the higher-boiling liquids may cause liberation of water by decomposition. Tausz and Rumm[6] and Fairbrother and Wood[7] describe methods of distillation with tetrachloroethane for products containing fairly large amounts of moisture, and give figures in comparison with those obtained by oven methods. In neither paper, however, is the question of possible carbohydrate decomposition considered.

Our purpose was to find a method suitable for baked cereal products (of low moisture-content) and for unbaked materials, the results for which could be correlated with baking losses.

Experiments

(1) Proportion of T.C.E. required.—Our first trials consisted of interrupted distillations of liquid and sample in different proportions. The distillations were carried on for a fixed time and then stopped. The volume of water was read off, and the distillation was continued for a further period, until no more tetrachloroethane could be distilled. Typical results are shown in Table I.

It is evident that, with sufficient liquid present, all the moisture can be distilled in 6 minutes, and that no decomposition takes place after a further 4 minutes' boiling. An amount of liquid insufficient to keep the contents of the flask mobile results in progressive decomposition and in a progressive increase in the amount of water distilled. At least 3 times as much tetrachloroethane as sample is required when distilling from a large quantity of sample.

TABLE I

THE EFFECT OF DIFFERENT PROPORTIONS OF LIQUID AND SAMPLE

Weight of sample g.	Tetrachloroethane ml.	Time of distillation Minutes	Volume of water distilled ml.	Volume of tetrachloroethane distilled ml.
180	350	6	Nil	
		9	1·95	
		12	2·55	
		15	2·85	270
150	350	3	2·1	
		6	2·7	
		9	2·7	
		10	2·8	245
150	450	3	1·9	
		6	2·4	
		9	2·4	
		12	2·4	300
50	250	5	6·75	
		6	6·9	
		7	6·9	
		10	6·95	200

(2) THE RATE OF DISTILLATION.—As decomposition can readily be caused to take place, it seemed advisable to determine how slowly the moisture could be distilled without influencing the result. Some results are shown in Table II. These were also interrupted distillations.

TABLE II

THE EFFECT OF THE RATE OF DISTILLATION

Weight of sample g.	Tetrachloroethane ml.	Time of distillation Minutes	Water distilled ml.	Rate of distillation ml. per minute
150	400	3	2·5	
		6	3·0	
		9	3·1	15
		12	3·2	
		15	3·3	
100	300	7	3·00	
		8	3·15	15
		9	3·20	
150	450	3	1·9	
		6	2·4	
		9	2·4	25
		12	2·4	
150	450	4	1·95	
		6	2·0	
		8	2·0	25
		10	2·0	

All the water is not driven off within 10 minutes when the rate of distillation is slow, and decomposition of carbohydrate material appears to take place after

10 minutes at the temperature of the boiling mass. This is contrary to the results of Tausz and Rumm, who distil slowly through a special still-head. Our results were obtained on biscuit material. The large quantities of sample were necessary because of the low moisture-contents.

(3) FINAL CHECK.—Having fixed the two conditions necessary to give consistent results, straight distillations of different portions of sample, taken from the same bulk, were made for times varying from 6 to 10 minutes. The following results were obtained:

TABLE III

Weight of sample. g.	Tetrachloroethane ml.	Time of distillation Minutes	Water distilled ml.
150	450	8	3·4
		8	3·3
		10	3·4
100	300	5	4·95
		6	4·95
		8	4·95
100	300	8	4·00
		8	4·05
		8	4·05

These duplicates agree as well as those obtained by any oven method, and, as will be seen later, bear a definite relationship to the boiling water oven figures.

METHOD OF DETERMINATION.—*Quantity of Sample.*—Sufficient sample to yield 2–5 ml. of water should be taken (usually 30–100 gms.). These quantities may be decreased somewhat if the sensitivity of the measuring apparatus is increased.

Preparation of the Sample.—As it is necessary to distil over the water in less than 10 minutes when carbohydrate material is present, the sample should be in a sufficiently fine condition to permit of the liberation of the water in this time. Meal and flour distil satisfactorily, whilst biscuit, cake, etc., should be ground and quickly transferred to the boiling-flask.

Quantity of Tetrachloroethane.—This will depend on the amount of the sample and on the technique used. There must be sufficient liquid left in the flask, after the water has been distilled, to keep the mass fluid and so prevent charring. Too much liquid slows up the distillation of the water. Generally, about 150 ml. for 30 g. of sample to 300 ml. for 100 g. are advisable.

Distillation Technique.—The sample and liquid are thoroughly mixed in a suitable boiling-flask connected by an ordinary cork or ground-glass connection to a still-head having a wide bore at its lower end to prevent splashing at the rate of distillation required. This is connected with a vertical condenser having a burette, partly filled with tetrachloroethane, fixed at the outlet. The tetrachloroethane is distilled at the rate of 20 to 25 ml. per minute. The water collects at the top of the distillate, and the level of liquid in the burette is maintained by a suitable adjustment of the burette-tap. When almost all the moisture has been distilled, the distillate, which is milky at first, suddenly clears. The distillation is continued for about a minute longer, when the cooling water of the condenser is

turned off. Heating is continued until the tip of the condenser becomes hot, when the gas is removed. The volume of water in the burette is measured, after cooling, by taking the readings of the top of the top meniscus and the bottom of the water and tetrachloroethane junction.

Another satisfactory technique is the use of the still-head of the American Association of Petroleum Technologists, described also by Fairbrother and Wood.[7] Tetrachloroethane is first introduced into the graduated portion and, on distilling, the water collects on this column, whilst the tetrachloroethane returns to the flask. Less tetrachloroethane is required by this method, as there is no loss from the flask.

Both types of still-head need an internal diameter of at least $\frac{3}{8}$ inch, and no constriction between the bulbs should be less than this.

Comparative results obtained by the method and by the use of the water-oven are shown in Table IV.

TABLE IV

COMPARISON BETWEEN THE DISTILLATION AND WATER-OVEN RESULTS

		Moisture		
		Distillation Per Cent.	Oven at 98·5° C. Per Cent.	Difference
Flour.				
	Manitoba	13·8	12·05	1·75
	Blend	13·15	11·2	1·95
	Australian	13·2	11·4	1·8
	English	14·25	12·45	1·8
				1·8
Baked products.				
	Bread (crumb) ..	49·6	48·0	1·6
		49·3	47·9	1·4
		48·3	47·0	1·3
				1·4
	Cake	5·7	4·5	1·2
		1·9	1·0	0·9
		4·0	2·7	1·3
				1·1
	Biscuit	2·25	1·0	1·25
		4·95	4·2	0·7
		2·50	1·70	0·8
		2·10	0·75	1·4
			Average of 30–40 tests	0·7
Fat—Cane sugar—Water systems.				
		25·1	25·1	Nil
		19·6	19·6	Nil
Cane syrups.	Steady decomposition.			

COMMENTS ON THE RESULTS.—The results for cereals appear to be similar to the maxima obtained by oven methods, and, at the same time, avoid the oxidation errors of the oven methods. The difference between the distillation and water-oven methods becomes less as dehydration by baking proceeds. The value of the method lies in the fact that a determination can be completed within about 15 minutes of the receipt of the sample.

SUMMARY AND CONCLUSIONS.—Accurate and reproducible results for moisture in cereal products of low moisture-content can be obtained by distillation with tetrachloroethane (b.p. 140° C.).

The essential conditions are moderately rapid distillation and sufficient solvent to leave a mobile residue when all the water has been driven off.

The results obtained for flour are 1·8 per cent. higher than those obtained by heating in a water-oven for 5 hours.

The method is not satisfactory when appreciable quantities of invert sugar are present.

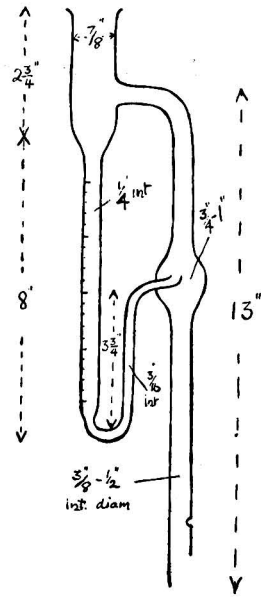

Fig. 1

Our thanks are due to Messrs. William Crawford & Sons, Ltd., for permission to publish these results.

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NOTE.—Since the paper was read a modified form of the continuous still-head has been used. This is shown in Fig. 1 above. The volume measurement is more accurate in this, and the return has been arranged so that a bubble of water cannot readily remain on the cold tetrachloroethane, as sometimes happened with the original apparatus. All diameters are internal measurements.

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The Oxalates of Calcium, Strontium, Barium, and Magnesium

By J. HASLAM, M.Sc., A.I.C.

(*Read at the Meeting of the North of England Section, October* 12, 1935)

Goy[1] found that when calcium oxalate is precipitated in the usual way from boiling solution the precipitate has the composition $Ca(COO)_2.H_2O$, and that this precipitate can be completely freed from adherent moisture, without loss of water of crystallisation, by filtration on a Gooch crucible, and drying for four hours at 100–105° C. From a cold solution, however, a mixture of $Ca(COO)_2.H_2O$ and $Ca(COO)_2.3H_2O$ is obtained.

Dick[2] has endeavoured to use this method as a rapid and accurate means of determining calcium as calcium oxalate monohydrate by filtering off the precipitate on a sintered glass crucible, removing adherent moisture by washing with alcohol and with ether, and weighing the precipitate after removal of the ether by suction or *in vacuo*.

Moser[3] tested Dick's method, but obtained results from 1·6 to 3 per cent. too high; he found it to be impossible to remove the whole of the adherent moisture except by actual drying in ovens.

Our own experiments were concerned with the relationship between the weight of the calcium oxalate precipitate and the titration of this precipitate in terms of standard potassium permanganate solution, and, further, the effect of the presence of barium, strontium or magnesium on this relationship.

To a known volume of standard calcium solution (pure Iceland spar dissolved in dilute hydrochloric acid) were added 5 ml. of concentrated hydrochloric acid and about 100 ml. of distilled water, followed by 20 ml. of saturated ammonium oxalate solution.

When a precipitate was produced in the cold, concentrated hydrochloric acid was added in 5-ml. portions until a perfectly clear liquid was obtained. This liquid was now diluted to 200 ml. and heated to boiling, and concentrated ammonia solution was added to the boiling liquid until it was just ammoniacal to methyl orange. The precipitate was digested by immersing the covered beaker in a boiling water-bath for ¾ hour, allowed to stand overnight, and then filtered off on a sintered glass crucible (1.G.3), washed five times with 0·1 per cent. ammonium oxalate solution (at about 50° C.), drained by suction, washed five times with water (at about 50° C.), and again drained by suction.

Adherent moisture was removed by washing five times with absolute alcohol (5 ml. each time), then draining, using the full suction of the vacuum pump, for two minutes. The washing was completed by treating the precipitate four times with ether (5 ml. each time), then draining, using the full suction of the vacuum pump, for five minutes. The crucible was wiped, placed in the desiccator for a few minutes, and then weighed.

Our results having confirmed Moser's conclusions as to the high results obtained by Dick's method, we titrated the oxalate ion in the precipitates as follows:

The sintered glass crucible containing the precipitate was placed in a large beaker (capacity 600 ml.), about 100 ml. of water were added, and then 20 ml. of dilute (20 per cent. by volume) sulphuric acid solution, the whole was diluted to 200 ml., and heated on the water-bath to about 70° C., and the permanganate titration was carried out as usual.

In the titrations with $N/10$ permanganate solution the odour of aldehyde could always be detected; this indicated the presence of traces of alcohol in the precipitates as weighed, which would, of course, tend to produce high results (both by weight and titration).

We therefore decided to heat the calcium oxalate precipitates at 100° C. to remove this alcohol, before proceeding to the permanganate titration. We found that the precipitates attained constant weight in the course of about one hour, and it has since been stated by Brunck[4] that the precipitate thus obtained (in his case dried at 105 to 110° C.) corresponds with $CaC_2O_4.H_2O$ in composition, and that this method of determination of calcium is comparable in accuracy with the ordinary methods; he does not, however, give any experimental results in support of this contention.

In our experiments, however, we noticed that after the precipitates had been heated to constant weight at 100° C., there was a slight discrepancy between the theoretical permanganate titration (assuming the dried precipitate to consist of pure $CaC_2O_4.H_2O$), and that actually obtained. The following results are typical:

Calcium oxide added g.	Calcium oxalate precipitate obtained by Dick's method g.	Calcium oxalate precipitate, after drying to constant weight at 100° C. (one hour) g.	Titration of dried calcium oxalate ppt., $N/10$ $KMnO_4$ ml.	Theoretical titration, assuming dried precipitate to consist of pure $CaC_2O_4.H_2O$, $N/10$ $KMnO_4$ ml.	Theoretical titration corresponding to calcium oxide added, $N/10$ $KMnO_4$ ml.
0·05882	0·1539	0·1536	21·0	21·03	20·97
0·1174	0·3075	0·3071	41·90	42·05	41·87
0·2932	0·7682	0·7676	104·55	105·1	104·6
0·2932	0·7683	0·7675	104·55	105·1	104·6

During the past two years we have carried out numerous comparisons along these lines, but we have always noticed the same general tendency, *i.e.* that the results obtained by the gravimetric method, even after the calcium oxalate precipitate has been dried to constant weight, are too high, and where large amounts of calcium oxide are in question (of the order of 0·3 g.) the use of this method may give rise to serious errors.

Briefly, we believe that the titration of the oxalate ion gives the most reliable indication of the amount of calcium in the precipitate, particularly where sintered glass crucibles are used, instead of filter paper, in the filtration of the precipitate.

STRONTIUM.—Strontium carbonate was carefully purified from barium and calcium and dissolved in dilute hydrochloric acid, and this solution was used in our experiments.

The following points should be noted in connection with the precipitation of strontium as oxalate:

(1) The precipitated strontium oxalate consists essentially of $SrC_2O_4.H_2O$. A precipitate weighing 0·5384 g., obtained after washing with alcohol and ether as in the calcium experiments, gave, after being heated for one hour at 100° C. to remove alcohol, a permanganate titration of 54·7 ml. of $N/10$ potassium permanganate solution. (Theoretical for pure $SrC_2O_4.H_2O$ = 55·6 ml. of $N/10$ permanganate solution.)

(2) The precipitated oxalate is not stable in an electric oven maintained at 100 ± 2° C.; 0·5387 g. of the precipitate lost 0·0479 g. after twenty-four hours at this temperature.

(3) Owing to the interference of insoluble strontium sulphate produced in the course of the titration, the oxalate, after being dried, does not show its full titration value in the sulphuric permanganate titration.

Thus, 0·5384 g. of the precipitate obtained after washing with alcohol and ether gave 0·5118 g. $SrSO_4$, corresponding with 55·72 ml. of $N/10$ permanganate solution. Actually, after drying to remove alcohol, the titration gave 54·7 ml. of $N/10$ permanganate from a corresponding amount of the strontium oxalate precipitate.

(4) Strontium is not completely precipitated as oxalate under conditions similar to those for complete precipitation of calcium.

Strontium oxide added g.	Strontium oxalate precipitated by Dick's method g.	Titration of dried strontium oxalate precipitate, $N/10$ $KMnO_4$ ml.	Theoretical titration corresponding with strontium oxide added, $N/10$ $KMnO_4$ ml.
0·0592	0·0980	10·02	11·42
0·1183	0·2090	21·57	22·83
0·2958	0·5384	54·7	57·10

BARIUM.—The barium solution used was prepared from $BaCl_2.2H_2O$ (Analar). The oxalate, precipitated under conditions similar to those outlined for calcium on p. 668, possesses essentially the composition $BaC_2O_4.\frac{1}{2}H_2O$.

The precipitated oxalate does not behave normally in the ordinary sulphuric acid permanganate titration, because the insoluble barium sulphate produced probably forms an external coating on the large crystals of barium oxalate, and this prevents the full realisation of the permanganate titration. However, if perchloric acid is substituted for sulphuric acid, the oxalate ion may be titrated without interference.

Thus, 0·3914 g. of the precipitate obtained, after washing with alcohol and ether as in the calcium experiments, gave a permanganate titration of 33·3 ml. of $N/10$, alcohol being removed by drying at 100° C. prior to the titration. This titration is equivalent to 38·28 per cent. of $(COOH)_2$.

Calculated for $Ba(OOC)_2.\frac{1}{2}H_2O$ = 38·40 per cent. of $(COOH)_2$.

Further, 0·4271 g. of the above precipitate yielded 0·4253 g. of barium sulphate = 65·37 per cent. of barium oxide.

Theoretical for $Ba(OOC)_2.\frac{1}{2}H_2O$ = 65·4 per cent. of barium oxide.

The precipitate appears to be fairly stable at 100° C., in which respect it resembles the corresponding calcium precipitate more closely than the strontium precipitate.

Under the normal conditions of complete precipitation of calcium, barium is very incompletely precipitated, as the following results show:

Barium oxide added g.	Barium oxalate obtained by Dick's method g.	Barium oxalate obtained after drying for one hour at 100° C. g.	Theoretical titration, assuming dried precipitate to consist of $BaC_2O_4.\frac{1}{2}H_2O$, $N/10$ $KMnO_4$ ml.	Titration of dried barium oxalate ppt., $N/10$ $KMnO_4$ ml.	Theoretical titration corresponding with barium oxide added, $N/10$ $KMnO_4$ ml.
0·0601	0·0722	0·0719	6·13	1·0	7·84
0·1201	0·1587	0·1584	13·52	4·65	15·66
0·3003	0·4260	0·4256	36·32	13·3	39·15

MAGNESIUM.—In these experiments, magnesium ammonium chloride (Analar) was used as the source of magnesium.

It was found that magnesium was precipitated essentially as $MgC_2O_4.2H_2O$. Thus, 0·5371 g. of the precipitate obtained after drying for one hour at 100° C. gave a permanganate titration of 71·85 ml. of $N/10$ $KMnO_4$, corresponding to 60·20 per cent. of $(COOH)_2$. Calculated for $MgC_2O_4.2H_2O$ = 60·67 per cent. of $(COOH)_2$.

Again, 0·2594 g. of the above dried precipitate yielded 0·5407 g. of magnesium hydroxyquinoline complex, $Mg(C_9H_6ON)_2$, corresponding with 16·22 per cent. of magnesium. Calculated for $MgC_2O_4.2H_2O$ = 16·40 per cent. of magnesium.

Of course, in the presence of ammonium chloride, magnesium oxalate is comparatively soluble, but even so, as is well known, it is also very liable to be carried down with calcium in an oxalate precipitation, and a double precipitation of calcium should always be carried out in the presence of magnesium.

PRECIPITATION OF CALCIUM IN THE PRESENCE OF BARIUM, STRONTIUM AND MAGNESIUM.—Known amounts of calcium were precipitated in the presence of known amounts of barium, strontium and magnesium, as outlined in the method on p. 668.

The following results were obtained:

Composition of mixture	Oxalate precipitate: obtained by Dick's method g.	Oxalate precipitate: after drying for 1 hour at 100° C. g.	Titration of dried oxalate ppt., $N/10$ $KMnO_4$ ml.	Calculated titration, assuming dried precipitate to consist of pure $CaC_2O_4.H_2O$, $N/10$ $KMnO_4$ ml.
0·2932 g. CaO 0·0594 g. SrO	0·8754	0·8744	114·95	119·8
0·2932 g. CaO 0·0601 g. BaO	0·8298	0·8275	108·83	113·3
0·2932 g. CaO 0·5 g. MgO	0·8083	0·8059	109·25	110·4

We have already pointed out that a slight discrepancy exists between the weight of a dried calcium oxalate monohydrate precipitate and its permanganate titration value, but the above results certainly indicate that this relationship is seriously affected by the presence of barium or strontium in the oxalate precipitate, and to a less degree by the presence of magnesium.

One interesting fact that has been observed is that the contamination of a precipitate of calcium oxalate with even very small proportions of magnesium always tends to cause the precipitate to adhere to the sides of the glass vessel used in the precipitation; with pure calcium oxalate this effect has not been observed.

I have to thank Mr. F. Sweeney for help in connection with the experimental work, and the directors of Imperial Chemical Industries, Ltd., for permission to publish the results of this investigation, which was carried out in the Research Department of their subsidiary company, I.C.I. (Alkali), Ltd., Northwich.

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Electrometric Determination of Thallium

BY WINIFRED R. A. HOLLENS, PH.D., AND JAMES F. SPENCER, D.SC.

SEVERAL methods for the electrometric determination of thallium are recorded in the literature; the most important are those due to Zintl and Rienäcker[1] and C. del Fresno and Valdés.[2] The reaction used by the former workers consists in the oxidation of the thallous ion by titration with potassium bromate using a platinum electrode and a N. calomel electrode to indicate the end-point. A second method due to the same authors involves the reduction of the thallic ion by means of titanous chloride in the presence of ammonium acetate, the same electrode system being employed. Fresno and Valdés oxidise the thallous ion by titration with potassium ferricyanide in alkaline solution.

The results of the latter authors are frequently 1·0 per cent. low, whilst the methods of Zintl and Rienäcker are rather involved. The bimetallic electrode system has been shown (Spencer and Pring[3]) to furnish accurate values for the titration of iodine by sodium thiosulphate and sodium arsenite, in connection with the electrometric determination of copper. Consequently, since thallium in the higher state of oxidation behaves like copper in its reaction with potassium iodide, it was decided to investigate the reaction as a possible means for the electrometric determination of thallium.

The method, which proved to be satisfactory, consists in converting the thallium to the higher state of oxidation, adding a suitable quantity of potassium iodide, and titrating with either sodium thiosulphate or sodium arsenite of concentration approximately equivalent to that of the thallium, and determining the

end-point by means of the Foulk and Bawden[4] bimetallic electrode system. In this case it was found that a potential of 15 millivolts imposed upon the electrodes gave a sharp and accurate end-point, provided that the electrodes were depolarised before use.

OXIDATION OF THALLIUM TO THE THALLIC STATE.—A solution of a thallous salt was precipitated as chloride and treated in the cold with washed chlorine until it had completely dissolved. A current of air was then bubbled through the solution to remove the dissolved free chlorine, until the emerging gas failed to react with starch iodide paper.

I. TITRATION WITH SODIUM THIOSULPHATE.—A series of titrations was carried out with solutions of thallic ion of concentration varying from 0·2 *N* to 0·002 *N*. A measured volume of the thallium solution was rendered slightly acid with acetic acid, an excess of potassium iodide solution was added, and the liberated iodine was titrated. It was also found that the liberated iodine could be satisfactorily titrated without electrodes by adding about 10 ml. of chloroform and titrating with sodium thiosulphate solution of normality approximately equivalent to that of the thallium, and shaking until the colour of iodine disappeared from the chloroform layer. The results of six series of titrations are recorded in Table I.

TABLE I

	25 ml. 0·2 *N* $TlCl_3$ + 2 g. KI + CH_3CO_2H		25 ml. 0·1 *N* $TlCl_3$ + 2 g. KI + CH_3CO_2H		25 ml. 0·05 *N* $TlCl_3$ + 2 g. KI + CH_3CO_2H	
Indicator.	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Thiosulphate used	25·10	25·20	25·15	25·20	25·10	25·25
,, ,,	25·15	25·25	25·15	25·30	25·10	25·20
,, ,,	25·15	25·20	25·20	25·20	25·15	25·23
Average ..	25·13	25·22	25·17	25·23	25·12	25·23

	25 ml. 0·01 *N* $TlCl_3$ + 1 g. KI + CH_3CO_2H		25 ml. 0·004 *N* $TlCl_3$ + 1 g. KI + CH_3CO_2H		25 ml. 0·002 *N* $TlCl_3$ + 1 g. KI + CH_3CO_2H	
Indicator	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Thiosulphate used	25·25	25·25	25·10	25·25	No satis-	25·25
,, ,,	25·30	25·25	25·10	25·25	factory	25·25
,, ,,	25·35	25·30	25·20	25·23	end-point	25·30
Average ..	25·30	25·27	25·15	25·23		25·27

The calculated volume of sodium thiosulphate solution required in all cases is 25·25 ml.

The normalities of thallic chloride given in the table are only approximate. A litre of the solution, named 0·2 *N*, was made from 23·8510 g. of thallous chloride, and the other solutions were prepared by diluting this as shown. The thiosulphate solution used with the 0·2 *N* thallium solution was 0·1968 *N*, and the solutions used in other cases were prepared by diluting the former to the same extent as the thallium solution.

The electrometric titrations show that, for concentrations down to 0·002 *N*, this method furnishes results which are accurate to 2 parts in 2,500, but at greater dilution the results are much less accurate. The results with chloroform as indicator are generally not so accurate, but even here values which differ by only about 0·25 per cent. from the calculated value are obtained. This is due to the fact that the end-point is difficult to determine, because the thallous iodide adsorbs iodine, giving a greenish precipitate, and making the disappearance of the colour in the chloroform a little uncertain. The method breaks down entirely at a concentration of 0·002 *N* thallic chloride.

EFFECT OF CONCENTRATION OF ACETIC ACID.—The effect of varying the amount of acetic acid added is given in the table below (Table II).

TABLE II

25 ml. 0·1 *N* $TlCl_3$ + 2 g. KI. Electrometric indication

Acetic acid added	None ml.	A few drops of 0·1 *N* acid ml.	2 ml. 2 *N* acid ml.	5 ml. glacial acetic acid ml.
Thiosulphate used	28·75	28·75	28·75	28·75
,, ,,	28·75	28·75	28·73	28·75
,, ,,	28·80	28·70	28·70	28·71
Average ..	28·77	28·73	28·73	28·74

The calculated volume of sodium thiosulphate required is 28·72 ml. A litre of the thallium solution was prepared from 12·3010 g. of thallous chloride, and the thiosulphate solution in this case was 0·0893 *N*. The results indicate that the concentration of the acetic acid may be varied over a very wide range, but that the presence of the acid is not essential.

EFFECT OF ACIDS OTHER THAN ACETIC ACID.—A further series of titrations was carried out with sulphuric and hydrochloric acids, respectively, and the results given below were obtained. Twenty-five ml. of thallic chloride solution (prepared by oxidising 12·6816 g. of thallous chloride and making up to 1 l.) and 2 g. of potassium iodide were used in each titration. The calculated volume of sodium thiosulphate is 28·34 ml.

	5 ml. 2 *N* acetic acid		5 ml. 2 *N* HCl		5 ml. 2 *N* H_2SO_4	
Indicator	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Thiosulphate used	28·30	28·25	28·35	28·45	28·35	28·40
,, ,,	28·35	28·30	28·30	28·40	28·35	28·42
,, ,,	28·35	28·30	28·35	28·40	28·30	28·40
Average ..	28·33	28·28	28·33	28·42	28·33	28·41

The end-point is a little high with the solutions containing hydrochloric and sulphuric acids, owing doubtless to the higher hydrogen ion concentration of these solutions, but even here the divergence from the calculated value is rather less than 0·3 per cent. The results with chloroform as indicator are considerably better.

TITRATION IN THE PRESENCE OF OTHER METALS.—Experiments were performed to ascertain whether thallium can be determined by the above method in the

presence of any or all of the metals which usually accompany it in its commercial form. The metals examined were zinc, lead, iron and copper. Known amounts of a soluble salt of these metals were added to a known solution of thallium, and the titration was performed as described above.

Twenty-five ml. of 0·1 *N* zinc chloride solution were added to 25 ml. of thallic chloride solution containing 2 g. of potassium iodide and 2 ml. of 2 *N* acetic acid.

	$TlCl_3$ ml.	$TlCl_3 + ZnCl_2$ ml.
Thiosulphate used	25·96	25·95
,, ,,	25·96	25·97
Average ..	25·96	25·96

The result in the presence of zinc is identical with that in its absence.

Solutions containing lead acetate in addition to thallic chloride gave no satisfactory end-point.

Ten ml. of 0·1 *N* ferrous ammonium sulphate solution were added to 25 ml. of thallic chloride solution containing 2 g. of potassium iodide. No acid was added in this case.

	$TlCl_3$		$TlCl_3 + FeSO_4(NH_4)_2SO_4.6H_2O$	
Indicator	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Thiosulphate used	25·15	25·20	25·25	24·20
,, ,,	25·15	25·30	25·20	25·25
,, ,,	25·20	25·20	25·20	25·25
Average ..	25·17	25·23	25·22	25·23

Attempts were made to determine thallium in the presence of ferric iron by Spencer and Pring's[3] method for copper, but were unsuccessful.

Twenty-five ml. of 0·1 *N* copper sulphate solution were added to 25 ml. of thallic chloride solution containing 2 g. of potassium iodide and a little acid.

	25 ml. $CuSO_4$ ml.	25 ml. $TlCl_3$ ml.	25 ml. $CuSO_4$ +25 ml. $TlCl_3$ ml.
Thiosulphate used ..	13·59	26·59	40·14
,, ,,	13·60	26·60	40·16
Average	13·59	26·59	40·15

The calculated quantity of sodium thiosulphate required is 40·18 ml.

These results show that the sum of the thallium and copper may be determined by this method, and, if the copper is determined electrolytically or by some other method, the value for thallium becomes known.

II. Titration with Sodium Arsenite.—A series of experiments was carried out to ascertain the suitability of the bimetallic electrode system to the titration of the iodine, liberated by thallic salts from potassium iodide, by sodium arsenite. It is essential that the solution should be alkaline during the titration. In the present case it has been found necessary to liberate the iodine before the addition of sodium bicarbonate, thereby preventing the precipitation of thallic

hydroxide. The titration was carried out as described above, using both chloroform and electrometric indicators to ascertain the end-point. The results are recorded in the table below.

Indicator	25 ml. 0·1 *N* $TlCl_3$		25 ml. 0·02 *N* $TlCl_3$	
	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Sodium arsenite used	26·00	26·00	26·00	26·00
,, ,, ,,	26·00	25·95	26·02	25·98
,, ,, ,,	26·00	25·93	25·99	25·97
Average ..	26·00	25·96	26·00	25·98

Indicator	25 ml. 0·01 *N* $TlCl_3$		25 ml. 0·002 *N* $TlCl_3$	
	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Sodium arsenite used	26·18	26·00	No satisfactory	25·95
,, ,, ,,	26·00	25·95	end-point	25·95
,, ,, ,,	26·10	25·95		25·97
Average ..	26·09	25·97		25·96

The calculated value of sodium arsenite solution required in all cases is 26·01 ml. The sodium arsenite used here was 0·0930 *N*. A litre of the thallic chloride solution was prepared from 12.2124 g. of thallous sulphate. The remarks made concerning the solutions under the titration by sodium thiosulphate apply here also.

The results show that this method is satisfactory down to concentrations of 0·002 *N* $TlCl_3$ with electrometric indicator, but only to 0·01 *N* with chloroform as indicator. At the latter concentration the end-point is a little delayed and rather difficult to define.

SUMMARY.—The bimetallic electrode system of Foulk and Bawden is satisfactory for the titration of iodine, liberated by thallic chloride from potassium iodide, with either sodium thiosulphate or sodium arsenite. Both reducing agents give good reproducible end-points with solutions of thallic salts of concentrations down to 0·002 *N*. In the case of sodium thiosulphate, the concentration of acetic acid may be varied between wide limits without affecting the end-point. The presence of zinc and ferrous iron has no effect on the titration value, but in the presence of copper, a titration value corresponding to the sum of the thallium and the copper is obtained. Consequently, the thallium may be determined in the presence of copper if the latter metal is subsequently determined by some other method.

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The Volumetric Determination of Nitrites by means of Ceric Sulphate Solution

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The advantages of ceric sulphate solution as a volumetric oxidising agent in place of permanganate solution have been pointed out in recent years by a number of workers, and especially by Willard and Young,[1] Furman,[2] and Berry,[3] who have made use of standardised ceric sulphate solution for the determination of nitrites and many other oxidisable substances. In the present paper the direct titration of a nitrite with ceric sulphate has been examined, a dyestuff of the triphenylmethane class being used as internal indicator in the solution, and the procedure has been extended to include the indirect determination of the small amounts of potassium obtained in the analysis of soil solutions and similar materials, the potassium being precipitated with sodium cobaltinitrite and the washed precipitate titrated with ceric sulphate and ferrous sulphate solutions.

Preparation of Ceric Sulphate Solution.—The ceric sulphate solution used for the experimental work was prepared (*a*) from technical ceric oxide and sulphuric acid, (*b*) from pure ceric ammonium nitrate by repeated evaporation with an excess of sulphuric acid.

The ceric sulphate solution was standardised against pure ferrous ammonium sulphate dissolved in air-free dilute sulphuric acid; the effect of atmospheric oxidation during the titration was found to be negligible. Erioglaucine was employed as internal indicator. 0·1 *N* ceric sulphate solution was used for the determination of the larger amounts of nitrite, 0·02 *N* solution for smaller amounts, and 0·01 *N* solution for the titration of the potassium cobaltinitrite precipitate. Solutions of ferrous sulphate of corresponding strengths were used in conjunction with the ceric sulphate solution.

The sodium nitrite ("Analar" B.D.H.) was dissolved in distilled water which had previously been boiled and cooled in a current of carbon dioxide to ensure freedom from air, and freshly-prepared solutions containing from 0·6 to 3·0 g. nitrite per l. were used for the determinations. The results were checked by parallel determinations with permanganate solution which had itself been standardised against sodium oxalate and ferrous ammonium sulphate, and figures in close agreement were obtained.

Method.—Twenty-five ml. of the standard nitrite solution were added to an excess of standard ceric sulphate solution containing a little 4 *N* sulphuric acid, the tip of the pipette being kept below the surface of the liquid during the addition. In some experiments the liquid was heated to boiling for one minute and then cooled; in others it was allowed to stand at the ordinary temperature for five minutes. In each case the excess of ceric sulphate was determined by titration with standard ferrous ammonium sulphate solution.

In the permanganate titrations the nitrite was added in the same way to a known volume of standard permanganate previously acidified with 5 ml. of dilute

(1 : 1) sulphuric acid, and the whole was slightly warmed. The liquid was well stirred and allowed to stand for a few minutes, after which an excess of sodium oxalate solution was added, and the whole was back-titrated with permanganate.

The following results are typical of the large number obtained:—

(*a*) Ceric sulphate solution, 0·195 *N* (1 ml. = 0·000673 g. of sodium nitrite).
50 ml. of ceric sulphate solution ≡ 48·8 ml. of ferrous ammonium sulphate solution.

Ceric sulphate ml.	Sodium nitrite added ml.	Ferrous solution used for back titration ml.
50	25	28·5
50	25	28·4

Ceric sulphate reduced ml.	Sodium nitrite in 25 ml. g.	Difference g.
20·80	0·140	—
20·69	0·139	−0·0001

(*b*) Permanganate solution, 0·0197 *N* (1 ml. ≡ 0·000681 g. of sodium nitrite).
15 ml. of sodium oxalate solution ≡ 7·63 ml. of permanganate solution.

Permanganate taken ml.	Sodium nitrite added ml.	Sodium oxalate added ml.
25	25	15
25	25	15

Permanganate for back titration ml.	Permanganate reduced ml.	Sodium nitrite in 25 ml. g.	Difference g.
3·1	20·47	0·139	−0·0001
3·2	20·57	0·140	—

In two of the series an excess of ferrous ammonium sulphate solution was added after the addition of the nitrite solution to the ceric sulphate, and the whole was back-titrated with ceric sulphate. In these experiments the results for sodium nitrite were usually a little higher (0·0001 to 0·0009 g.) than in the other tests, but were still quite satisfactory.

DETERMINATION OF POTASSIUM.—Preliminary experiments with a solution prepared from potassium sodium cobaltinitrite showed that reproducible results (*e.g.* 0·149, 0·147, 0·149 mg. in 5 ml.) were obtainable if the cobaltinitrite solution was added to an excess of 0·01 *N* ceric sulphate containing 3 ml. of 4 *N* sulphuric acid and the mixture was boiled for a minute. After cooling, 5 ml. of standard ferrous ammonium sulphate were added, and the excess was titrated with ceric sulphate, erioglaucine being used as indicator. With 0·01 *N* ceric sulphate the fading of the orange-pink colour after the end-point has been reached is more pronounced than with 0·02 *N* solution, but, despite this, the colour-change at the end-point is quite sharp.

A series of determinations was then made on a potassium chloride solution containing 0·1600 g. of the salt per l. The potassium was precipitated by the method used in the Agricultural Laboratory of this College. The potassium

chloride solution was measured into a centrifuge tube and evaporated to 2 ml. Two drops of glacial acetic acid were added, and the tube was cooled in ice for 5 minutes, after which 0·75 ml. of sodium cobaltinitrite reagent was added slowly, the solutions being mixed by inclining the tube and then rapidly returning it to a vertical position. The tube was left in ice-water for 30 minutes and then centrifuged for 5 minutes, and the supernatant liquid was removed by means of a glass tube drawn out to a fine jet and attached to a suction-pump. The precipitate was washed twice with 2 ml. of water, the tube being centrifuged for 2 minutes at each washing. The precipitate was then washed into a 100-ml. beaker and dissolved by heating with 10 ml. of 0·01 *N* ceric sulphate and 4 ml. of 4 *N* sulphuric acid. The solution was cooled, 5 ml. of 0·02 *N* ferrous ammonium sulphate solution were added, and the excess of this was titrated with ceric sulphate after addition of erioglaucine as indicator.

Ceric sulphate solution, 0·00992 *N*. 1 ml. ≡ 0·0705 mg. potassium. The ceric sulphate solution was standardised with ferrous ammonium sulphate. The following results are typical:—

Potassium chloride solution taken ml. mg.	Ceric sulphate reduced ml.	Potassium found mg.	Difference mg.
2 = 0·168	2·43	0·171	+0·003
2 = 0·168	2·45	0·173	+0·005
7 = 0·587	8·87	0·625	+0·038
7 = 0·587	8·96	0·632	+0·045

A comparative series of determinations in which the cobaltinitrite precipitate was titrated with permanganate solution also gave results that were quite satisfactory for small amounts of potassium (0·17 to 0·40 mg.), but tended to become irregular with larger amounts.

In two series of experiments, in which the potassium was precipitated with Kramer's solution (a solution of cobaltinitrite made from cobalt nitrate and sodium nitrite), the results were invariably higher than when a precipitant prepared from solid sodium cobaltinitrite was used. It is evident that the composition of the precipitate varies with the conditions of precipitation and the composition of the reagents used. In several of the series it was possible to calculate for the ceric sulphate a potassium factor which afforded satisfactory values throughout the whole range of that particular series, but could not be used for any other series of determinations made under even slightly differing conditions.

Considered as a whole, our results confirm those of previous workers when using permanganate solution in the titration of the cobaltinitrite precipitate,[4] and clearly indicate that accurate determinations of these small amounts of potassium can be attained only by rigid control of the conditions of precipitation and filtration, and by standardising the permanganate or ceric sulphate solutions against a solution of pure potassium chloride treated in exactly the same way as in the actual determination.

The method finally recommended for the titration of the cobaltinitrite precipitate is as follows:—The washed precipitate is dissolved by heating it with 10 ml. of 0·01 *N* ceric sulphate solution and 4 ml. of 4 *N* sulphuric acid. Five ml. of

standardised ferrous sulphate solution are added to the cooled solution, and the excess of the ferrous solution is titrated with the ceric sulphate solution. This procedure has the advantage of avoiding danger of decomposition of the standard solution in the hot liquid, which is the drawback of the customary permanganate method.

SUMMARY.—Soluble nitrites may be accurately determined by titration of their solutions with ceric sulphate solution, erioglaucine being employed as internal indicator.

In the determination of small amounts of potassium in soil solutions, etc., by the cobaltinitrite method, ceric sulphate may advantageously replace permanganate in the titration of the potassium cobaltinitrite precipitate.

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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.

CURVES FOR USE IN THE COLORIMETRIC ESTIMATION OF CAROTENE

THE colorimetric estimation of carotene has been carried out for many years by comparison with potassium dichromate solution. Many workers have prepared crystalline carotene and with its help constructed curves, potassium dichromate of varying strengths being used for matching. While this may be satisfactory when the worker is engaged in experiments in which relative carotene-contents are examined, variation in the purity of the samples of carotene used for the construction of the curves may lead to conflicting results when comparative work on absolute amounts of carotene is carried out by several workers.

It was decided to construct a curve with highly purified carotene, which might act as a standard for future work, the Lovibond Tintometer (B.D.H. Pattern) being used for the purpose. At the same time a comparison was made against the usual potassium dichromate solution.

Several samples of carotene were examined, but one, for which I am indebted to Professor A. C. Chibnall and Dr. A. Pollard, of the Imperial College of Science and Technology, was of outstanding purity.

This carotene,* prepared from cocksfoot grass (*Dactylis glomerata*), was entirely in the β-form, and its melting-point was 180–182° C. (182° corr.).

* The carotene was isolated during an extensive fractionation of all the ether-soluble material from cocksfoot (*Dactylis glomerata*). Details will be published later.

The intensity of absorption of light at $463m\mu$ was taken as the criterion of purity. Mr. A. E. Gillam, of Manchester University, kindly made the spectroscopic examination. He reports the sample to be the purest he has met with. The absorption data in chloroform were as follows:

$E\,{}^{1\%}_{1\,\text{cm.}}\,(463m\mu) = 2200$,* where $E = \log \frac{I_0}{I}$, I_0 = the intensity of incident light, and I = the intensity of transmitted light in a cell 1 cm. in thickness.

Expressed as the molar extinction coefficient, E_1, this equals 118,000 $[E_1 = \log \frac{I_0}{I} \div (\text{molar concentration} \times \text{cell thickness in cm.})]$.

This sample was used for the construction of the curves; 10·15 mg. were dissolved in about 20 ml. of chloroform, and the volume was made up to 500 ml. with petroleum spirit (b.p. 40°–60° C.). From this solution seventeen dilute

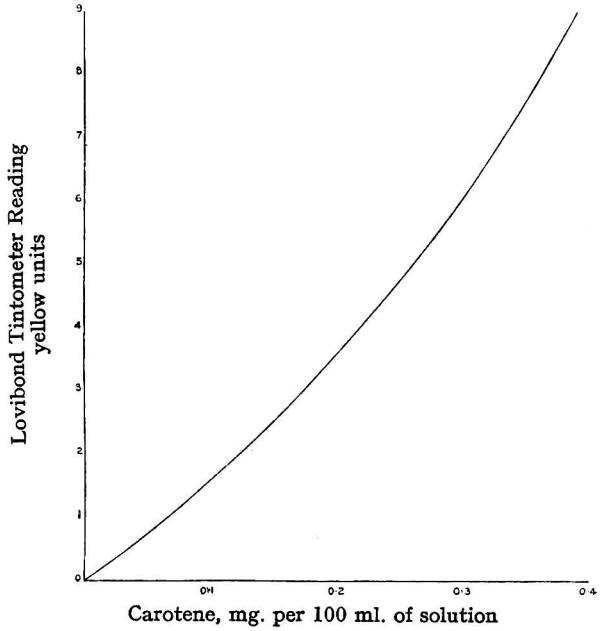

Fig. 1

solutions were prepared by dilution with petroleum spirit and matched in the Lovibond Tintometer, daylight from a north window being used as the source of light. Readings were made by three independent observers, and the results were averaged. The individual readings usually lay within 0·1 unit, but a maximum difference of 0·4 unit was obtained with two of the more concentrated solutions. To obtain perfect matching, it was necessary to make use of the red slides in amounts varying from 0·2 unit in the more dilute solutions to 0·5 unit in the strongest solutions. These amounts are small, and only the yellow units were used for the curve.

The curve is shown in Fig. 1. The values go no higher than 9 Lovibond yellow units, owing to the difficulty of matching accurately above that density;

* The highest value Mr. Gillam had obtained previously in his wide experience was $E\,{}^{1\%}_{1\,\text{cm.}}\,463m\mu = 2000$.

experience has shown that the most accurate values are obtained when the colours lie within the range of 2 and 5 yellow units.

POTASSIUM DICHROMATE SOLUTION AS STANDARD.—From a freshly-prepared carotene solution ten further dilute carotene solutions were made up, and these were compared against 0·1 per cent. potassium dichromate solution in a Klett colorimeter, the source of light being north, as before.

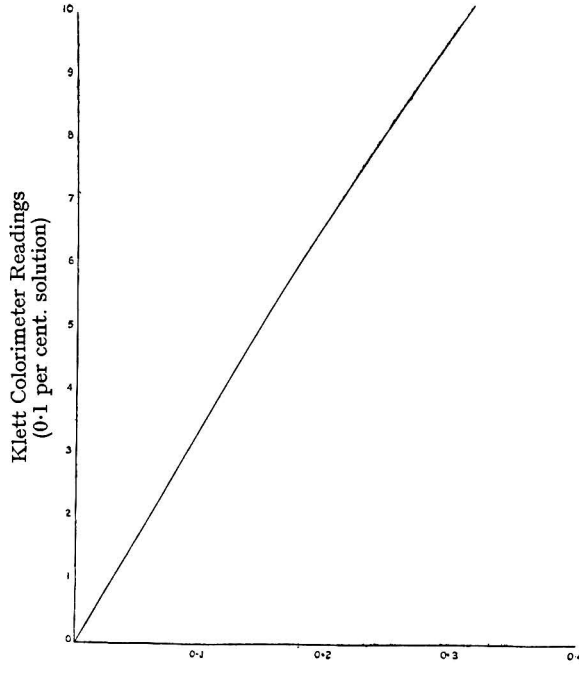

Fig. 2

The carotene solutions were set at 20 mm. on the scale, and the matching was done by varying the height of the potassium dichromate column. This method has

TABLE I

DATA FOR CONSTRUCTION OF CURVE (TINTOMETER)

Carotene per 100 ml. mg.	Tintometer reading, yellow units	Carotene per 100 ml. mg.	Tintometer reading, yellow units
0·0609	0·95	0·2436	4·55
0·0812	1·30	0·2639	5·00
0·1015	1·60	0·2842	5·70
0·1218	2·05	0·3045	6·10
0·1421	2·30	0·3248	6·90
0·1624	2·80	0·3451	7·35
0·1827	3·20	0·3654	8·05
0·2030	3·70	0·3857	8·75
0·2233	4·05		

been found very convenient, and it has given satisfactory results in a number of comparative tests with the Lovibond tintometer method.

The curve is shown in Fig. II. It was again found that the matching was easier and more accurate at the lower concentrations.

To enable workers to construct their own curves on a larger scale than that published here, the actual figures obtained in the work are given in Tables I and II.

TABLE II

DATA FOR CONSTRUCTION OF CURVE (KLETT COLORIMETER)

Carotene per 100 ml. mg.	Depth of 0·1 per cent. $K_2Cr_2O_7$ column, mm.	Carotene per 100 ml. mg.	Depth of 0·1 per cent. $K_2Cr_2O_7$ column, mm.
0·0483	1·60	0·1800	6·04
0·0676	2·26	0·2029	6·85
0·0966	3·21	0·2318	7·65
0·1256	4·19	0·2705	8·79
0·1546	5·16	0·3280	10·50

My thanks are due to Mr. E. Sampson and Mr. F. Reed for assistance in the colour matchings and to Messrs. Imperial Chemical Industries, Ltd., for permission to publish this note.

W. S. FERGUSON

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TIN AND LEAD IN CANNED FISH

ONE hundred and forty-six samples, mostly purchased at random, and comprising about 100 different brands of various kinds of canned fish, have been examined recently for metallic contamination by Mr. H. G. Harrison and myself; 20 were reported upon adversely, the results being summarised below:

Sardines.—Of 28 samples analysed, none contained more than small amounts of tin, but 10 contained lead in excess of 7 parts per million, *viz.* 8, 9, 10, 10, 15, 15, 16, 20, 21, and 43 p.p.m., respectively.

In determining the lead in canned fish it was found that the direct colorimetric method on the clear solution obtained by the acid-destruction of 5 g. of the thoroughly mixed sample, with the use of appropriate reagents to prevent interference from iron, copper, phosphates, etc. (Lampitt and Rooke, ANALYST, 1933, **58**, 736), gave results closely agreeing with those given by the diphenylthiocarbazone method of Allport and Skrimshire (ANALYST, 1932, **57**, 443), and the former method would appear to be satisfactory for general routine, provided that colourless solutions are obtained.

The sardines containing the higher proportions of lead were all packed in Portugal, and the cans showed no obvious signs of corrosion or exposed solder; the explanation of the contamination doubtless lies in the Portuguese method of steam-cooking on lead-containing grills, as explained by Lampitt and Rooke (*loc. cit.*).

A further point of interest was that two samples, sold as sardines, bore unusual markings and were accordingly submitted to further examination to establish their identity. The pieces of fish submitted were more slender in shape, lighter in colour, and less scaly than sardines; a long dorsal fin extending almost to the tail and long pointed pectoral fins were observed on dissection, but the most characteristic features were pronounced spiny projections all along the lateral line, and a sharp curve downward in the middle of this line. From information obtained

at the Fishmongers' Hall, and by comparison with specimens with Mr. J. R. Norman's kind assistance at the Natural History Museum, it was definitely established, even in the absence of their heads and tails, that the fish belonged to a species of *Trachurus*, a horse mackerel or scad (family, *Carangidae*), a fish of different natural order from the sardine, and far inferior in flavour and value.

In fairness to the packers it should be stated that both samples proved to be of the same brand and to be sold in tins labelled "Portuguese Fish in Oil." Nothing can be said at the time of writing as to the value of this declaration as a defence for the vendor.

Brisling, etc.—Eight samples of brisling in oil, 7 of pilchards in tomato sauce, 15 of herrings in tomato sauce, 10 of crab, 4 of salmon, 2 of lobster, 1 of oysters and 1 of mackerel, were all free from more than traces of lead or tin. It appears that the distinction between sardines and pilchards and between sild and herring is merely one of size (*cf.* Hattersley, ANALYST, 1935, 69).

Sild.—Seventy samples of tinned sild showed no excessive amounts of lead; 12 samples, however, contained more than 2 grains of tin per pound, the results being as follows:

Tin-content in grains per pound	Number of samples
Less than 1	41
From 1 to 1·9	15
,, 2 to 2·9	4
,, 3 to 3·9	4
,, 4 to 6·7	5

The tin was determined by the gravimetric method of Buchanan and Schryver (L.G.B. Report, No. 7, 1908; Abst., ANALYST, 1909, **34**, 121). It may be of interest to mention here that quantities of tin approaching and exceeding 2 grains per lb. can usually be detected visually by the yellowness of the ash when hot; also, that the ignited sulphide precipitate from a hydrochloric acid extract of the ash, determined in 20 cases in an attempt to find an expeditious method, gave from two-thirds to three-quarters of the tin found by the former method. A volumetric process involving an iodimetric titration of the stannous chloride formed by the reduction by aluminium wire of the hydrochloric extract from the ash, in an atmosphere of carbon dioxide, proved quite unreliable, no doubt on account of incomplete solution of the tin and interference by iron, etc.

Of the samples containing excessive amounts of tin, one (tin, 2·6 grains per lb.) was stated to be British and contained tomato sauce, which might have accounted for some corrosion, whilst the remainder were cheap brands of Norwegian origin. It was observed that in most of the latter the oil used was not olive oil, and appeared to be deficient in quantity; this may account for the presence of tin, for the cans, although evidently not from old stock, showed marked signs of corrosion in patches where the fish had been in contact with the sides, suggesting that the oil was insufficient in quantity to protect the tin from the action of the salts, etc., in the fish. Indeed, three corroded cans contained scarcely any oil.

In most of these cases of metallic contamination appropriate action taken by the authorities concerned has prevented the further sale or importation of such consignments, thus avoiding the necessity for actual prosecutions.

A Suggested Standard for Lead in Canned Fish.—While it is obvious that the contamination of fish intended for human consumption with a poisonous metal, such as lead, should be entirely prevented, it is necessary to choose a certain degree of contamination to serve as a limit for practical administrative purposes.

It is very desirable that the same limit should be adopted in all districts, and in the absence of a legal or authoritative ruling, I venture to suggest that one-tenth of a grain of lead per pound might be generally adopted as a maximum limit,

pending the promulgation of an official or semi-official standard. This figure is equal to approximately 14 parts per million. There seems to be no reason why the proportion of lead in tinned fish could not be kept well within such a figure and, this being about twenty times that generally regarded as dangerous for drinking water and over ten times the proportion found in cider responsible for the 1932 outbreak of lead poisoning (*Lancet*, 1932, **223**, 717), it can hardly be regarded as a stringent limit, and would only exclude definitely contaminated fish. On the other hand, the universal enforcement, at this stage, of a materially lower limit would apparently prove extremely difficult and likely to cause considerable hardship.

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ANALYSIS OF TURPENTINE LINIMENT

EVERS and Elsdon, in "The Analysis of Drugs and Chemicals," state that the turpentine and camphor in this liniment may be determined together by distilling 50 g. of the liniment with steam. In practice, it has been found difficult to control frothing, but the addition of 0·5 ml. of syrupy phosphoric acid breaks the emulsion and prevents the trouble. The distillation may then be carried out much more rapidly. Identical results are obtained by the two methods.

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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 special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF LEEDS

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1934

LABELLING OF LARD SUBSTITUTES.—An imitation vegetable substitute, prepared by hardening cotton-seed oil, was sold as lard. The shopkeeper's explanation was that all her customers knew that they were receiving, not lard, but "lardine." She was subsequently warned by the Medical Officer of Health that in future this commodity must be suitably labelled. In view of the quantity of lard substitutes now on the market, it seems most desirable that they should be required by law to be sold in wrappers distinctively labelled in letters of a specified size, so that the same distinction may be made between lard and its substitutes as is now made between butter and margarine.

FLAVOURING ESSENCES.—On account of questions asked in the House of Commons in December, 1933, regarding flavouring essences, informal samples of rum, raspberry, and lemon essences from a local store were submitted for analysis and found to contain 70, 30 and 35 per cent. of isopropyl alcohol, respectively. No excise licence is needed, and the only requirement relating to the use of isopropyl alcohol is that, according to the Isopropyl Alcohol Regulations, 1927, manufacturers and sellers must make a six-monthly return to the Excise Authorities of the quantities used. Hence, this alcohol has recently been widely used both

for perfumery and culinary flavours, with material falls in the prices of the articles. Isopropyl alcohol is stated to be safe for internal use in small doses in dilute form, and to be a solvent that might be used for making tinctures.

CAMPHORATED OIL.—A sample was found to contain 19·3 per cent. of camphor and 80·7 per cent. of olive oil, instead of the 20 per cent. of camphor required by the B.P., 1932. This sample was interesting from the fact that advantage had been taken of the permission given in the B.P., 1932, to use artificial camphor for the preparation of this liniment.

IDENTIFICATION OF FACE POWDER.—In the case of *Rex* v. *Blake*, tried at the West Riding Assizes in December, 1934, the prisoner was convicted of the murder of a woman. Certain powders were analysed in connection with the case, one of them being a face powder contained in a "Phul-Nana" powder box found in the prisoner's possession and identified as the dead woman's property by the shape of a tear on the lid. The defence having submitted that the box and powder belonged to the prisoner's wife, who stated that she had mixed some white Yardley compact with the "Phul-Nana" powder in her box, evidence was given to the effect that the white lumps in the box were not those of another face powder, but consisted of boric acid, which constituted 85 per cent. of the mixture. Neither of the face powders mentioned contains boric acid.

C. H. MANLEY

CITY OF LEICESTER

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1934

DYED SUGAR.—A sample was submitted under Sec. 17 (2) of the Food and Drugs (Adulteration) Act, 1928, because of its green appearance after wetting, especially when the wetting medium was milk. The trouble was found to be due to a film of spirit-soluble dye on the surface of the crystals.

STERILISED MILK.—The standard, adopted some years ago, of a maximum count of 1000 organisms per ml., seems fair, and most supplies comply with it. Four of 16 samples failed to reach this standard, and one had a count of 570,000 per ml.

BATH WATERS.—The following standards and system of sampling, adopted early in 1932 for indoor swimming baths, have been found workable:

Standards.—(i) The free chlorine shall not exceed 0·5 part per million.

(ii) The total number of colonies developing in 24 hours on nutrient agar at blood heat shall not exceed 1000 per ml.

(iii) *Bacillus coli* shall not be present in more than two out of five 10-ml. tubes.

System of Sampling.—Each bath is sampled the first week it is open to the public for the year. If the water fails to comply with any one of the above tests, it is sampled again weekly until a satisfactory sample is obtained. It is then sampled again after a fortnight, and, if still satisfactory, it is sampled thereafter once a month. If the first sample from a bath is satisfactory, it is sampled again after a fortnight, and thereafter monthly while it remains satisfactory. It thus follows that the number of samples required to be taken is inversely as the quality of the water; and the drop in the number of samples taken in 1934 is explained.

A large privately-owned open-air swimming pool was opened to the public in the summer just inside the City boundary at Knighton. Up-to-date filtration and chlorinating plant was installed, but, for some reason, was not put into commission. Consequently the water failed to reach the necessary bacterial standards. It is expected that this will be remedied in 1935.

SUSSEX GROUND OATS.—Three samples, taken informally under the Fertilisers and Feeding Stuffs Act, 1926, contained excessive amounts of fibrous material.

The maximum amount of fibre likely to occur in genuine Sussex ground oats is 12 per cent., whereas these three samples contained, respectively, 15·4 per cent., 15·4 per cent. and 17·3 per cent. No declaration of fibre-content is required under the Act for Sussex ground oat samples, but added husks or glumes have to be declared. It was not possible to state conclusively whether the high fibre was due to grinding very thin oats, or whether extraneous husk had been added, but the figures obtained raised a very strong presumption that the latter was the case.

SULPHUR IMPURITIES IN THE ATMOSPHERE.—The relatively simple method of the Building Research Station for measuring sulphur gases in the atmosphere was tried throughout the year and found to have many advantages. Briefly, it consists in exposing a cylinder, of known superficial area, covered with an absorbent surface of lead peroxide, to the atmosphere for a definite period, and then determining the amount of lead sulphate formed by absorption of the sulphur gases (*cf.* ANALYST, 1933, **58**, 284). The amounts of sulphur dioxide found in the atmosphere by the volumetric method developed in the Government Laboratory were as follows:—January (average), 17·0; February (foggy), 109·0; (fog clearing) 64·0; (warm, bright, clear) 15·0; May (fine, sunny), 4·0; October (average), 12·0; (night reading), 6·0; November (average), 17 parts per 100,000,000.

"SPECIAL COFFEE."—Three samples of coffee from a stall were sent in by the Chief Constable. One shilling per cup was charged for this "special" line, instead of the usual twopence. Rum was found in each sample, and the vendor was convicted for selling intoxicating liquor by retail without having a Justices' licence.

F. C. BULLOCK

Department of Scientific and Industrial Research

REPORT OF THE FOOD INVESTIGATION BOARD FOR 1934*

THE Report of the Food Investigation Board aims at presenting a concise statement of the progress of the investigations carried out during the year 1934. The results of the investigations are published in full from time to time on completion. The arrangement of the Report differs from that of previous years, the various investigations being grouped according to subject-matter instead of under the names of the laboratories concerned.

SECTION I. MEAT.—The experiments on the storing of chilled meat in air enriched with carbon dioxide have resulted in the carrying of 4400 tons of chilled beef from Australia and New Zealand during 1934. The problem of gas leakage now appears capable of practical solution, but a number of problems connected with the proper conditions of cooling, humidity and air circulation for preservation to the fullest possible extent of the natural appearance of the meat are still being investigated.

In connection with palatability of meat, methods for determining the amounts of individual proteins have advanced sufficiently to permit of such changes as denaturation being followed with some certainty. Ozone has been found to be germicidal to bacteria in concentrations of the order of 100 to 1000 parts per million, whilst the mortality of bacteria rapidly frozen in solid carbon dioxide is greatest at 0° to −5° C. Work has been carried out on the use of non-toxic anti-oxidants, *e.g.* sodium citrate, sodium malonate and glycine, in connection with the preservation of edible fats.

SECTION II. EGGS.—A preliminary study of the changes taking place when eggs are stored in air and in air enriched with carbon dioxide shows that, in order

* H.M. Stationery Office, Adastral House, Kingsway, W.C.2. 1935. Price 4s. net.

to maintain the *p*H of the white at 7·9, eggs must be stored in atmospheres containing approximately 10 per cent. of carbon dioxide at 20° C., or 3 per cent. at 0° C. The strength of the membrane enclosing the yolk is an important factor in the preservation of eggs, and the average thickness is about 64/100,000 of an inch, and in a fresh egg its bursting strength is about 0·065 lb. per sq. in. This falls on storage, and, when it is only a little over half the strength, the yolk breaks easily. The whites of eggs were found to be sterile, except those of a few imported eggs, whilst the yolks tended to be sterile or nearly so in July, but had a larger bacterial count in September.

SECTION III. PORK, BACON AND HAMS.—An investigation, in collaboration with the Cambridge School of Agriculture, has been started, of the factors affecting the quality of the pig carcase, and it has been already shown that fat sides lose slightly less weight during maturation than lean sides. A new method for determining the distribution of fat in lean meat is to measure the electrical resistance of the meat, since the resistance of the fat is several times greater than that of the lean. It has been found that by using an atmosphere of carbon dioxide at a temperature of 5° C., at least 3 weeks can be added to the storage life of mild-cured bacon.

SECTION IV. FISH.—Much work has been done in connection with the herring industries. Herrings that had been brine-frozen at the usual temperature of −5° F. made good kippers after at least 5 months' storage, and experiments under commercial conditions are being conducted. The metabolism of fats in fish has continued to receive attention. Marked specific resemblances have been found between fats of fresh-water algae and zooplankton and those of fresh-water fish, in contrast with corresponding resemblances between those from marine sources. The fats of the porpoise and dolphin have received particular attention. In the study of the transport of fish it has been found that a saving of ice may be effected by the use of vegetable parchment paper enclosing the mass of fish and ice in the box, owing to the protection afforded against currents of air.

SECTION V. FRUIT AND VEGETABLES.—Only a few of the many investigations under this heading can be mentioned. The trials of English varieties of apples in gas storage have shown that for most varieties an atmosphere containing 5 per cent. of carbon dioxide and 2·5 to 5 per cent. of oxygen is best, and a table is published showing recommended temperatures and atmospheres for 8 culinary and 6 dessert varieties. One result of the further study of the critical changes occurring at the climacteric in the apple is the identification of ethylene as the active substance that is given off by apples at this point; this substance also stimulates this change in other apples. It has been established that, prior to the development of the disease known as "low-temperature breakdown," the amino acids reach a maximum concentration in the tissues, owing to a change in the relative proportions of the components of that fraction of the nitrogenous constituents which is soluble in alcohol.

In connection with the rotting of fruit in storage it has been found that wraps treated with iodine retard the development of fungal rotting in various types of fruit without impairing the appearance or flavour, or hastening ripening (*J. Pomol.*, **1934, 12, 311**). Grapes, tomatoes and oranges all showed marked improvement, as also did certain varieties of plums and peaches, but other varieties failed to ripen properly, and some even turned brown. Papers may be soaked in a solution containing 12·7 g. of iodine, 10·0 g. of potassium iodide, 200 ml. of water, and 800 ml. of rectified spirit. At a temperature of 15° C., tomatoes in plain papers developed mould in 38 days, but those in iodised papers required 72 days. Experiments are now being carried out on a commercial scale. This method cannot be applied to the storage of prepared foods or meat.

In the study of the stored-apple diseases it has been shown that "scalding"

results from changes in the tissues occurring weeks or months before the injury is apparent, and that prevention by oiled paper wrappings is efficient chiefly during these early stages. Scald is regarded as due to an excessive accumulation of some volatile substance in the tissues.

The vitamin *C* content of apples, which is known to increase as the skin is approached from the core, has been found to vary in the red and green peel of Bramley Seedling apples. Red peel was found to be more than twice as active as regards vitamin *C* as green peel, although no difference could be found in the activities of the pulps. Storage of Bramley Seedling apples from mid-September to mid-December in pure oxygen and pure nitrogen (less than 0·5 per cent. of oxygen) in containers continuously ventilated with these gases at 1° C. had no effect on their vitamin *C* potency.

SECTION VI. CANNING.—Synthetic vitamin *C*, which is now known to be identical in chemical structure and in biological activity with the natural vitamin, added to such foods as runner beans, apples or apple jelly, remained substantially stable during the canning, and the loss was in no case greater than 25 per cent. Antiscorbutically-active products may thus be obtained equal to such natural sources of vitamin *C* as the citrus fruits.

Tests with plain and lacquered aluminium cans and the principal English fruits go to show that plain and once-lacquered cans are unsatisfactory, and that aluminium is even more dependent than tinplate on the protection the lacquer affords. Work on the diffusion of hydrogen through mild steel sheet and tinplate shows that hydrogen evolved during corrosion can diffuse comparatively rapidly through steel, and, to some extent, through tinplate. The rate of diffusion varies with different steels, and is affected by addition of substances known to accelerate or inhibit acid corrosion. The diffusing hydrogen appears to be in a specially active state, probably atomic. The changes in the setting value of the pectin in fruits during storage have been further studied, and a table is given summarising the changes for raspberries, gooseberries and apples.

SECTION VII. ENGINEERING.—The influence on the relative humidity in cold stores of the heat produced by the stored material has been studied in detail, and since heat leaking in from outside exerts similar effects, a jacketed construction has been proposed for cold stores where high relative humidities are required. A new method of cooling ships' holds, suitable for a large range of cargoes, has been suggested; it involves a two-stage system of air circulation, the air-stream passing vertically down through the cargo and returning to the cooler by way of a jacket, lining the sides, in which the heat of leakage is removed. The method is being adopted in some of the new steamers, with modifications according to the particular cargo.

D. G. H.

Alkali &c. Works

ANNUAL REPORT OF THE CHIEF INSPECTORS FOR THE YEAR 1934*

THIS is the 71st Annual Report of the Chief Inspectors under the Alkali etc. Works Regulation Act, and the Alkali etc. Works Order, 1928, to the Minister of Health, and to the Department of Health for Scotland. For the first time since 1917 there has been an increase in the number of works registered over that of the previous year. The number of works registered in 1934 was 918, involving the operation of 1759 separate processes.

A draft Order† was prepared by which it is proposed to add to the list of noxious or offensive gases:

(1) Fumes containing silicon, calcium or their compounds.

(2) Fumes from paraffin oil works containing any sulphur compound.

It is proposed, further, to extend the list of scheduled works to include "Cement Production Works" (under a new definition) and to widen the definitions of muriatic acid works (*a*), bisulphide of carbon works and paraffin oil works.

As in previous years, much of the District Inspectors' time has been occupied by visits and inquiries in connection with unregistered processes.

The number of cases in which statutory limits of acidity tolerated by the Act have been exceeded, or in which other infringements have occurred, was less than in the previous year, and no case was sufficiently serious for legal proceedings to be taken.

There is no doubt that the public is more concerned than ever about air cleanliness, as regards pollution both by smoke and by dust, as well as by offensive gases. Local authorities, too, have frequently appealed to the Ministry for advice and assistance in dealing with difficult problems.

FUMES FROM WIRE ENAMELLING.—The characteristic harshness of these fumes is probably due to acroleinic substances and hydrocarbons. Complaints have been reduced by re-designing the drying stoves and by an improved system of draughting.

POWER STATIONS.—Regular determinations have been made of the sulphur oxides content of waste gases emitted from the stacks of the Battersea Power Station. The washing plant installed at the station has operated continuously and efficiently. The acidity of the chimney gases has been satisfactorily low, and there has been an almost complete absence of smoke.

Determination of Sulphur Oxides in Chimney Gases.—The method used for the determination of sulphur oxides in the chimney gases was as follows:

A 120-ml. Dreschel wash bottle, fitted with a sintered glass septum 2 cm. in diameter, sealed to the inlet tube, was used as an absorber. Twenty ml. of 10-vol. hydrogen peroxide and 50 ml. of water were placed in the Dreschel bottle, and a similar amount retained for a blank determination. Gas was drawn from the chimney through the absorber and a meter by means of a pump at a rate of about 1½ cb. ft. per hour. (The Dreschel bottle and solution offers a resistance equivalent to 12-in. water pressure.) When about 2 cb. ft. of gas had been washed the pump was stopped, the meter read, and the solution from the washer was transferred to a titrating flask. The acidity or alkalinity of the blank was determined by titration with $N/20$ acid or alkali. The sample was then similarly titrated, the blank being used as a standard for colour.

* Report by Dr. W. A. Damon and Dr. B. Wylam, pp. 44. H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. 1935. Price 9d. net.

† The Order (Statutory Rules and Orders, 1935, No. 162) came into operation on April 1st, 1935.

By a long series of experiments it has been proved that this method is reliable. The presence of carbon dioxide has no effect on the absorption, and the oxidation of sulphurous to sulphuric acid appears to be instantaneous.

Pulverised Fuel.—The use of pulverised fuel makes the employment of dust-arrestment plant imperative if falling dust in the atmosphere is to be avoided. With a high chimney it is improbable that any inconvenience would be caused at ground level by sulphurous fumes, but a chimney, however tall, does not lessen atmospheric pollution.

ALKALI AND COPPER (WET PROCESS) WORKS.—The average escape of hydrochloric acid gas into the atmosphere has been satisfactorily low (0·069 grain HCl per cb. foot). The question of the 95 per cent. condensation figure required by the Act was discussed in the 68th Report. Since then manufacturers have been asked to make returns of salt used and acid produced, and efficiencies have been calculated from those figures. These show considerable variation. It is realised, of course, that a figure based on such data is not necessarily the same as a condensation figure, because there may have been leakages and other losses of condensed acid; nevertheless, it is a useful figure on which to base comparisons.

The moisture and purity of the salt used vary at different works, as also does the proportion of undecomposed chloride in the salt-cake. Taking a round figure of 90 per cent. for the sodium chloride-content of the salt and ignoring that in the salt-cake, the average efficiency for all salt-cake processes works out at 94·1 per cent. Individual results vary from 83·5 per cent. to 104·6 per cent., showing that there is room for much improvement at some works.

FUMES FROM A COPPER REFINERY.—In the investigation of a complaint, the method of estimating atmospheric pollution devised by the Building Research Station has been used (*cf.* ANALYST, 1933, **58**, 284). The results up to date are somewhat inconclusive, but they certainly have afforded no definite evidence that the locality from which many complaints emanated is suffering from the fumes.

SULPHURIC ACID WORKS.—The production of sulphuric acid in England and Wales during 1934 was 730,000 tons—an increase of 81,500 tons compared with the production in 1933.

Determination of Total Acidity of Chamber-Plant Escapes.—The method of testing hitherto employed by District Inspectors is unsatisfactory, since it does not include all the acidity due to the oxides of nitrogen. The following modified test (described in Appendix V) has therefore been devised, and, should it prove satisfactory in practice, it is proposed to adopt it as the official method. Section 6 (1) of the Act distinctly provides that "the acid gases of sulphur or of sulphur and nitrogen . . . shall not exceed the equivalent of 4 grains of sulphuric anhydride."

A Winchester quart of known capacity is fitted with an aspirator attachment consisting of an inlet and outlet tube of glass tubing, 1 cm. in diameter. The bottle is dried by means of alcohol and ether, and a sealed tube containing 10 ml. of 10-vol. hydrogen peroxide is placed in it. The inlet-tube, *i.e.* the one reaching to the bottom of the bottle, is connected with the sampling tube, and the outlet with a Fletcher's bellows. Four aspirations are made to ensure replacement of air in the bottle by exit gas, and the inlet and outlet are then closed by clips and disconnected. The bottle is shaken to break the tube of peroxide and to wet the walls. It is allowed to lie on its side for 20 minutes with occasional shaking, and the contents are then washed out into a basin. Ten ml. of $N/10$ caustic soda are added, and the excess is determined by back-titration with $N/10$ acid, methyl red being used as indicator.

Should there be any sign of entrained acid in the exit gases, the inlet-tube should be fitted with a plug of glass wool. This may be washed and the washings titrated separately, one-fourth of the acidity being added to the figure obtained for acidity of the gas contained in the bottle.

Such tests as have already been made indicate that a normal escape of from 1 to 2 grains of sulphur dioxide is usually accompanied by 0·5 to 1 grain of oxides of nitrogen (expressed as NO_2). It will be found that this amount of escape corresponds roughly with a nitre-consumption figure of 3 lbs. $NaNO_3$ per 100 lbs. of sulphur burned, so that there are some grounds for thinking that the loss of nitre viâ the exit very nearly balances that supplied (as make-up) to the plant.

Manufacturers would do well to introduce the modified method of testing at their works, either instead of, or in addition to, the ordinary quick test. Not only does it give a truer estimate of acidity, but it also affords an indication of the loss of nitre.

Sulphuric Acid as a Spray for Cereal Crops.—The use of sulphuric acid for spraying cereal crops to kill charlock and other annual weeds has been extended; the sales of acid for this purpose have been quadrupled, compared with those of the previous year.

CHLORINE.—The use of chlorine in industry is expanding, and a number of new works have been registered.

The application of chlorine for the purpose of slowing down the rate of decomposition has lately been practised at a certain sewage works. The chlorine cylinders are housed in structures which are situated in the public road, but they are protected against impact by steel barriers. It is understood that the process is experimental, and that, if successful, the cylinders will be housed in underground structures.

To avoid corrosion of chlorine feed-pipes in the manufacture of calcium hypochlorite, various materials have been tried. Of these, tellurium lead (*cf.* ANALYST, **1933, 58**, 367) has offered the greatest promise, but most manufacturers still prefer to use pipes of mild steel or wrought iron and to renew them frequently.

CARBON DISULPHIDE WORKS.—Recovery from the sodium methyl xanthate is practised at only a few works. Some difficulty has been experienced in disposal of the recovered material, and fears are entertained lest the excessively foul gases liberated in the process may occasion trouble.

An investigation (detailed in Appendix IV) indicates that an alkaline xanthate on storage breaks down to sulphide and carbonate. On acidification, therefore, the quantity of hydrogen sulphide liberated increases with the age of the xanthate, while the recoverable carbon disulphide decreases. A neutral xanthate is more stable, but exhibits a tendency towards production of the even more objectionable mercaptans. Clearly, every precaution should be taken to deal with gaseous emissions from this process. There is no insuperable difficulty in doing so, as has been demonstrated at two works where the process has been operated without any offence during the past year.

Milk Act, 1934

[24 & 25 GEO. 5, CH. 51]*

AN Act to provide for temporarily securing to producers of milk, by means of payments out of moneys provided by Parliament, a minimum return in respect of milk used in the manufacture of milk products; for conditionally requiring repayment to the Exchequer of the amount of such payments; for making, out of moneys so provided, payments for the purposes of improving the quality of the milk supply and increasing the demand for milk; for regulating the manner in which milk is described for the purposes of advertisement and sale; for imposing and conferring certain duties and powers on boards administering milk marketing schemes; and for purposes connected with the matters aforesaid. [31st July, 1934.]

The arrangement of the sections of the Act is as follows:

Section 10 provides that the following section shall have effect in substitution of sec. 3 of the Milk and Dairies (Amendment) Act, 1922:

"3.—(1) The Minister of Health, after consultation with the Minister of Agriculture and Fisheries, may by order—

(*a*) prescribe, in relation to milk of any description, such designation (hereinafter referred to as a 'special designation') as he considers appropriate; and

(*b*) as respects any special designation, provide for the granting by the Minister of Health or local authorities of licences (hereinafter referred to as 'milk licences') authorising the use of that special designation; and

(*c*) prescribe the periods for which, and the conditions (including conditions as to the payment of fees) subject to which, milk licences in general or milk licences of any particular class are to be granted;

(*d*) provide for the revocation or suspension of a milk licence in the event of a breach of any condition subject to which the licence was granted; and

(*e*) provide for entitling any person aggrieved by the refusal, suspension or revocation of a milk licence by a local authority to appeal to the Minister of Health; and

* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 4d. net.

(*f*) provide for such matters as are necessary for giving effect to, or are incidental to, or consequential on, any provisions contained in the order by virtue of the foregoing provisions of this subsection.

"(2) No person shall, for the purpose of the sale or advertisement of any milk—

(*a*) use a special designation in any manner calculated to suggest that it refers to that milk, unless there is in force a milk licence authorising the use of that designation in connection with that milk; or

(*b*) refer to that milk by any such description, not being a special designation, as is calculated falsely to suggest either that the cows from which the milk is derived are free from the infection of tuberculosis or of any other disease, or that the milk is tested, approved or graded by any competent person.

"(3) In any proceedings taken by virtue of paragraph (*b*) of the last foregoing subsection it shall lie on the defendant to prove the truth of any suggestion which, in the opinion of the court, his acts or conduct as proved by the prosecution are or is calculated to convey."

(2) Section 14 of the Milk and Dairies (Amendment) Act, 1922 (which provides that, in the application of that Act to Scotland, references to the Department of Health for Scotland shall be substituted in the Act for references to the Minister of Health) shall have effect as if at the end of paragraph (*a*) of that section there were inserted the words "and the Department of Agriculture for Scotland shall be substituted for the Minister of Agriculture and Fisheries."

(3) Any order under sec. 3 of the Milk and Dairies (Amendment) Act, 1922, which is in force immediately before the commencement of this Act shall continue in force until revoked.

Statutory Rules and Orders

1934, No. 1317*

MILK AND DAIRIES, ENGLAND

THE MILK (SPECIAL DESIGNATIONS) ORDER, 1934, DATED NOVEMBER 28, 1934, MADE BY THE MINISTER OF HEALTH UNDER SEC. 3 OF THE MILK AND DAIRIES (AMENDMENT) ACT, 1922 (12 & 13 GEO. 5, C. 54).

The Minister of Health after consultation with the Minister of Agriculture and Fisheries in exercise of the powers conferred on him by sec. 3 of the Milk and Dairies (Amendment) Act, 1922, as enacted in sec. 10 of the Milk Act, 1934 (*a*), and of any other powers enabling him in that behalf hereby orders as follows:

1. This Order may be cited as the Milk (Special Designations) Order, 1934, and shall come into operation on the date hereof.

2. In this Order "the Minister" means the Minister of Health.

3. The special designations which may be used in relation to milk under a licence granted by the Minister are "Certified" and "Grade A (Tuberculin Tested)".

4. The Minister may grant licences to producers to use the special designations "Certified" and "Grade A (Tuberculin Tested)" in relation to milk.

5. This Order shall have effect as if the following Articles and Schedules of the Milk (Special Designations) Order, 1923(*b*), were with any necessary modifications incorporated herewith, that is to say, Articles 2, 5, 6, 7, 8, 9(1) and 12 and the First Schedule (Form A), the Second Schedule, the Third Schedule, Part I, Part II, Part IIIA(7) and C(2) and the Fourth Schedule.

6. Any licence heretofore issued by the Minister on or after the fifteenth day of August nineteen hundred and thirty-four authorising the sale of milk as "Certified" or "Grade A (Tuberculin Tested)" shall if the period for which the licence was issued has not expired on the date of this Order be deemed to have been granted under this Order and shall for the remainder of such period have effect as if it were a licence granted under the appropriate provisions of this Order.

(*a*) 24–5 G. 5, c. 51. (*b*) S.R. & O. 1923 (No. 601), p. 564.

* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 1d. net.

Fruit and Vegetable Preservation Research Station, Campden

ANNUAL REPORT, 1933–1934*

IN 1930 the canning industry became more intimately associated with the management of the Station, and, as a result of the financial support received from commercial firms, the scope of the work has increased year by year. The Report reviews the progress that has been made during the last four years. The Station now possesses chemical, biochemical, physical and bacteriological laboratories, and experimental rooms fitted with machinery for canning fruit and vegetables and milk products on a moderately large scale. Experimental and research work on problems in connection with the canning of food products has been continuously carried out, and the results have been published in various bulletins. An account of some of the important lines of research work is given in the present report, with brief notes on results obtained in various investigations.

HYDROGEN SWELLS.—A second bulletin incorporating certain fundamental features is to be published shortly. It deals *inter alia* with the influence of the tinplate, effects produced by the can-making process, by the raw products, and by the canning processes, and chemical studies of corrosion effects in tins.

The chemical composition of the base plate, particularly in respect of the presence of small amounts of other metals, appears to be of extreme importance. This has led to the testing of cans made from a new type of tinplate, known as strip-plate, in which the less desirable elements are present in smaller quantities.

LACQUER TESTS.—Very satisfactory results have recently been obtained with new lacquers, and in the latest experiments lacquer surfaces have remained intact and purple fruits free from discoloration after 5 months' storage at 95° F.

CANE AND BEET SUGAR.—As many canners were decidedly prejudiced against the use of beet sugar, comparative tests with syrups containing beet and cane sugar were made. These showed conclusively that beet was as satisfactory as cane sugar from every point of view, and at present British beet sugar is probably more extensively used than the imported cane sugar.

RIPENING OF PEAS.—An investigation is in progress to ascertain the tendency of each variety of peas to ripen at a fast or slow rate. The ripening of the crop as a whole and the stages of ripening of pods of the same maturity are both being studied.

INFLUENCE OF SOIL ON COLOUR OF VEGETABLES.—Beetroots and carrots have been grown under similar conditions in the Campden area. The colour of the canned products is being determined by means of the tintometer, and an attempt will be made to correlate the results with the chemical and physical properties of the soils.

CHANGES IN HYDROGEN-ION CONCENTRATION IN SYRUPS.—The results obtained in an investigation are summarised in the following table. In each case

* Published by the University of Bristol. Pp. 85. Introduction by F. Hirst, M.Sc. (*Director*), and contributions by W. B. Adam, M.A., A.I.C., G. Horner, M.Sc., R. Hull, B.Sc., and G. Stanworth.

12 ounces of fruit were packed in A2 cans, the filling temperature being 170° F., the exhaust 6 minutes at 180° F., and the sterilising time the normal period of stationary cooking for each class of fruit.

	End of exhaust	Mid-cook	End of cook	1 hr. cool	1 day's storage	5 days' storage
Gooseberries ..	3·36	3·14	2·93	2·85	2·82	2·82
Strawberries ..	—	3·84	3·63	3·60	3·55	3·55
Raspberries ..	4·25	3·70	3·43	3·34	3·10	3·10
Loganberries ..	3·42	2·90	2·72	2·70	2·70	2·70
Blackcurrants ..	3·86	3·48	3·24	3·18	3·16	3·16
Cherries (sweet) ..	—	5·83	4·33	3·99	3·72	3·70
Pershore plums ..	5·96	3·03	3·00	2·94	2·90	2·87
Victoria plums ..	5·48	3·12	3·08	3·02	2·97	2·95
Damsons ..	3·55	3·05	2·98	2·94	2·93	2·93
Blackberries ..	3·44	2·98	2·86	2·84	2·84	2·83
Bilberries ..	3·56	3·15	3·10	3·02	3·00	3·00

By the end of the full cooking period nearly all the syrups were very close to the constant *p*H value; exceptions were noted for raspberries and cherries, with which the diffusion process was rather slow. The *p*H value appears to be virtually stable in nearly all cases within 1 to 2 days after canning.

CHANGES IN ACIDITY.—The following table shows the rate of diffusion of acid into syrup of various fruits:

	Acidity expressed as per cent. citric acid				
	Mid-cook	End of cook	1 hr. cool	1 day's storage	5 days' storage
Gooseberries	0·23	0·49	0·70	1·15	1·15
Strawberries	0·13	0·20	0·29	0·33	0·41
Raspberries	0·08	0·10	0·22	0·60	0·63
Loganberries	0·36	0·52	0·85	1·48	1·62
Blackcurrants ..	0·48	0·66	0·78	0·95	1·30
Cherries (sweet) ..	0·02	0·03	0·03	0·09	0·18
Pershore plums ..	0·20	0·29	0·52	1·01	1·17
Victoria plums ..	0·28	0·33	0·55	0·86	0·90
Damsons	0·35	0·52	0·88	1·48	1·83
Bilberries	0·22	0·28	0·32	0·43	0·57

The rise in acidity of the syrup corresponds very closely with the fall in density, stability being reached most rapidly with most soft berries, and more slowly with stone fruits and currants.

INVERSION OF SUGARS.—After short stationary cooking periods the extent of inversion immediately after canning and cooling ranged from 2 per cent. for cherries to 20 per cent. for blackcurrants. Long stationary cooking periods gave about twice these figures. The percentages increased considerably during the next few days (10 to 15 per cent. for cherries and strawberries to 35 per cent. for blackcurrants). Subsequent conversion of sucrose into invert sugar goes on slowly during storage. A very high percentage of invert to total sugars in a can is usually a sign of excessive heating during processing, or of a high temperature or long period of storage. The following table shows results of tests on the rate of inversion of canned fruits stored at normal temperatures:

Inversion expressed as per cent. of total sugars

	*p*H	4 months' storage	6 months' storage	8 months' storage
Gooseberries	2·72	61·8	67·3	—
Raspberries	3·35	24·5	24·7	26·1
Loganberries	2·88	45·5	49·6	—
Cherries (sweet) ..	4·00	27·9	27·9	28·0
Blackcurrants ..	3·17	39·5	46·1	4·80
Greengages	3·08	32·1	33·8	38·5
Pershore plums ..	2·80	37·0	38·2	46·8
Victoria plums ..	2·88	35·7	38·9	47·2
Damsons	2·93	39·5	53·1	62·6
Blackberries	2·95	36·3	43·0	46·0

TEXTURE OF CANNED FRUITS AND VEGETABLES.—An apparatus for measuring the toughness of fruits and vegetables has been designed, and is described in the report. It has been found that different parts of the skins of fruit are of different toughness. Hard water used in preparing the syrup or brine does not appreciably toughen the skins of fruits or most fresh vegetables, but the toughness of the skins of fruits increases with the strength of the sugar syrup used.

GASES IN CANNED FOODS.—A description is given of an apparatus designed for the collection of the headspace gases from canned fruits and vegetables. The composition of the gases immediately after canning depends largely upon the relation between the size of can, fill and headspace. When the headspace is large, the proportion of entrapped air is high and the percentage of carbon dioxide low. The ratio of oxygen to nitrogen can never have a value as high as that for air (0·264), as the gas from the tissues of the fruit contains only traces of oxygen as against considerable amounts of nitrogen.

The changes that take place in the headspace of canned fruits are due largely to some corrosive process. The oxygen-content usually decreases to zero before any appreciable amount of hydrogen is evolved. When the oxygen has almost disappeared, therefore, the headspace contains only carbon dioxide and nitrogen, and the vacuum is usually perceptibly higher than when the cans were first packed. These changes are illustrated by a series of tables. The results show that the oxygen is removed from the can by about 7 to 10 days' storage in plain cans and 4 to 6 weeks in lacquered cans, whilst, in the earliest stages of hydrogen development, the rate of corrosion, as measured by the gas changes, is greater in plain cans. It is well known, however, that lacquered cans give much greater losses from hydrogen swells than plain cans, and, therefore, at some period of storage the rate of development in lacquered cans must show an increase.

SPOILAGE OF PROCESSED FRUIT BY *Byssochlamys fulva*.—An investigation made with the object of determining the possibility of factory control led to the following conclusions:—A small percentage germination of ascospores took place slowly at 65° C. At 70° to 80° C. the rate of germination and percentage germination were stimulated; above this maximum, heating retarded germination and killed the ascospores. Increase of time of heating at 65° to 70° C. had a stimulating effect, but increase of time of heating at 75° C., 80° C. and 85° C. led to decreased rate of germination and percentage germination.

MEASUREMENT OF VACUUM IN SEALED CANS.—Two methods of measuring the vacuum were investigated, *viz.* the "flip" method and a method based on the depression of the ends of the cans, the standard surface from which the readings were taken being the flat portion of the countersink. It was found that the movements of the ends—up to a vacuum in the region of 15 inches—bore a definite relationship to the vacuum within the can. Above that vacuum the ends become permanently strained inwards. Experiments on the effect of vacuum on the volume of the can are recorded.

U.S.A. Department of Commerce

NATIONAL BUREAU OF STANDARDS

IRON GALLATE INKS—LIQUID AND POWDER*

In view of complaints by the U.S. Post Office Department of excessive corrosion of steel pens caused by the ink used in their stations, a general study of writing inks has been undertaken in an attempt to prepare one that would be less corrosive than the standard ink, and which could also be prepared in the form of a powder and still comply with the requirements of the specification (Federal Specification TT–I–563, Ink; Writing).

The standard writing ink contains 3 g. of iron per l., and this proportion was used in all the experimental work. The characteristics of the inks were tested by the Specification methods, and an attempt was made to evaluate the stability in terms of the number of days required for sediment to appear. Although the results for individual inks were not strictly reproducible, they always placed the inks in the same order of stability.

Since gallic acid inks are known to be more stable than inks made from tannic acid, preparations containing increasing amounts of gallic acid and decreasing amounts of tannic acid were tested, and the following results were obtained:

	Composition of ink in g. per litre						
	Tannic acid	Gallic acid	Ferrous sulphate, $FeSO_4.7H_2O$	Ferric sulphate, anhydrous	Oxalic acid	Tartaric acid	Stability as approx. days for sediment to form
1* ..	11·7	3·8	15	—	—	2·6	5
2 ..	8·4	7·7	15	—	—	2·6	5
3 ..	—	10	15	—	—	2·6	10
4 ..	11·7	3·8	—	10·7	2·16	—	7
5 ..	8·4	7·7	—	10·7	2·16	—	35
6 ..	—	10	—	10·7	2·16	—	42†

* Standard ink is similar to this, excepting that 12·5 g. of U.S.P. hydrochloric acid is substituted for tartaric acid, and 3·5 g. of dye and 1 g. of phenol are added.

† Test stopped before sediment appeared.

Rupert (*Ind. Eng. Chem.*, 1923, **15**, 489; Abst., ANALYST, 1923, **48**, 459) found that inks containing gallic acid without tannic acid were not very permanent when exposed to atmospheric conditions. In the present experiments, however, stripes of the inks were exposed for 150 hours in a Fade-ometer, and the two types of ink were equally permanent.

In comparative experiments with inks respectively containing Walther's patent ferric chlorosulphate hexahydrate (*Chem.-Ztg.*, 1921, **45**, 842), ferric chloride and ferric sulphate, no marked differences were observed in keeping qualities or corrosive action, but ink powder prepared with ferric chlorosulphate began to cake after 2 months' exposure to an atmosphere with 50 per cent. relative humidity, whereas powders containing the other two salts remained loose.

Inks stabilised with tartaric, citric or succinic acid kept as well as the standard ink. In Walther's formulae inks made with ferric chlorosulphate require to be stabilised with oxalic acid. The amount of hydrochloric acid in the Specification standard ink is chemically equivalent to 2·16 g. of crystallised oxalic acid or 2·58 g.

* Research Paper R.P. 807, by E. W. Zimmerman, July, 1935.

of tartaric acid, and these acids are suitable for stabilising ink powders. Oxalic acid is an effective stabilising agent for inks made with ferric salts, because it also retards the corrosion of pens by forming a protective film of ferrous oxalate upon them. The corrosion decreases with increase in the concentration of oxalic acid. On the other hand, oxalic acid has been shown to have a deleterious effect upon the ageing of paper (*J. Research National Bureau of Standards*, 1935, **14**, 463; RP 779), and this type of ink is therefore unfit for use in making permanent records.

The following formulae were worked out for ink, in liquid or powder form, from the data obtained in these experiments:

	Ink		
	No. 16	No. 17	No. 18
	g.	g.	g.
Gallic acid	10·0	10·0	10·0
Ferric sulphate, anhydrous	10·7	—	—
Ferrous sulphate, $FeSO_4.7H_2O$	—	15·0	15·0
Oxalic acid	2·0	—	—
Tartaric acid	—	1·0	—
Sulphuric acid, as anhydrous H_2SO_4	—	—	0·654
Soluble blue (C.I. 707)	3·5	3·5	3·5
Water to make	1 litre	1 litre	1 litre

Ink No. 16 and 17 can be prepared as powders which, when dissolved in the proper amount of water, will make inks that comply with the Federal Specification requirements. Ink No. 18 cannot be prepared in powder form. To make 1 gallon (U.S.A.)* of ink, the figures given must be multiplied by 3·79. All the inks are more stable and less corrosive to pens than the standard ink. Ink No. 17 is less stable than the other two, and it contains oxalic acid, which attacks paper and tends to form a crust on steel pens.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Ammonium Salts as an Indication of the Quality of Milk. A. I. Burstein and F. S. Frum. (*Z. Unters. Lebensm.*, 1935, **69**, 421–431.)—The methods of Tillmans, Splittberger and Riffart (Abst., ANALYST, 1914, **39**, 173) and of Grünhut (*Z. Unters. Nahr. Genussm.*, 1919, **37**, 304) are tedious and complicated, and the authors have therefore used Folin's rapid method (*Chem.-Ztg.*, 1924, **48**, 557) in this investigation. Three g. of sodium permutit are placed in a 200-ml. graduated flask and washed by decantation first with a little 2 per cent. acetic acid and then two or three times with water. Fifty ml. of milk are added and shaken well with the permutit for several minutes, and, after the permutit has settled out completely, the milk is decanted and replaced by water, the shaking and decantation being repeated with additional quantities of water until the decanted liquid is quite clear. Ten to 20 ml. of water are added to

* The U.S. gallon = 0·833 imperial gallon.

the permutit and 5 ml. of 10 per cent. sodium hydroxide solution, to liberate ammonia from the ammonium permutit, the flask is then nearly filled with water, 5 ml. of Nessler's reagent are added, and the volume is made up to 200 ml. A standard comparison solution is prepared in the same manner, 1 ml. of an ammonium sulphate or ammonium chloride solution corresponding with 0·1 mg. of ammonia being used instead of the milk (3·8792 g. of ammonium sulphate or 3·147 g. ammonium chloride per l., the working solution being prepared from this by ten-fold dilution). The solution prepared from the milk is compared colorimetrically with the standard solution. The water and acetic acid used must be freed from ammonium salts by treatment with permutit. The determination takes from 30 to 40 minutes, and the authors have established by experiment that no material amount of ammonium compounds remains in the milk.

A series of determinations showed that the concentration of ammonia in quite fresh milk (30 to 40 minutes after milking) is 0·10 to 0·12 mg. per 100 ml., thus contradicting statements in the literature that fresh milk contains no ammonium compounds. The dependence of the concentration of ammonia upon the time and temperature of storage of milk was investigated. Milk stored in the laboratory at 10 to 12° C. gave on the first day an acidity (Thörner scale) of 16·42, and an ammonia-content of 0·184 mg. per 100 ml. On the sixth day the acidity was 39·61, and the ammonia-content 0·575. The intermediate values, when plotted on graph paper, form curves which are approximately parallel. With milk stored at 18 to 20° C. the acidity rose from 21·25 initially to 113·99 on the fourth day, the initial and final concentrations of ammonia being 0·180 and 0·470 mg. per 100 ml. In this instance the acidity curve indicates a sharp rise to the curdling point on the second day, the ammonia curve showing a similar, but relatively smaller rise. The curves are again similar in shape. Milk kept at 2 to 3° C. showed very little change in acidity in 4 days, but the ammonia concentration rose from 0·156 to 0·308 mg. per 100 ml. These results are in accordance with the known temperature limits of the activities of the bacteria causing the souring of milk. At the higher temperatures the lactic acid bacteria are most active, whilst at lower temperatures the proteolytic bacteria develop. As might be expected, the concentration of ammonium salts rises more rapidly in unclean than in clean milk. The addition of sodium carbonate as a preservative (1 mg. per ml.) tends to cause a slight increase in the rate of formation of ammonium compounds. Alteration of the *p*H value towards the basic side favours the development of proteolytic bacteria.

On the basis of these results the authors suggest the division of milk samples into 3 classes: (*a*) Milk of the best quality, 0·10–0·12 mg. of ammonia per 100 ml.; (*b*) milk of medium quality, 0·15–0·18 mg. per 100 ml.; (*c*) milk admissible for immediate use, 0·22–0·23 mg. per 100 ml. A. O. J.

Detection of Coal-tar Colours in Hens' Eggs. J. Grossfeld and H. R. Kanitz. (*Z. Unters. Lebensm.*, 1935, **69**, 582–584; *cf.* ANALYST, 1935, 253.)—An emulsion sold as "Regina red" for adding to poultry food in order to colour the yolks of the eggs obtained, is found to contain a colouring matter of the Soudan class. The dye does not find its way into the egg immediately, but after the

material had been employed for some time the dye could be detected in 17 of 20 yolks examined. For testing, the separated yolk is mixed thoroughly with a mixture of 10 ml. of 95 per cent. alcohol and 30 ml. of ether, and the extract is filtered off. About 5 ml. of the filtrate are treated, in a test-tube, with 1 ml. of 5 per cent. sodium nitrite solution and a few drops of hydrochloric acid, and vigorously shaken. The nitrous acid bleaches the natural colouring matters of the yolk and the Soudan dyestuff is shown by its bright red colour, which persists unchanged even after 24 hours.

Another procedure consists in extracting two yolks with the above alcohol-ether mixture, evaporating the solvent from the extract, saponifying the residue with alcoholic potassium hydroxide, adding water, and shaking with petroleum spirit. The natural yellow colouring matters in the petroleum spirit extract are then destroyed by nitrous acid, a pink colour appearing. After the solvent has been evaporated, the residue is taken up in 5 ml. of hot alcohol, and the solution is cooled in ice. Most of the cholesterol is thus separated, and, after removal of this by filtration, the red alcoholic solution is poured into 75 ml. of water acidified with tartaric acid. The cholesterol still present, together with part of the artificial colouring matter, is thrown out, and the remaining solution slowly imparts a pink colour to woollen yarn immersed in it. In alcohol-ether extracts prepared as above from the natural colouring matters, capsanthin, carotene, and bixin, these are almost completely decolorised by nitrous acid. T. H. P.

Decomposition and Preservation of Eggs. A. Tanke and L. Jirak. (*Z. Unters. Lebensm.*, 1935, **69**, 434–452.)—During the storage of eggs two different processes affecting their quality take place, *viz.* loss of water from the white and exchange of material between yolk and white. These result in a decrease in the refractive index of the yolk and an increase in that of the white. Since, in fresh eggs, the yolk has a distinctly higher refractive index than the white, these changes cause a decrease in the difference between the two refractive indices. If n_D^D is the refractive index of the yolk and n_D^K that of the white (both determined with sodium light) the expression 1000 (n_D^D–n_D^K) is termed the "quality number" (*Wertzahl*) of the egg, and is denoted by WZ. The minimum value of the refractive index of the yolk of fresh eggs is 1·420 at 17·5° C. The expression 1000 (1·420–n_D^D) is termed the "age number" (*Älterungzahl*), and is denoted by AZ. Negative values of AZ are recorded as zero. The procedure for the determination of these values is as follows:—The egg, after examination by transmitted light to detect infection, is broken, and the white is separated from the yolk. The white is homogenised by drawing it up several times into a pipette having a fine orifice. A drop is then placed between the prisms of a refractometer (the Abbé type is recommended), and the observation is made at room temperature. A specimen of the yolk, taken by piercing the yolk-sac by means of a finely-drawn-out glass tube, is mixed well and homogenised, and the refractive index is determined. The following minimum values for the refractive index of fresh yolk are given:

Temperature	15° C.	16° C.	17·5° C.	18° C.	20° C.	22° C.	24° C.	26° C.
$(n_D)^D$	1·4204	1·4203	1·4200	1·4199	1·4195	1·4190	1·4185	1·4182

These may be used in the determination of AZ at room temperature.

The value of WZ for fresh eggs should be at least 55 and the value of AZ should not exceed 5. By this method the authors investigated the effects of different methods of storing eggs upon their quality. The decisive factors which determine the degree of freshness of an egg are the amount of internal evaporation, the extent to which exchange of material between yolk and white has taken place, and the degree of contamination by micro-organisms. For the cleansing of the outer surface a sodium hypochlorite solution (10 mg. active chlorine per l.) proved the best, but it is difficult to attain complete sterilisation when contamination has penetrated to the inner shell membrane.

Moist preservation completely prevents evaporation from the interior, but there is slight penetration of the aqueous solution into the interior of the egg, and this may cause rupture of the yolk-sac, impairing of the taste, and, in water-glass preservation, discolouring of the albumen. The complete elimination of these undesirable effects by first impregnating the shell with vaseline or paraffin preparations is apparently not attainable. Bacterial infection causes very little loss with these methods, but the ageing process (represented by the AZ value) is scarcely retarded. Lowering the temperature of the store room certainly retards the ageing process, and thus "cold-storage" eggs have the lowest AZ values. Eggs stored at +1° C. showed by the refractometric method values just as good as those stored at about 14° C. for only 40 days. It is suggested that the main disadvantage of cold storage, *viz.* absorption of odour from the filling material in the boxes, could be removed by substituting steel springs for the packing material. A diminution of the internal evaporation by closing the pores in the shell can be effected in various ways. For large-scale operations liquid paraffin alone, or as a solvent for other preparations, is most suitable when mechanical appliances are used to rotate the eggs during spraying. Aqueous preparations, such as thin emulsions, do not spread evenly, and are of use in spraying processes only if the egg is previously coated with a film of such preparations as Tylose or Colloresin. These methods reduce internal evaporation and bacterial infection, but have no marked effect upon the AZ value, unless cold storage is simultaneously adopted. Paste-forming emulsions applied by smearing give good results; losses due to evaporation and infection are diminished, changes due to age are markedly retarded, and no foreign matter is introduced into the interior of the egg. This method has the additional advantage of requiring no special apparatus. A. O. J.

Detection of Rye and Wheat Flour in Mixtures by the Trifructosan-content. H. Werner and H. Volger. (*Z. Unters. Lebensm.*, 1935, **69**, 555–562.) —The method described by Strohecker (*ibid.*, 1932, **63**, 514) for determining rye meal in flour or baked wares depends on determination of the trifructosan found in rye by Tillmans and his co-workers. The modified form of this method used by the present authors is as follows:—Ten g. of the flour are mixed to a uniform paste with 100 ml. of water and then treated with 5 ml. of dialysed colloidal ferric hydroxide solution (to precipitate the proteins), and filtered after 10 minutes through a pleated filter into a 100-ml. measuring cylinder. Of the filtrate, 25 ml. are made up to 90 ml. with 96 per cent. alcohol and, after 10 minutes, filtered into a 50-ml. cylinder. To 45 ml. of the filtrate are added 5 ml. of alcoholic 0·5 *N*

potassium hydroxide, the mixture being left for 30 minutes, and then filtered through an Allihn tube and the precipitate washed with two 5-ml. quantities of 96 per cent. alcohol. The precipitate is next dissolved in 20 ml. of hot water, and the solution is collected in a test-tube, inverted by heating with 1 ml. of hydrochloric acid (sp.gr. 1·19), neutralised, and washed with a little water into a beaker. The solution is then boiled for 2 minutes with an equal volume of Fehling solution and the cuprous oxide collected and weighed as cupric oxide in the usual way. If a is the weight of CuO, and w the percentage of dry matter in the flour, the amount of cupric oxide corresponding with 1 g. of dry substance is given by $100a/1{\cdot}19w$.

For a number (17) of wheaten flours the values thus obtained varied from 25 to 33 mg., and for 19 commercial flours from 19 to 35 mg., the mean being 27 mg. Of 18 rye meals, purchased retail, one gave the figure 59 and the rest values ranging from 75 to 111; 32 per cent. lay between 91 and 100 and 23 per cent. between 101 and 110. From the trifructosan-content, it is, therefore, not possible to determine the proportions of rye and wheat meal in a mixed flour. Loss of trifructosan occurs during baking, and the method is inapplicable to bread, etc.

T. H. P.

Occurrence of Acetaldehyde in Tropical Fruits. A. Steinmann. (*Z. Unters. Lebensm.*, 1935, **69**, 479–481.)—In applying Griebel's method (Abst., ANALYST, 1924, **49**, 486) the period of cooling should be extended to 45 minutes before the crystallisation test can be regarded as negative. In most instances Griebel's observation, that acetaldehyde generally occurs in fruits which have a sharp, sour taste when unripe, the sourness disappearing as the fruit ripens, has been confirmed. Negative results were obtained with fruits of the N.O. *Palmae* and *Zingiberaceae*, in which there is no transition from sour to sweet taste, also with *Dialium indicum* (*Leguminoseae*), which retains a sour taste when ripe, with the *Leguminoseae* in general and with the *Cucurbitaceae*. It is remarkable that all the representatives of the *Solanaceae* investigated gave either a negative or only a faintly positive reaction. Certain fruits, *Lansium domesticum* (*Meliaceae*), *Spondias dulcis* (*Anacardiaceae*), *Persea gratissima* (*Lauraceae*), and some others gave a negative result in the unripe state and a positive reaction when ripe. Here, probably, acetaldehyde does not occur until the fruit is ripe. With other fruits: *Areca catechu* (*Palmae*), *Nicolaia* (*Zingiberaceae*), *Artocarpus communis* (*Moraceae*), in the cocoa bean, and in the husk of *Garcinia mangostana* (*Guttiferae*), it was observed that, instead of crystals, yellow droplets were formed, which on standing for a long time gave place to thick yellow crystals of the hydrazone. Probably in these instances other volatile substances which hinder the formation of crystals occur in the reaction mixture.

A. O. J.

Determination of Acetaldehyde in Wines and Spirits. P. Jaulmes and P. Espezel. (*Ann. Falsif.*, 1935, **28**, 325–335.)—The influence of varying conditions on the various stages involved in the determination of acetaldehyde in wine and spirit by the bisulphite and iodine method has been studied. The method evolved from the results obtained is a direct iodimetric method, and comprises three stages: combination in a neutral medium of the aldehyde with

sodium bisulphite (in excess), oxidation in an acid medium (*p*H below 2) of the excess of sulphite by iodine solution (either standard or not), and titration with standard iodine in an alkaline medium (*p*H 9·5) of the sodium sulphite formed by the dissociation of the aldehyde-sulphite compound. The reagents required are: (1) 0·1 *N* iodine solution; 1 ml. ≡ 2·2 mg. of acetaldehyde; (2) dry neutral sodium sulphite 18·9 g., *N* sulphuric acid 150 ml., water to 1000 ml.; (3) KH_2PO_4 3·35 g., $Na_2HPO_4.12H_2O$ 15 g., water to 1000 ml., or $Na_2HPO_4.12H_2O$ 24 g., *N* H_2SO_4 25 ml., water to 1000 ml.; (4) hydrochloric acid of 22° Baumé [sp.gr. 1·18] 250 ml., water to 1000 ml.; (5) boric acid 17·5 g., *N* sodium hydroxide 800 ml., water to 2000 ml.; (6) freshly made 0·2 per cent. starch paste.

Fifty ml. of solution (3), 10 ml. of (2) and a definite volume of the aldehyde solution containing 0·01 to 0·03 g. of acetaldehyde are placed in a 250-ml. Erlenmeyer flask, which is stoppered, well shaken, and left for 20 minutes. One ml. of starch paste, 100 ml. of water, and 10 ml. of reagent (4) are added, and solution (1) is run in from a burette until a blue colour just appears. On addition of 1 drop of phenolphthalein solution and 100 ml. of solution (5), the blue colour disappears and the liquid turns pink. The liquid is then titrated with 0·1 *N* iodine solution (*n* ml.) to a blue-violet colour; acetaldehyde taken = 2·2 *n* mg. With wines, the aldehyde should be separated before applying the above method. Two hundred, or 100, or 50 ml. of the wine, according to the acetaldehyde-content, are mixed with 5 per cent. of phosphoric acid and distilled down to the half volume, the distillate being collected in the bisulphite solution and buffer mixture indicated above. Spirits are either treated directly or distilled to concentrate the aldehyde, if this is low in amount. T. H. P.

Occurrence of Sorbitol in Pure Grape Wines. E. Vogt. (*Z. Unters. Lebensm.*, 1935, **69**, 587–591.)—Forty-four wines, mostly of good vintage years, were examined by Litterscheid's method (ANALYST, 1932, **57**, 178), and in only 5 of them—Rülander wines of 1928, 1929, and 1931—was sorbitol found in appreciable quantity. From 600 ml. of the wine, from 30 to 86 mg. of chlorobenzylidenesorbitol, or from 12 to 30 mg. of hexacetylsorbitol were obtained. These amounts are too small to be mistaken as evidence of adulteration with fruit wines, even if such adulteration were likely with these high-grade wines. The value of the sorbitol test is thus confirmed. T. H. P.

Determination of Hydroxymethylfurfural and of Laevulosin in Port Wines and other Sweet Wines. C. I. Kruisheer, N. J. M. Vorstman and L. C. E. Kniphorst. (*Z. Unters. Lebensm.*, 1935, **69**, 570–582.)—To determine hydroxymethylfurfural, 50 ml. of the wine are neutralised to litmus paper by addition of *N* sodium hydroxide and extracted for two days with ether in a percolator. To the percolate (about 50 ml.) are added 10 g. of anhydrous sodium sulphate and, with swirling, 25 ml. of petroleum spirit (b.p. 40 to 60° C.). The next day the dried liquid is filtered into a 200-ml. Erlenmeyer flask, and the precipitate is washed several times with a 1 : 1 mixture of the petroleum spirit and ether. The total filtrate is distilled on a water-bath, the last traces of liquid being expelled by immersing the flask as far as possible in the boiling water and passing through the flask for 10 minutes a current of dry, oxygen-free carbon

dioxide. The flask is quickly cooled and, after addition of 10 ml. of 16 per cent. hydrochloric acid, whisked round for a short time, the liquid being then filtered through a small filter-paper, which is washed with about 10 ml. of the acid in small amounts. A fresh, filtered solution of 0·25 g. of phloroglucinol in 30 ml. of hydrochloric acid (16 per cent.) is next added, to give a total volume of 50 ml. The presence of hydroxymethylfurfural is shown by a red colour, changing to an opalescence, and later to a red precipitate; otherwise no precipitate appears even after 24 hours. On the following day the precipitate is collected in a crucible with a porous porcelain bottom (Schott 1G4), if necessary with gentle suction, and is washed with a total of 15 ml. of about *N* hydrochloric acid, dried at 100° C. and weighed. Two, 4, 6, . . . 36 mg. of the phloroglucide correspond respectively with 2·3, 3·3, 4·3, . . . 16·3 mg. of hydroxymethylfurfural, the relationship being linear between 6 and 36 mg. of the phloroglucide.

A useful orienting test may be made beforehand by treating 2 ml. of the wine (if dark, this should be first decolorised with a little norit) in a test-tube with 2 ml. of hydrochloric acid (30 per cent.) and 1 ml. of a fresh 0·5 per cent. solution of phloroglucinol in hydrochloric acid (16 per cent.). If an opalescence appears within 15 minutes or, with a decolorised wine, within 1 hour, the presence of hydroxymethylfurfural is probable. When hydroxymethylfurfural is added to a wine, the above method indicates, not the whole, but the bulk of the addition (240 mg. added; 214 mg. or, in presence of much sulphite, 198 mg. found). Pure ports, free from caramel or added boiled-down must, contain little or no hydroxymethylfurfural, 50 mg. per litre being exceptional. Neither pasteurisation nor long storage affects the content.

Pure ports contain no laevulosin, but in certain sweet wines made with the help of boiled must, this compound occurs in conjunction with hydroxymethylfurfural. To determine laevulosin, 50 ml. of the wine, mixed with 150 ml. of water, are fermented with 10 g. of pure pressed yeast for 2 days at about 30° C., and then neutralised to neutral red by means of baryta solution, centrifuged, and evaporated to about 100 ml. on a water-bath. The subsequent procedure is that previously described (ANALYST, 1933, **58**, 231). T. H. P.

Differentiation of Spirit Vinegar and Artificial Vinegar. A. Schmidt. (*Z. Unters. Lebensm.*, 1935, **69**, 472–478.)—The procedure followed is that of Wüstenfeld (*Lehrbuch der Essigfabrikation*, 1930, Verlag P. Parey, Berlin). The "oxidation value" is the number of ml. of 0·1 *N* potassium permanganate solution required to impart a permanent red colour to 50 ml. of vinegar containing 3 per cent. of acetic acid, in the presence of dilute sulphuric acid. Artificial vinegar prepared from "vinegar essence"* requires not more than 1 or 1·5 ml., whilst spirit vinegar requires 8 ml. or more. As vinegar containing caramel as colouring matter gives very high values (12 to 14 ml.), the oxidation value was determined both before and after treatment with active carbon for 2 minutes at room

* "Vinegar Essence" is the commercial name of a product containing 12 per cent. of acetic acid (made by the distillation of wood or by a synthetic process) and coloured with caramel or an aniline dye. Some years ago "Essigsprit" (a 12 per cent. spirit vinegar) was also sold as "vinegar essence." "Spirit acid" was the concentrated acetic acid obtained by the distillation of *Essigsprit*.—EDITOR.

temperature. Pure glacial acetic acid diluted to 3 per cent. with distilled water gave an oxidation value of 0·2 before treatment with active carbon, and 0·19 after treatment. Fourteen samples of commercial "vinegar essence," containing 3 to 3·5 per cent. of acetic acid and coloured with synthetic dyes, gave oxidation values of 0·9 before treatment with active carbon, and 0·78 after treatment. Sixty samples of commercial vinegar, labelled "fermentation vinegar," containing 2·6 to 3·5 per cent. of acetic acid and coloured with synthetic dyes, gave oxidation values of 5·0 to 7·0 before treatment with active carbon, and 3·2 to 4·1 after treatment.

The iodine value is also determined, as described by Wüstenfeld (*loc. cit.*). Excess of 0·01 *N* iodine solution is added to 25 ml. of vinegar which has been made alkaline, the mixture is allowed to stand for 15 minutes and acidified with dilute hydrochloric acid, and the iodine is titrated back with 0·01 *N* sodium thiosulphate solution. The determination is made both before and after treatment with active carbon for 2 minutes at room temperature, and samples of vinegar containing more than 3 per cent. of acetic acid are diluted to that concentration. Spirit vinegar gives an iodine value of 30 to 60 or more. If the value falls below 20, the sample may be regarded with suspicion. Fifteen samples of artificial vinegar prepared by dilution of glacial acetic acid gave iodine numbers of 5 to 7 before treatment with active carbon and 4 to 6 after treatment. Twenty-four samples of 3 per cent. vinegar prepared by dilution of a 12 per cent. commercial "vinegar essence" gave iodine values of 3 to 5 before treatment with active carbon, and 3 to 4·5 after treatment. Forty-eight samples of commercial fermentation vinegar gave iodine values of 38 to 44 before treatment with active carbon, and 34 to 40 after treatment. The oxidation and iodine values thus afford means of distinguishing between spirit vinegar and artificial vinegar, especially when interpreted in conjunction with other analytical data. (*Cf.* ANALYST, 1927, **52**, 93, 260; 1932, **57**, 722; 1933, **58**, 619.) A. O. J.

Itoyo Fish Oil. S. Ueno and S. Komori. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 345–352B.)—Itoyo oil is obtained from the Gasterostenus family, and the sample of oil used in this investigation was obtained from *G. aculeatus* (Limeoseus). The oil was an orange-red liquid, of sp.gr. 20/4° C., 0·9232, n_D^{20} 1·4789, saponification value 186·9, iodine value (Wijs) 165·0, acid value 0·75, and unsaponifiable matter 1·01 per cent. The mixed fatty acids (free from unsaponifiable matter) had iodine value 171·9, and neutralisation value 190·5. The solid (14·3 per cent.) and liquid (85·7 per cent.) acids were separated by the lead salt and alcohol method. The methyl esters of the fatty acids were prepared and fractionally distilled, and the fractions were analysed. The approximate composition of the oil is regarded as: total saturated acids, about 18·2 per cent., consisting of myristic, 3·7; palmitic, 12·8; stearic, 1·7; and a minute quantity of C_{20} (?) acid. The unsaturated acids contained an acid $C_{16}H_{30}O_2$ (probably zoomaric acid), oleic and catoleic acids, and highly unsaturated acids, $C_{18}H_{28}O_2$ (probably moroctic acid), and $C_{22}H_{34}O_2$ (probably clupanodonic acid). The sterol portion of the unsaponifiable matter was cholesterol, and the liquid portion contained oleyl alcohol, together with a new higher and highly unsaturated alcohol. D. G. H.

New Reaction of *Helvella esculenta*. G. Reif. (*Z. Unters. Lebensm.*, 1935, **69**, 585–586.)—A number of fungi have been tested with the solution of selenious acid in sulphuric acid suggested by Mecke (*Z. öffentl. Chem.*, 1899, **5**, 351) as a sensitive reagent for opium alkaloids and shown later by Levine (*J. Lab. Clin. Med.*, 1925–1926, **11**, 809) to react also with various phenols. Of the fungi examined, only *Helvella esculenta* showed any reaction with the reagent, giving first a red colloidal solution of selenium and later a red precipitate of amorphous selenium. Failure to react was displayed by *Amanita phalloides, A. mappa, A. muscaria, A. pantherina, A. rubescens, Psalliota campestris, Boletus edulis, Tricholoma equestre, Russula vesca, R. emetica,* and various *Morchella* species, including the edible morel (*M. esculenta*), *M. conica,* and *M. semilibera.* The reaction thus provides a means of distinguishing between *Helvella esculenta* and *Morchella* species. The reacting substance remains in the residual solid when the fungus is pressed, but is completely removed by extraction with hot water. It occurs in both the stem and the cap of the fungus and is not destroyed by drying the fungus. In applying the test, 2(0·2) g. of the finely-sliced fresh (dried) fungus are heated with 15 ml. of water on a water-bath for 15 minutes, the cold filtered extract being treated with 15 drops of a solution of 0·5 g. of selenious acid in 100 g. of concentrated sulphuric acid and heated similarly. T. H. P.

Determination of Oxydimorphine. B. Drevon. (*J. Pharm. Chim.*, 1935, **127**, 97–106.)—Oxydimorphine or its salt is dissolved in 1 to 2 ml. of sulphuric acid (sp.gr. 1·83), and on to the surface 0·1 to 0·2 ml. of acetic anhydride is pipetted, the tube being kept cool. A bright green colour appears at the line of separation and gradually spreads through the solution, attaining its maximum intensity in 30 minutes at ordinary temperature. The colour disappears on addition of water, re-appearing with further additions of sulphuric acid. Morphine itself gives no colour under the same conditions. For purposes of comparison the alkaloid must always be dissolved in the same volume of reagent (20 ml. of sulphuric acid and 1 ml. of pure acetic anhydride are mixed without allowing the temperature to rise and used immediately). The green colour developed in this reaction may be compared with stable standards prepared from a mixture of 1 ml. of copper nitrate solution (15 per cent.), 1 ml. of nickel nitrate solution (20 per cent.), and 0·3 ml. cobalt nitrate solution (10 per cent.). The colorimetric determination of oxydimorphine necessitates the isolation of the substance in an insoluble form, and the subsequent application of the above method. To 5 ml. of the solution under examination are added 5 drops of a 5 per cent. solution of silicotungstic acid and about 0·03 g. of potassium bicarbonate. The tube is placed in ice for about 30 minutes, and one drop of a suspension of gelatinous barium sulphate containing about 10 per cent. of the dry product is added. The whole is mixed and centrifuged for three minutes (3000 revolutions), another drop of the suspension is added and centrifuging is repeated so that the alkaloidal precipitate is covered with a layer of barium sulphate. The clear supernatant liquid is withdrawn, and the tube is dried by means of filter paper. After the tube has been cooled in ice, 2 ml. of the acetosulphuric reagent are added, and, after a few minutes' cooling, the mass is brought into suspension by means of a glass rod, when the barium

sulphate and oxydimorphine dissolve. The tube is allowed to attain laboratory temperature, and after 30 minutes the colour developed is compared with the standards. Optimum conditions are obtained when 5 ml. of the solution to be examined contain 0·4 to 0·1 mg. of oxydimorphine. The error is of the order ±5 per cent. D. G. H.

Gravimetric and Volumetric Determination of Quinidine. R. Monnet. (*J. Pharm. Chim.*, 1935, **127**, 112–119.)—An excess of potassium thiocyanate is added to an aqueous solution of a basic salt of quinidine, and the resulting precipitate is separated and weighed. One g. of the salt weighed corresponds with 0·8468 g. of quinidine. The quinidine solution (containing not more than 0·29 g. of quinidine) is concentrated to about 20 ml., and if acid to litmus, is neutralised with 0·01 *N* sodium hydroxide solution. After addition of 3 g. of potassium thiocyanate and mixing, the solution is again neutralised, if necessary. After 2 hours the liquid is filtered, the precipitate is washed twice with water and 8 times (2 ml. each time) with a saturated solution of quinidine thiocyanate hydrate, dried and weighed. In the presence of quinine, cinchonidine and cinchonine, the determination is carried out in the same way, but after the precipitate has been washed with the saturated quinidine thiocyanate hydrate solution it is washed six times (1 ml. each time) with 96 per cent. alcohol saturated with quinidine thiocyanate hydrate. If present in large quantities, quinine and cinchonidine may be precipitated as basic tartrates. Emetine, papaverine, strychnine, veratrine and berberine are precipitated by thiocyanate in the neutral medium, but aconitine, atropine, brucine, caffeine, cocaine, codeine, coniciene, eserine, hydrastine, hyoscyamine, morphine, pelletierine, pilocarpine, sparteine, thebaine, theobromine, and yohimbine are not precipitated by thiocyanate. No precipitates are given by digitalin, strophanthin, convallamarin, salicin, acetanilide, adrenaline, antipyrine, cryogenine, exalgine, novocaine, phenacetin, pyramidone, stovaine, urea, urethane, and veronal.

For the volumetric determination of quinidine, the solution, containing the quinidine as nitrate or basic sulphate, is concentrated to about 20 ml., and should then contain not more than 0·15 g. Twenty ml. of a 0·1 *N* solution of potassium thiocyanate are added, the solution neutralised if necessary, made up to 50 ml., and filtered after shaking 4 or 5 times during a 20 minutes' period. The first portion of filtrate is neglected, and 25 ml. are used for titrating the excess of thiocyanate by the Charpentier–Volhard method after addition of 10 ml. of 0·1 *N* silver nitrate solution. Then, if n is the number of ml. of 0·1 *N* potassium thiocyanate added, $32{\cdot}4 \times 2 \times n$ is the quantity of quinidine in the sample. This method cannot be applied in the presence of other cinchona alkaloids or of other substances precipitated by potassium thiocyanate in neutral solution. If salts precipitated by silver nitrate in nitric acid medium are present, the alkaloid must be extracted and dissolved in sulphuric or nitric acid. A sufficient excess of salt is not present for the precipitation of the whole of the quinidine, and a correction may be made by adding 6·5 mg. to the weight of quinidine found. The method is simpler and quicker than the gravimetric procedure. D. G. H.

New Specific Reaction for Yohimbine. Pesez. (*J. Pharm. Chim.*, 1935, **22**, 164–165.)—The method, which is analogous to the Pettenkofer reaction, is based on the condensation of yohimbine with chloral in the presence of sulphuric acid. To a mixture of 3 ml. of concentrated sulphuric acid and 0·2 ml. of a 20 per cent. aqueous solution of chloral, is added 0·5 ml. of a solution of a salt of yohimbine, a drop at a time, with continuous agitation. The solution is then warmed at 50° to 60° C., when the rose colour changes to a greenish-blue shade, which gradually turns to a very stable and more pronounced blue. With preparations containing yohimbine it is necessary first to isolate the alkaloid, on account of the interfering effect of any sugars present. A solution in 5 ml. of hot water is therefore extracted with 1 ml. of ammonia and 2 ml. of chloroform, the chloroform layer being washed with water and the test applied to the residue after evaporation. Dilution with 3 ml. of water is without effect, but addition of 10 ml. causes the colour to disappear. The reaction is sensitive to 0·02 mg. of yohimbine hydrochloride, and is specific for this alkaloid; others usually give a yellow to brown colour, or in the case of those which condense with aldehyde compounds (*e.g.* morphine, veratrine or picrotoxine), a red shade. When other aldehydes are used as condensing agents, yellow to brown shades are also usually obtained, although vanillin and salicylaldehyde give a carmine red; these reactions are not specific for yohimbine. J. G.

Test for Citric Acid and a Reagent for the Opium Alkaloids and Phenols. Pesez. (*J. Pharm. Chim.*, 1935, **22**, 160–163.)—The reaction is based on the conversion of citric acid into glyoxal by the formation, first of pentabromoacetone and then, by hydrolysis, of the compound CHO.CO.COOH, which is decomposed into glyoxal (*cf.* Denigès, *Bull. Soc. Chim.*, 1902, **27**; Polonovski, ANALYST, 1921, **46**, 464). In a test-tube are placed 0·1 ml. of the test solution, 0·05 ml. of saturated bromine water, 3 drops of concentrated sulphuric acid and 0·05 ml. of a saturated solution of potassium permanganate, and the mixture is boiled gently. The colour should disappear, but, if the concentration of citric acid exceeds 2 per cent., a precipitate is formed, and in that case 2 ml. or more of sulphuric acid should be added and the heating continued until complete solution is obtained. The liquid is cooled and 0·1 ml. of a 0·05 per cent. solution of codeine is added, and, if no rose colour appears after a few seconds, the solution is warmed on the water-bath, when a blue to violet colour develops. Codeine may be replaced by other reagents, the respective colours in the cold and on the water-bath being as follows:—Resorcinol, rose, wine-red with a pale green fluorescence; thymol, no reaction, blood-red; β-naphthol, very pale green, deeper emerald-green; salicylic acid, no reaction, red to violet; methyl salicylate, rose to violet, greater in intensity. The reaction is almost quantitative, and is sensitive to 0·0002 g. of citric acid, the most sensitive reagent in this case being the warm methyl salicylate; when the amount of citric acid is so small, however, any colour remaining in the solution when it is warmed with the potassium permanganate must be removed by adding a drop of a saturated solution of oxalic acid. The reaction is specific for citric acid, whilst lactic, acetic, tartaric, oxalic, benzoic, salicylic and uric acids produce only a yellow colour in the cold, which turns

brown on the water-bath, and is due to liberation of bromine. The reaction may also be used to prepare a solution of glyoxal for use as a test for the phenols mentioned above, or to replace the Denigès methyl glyoxal reagent for the opium alkaloids, the colours obtained being identical in both cases. A mixture of 10 ml. of 10 per cent. citric acid solution, 30 ml. of bromine water, 1 ml. of sulphuric acid, and 10 ml. of a 4 per cent. solution of potassium permanganate is warmed until the colour disappears, 5 ml. of concentrated sulphuric acid being then added and the mixture boiled for a few seconds. J. G.

Separation and Detection of Cocaine in Mixtures of Cocaine and Procaine. C. H. Riley. (*Amer. J. Pharm.*, 1935, **107**, 271–279.)—Small amounts of cocaine hydrochloride may be identified, after separation from large amounts of procaine hydrochloride, by dissolving 200–250 mg. of the sample in 15 ml. of water, and placing the solution in a separating funnel. To this, 0·5 ml. of 0·5 *M* sodium phosphate (Na_2HPO_4) solution and 15 ml. of chloroform are added, and the whole is well shaken. In a second funnel, 15 ml. of a solution, made by mixing 50 ml. of 0·5 *M* citric acid solution and 90 ml. of 0·5 *M* sodium phosphate solution, are placed. A third funnel containing 10 ml. of this solution, and a fourth containing 5 ml. of water, are also required. A plug of cotton-wool is placed in the stems of funnels No. 3 and No. 4. The chloroform in funnel No. 1 is drawn off into funnel No. 2, shaken, and allowed to separate. It is then drawn off into funnel No. 3, and the process repeated. The chloroform is finally shaken with the water in funnel No. 4, and is then run into an evaporating dish. The whole process is repeated, but with 10 ml. of chloroform. To funnel No. 3, 1 to 2 ml. of chloroform are added, and this is then passed into funnel No. 4, and thence to the evaporating dish. The mixed chloroform solutions are evaporated to dryness. If the residue is large (over 10 mg.), a portion is dissolved in 2 *N* hydrochloric acid on a microscope slide, platinic chloride solution is added, and the crystals are examined under a microscope. If the residue is small, it is dissolved in the dish in two drops of the acid, and this is decanted on to the slide and again examined. All the separator stopcocks must be free from grease. If cocaine is suspected in the form of the free base, the sample is dissolved in 15 ml. of chloroform and separator No. 1 is omitted. A more rapid, but less efficient, method is to dissolve the sample in 5 ml. of water, and to pour the solution into a separating funnel of 100 to 200 ml. capacity. To this are added 5 ml. of 0·5 *M* citric acid solution and 5 ml. of 0·5 *M* sodium phosphate solution. The solutions are thoroughly mixed, 10 ml. of chloroform are added, and the whole is well shaken. A plug of cotton-wool is inserted into the stem of the separating funnel, and the chloroform layer is then drawn off into a second funnel containing 5 ml. of distilled water. The contents of the second funnel are shaken, and the chloroform is again drawn off through a plug of cotton-wool into a small evaporating dish. The initial solution is extracted with 5 ml. of chloroform, which is run off into the second funnel as before. After shaking, the chloroform is drawn off into the evaporating dish. The combined chloroform extracts are evaporated to dryness on the water-bath, the dish is cooled, and the residue is treated with two drops of 2 *N* hydrochloric acid solution. This solution is placed on a microscope

slide, one drop of 8 per cent. platinic chloride solution is added, and the slide is examined under the microscope for characteristic cocaine crystals. For the determination of the amount of cocaine present, 200 to 250 mg. of the sample are dissolved in 12 ml. of water in a separating funnel. To the solution are added 3 ml. of 0·5 *M* sodium phosphate solution. In a second funnel are placed 15 ml. of a mixture of 10 ml. of 0·5 *M* citric acid solution and 20 ml. of 0·5 *M* sodium phosphate solution; in a third funnel 10 ml. of this solution, and in a fourth 5 ml. of water. Extractions are made with 15 + 10 + 10 ml. of chloroform as before. The chloroform extracts are evaporated to dryness, and the residue is dried and weighed. The residue is then dissolved in neutral alcohol, 20 ml. of 0·5 *N* sulphuric acid solution added, and the excess is titrated with 0·02 *N* sodium hydroxide solution, methyl red being used as indicator. Each ml. of 0·5 *N* sulphuric acid absorbed by the residue is equivalent to 0·015158 g. of cocaine or 0·01698 g. of cocaine hydrochloride. S. G. S.

Quantitative Determination of Diaminoacridine in Euflavine. F. Reimers. (*Quart. J. Pharm.*, 1935, **8**, 218–230.)—Inaccuracies in the methods of Gaillot (*Quart. J. Pharm.*, 1934, **7**, 63) and Hall and Powell (*Quart. J. Pharm.*, 1933, **6**, 389; 1934, **7**, 522; Abst., ANALYST, 1935, 108) are pointed out. The difference between the basic strengths of the components of diaminoacridine hydrochloride, as determined from measurements with the glass electrode, may be utilised as the basis of a rapid method which can be employed as a check on the accuracy of other methods. The amount of diaminoacridine hydrochloride in euflavine may be determined more accurately than by previous methods, by dissolving 0·5 g. to 0·7 g. of the euflavine in 10 ml. of boiling water in a 250-ml. flask. To this are added 90 ml. of isopropyl alcohol and 2 ml. of thymol blue solution, and the mixture is titrated with 0·1 *N* sodium hydroxide solution to a definite colour-change, *i.e.* to a colour that is murky brown. The titration must be made in strong electric light. The solution is then titrated back with 0·1 *N* hydrochloric acid solution until the colour no longer changes. As a rule, 0·2 to 0·5 ml. are required for this. The difference between these titrations, multiplied by 0·02462, gives the amount of diaminoacridine hydrochloride in the sample taken. S. G. S.

Biochemical

Presence of Manganese in Cane Sugar and Maple Sugar. P. Riou and J. Delorme. (*Compt. rend.*, 1935, **200**, 1132–1133.)—Crude cane sugar and maple sugar both contain manganese, the amount varying in the former up to 4 parts per million, and in the latter from 10 to 125 parts per million. Refined cane sugar contained no manganese, and therefore the small amounts present in the crude sugar are removed during the refining processes. The plant tissues of both the sugar cane and the sugar maple contain manganese, and the authors are extending their work with a view to ascertain if this element has any catalytic effect on the formation of sugar in the plant cells. S. G. S.

Study of the Concentration and Properties of Two Amylases of Barley Malt. M. L. Caldwell and S. E. Doebbeling. (*J. Biol. Chem.*, 1935, **110**, 739–747.)—If extracts of barley malt are subjected to repeated fractionations by ammonium sulphate with intervening dialyses, followed by fractional precipitation with alcohol, it is possible to obtain two distinct amylases. The amylases so prepared are free from carbohydrates, but both give positive protein colour reactions, and both are rapidly inactivated by heat in aqueous solutions. In the presence of 0·01 *M* acetate, and at 40° C. *p*H values of 4·3 to 4·6 favour the saccharogenic action of both types of enzyme. The amylase having a preponderance of an amyloclastic activity also has an optimum *p*H of 4·3 to 4·7. S. G. S.

Measurement of Phenolase Activity. R. Samisch. (*J. Biol. Chem.*, 1935, **110**, 643–654.)—During the study of some of the variables involved in the oxidation of phenols by gaseous oxygen in the presence of plant phenolase, it was found that the rate of enzymic oxidation could be increased if the partial pressure of oxygen was increased to between 60 and 70 per cent. O_2. The oxygen absorption was increased by increasing the concentration of the substrate, but this had an optimum value, beyond which a further concentration of the substrate inhibited enzyme activity. The optimum *p*H value for the activity of the enzyme was found to vary with the source of the enzyme, and also with the nature of the substrate. At moderate temperatures, phenolase activity is destroyed by a reaction which appears to be chemical in nature, and not a heat coagulation. The activity is also inhibited by the halides of neutral salts, the effects of these being in the inverse ratio of their atomic numbers. A phenolase unit is proposed, and is defined as the velocity constant K (= O_2 absorbed/log t) measured in an atmosphere of pure oxygen, at 25° C., at the optimum *p*H value, and with the optimum concentration of the substrate. S. G. S.

Enzymic Method for the Estimation of True Vitamin *C*. H. Tauber and I. S. Kleiner. (*J. Biol. Chem.*, 1935, **110**, 559–563.)—The substances interfering with the chemical determination of vitamin *C* may be eliminated, now that a specific ascorbic acid oxidase has been isolated (ANALYST, 1935, 625). The enzyme is prepared from the pericarp of the Hubbard squash by extracting 250 g. with 750 ml. of 30 per cent. alcohol, and filtering. 0·5 mg. of ascorbic acid should be completely oxidised by 10 ml. of this extract in 30 minutes at 38° C. If the enzyme solution is weaker, incubation time must be increased accordingly. Samples for analysis are prepared by the Emmerie and van Eekelen mercuric acetate method. A standard solution of ascorbic acid is prepared by dissolving 25 mg. of pure ascorbic acid and 50 mg. of cystine in 90 ml. of boiling 0·01 *N* hydrochloric acid solution, cooling and diluting to 100 ml. This solution keeps only for one day. The fluid to be analysed is adjusted to *p*H 5·0 and titrated with 2, 6-dichlorophenone indophenol. This is prepared by extracting 50 mg. of the dye with 150 ml. of boiling water, and is standardised against the standard ascorbic acid solution. It will keep for four days. Another portion of the fluid under examination is treated with 1 ml. of *M* acetate buffer solution of *p*H 6·0 and 10 ml. of the enzyme solution. It is kept at 38° C. for 30 to 60 minutes. The enzyme activity is then stopped by the addition of 1 ml. of 2 per

cent. sulphuric acid solution, and the residual reduction is determined by titration with the dye. The difference between these two titrations is calculated as ascorbic acid. S. G. S.

Biological Utilisation of Esters of Vitamin *E*. H. S. Olcott. (*J. Biol. Chem.*, 1935, **110**, 695–701.)—The presence of a hydroxyl group in vitamin *E* is demonstrated by its ability to form esters. The acetic or benzoic esters are biologically active, although the methyl and ethyl ethers are inactive. The urethane derivative is inactive, but on alkaline hydrolysis the active vitamin is regenerated. Rats cannot utilise the urethane derivative, although the acetyl and benzoyl esters can replace the vitamin itself. Hydrogenation at 230° C. and at 250 to 280 atmospheres pressure neither destroys the vitamin nor saturates the concentrates. The band at 294$m\mu$, which is found in the absorption spectrum of concentrates from wheat germ and cotton-seed oils, is shown to be uncorrelated with the vitamin. S. G. S.

Toxicological and Forensic

Biological Methylation of Compounds of Arsenic and Selenium. F. Challenger. (*Chem. and Ind.*, 1935, **54**, 657–662.)—Cases of poisoning due to domestic wall-papers containing arsenical pigments have been known since 1815, and inhalation of arsenic particles, arsine, cacodyl oxide, ethyl arsines, diethyl arsine oxide or monomethyl arsine has been suggested to account for them. Early and current work on the subject is now critically reviewed, and the conclusion is reached that the gas evolved ("Gosio gas") is trimethyl arsine, and that when it reacts with mercuric chloride solution containing hydrochloric acid the compound $(C_2H_5)_2As,HgCl,HgCl_2$ is formed, free calomel being absent (*cf.* Challenger, Higginbottom and Ellis, Abst., ANALYST, **1933**, **58**, 235). This conclusion is confirmed by comparison of the m.p. and mixed m.p. of derivatives prepared from Gosio gas and synthetic trimethyl arsine; these include hydroxytrimethyl arsonium nitrate and picrate; trimethyl arsine oxide (produced by the action on the gas of hydrogen peroxide), and its picrate (m.p. 218° to 219° C.); and trimethylbenzyl arsonium picrate, which is prepared by reaction with benzyl chloride. Average yields of trimethyl arsine obtained by allowing bread culture experiments (*loc. cit.*) to proceed until no further precipitate was produced in acid mercuric chloride solution after a week were 22, 24 and 15·5 per cent., with arsenious oxides, sodium methyl arsonate and sodium cacodylate, respectively. They were obtained by weighing the dimercurichloride (*supra*), or the hydroxytrimethyl arsonium nitrate produced by absorbing the gas in nitric acid. No evidence of alkylation was obtained when antimony, sulphur, phosphorus, bismuth, lead or mercury in various forms of combination was substituted for arsenic, but it is recognised that this may occur but not be apparent because of the difficulty in reducing the compound to the gaseous state. Other cases of biological methylation are discussed, *e.g.* the production of odorous compounds by the action of *P. brevicaule* on breadcrumbs containing selenium, or in the breath of animals fed with selenium, tellurium or bismuth compounds; and the conversion of nicotinic

acid into trigonelline by dogs (*cf. loc. cit.* and *J. Chem. Soc.*, 1934, 68). In connection with the Forest of Dean case (*cf.* ANALYST, **1932, 57**, 163; Lerrigo, *id.*, 155) it is concluded that the cause of poisoning was trimethyl arsine, which is however less poisonous than hydrogen arsenide (*cf.* Huss, *Z. Hyg.*, 1914, **76**, 361). The source of the arsenic was the coke-breeze in the plaster on the walls, and the wall-paper was relatively unimportant from this point of view, although this and the adhesive supplied the organic matter necessary for growth of the mould. The danger of the use of coke-breeze slabs for papered walls which are likely to become damp is emphasised. As examples of potential dangers of this nature, 3 patents are cited (Smitt, B.P. 412,091; Stälhane U.S.P. 1,900,690, and Curtin, U.S.P. 1,900,162) concerned with the use of arsenious oxide in wall-boards and in cement to increase its setting rate and insolubility. J. G.

Dermatitis in Relation to Knitted Woollen Goods. S. R. Trotman. (*J. Soc. Dyers and Col.*, 1935, **51**, 284–287.)—The difficulties of diagnosing the cause of irritation or dermatitis by woollen garments are discussed, and physical, chemical and micro-biological irritants are considered in turn. (1) *Physical.*—Such agents as sunlight and ultra-violet rays do not concern the hosiery manufacturer directly, but excessive sun-bathing seems to produce changes in the skin, rendering it more susceptible to the action of other irritants or to the growth of micro-organisms. Moreover, the free edges of the epithelial scales of wool may cause irritation or a condition simulating dermatitis. In certain cases where no chemical agent could be found, the garments complained of were made of a coarse wool with well-marked epithelial scales and containing a number of hair-like fibres. (2) Chemical irritants include acids, alkalis, salts, amines, phenols, formaldehyde, dyes, tar oils, nitro-compounds, arsenic and certain vegetable tissues. In order that a chemical may act as an irritant, it must be soluble in moisture, perspiration or skin grease. Woollen underwear which has been stoved and dried without washing may contain as much as 0·5 per cent. of sulphurous acid, as well as traces of sulphuric acid, and very prolonged washing with water is required to remove the acid. With undyed goods, complaints refer almost always to low-grade, stoved wool, fine wools bleached with peroxide rarely causing trouble unless subsequently stoved. As regards dyed wools, the affinity of wool for the residual sulphuric acid, and the difficulty of removing this by washing with water, demand attention. The usual method of rinsing cannot be expected to remove more than a fraction of the absorbed acid, and, unless alkali is used, it is practically impossible to make acid-dyed wool neutral. Formic acid may also be present in dyed woollens. Alkali may be introduced during washing as sodium carbonate, which may undergo hydrolysis yielding a little sodium hydroxide, and the same would occur with residual soap. Tests are described which indicate that the liberation of bases from wool dyes is unlikely to occur. Most of the known pure synthetic dyes are innocuous to the skin, and dye dermatitis is often probably due to unremoved chemicals used as assistants, rather than to the dyes themselves. Skin trouble is, however, set up by chrysoidine, safranine, Bismarck brown, fuchsine, and aurantia. Certain lubricating oils which are used for treating rayon and may contain free fatty acids, vegetable or mineral oil, a hydrogenated

aromatic hydrocarbon and sulphonated oil or soap, irritate the hands of those dealing with the goods. Oxidised oils, frequently present in knitted goods, may be irritant, as they contain free fatty acids, hydroxy-fatty acids, aldehydes and peroxides. (3) *Micro-organisms.*—Members of the *Pyogenes aureus* family of cocci, which are widely distributed and often present on the skin, may be the cause of trouble, and are generally associated with the formation of pus. Their rôle is secondary rather than primary, as they do not grow on the skin unless superficial damage has already been effected. Even then, their development is dependent on the general vitality of the infected person. T. H. P.

Agricultural

Palatibility and Possible Toxicity of different Species of *Crotalaria*. R. B. Becker, W. M. Neal, P. T. D. Arnold and A. L. Shealy. (*J. Agric. Res.*, 1935, **50**, 911–922.)—Four species of *Crotalaria* are known to be toxic to live stock, but the toxic principles vary, producing different symptoms and lesions; *C. sagitallis* causes "Missouri River bottom disease," resulting in death among horses; seeds of *C. juncea* L. fed to sheep may cause death; *C. burkeana* Benth. causes death among cattle; and *C. dura* is also definitely toxic. In this investigation nine species of *Crotalaria* were planted in adjacent rows in a fenced 2-acre field, and from time to time during the grazing season two head of cattle were transferred to the field, usually for 14 days, and the extent of the grazing on the separate species was noted. No supplementary feeds were allowed, water was accessible, and some grasses and plants not killed by cultivation were grazed. Eight of the 11 species of *Crotalaria* were dried and fed as hay. It appears that eight of the ten species are not toxic; *C. anagyroides* H.B.K.; *C. goreensis* Guill. and Perr.; *C. grantiana* Harvey; *C. incana* L.; *C. intermedia* Kotschy; *C. lanceolata* E. Mey; *C. maxillaris* Klotzsch; *C. striata* D.C.; and *C. usaramoensis* Baker. *C. spectabilis* Roth is definitely toxic, and one acute and three chronic cases of poisoning by this species are discussed and typical lesions are illustrated. D. G. H.

Quantitative Relationship between the Constitution and Toxicity of some Rotenone Derivatives. W. A. Gersdorff. (*J. Agric. Res.*, 1935, **50**, 893–898.)—The comparison of toxicity of the eight rotenone compounds was made by means of the minimum product of concentration and survival time, the value corresponding with a point at which neither tolerance factor is preponderant. Tests were made with goldfish at a temperature of 27° C., and the following relative toxicities were found:—Dihydrorotenone, 1·4; rotenone, 1·0; acetyldihydrorotenone, 0·81; acetylrotenone, 0·55; dihydrorotenolone, 0·15; rotenolone, 0·097; acetyldihydrorotenolone, 0·082; and acetylrotenolone, 0·055. Each change in chemical constitution was found to effect a change in toxicity independent of the effect of any other change, and the combined effect on toxicity of more than one change in constitution was equal to the product of the individual effects; *e.g.* the dihydroacetates have 0·83 of the toxicity of the parent compounds; the dihydrohydroxy derivatives, 0·15; the acetylhydroxy derivatives have 0·057 the toxicity of the parent compounds, and acetyl hydrorotenolone (which includes

all three changes in constitution) 0·082 the toxicity of rotenone. Dihydro derivatives obtained by saturation with hydrogen of the double bond in the side chain have 1·5 times the toxicity of the corresponding unsaturated compounds; the acetates (both the enol type and acetyl derivatives of hydroxy compounds) have 0·56 the toxicity of the parent compounds, and the hydroxy derivatives have 0·10 the toxicity of the parent compounds. D. G. H.

Soya-bean Proteins. M. Mashino. (*J. Soc. Chem. Ind.*, 1935, **54**, 236–238T.)—Methyl alcohol is the most suitable solvent for the extraction of carbohydrates and substances responsible for the characteristic odour, taste and colour of soya-bean oilcakes, a total extract of 11·49 per cent. (carbohydrates, 9·73; crude oil, 0·06; and nitrogen, 0·32 per cent.) being obtained. Additions of water increase the yields of extract progressively, and the use of 0·02 *N* hydrochloric acid in 60 per cent. methyl alcohol prevents the dispersion of the protein, which normally occurs in the presence of water (total extract, 20·00; crude protein, 15·19; ash, 2·81; other substances, 1·99 per cent.). The residue after extraction with benzene and methyl alcohol is a non-hygroscopic, odourless, almost white solid. The greatest yields of oil were obtained at 40° to 50° C. from mixtures of 46, 48 and 50 per cent. by wt. of methyl alcohol in petroleum spirit, b.p. 60° to 70°, 70° to 80°, and 80° to 90° C., respectively. The expression $(125–T)/0·71$ gives the percentage of hydrocarbon in the azeotropic mixture in terms of its average b.p. (T); separation into 2 layers does not occur if T exceeds 104° C. The solvents form one layer during extraction, and subsequently separate, at room temperature, into a petroleum spirit layer containing mainly oil, and an alcohol layer containing carbohydrates, phosphatides and colouring matters. The residue contains about 60 per cent. of proteins, and appears to be a suitable raw material for bread or biscuits. Pre-treatment with superheated steam does not greatly affect the rate of decomposition by hydrolysis of the protein contained in the residue after extraction. The liquid obtained after hydrolysis with 25 per cent. sulphuric acid was neutralised with barium hydroxide and concentrated under reduced pressure to obtain the tyrosine, the resulting filtrate being extracted with *n*-butyl alcohol for 97 hours. Arginine, histidine and lysine were then precipitated from the extract by phosphotungstic acid and isolated as picrolonate, picrolonate and picrate, respectively; dibasic acids were not extracted, leucine and phenylalanine were obtained from the soluble portion of the extract, and proline from the insoluble portion. The following average figures show the distribution of the nitrogen in soya-bean proteins:—Amide, 9·58; humin, 6·14; cystine, 1·74; arginine, 15·55; histidine, 7·03; lysine, 6·08; monoamino, 49·19; non-amino, 5·19; diamino, 30·40 per cent. An ethereal solution of the methyl esters of the amino-acids produced after hydrolysis with 38 per cent. hydrochloric acid yielded on evaporation an unknown substance $C_{10}H_{16}O_8$ as monoclinic crystals, m.p. 78° C., soluble in water, methyl alcohol or benzene, and slightly soluble in ethyl alcohol. The following percentage yields of crystalline glutamic acid hydrochloride were obtained before and after acid hydrolysis, respectively, in the presence of the carbohydrates mentioned:—Glucose, 36·51, 60·43; fructose, 54·45, 62·79; sucrose, 35·58, 48·85; starch, 44·94, 61·40; none, 75·06. These figures explain why soya-cake is not

used as a source of glutamates, although 40 to 45 per cent. thereof consists of protein containing about 20 per cent. of the acid; 96 per cent. yields are, however, obtainable in the laboratory from cakes which have been extracted with methyl alcohol. The solubility of soya-bean protein at 30° C. in alkali and in solutions of various electrolytes is "affected" (decreased ?) by heat pre-treatment (at 120° C.), but not by extraction with solvents. Adhesives prepared from soya-protein by treatment with 0·2 per cent. sodium hydroxide solution, followed by coagulation with 0·5 per cent. sulphuric acid, had a lower Amsler shearing strength than similar casein products, unless they were prepared by extraction with the azeotropic mixture of solvents (cf. *supra*), when the strengths were the same. Similar differences were obtained with water-paint products for the solubility and surface produced after drying, and for the hardness and transparency of condensation products with formaldehyde. J. G.

Organic

Ethylene Glycol Monoacetate as a Selective Solvent for the Separation of Paraffins from other Oils. K. B. Edwards and R. Lacey. (*J. Soc. Chem. Ind.*, 1935, **54**, 253–254T.)—Ethylene glycol monoacetate is now produced commercially as a colourless, inert almost odourless liquid, of sp.gr. 1·109 at 15° C. It is soluble in water, and when used as a solvent it enables the solute to be recovered by dilution with water, and it therefore serves for the separation of both the soluble and insoluble portions of a mixture. All high-temperature carbonisation creosotes are soluble, whilst the solubility of petroleum and paraffin products decreases with increasing b.p.; the solubility of kerosene is 0·5 to 0·7 per cent. (spindle oils, 0 to 0·25 per cent.). The optimum concentration for use with tar oils and light lubricating oils is 8 vol. of solvent to 1 vol. of oil, and it is convenient to use flasks with graduations on the neck between 80 and 90 ml., the mixture being shaken very vigorously and the readings taken after a settling-period of at least 12 hours. Experiments with synthetic mixtures of anthracene oil and 25 to 90 per cent. of spindle oil showed that, if the solubility-factor is known, very accurate results are obtainable. Down to 2·5 per cent. of petroleum oil in anthracene oil may be detected and determined with an accuracy exceeding that of any other known method; the sp.gr. of the anthracene oil after recovery was 1·084 (1·089 originally). Phenols and acids should first be removed, as large quantities of the former invalidate the test, and as aromatic hydrocarbons separate with the paraffin, the method cannot be used for mixtures of low b.p. petroleum products with benzene, toluene or naphtha. Satisfactory results are obtained for the detection of low-temperature carbonisation in admixture with high-temperature products, since the former contain paraffins. These paraffins may also be separated and examined, but they cannot be differentiated with certainty from the paraffins contained in petroleum, although the sp.gr./b.p. curve method (Edwards, *id.*, 1924, **43**, 143T) enables the proportions of high and low-temperature carbonisation products to be estimated. Possibilities also exist in connection with other types of oils; *e.g.* most American pine oils are soluble, whilst Russian oils are not. J. G.

Determination of Urushiol in Lacquer. V-VI. S. Hirano. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 307B.)—The method of determining urushiol by polymerisation with sulphuric acid, whereby a 90 per cent. yield of substances insoluble in a mixture of alcohol and benzene is obtained, yields consistent results only when pure samples are taken direct from the trees, and if oil (*e.g.* perilla oil) has been added to the lacquer, the following adaptation of the method should be used. The lacquer is extracted with absolute alcohol, and to 0·2 g. of the extract and 0·5 g. of paraffin is added 1 ml. of absolute alcohol containing 2 ml. of concentrated sulphuric acid per 100 ml. The alcohol is evaporated, the flask is kept at 100° C. for 30 minutes, and the film formed is treated in the usual way. The percentage of urushiol is obtained by multiplying the figure for insoluble matter by 1·1. Urushiol cannot be determined in a finished lacquer by titration with baryta, since the acid value decreases in the finished product. No such drawback attends the polymerisation method, which gave fairly consistent results. The polymerisation should be carried out at 110–115° C., to ensure all alcohol being expelled. (*Cf.* ANALYST, 1935, 572.) D. G. H.

Inorganic

α-Naphthoflavone as an Indicator for Bromate Titrations. E. Schulek. (*Z. anal. Chem.*, 1935, **102**, 111–113.)—The reagent may be applied as an indicator in the volumetric determination of arsenic or antimony. The solution, containing 5 ml. of strong sulphuric acid in a total volume of 30 ml., is treated with 0·2 g. of potassium bromide and 2 drops of a 0·5 per cent. solution of naphthoflavone in 96 per cent. alcohol. The liquid is titrated with potassium bromate solution until the faint green opalescence changes to a decided rust-brown colour; at the equivalence point the bromo-substitution product flocculates. The reaction is reversible, the colour disappearing on addition of the necessary quantity of arsenious or antimonious salt solution. In the determination of antimony, the liquid should contain 0·5 g. of tartaric acid. Hydrochloric acid in substantial quantity (over 5 per cent.) decreases the sensitiveness of the indicator.

W. R. S.

Volumetric Determination of Manganese by Conversion into Manganic Salt. R. Lang. (*Z. anal. Chem.*, 1935, **102**, 8–16.)—The process is based on induced oxidation of manganous to manganic salt by dichromate in presence of arsenite in metaphosphoric acid solution, and titration of the manganic salt with ferrous sulphate; it follows the lines of the author's method for the determination of cerium (ANALYST, 1934, **59**, 646). The same dichromate, arsenite, ferrous sulphate solutions, and diphenylamine indicator are used. The manganous solution must be free from chloride, but may contain 5 to 40 ml. of strong sulphuric, or 10 to 50 ml. of strong nitric, acid free from nitrous oxides; it is cooled to room temperature, and treated with a solution of metaphosphoric acid in 20 to 25 ml. of water. After addition of 0·1 ml. of indicator, it is treated first with dichromate,

then with an excess of arsenite, solution. The following quantities of reagents are used:

For 0·08 g. Mn: HPO_3 5 g., $K_2Cr_2O_7$ 35 ml., As_2O_3 40 ml.
,, 0·2 ,, ,, : ,, 8 ,, ,, 60 ,, ,, 65 ,,
,, 0·25 ,, ,, : ,, 10 ,, ,, 75 ,, ,, 80 ,,

The red solution is titrated with ferrous sulphate solution, the colour changing to violet, blue, and, finally, grass-green. Other metals do not interfere, with the exception of tungsten, which prevents a sharp end-point when the volume of dichromate solution required exceeds 30 ml. In presence of ferric salt the addition of metaphosphoric acid must be increased, one part of iron requiring ten of the acid. The process is suitable for iron alloys and special steels containing chromium and cobalt. The following quantities are recommended, (1) for metal with less than 5 per cent. of manganese, (2) for metal with more than 5 per cent., and (3) for ferromanganese:

(1) 0·6 g. alloy: HPO_3 10 g., $K_2Cr_2O_7$ 30 ml., As_2O_3 35 ml.
(2) 0·4 ,, ,, : ,, 12 ,, ,, 60 ,, ,, 65 ,,
(3) 0·3 ,, ,, : ,, 12 ,, ,, 70 ,, ,, 75 ,,

W. R. S.

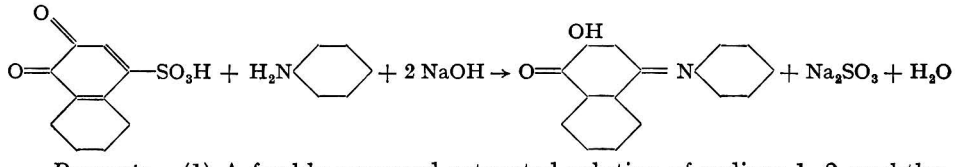
Determination of Caesium as Iodobismuthate. R. W. Feldmann. (*Z. anal. Chem.*, 1935, **102**, 102–108.)—The work of Tananaeff and Harmasch (Abst., ANALYST, 1932, **57**, 672) was submitted to critical re-examination. In spite of various modifications in the procedure, which are set out in this paper, the author was unable to effect a recovery of more than 94 per cent. of the caesium taken; the filtrates from the iodobismuthate gave a positive reaction for caesium. Further, it was found that rubidium is precipitated to a certain extent; test separations of caesium from rubidium yielded products containing 7 to 10 per cent. of rubidium in terms of the chloride. It is concluded that the proposed method cannot be described as accurate. W. R. S.

Volumetric Determination of Boron Nitride. B. Ormont and A. Ssamoilow. (*Z. anal. Chem.*, 1935, **102**, 20–24.)—The process, which is based on the conversion of the nitrogen into ammonia, utilises fusion with potassium hydroxide at low temperature in a porcelain crucible in a stream of moist hydrogen. The material (0·05 to 0·1 g.) is weighed in the crucible in a closed weighing bottle. Dry potassium hydroxide (5 to 6 parts) is added, and the crucible is introduced into a wide test-tube closed with a two-holed stopper and placed in a small electric furnace. The stopper carries two tubes bent at right angles; a longer one for the admission of hydrogen, reaching down into the crucible, and a shorter exit tube connected with a conical receiver containing a known excess of standard acid and a little phenolphthalein. Since complete decomposition of the nitride requires 2 hours or more at 250° to 300° C., the receiver is so constructed that a few drops of standard acid can be blown into the knee-bend of the exit tube during a momentary interruption of the hydrogen current. When this is turned on again, any ammonia carried over will colour the indicator after a few minutes. When decomposition is complete, heating is continued for another 15 minutes; the receiver is withdrawn, the tube rinsed through, and the excess of acid is measured with standard alkali.
W. R. S.

Detection of Japanese Acid Clay by the Colour Reaction of Benzidine Solution. K. Kobayashi and H. Ishikawa. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 308–309B.)—Owing to the powerful adsorption properties of Japanese acid clay, this clay may be distinguished from ordinary kaolinitic clays by several reagents, and particularly by a solution of benzidine in alcohol. Dried clays should be treated with a 0·05 per cent. solution of benzidine in 50 per cent. alcohol, and wet clays with a 0·1 per cent. solution, when Japanese acid clay will develop an intense blue or greenish-blue colour, whilst no colour develops with kaolinitic clays, even after several hours. D. G. H.

Microchemical

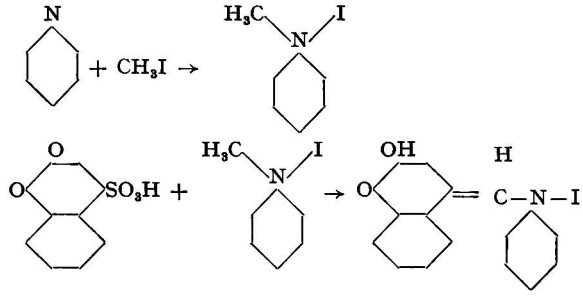
Spot Tests for Organic Compounds (VII) Tests for CH_2– and NH_2–Groups. F. Feigl and O. Freyden. (*Mikrochem.*, 1935, **16**, 79–86.)—The test utilises the reaction between 1, 2-naphthoquinone-4-sulphonic acid in alkaline solution and CH_2– and NH_2– compounds with a replaceable hydrogen atom, giving deeply-coloured quinonoid condensation products:



Reagents.—(1) A freshly-prepared saturated solution of sodium 1, 2 naphthoquinone-sulphonate in 50 per cent. alcohol. (2) 0·5 *N* sodium hydroxide solution. (3) 2 *N* acetic acid. *Method.*—A small amount of the solid test substance, or a drop of the solution is treated in a micro-crucible with two drops of solution (1), and then rendered alkaline with two drops of the alkali, when an intense colour results. On acidifying with acetic acid there is a distinct colour change, usually accompanied by precipitation. Colours and limits of identification are shown in the table.

Compound	Identification limit γ	Colour: With alkali	Colour: With acetic acid	Remarks
Ethyl malonate	1·2	Deep violet	Yellow and yellow ppt.	—
Rhodanine	0·6	Dark blue-violet	Red-yellow ppt.	—
Ethyl acetoacetate ..	1·2	Blood-red to violet	Yellow and yellow ppt.	Slow reaction
Thiocyano acetic acid ..	0·6	Red-brown	Orange	—
Dibenzoyl methane ..	12	Red-violet	Yellowish-white ppt.	Very slow
m-Nitraniline	6	Yellow-brown	Carmine ppt.	Allow to stand
Benzylamine	0·6	Green	Brown-red	—
Semicarbazide	0·6	Orange-red	Light yellow	—
Aniline	0·12	Auburn red	Light orange	—
β-Naphthoquinoline methiodide	1·2	Dark violet to blue-green	Yellow-brown ppt.	—
β-Napthylamine ..	0·6	Yellow-red or brown	Carmine ppt.	—
Indole	0·6	Green	Violet	—
Piperidine	0·6	Red	Light-red ppt.	Intense colour reaction without alkali
Pyrrole	0·6	Dark violet	Olive-green	Intense colour

The same reaction may also be utilised for the detection of tertiary ring bases after their conversion into quaternary compounds with methyl iodide or dimethyl sulphate:



Reagents.—(1) Methyl iodide or dimethyl sulphate. (2) Same as (1) above. (3) Same as (2) above. (4) *N* acetic acid. *Method.*—A small amount of the test solution or solid is mixed in a micro-crucible with 5 or 6 drops of methyl iodide or dimethyl sulphate and heated to gentle boiling over an asbestos plate. Some substances very difficult to convert must be heated with the methyl iodide for some hours in a sealed capillary tube in a boiling water-bath. The test is then carried out as described above. The following table shows a number of compounds tested:

Compound	Identification limit γ	Colour: With alkali	Colour: With acetic acid	Remarks
Pyridine	12	Red to violet	Orange	—
α-Picoline	12	Dark blue-violet	Yellow	—
Quinoline	25	Brown to black-green	Red	—
Quinaldine	12	Violet to blue-green	Greenish-yellow	—
α-6-Dihydroxypyridine-4-carboxylic acid	25	Dark green	Red striations then green ppt.	Use CH_3I
Dimethylpyrone	25	Brown-violet, turning green	Red coloration then ppt.	—
Chelidonic acid	25	Dark green	Red	Use CH_3I
o-Nitraniline		Yellow-green ppt.		$(CH_3)_2SO_4$
p-Nitraniline		Dark green		,,
Atophan		Milky ppt., turning orange	Yellow	CH_3I in sealed tube
Cinchonine	100	Red	,,	,, ,,
Papaverine		Violet-brown ppt., turning orange on standing	,,	,, ,,

J. W. M.

Crystal Formation by "Salting out." L. Rosenthaler. (*Mikrochem.*, 1935, **16**, 37–44.)—"Salting out" is used to precipitate the alkaloids from pharmaceutical preparations. A drop of an approximately 1 per cent. solution of the preparation is put on a microscope slide, and sufficient of the salt for a little to remain undissolved is added. The drop is then covered with a cover-slip, and the crystal formation is observed under the microscope. The following

table shows the salts used and the concentration limits when crystals were formed:

Test substance	Sulphates of			Chlorides of			Nitrates of		
	Ammonium	Potassium	Sodium	Ammonium	Potassium	Sodium	Ammonium	Potassium	Sodium
Aconite nitrate	1:1000	—	—	—	—	1:200–1:300	1:750–1:1000	1:200–1:300	1:750
Alipine hydrochloride	—	—	—	—	—	1:100–1:200	1:100–1:200	—	1:750
Apomorphine ,,	1:1000–1:1500	1:200–1:300	1:500–1:750	1:2000	1:2500	1:4000	1:1500	1:1500	1:7000
Berberine ,,	1:4000	1:200–1:500	1:200–1:500	1:10,000	1:2500	1:8000	1:5000	1:10,000	1:5000
Brucine sulphate	1:5000	1:100–1:200	1:750	1:100–1:200	1:200–1:300	1:500–1:1000	—	1:200	1:100–1:200
Quinidine ,,	1:1500–1:2000	1:200–1:500	1:750	1:750	1:2000	1:2500	1:500–1:750	1:750–1:1000	1:2000
Quinine ,,	1:3000	1:1000	1:3000	1:500	1:1000	1:1000	1:300	1:500–1:750	1:1000
Cinchonidine ,,	1:1500	1:200–1:500	1:750	1:200–1:500	1:500	1:1000	1:200–1:500	1:200–1:500	1:750
Cinchonine ,,	1:1000	1:100–1:200	1:200	1:300–1:500	1:1000	1:1000	1:200	1:200	1:1000
Codeine phosphate	1:500	—	—	—	1:100–1:200	1:100–1:200	—	—	1:100–1:200
Caffeine	1:5000	—	1:300	—	—	1:100–1:200	—	—	—
Caffeine sodium benzoate	1:1000	—	—	—	—	—	—	—	—
Diocaine hydrochloride	1:3000 (amorphous)	—	1:500 (amorphous)	1:1500	1:1500	1:3000 (amorphous)	1:2000 (amorphous)	1:2000 (amorphous)	1:2000 (amorphous)
Eucaine A ,,	1:500	—	—	1:300	1:300	1:750	1:500	1:300–1:500	1:1500
Eucaine B ,,	1:750	—	—	1:100–1:200	1:400	1:3000	1:100–1:200	1:100–1:200	1:500
Larocaine ,,	1:250–1:500	—	—	—	—	1:250–1:500	1:100–1:200	—	1:250–1:500
Morphine ,,	—	—	—	—	—	1:200	—	—	1:200
Novocaine ,,	(amorphous)	—	—	—	—	1:100	—	—	(amorphous)
Panthesin	1:1000	1:100 (amorphous)	—	—	1:200	1:750	1:300–1:500	1:200	1:1000
Psicaine hydrochloride	1:500–1:1000 (amorphous)	—	—	1:500–1:1000	1:500–1:1000	1:1500	1:500–1:1000	1:500–1:1000	1:2500
Aminopyrine	1:1000	—	1:200	—	1:200	1:250–1:500	—	—	1:250–1:500
Stovaine hydrochloride	—	—	—	—	—	1:100–1:200	—	—	1:200
Strychnine ,,	1:1500	—	1:200–1:400	1:500–1:1000	1:1000–1:2000	1:1000–1:2000	1:200–1:400	1:200–1:400	1:500–1:100
Atropine	—	—	—	—	—	—	—	—	—
Hexamethylene tetramine	—	—	—	—	—	—	—	—	—
Antipyrine	1:100 (drops only)	—	—	—	—	—	—	—	—
Emetine hydrochloride	1:100 (amorphous)	—	—	1:100 (amorphous)	1:100 (amorphous)	1:100 (amorphous)	1:100 (amorphous)	1:100 (amorphous)	1:100 (amorphous

J. W. M.

Physical Methods, Apparatus, etc.

Standardisation of Photochemical Methods for the Measurement of Solar Ultra-violet Radiation. H. S. Mayerson. (*Amer. J. Hygiene*, 1935, **22**, 106–136.)—The acetone and methylene blue method (Webster, Hill and Eidinow, *Lancet*, 1924, **1**, 745), the zinc sulphide method (Clark, ANALYST, 1929, **54**, 493), and the oxalic acid method (Anderson and Robinson, *J. Amer. Chem. Soc.*, 1925, **47**, 718) for the measurement of solar ultra-violet radiation have been calibrated against a radiometric (thermopile-screen) method, and are now compared. The first method is the simplest and most convenient and, being slow, it requires little attention. However, it gives only approximate results, because the reaction is reversible in the dark; the temperature-coefficient (1·25 per 10° C. rise) is high, and the correction is difficult to apply; the rate of bleaching is not uniform and decreases as the reaction proceeds; and the maximum sensitiveness is to light of wave-length below 270$m\mu$, which is absent from solar radiations. Methods for controlling these errors are suggested. The reaction is sensitive to visible radiation between 570 and 710$m\mu$, and it is suggested that 700 ergs per square cm. per second should be taken as the antirachitic energy shorter than 313$m\mu$ required to bleach the standard acetone and methylene blue solution by 1 unit in 1 hour; that radiations should always be measured at normal incidence; and that the bleaching due to the visible spectrum should be determined by simultaneous exposure of a glass control tube and an allowance made. The zinc sulphide method is simple, rapid and convenient, so long as apparatus for making accurate measurements of reflection factors is available, since colour-charts are unsatisfactory. It is irreversible and is sensitive only to ultra-violet radiation (and particularly to the antirachitic constituents); under the conditions specified the change observed is proportional to the intensity of the radiation. It is suggested that "green glass" slides should be used to isolate the radiations of wave-lengths below 313$m\mu$, and that in correcting for the difference between the readings obtained in quartz and glass vessels the difference value should be reduced by the factor 0·13. Disadvantages are the variations in the sensitiveness of different batches of zinc sulphide, and the changes in colour which they undergo on storage in the dark. One unit, for wave-lengths of 290 to 350$m\mu$, is equivalent to a radiation intensity of 735,000 ergs per square cm. The oxalic acid and uranyl sulphate method is in all respects the most desirable. The apparatus is simple, the reagents are readily available in the pure state, and the final result is obtained by means of a standard accurate titration. Unless allowance is made for radiation from the sky, measurements of solar radiation at normal incidence are not comparable, and this difficulty may be overcome by means of a blank test (cf. *supra*), or by an arrangement of black metal discs with concentric openings. The intensity of radiation, as measured by this method, may be expressed in ergs per square cm. per second by multiplying the number of mg. of oxalic acid decomposed per sq. cm. in 30 minutes by 18,300 (for wave-lengths between 290 and 390$m\mu$). The reaction depends on the decomposition of 0·1 N oxalic acid in the presence of a 0·01 N solution of uranyl sulphate as a photosensitiser; Moss and Knapp (*J. Soc. Chem. Ind.*, 1935, **44**, 453T), however, recommend uranium acetate. The liquid is

exposed in a quartz cell, 1·5 to 2 cm. thick (or in a glass cell with a Corex glass face), and the oxalic acid is titrated with 0·1 *N* potassium permanganate solution; the unit is the number of mg. of oxalic acid decomposed per unit time per square cm. of surface exposed. The amount of decomposition is directly proportional to the intensity of the radiation, so long as not more than 50 per cent. of the oxalic acid is decomposed. The absorption of the solution does not change materially during prolonged exposure, and variations due to differences in temperature are negligible. To facilitate intercomparison of data obtained in different localities by different methods, it is suggested that all results should in future be expressed in absolute units by means of the factors given. J. G.

Reviews

CHEMISCHE GRUNDLAGEN DER LEBENSVORGÄNGE. Eine Einführung in biologische Lehrbücher. CARL OPPENHEIMER. Pp. vii + 298. Leipzig: Georg Thieme. Price R.M. 22·50.

The increasing refinements of analytical methods have had a profound influence on biochemical theory. At the beginning of this century most biochemical textbooks opened with a bold statement that "protoplasm" was built up from carbon, hydrogen, oxygen, nitrogen, sulphur and phosphorus. By slight stretching of the imagination, iron, calcium, sodium, potassium and magnesium were also included among the biologically essential elements. To-day, following on the development of analytical technique which has allowed of the determination of smaller and smaller quantities, it is realised that copper, manganese and iodine must also be included in the list. Barium, zinc, arsenic, aluminium, bromine and fluorine are almost invariably present in living tissues, but whether as essential or incidental factors is not fully known. The same can be said of the long list of elements found, by spectroscopic methods, freely distributed in the tissues of marine animals.

Professor Oppenheimer's book sums up present knowledge of the elementary composition of living matter and gives a broad review of the working of the chemical machine. He takes up the position that no sharp line is to be drawn between chemical combination and adsorption, or between the substance of the life-machine and the other constituents that are required to keep it working. He devotes a section to the chemical components of living matter, and others to the processes of metabolism and to catalysts and enzymes, with particular attention to the problem of cell oxidation. A section on the energetics of living matter brings to an end a book which is well balanced and well written and full of interest on every page. DOROTHY JORDAN LLOYD

THE APPLICATION OF ABSORPTION SPECTRA TO THE STUDY OF VITAMINS AND HORMONES. R. A. MORTON. Pp. 70. With 6 plates. Adam Hilger, Ltd. 1935. Price 10s. net.

Since the days of Bunsen, spectroscopy has been, in a sense, part of the analyst's territory; it may, however, be considered to have been given *de jure*

recognition at the Society's meeting on 7th November last. Dr. Morton's monograph, though it covers only part of the domain, has nevertheless a double appositeness, for members of the Society are becoming increasingly involved in the physical and chemical methods of estimating vitamins, hormones and other substances first recognised and measured by their physiological activity.

In his 66 pages Dr. Morton has been able to outline the relevant researches that have led to the present position and to define that position in some detail and with the necessary qualifications, which are laid down in a commendably accurate manner. He makes it clear that spectrophotometric assay is the most accurate method available for measuring vitamin *A*, in most natural sources, provided steps are taken to estimate any significant quantities of carotene that may also be present; that it is an essential part of any attempt to assess the purity of calciferol, the crystalline artificial vitamin *D*; that its possibilities in the determination of vitamins B_1 and *E* are worthy of further exploration; that the peculiar properties of ascorbic acid (vitamin *C*), in that its ultra-violet spectrum changes with *p*H, render its spectrometric examination of analytically diagnostic value; and that the possibilities of its use in hormone bio-chemistry are by no means to be ignored.

All the known substances comprised under the terms hormones and vitamins, except the "flavins," are colourless, or nearly so, and it therefore follows that the methods of ultra-violet spectroscopy and spectrophotometry are alone in question; with the great improvements effected in this technique during the last two decades —improvements towards which the publishers of this book have contributed very largely—this use of the invisible spectrum to-day involves substantially no more serious problems of method and equipment than does the use of the visible.

It is to be hoped and expected that more than one edition of Dr. Morton's interesting and lucid exposition will be called for. When it is, we trust that the opportunity will be taken to eliminate the rather manifold signs of haste in production from which it must be admitted to suffer. There is evidence of inadequate proof-reading, which has led to the appearance on p. 28 of a structural formula for vitamin *A* that is not only wrong, but impossible, to the writing of "inactive" for "active" on p. 7 (par. 3, line 5), to an incorrect "legend" to figure 3 (p. 14), to the omission of the essential words "for the oil" from the beginning of line 3 on p. 24, to the appearance of "Fig. 20" under two different diagrams (pp. 51 and 57; the second should be "Fig. 21"), and to certain minor "literals."

In his quite legitimate anxiety to take into account the most recent work Dr. Morton has, on p. 12, summarised the evidence that makes the existence of vitamin *D* in more than one form very probable; unfortunately this completely invalidates the statement made seven pages earlier, that *calciferol* circulates in the blood-stream after irradiation of the animal organism. We simply do not know which of the several possible forms of "vitamin *D*" is natural to man and other mammals. Any new edition will, doubtless, be able to carry the story of vitamin *D* some stages further; there is at present quite a vigorous controversy raging between the experts on the nature of the chemical changes following the irradiation of ergosterol, and consequently on the precise constitution of calciferol.

Again, it is surely not legitimate for Dr. Morton, or anyone else, to depart from factors having the international sanction of the Permanent Commission on

Biological Standardisation, unless he makes it abundantly clear that he has done so. Dr. Morton gives the biological activity of pure vitamin *A* as 1·8 million international units per gram (pp. 22 and 26), and the factor for converting $E^{1\%}_{1\,cm.}$ 328*mμ* to international units as 1100; the figures fixed by the conference of June, 1934, were 2·56 million and 1600, respectively. The work on which Dr. Morton obviously bases his departure from these figures was presented by himself and Mr. R. S. Morgan to the Biochemical Society early this year; but, though this work has just been published, Dr. Morton is likely only to confuse the unwary by making this departure without anywhere stating that he has done so.

The list of carotenoids and related substances, with their more important properties (Table III, pp. 31–33), is a valuable feature of this book, and should be sufficient by itself to recommend it to plant chemists. Doubtless any new edition will see a considerable extension of this list, which might then be printed across two pages, with an extra column for stating the known more important sources of each substance; in this edition no source is given for several of them.

Although we have criticised above a number of inaccuracies and mis-statements, most of which are, we suggest, simply due to haste in production, the selection of facts in this book and their method of presentation are such as to make it quite clear that any future edition will not be allowed to lag behind current research. Dr. Morton is to be congratulated on the precision with which he has, in general, defined and carried out his survey, but it might be suggested to the publishers that the cost is somewhat excessive for 70 pages of even so excellent a piece of work; it seems quite likely that its sale might be trebled or quadrupled if the price were halved.

A. L. BACHARACH

A GERMAN-ENGLISH DICTIONARY FOR CHEMISTS. By AUSTIN M. PATTERSON, Ph.D. Second Edition. Pp. 411. London: Chapman & Hall. 1935. Price 15s. net.

The first edition of this useful little handbook was published in 1917, and has been repeatedly reprinted. The fifth (1924) issue, which contained 27 pages of addenda, was reviewed in THE ANALYST (**1925, 50**, 260), and now we have a revised second edition in which the supplementary pages have been incorporated in the body of the book, and a large amount of new matter has been added. During the years that have passed since the last revision there have been great changes of concept in chemistry, especially in chemical physics, with a corresponding coinage of new words. Most of these will be found in this new edition, which now comprises some 42,000 entries, and has 68 more pages than its predecessor, notwithstanding the fact that some space has been gained by omission of numerous words that are rarely met with in technical literature.

In revising the dictionary Dr. Patterson has consulted not only the standard scientific and technological dictionaries, but also specialised dictionaries on metallurgy, biology and bacteriology (*e.g.* Partridge's *Dictionary of Bacteriological Equivalents*), and he has succeeded in producing a book that is well nigh invaluable to all who wish to study German chemical publications. In particular, mention should be made of the very large number of abbreviations, with their English

equivalents, which have been included; abbreviations such as "ä.W.," "Dz," "Q.S.," and "KZ" are too often a stumbling block to the foreign reader of German technical books.

We can fully endorse all that was said in praise of this dictionary when it was last reviewed. It is clearly printed and singularly free from typographical errors, is in a binding that is easy to handle and, when consulted, will seldom be found wanting. EDITOR

ANNALI DI MERCEOLOGIA SICILIANA. Vol. II. 1933–1934. Pp. 319. Catania.

In this volume various industries carried on in Sicily and elsewhere in Italy are discussed in turn by different authors. Attention is directed first to cotton, which was introduced into several districts of Italy and into Sicily by the Arabs, probably over 800 years ago. The soil and climate of Sicily are well suited to the growing of cotton, which at one time was carried on there on a considerable scale. In Italy itself the cultivation has been relinquished, but in Sicily, although greatly restricted, it still persists. Now that the spinning and weaving of cotton are being developed in the countries where the main bulk of the raw material is grown, expansion of the cultivation in Sicily, and abolition of the tax on cotton-seed oil, are urged.

An excellent account is given of the citric acid position throughout the world and of the way in which the biological manufacture of the acid has affected what was once virtually a Sicilian monopoly. Other industries discussed are those of sea-salt, sheep-raising, limestone, antimony, tunny fishing, papyrus, and the de-tinning of tinned-sheet scrap. Communications are also included describing a new volumetric method of determining mercuric chloride (by C. Chines), and a densimeter for use with small amounts of liquid (G. Ajon). T. H. POPE

CEREAL LABORATORY METHODS. COMMITTEE OF METHODS OF ANALYSIS, AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Third Edition. Pp. vii + 204. American Association of Cereal Chemists, Omaha Grain Exchange, Nebraska. 1935. Price $3.

Those chemists interested in cereal work in England will welcome the third edition of this publication dealing with the methods they normally employ. In general the methods are distinctly American, and but little reference has been given to other accepted methods used by chemists in Europe. It is also a pity that dough-testing methods have not progressed sufficiently or been sufficiently accepted to have been included and described.

The present edition has the following chapters and headings:—I, Wheat and other Whole Grains; II, Feeds and Feeding Stuffs; III, Wheat Flour, Semolina, and Similar Products; IV, Enzymatic, Physico-chemical, and Miscellaneous Methods; V, Baking Tests; VI, Baked Cereal Products; VII, Macaroni Products; VIII, Fats and Softening Materials; IX, Leavening Agents; X, Yeast Foods, Flour Improvers, etc.

The appendix contains a number of useful tables dealing, amongst other things, with the Munson–Walker equivalents for sugar, correction factors for the

determination of carbon dioxide, percentage of protein and ash with varying moisture, etc.

Some of the methods deal with aspects of problems with which we are little concerned in this country, and so may not appeal directly to English chemists.

The third edition is undoubtedly arranged in a more attractive manner than the second edition, although it is not much larger. For example, the first chapter on Wheat and other Whole Grains is curtailed and deals only with essentials. Much work on the nature of the proteins present and the like has been cut out, since it really appears under the section on flour and semolina. The chapter dealing with Feeds and Feeding Stuffs consists mainly of methods recommended by the Association of Official Agricultural Chemists.

In Chapter III, full and useful methods are given. It is interesting to note that the Rask method for the determination of starch is given as originally proposed, and that no mention is made of the use of sand, without which, particularly with soft flours, it is sometimes difficult to obtain accurate results. In the estimation of chlorine in flour extraction is advocated with anhydrous alcohol-free ether instead of with the petroleum spirit generally used in England. Similarly, in the chapter on Enzymatic and Physico-chemical Methods, no mention is made, in the description of the determination of maltose, of the procedure by Lane and Eynon with methylene blue, which is common practice in England, especially when this test is used for routine work.

The chapter on Baking Tests is mainly concerned with the standard American baking test employing 100 grammes of flour, which method so far has not commended itself in Europe.

The book will, however, be much appreciated by those chemists in flour mills and bakeries, and others, who are faced with the problems of the analysis of cereal products, as the methods given are clearly described and are, in general, of proved usefulness. The Committee of Methods of Analysis of the American Association of Cereal Chemists, under the chairmanship of C. E. Mangels, is, therefore, to be congratulated.

D. W. KENT-JONES

Publications Received

INORGANIC COLLOID CHEMISTRY. Vol. II. HYDROUS OXIDES AND HYDROXIDES. By H. B. WEISER. Pp. vii+429. London: Chapman & Hall. Price 23s. 6d. net.

PLANT PHYSIOLOGY. By MEIRION THOMAS. Pp. xii+494. London: J. & A. Churchill, Ltd. Price 15s.

SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS. By F. SUTTON. Twelfth Edition. Revised by A. D. MITCHELL. Pp. xvi+631. London: J. & A. Churchill, Ltd. Price 35s.

STRUCTURE AND COMPOSITION OF FOODS. Vol. II. VEGETABLES AND FRUITS. By A. L. and K. B. WINTON. Pp. xiv+904. London: Chapman & Hall. Price 75s. net.

MIKRO-MASSANALYTISCHE BESTIMMUNG DES KOHLENSTOFFES UND WASSERSTOFFES. By J. LINDNER. Pp. vii+374. Berlin: Verlag Chimie G.M.B.H. Price RM. 20.