THE ANALYST

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

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, May 7th, the President, Dr. J. T. Dunn, being in the chair.

Certificates were read for the first time in favour of:—John Herbert Bushill, M.Sc., A.I.C., Edward Quentin Laws, B.Sc., A.I.C., and Hubert Taylor, B.Sc., A.I.C.

Certificates were read for the second time in favour of:—Lionel Stuart Davis, Arthur Smith, B.Sc., A.I.C., and Snow Blagburn Tallantyre, B.Sc., A.R.C.Sc., F.I.C.

The following were elected members of the Society:—Charles Ambrose Adams, B.Sc., F.I.C., Janet Warden Brown, Ph.D., A.I.C., and John Alexander Reddie, F.I.C.

The following papers were read and discussed:—"The Diastatic Activity of Honey," by L. H. Lampitt, D.Sc., F.I.C., E. B. Hughes, M.Sc., F.I.C., and H. S. Rooke, M.Sc., A.I.C.; "A New Method for the Separation of Titanium from Zirconium and Hafnium," by A. R. Powell and W. R. Schoeller, Ph.D.; "The Composition and Polymerisation of Chinese Wood (Tung) Oil," by E. R. Bolton, F.I.C., and K. A. Williams, B.Sc., A.I.C.; and "The Examination of Milk for Tubercle Bacilli," by D. R. Wood, F.I.C.

The Composition and Polymerisation of Chinese Wood (Tung) Oil.

By E. R. BOLTON, F.I.C., and K. A. WILLIAMS, B.Sc., A.I.C.

(*Read at the Meeting, May* 7, 1930.)

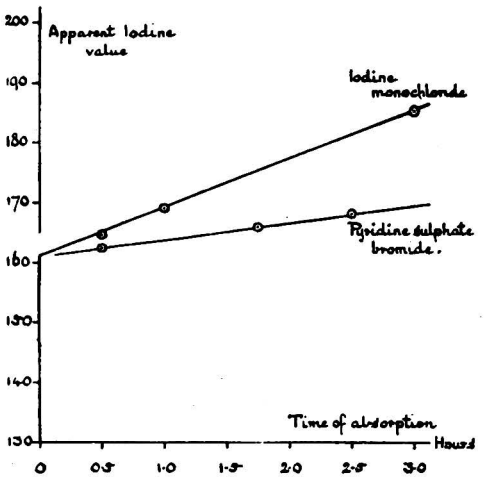
In a previous communication (Analyst, 1926, **51**, 335) we have described a method for the determination of the polymerisable matter in Chinese wood oil, and have shown that the proportion varies within such narrow limits (70 to 74 per cent.) that its determination affords a satisfactory criterion of the purity of an oil. We have further suggested the proportion of polymerisable matter to be a measure of the commercial value of the oil.

During the past 4 years we have had further opportunities of examining a large number of samples, with results in confirmation of those given in our original communication.

Chinese wood oil is characterised by containing a large proportion of glycerides of elaeostearic acid, to which its power of polymerising to a solid mass is due. It seemed to us, therefore, that if a correlation of the commercial value of the oil and the proportion of elaeostearic acid could be established it would provide a more satisfactory basis for the assessment of the commercial value than the general consideration of conventional constants that is at present customary. It was on this account that we sought to establish a relation between the proportions of polymerisable matter and elaeostearic acid in the oil; and we have succeeded in showing that these two quantities are, within experimental error, the same for every oil in which we have so far determined both.

Determination of Elaeostearic Acid.—Of the methods available for the determination of elaeostearic acid that described by Toms (Analyst, 1928, **53**, 69) has yielded results which we believe to be more consistent and accurate than any other yet published. This method is based on the assumption that a molecule of elaeostearic acid absorbs 6 atoms of bromine from bromine vapour, but only 4 atoms of halogen from Wijs iodine monochloride solution, and that all other fatty acids present absorb equivalent proportions of halogens from both reagents. While there seems to be no doubt that exactly 6 atoms are absorbed from bromine vapour, it is generally recognised that the absorption from Wijs solution, as usually applied, is by no means so simple as Toms has assumed, the iodine value usually obtained representing the absorption of rather more than the 4 atoms required by theory. Thus, Boughton (Seventh Int. Congr. Appl. Chem., London, 1909) has shown that the apparent iodine value of Chinese wood oil depends upon such experimental conditions as temperature, time of contact of oil and reagent, and concentration

of the halogenating solution. It follows that Toms' method leads, in general, to low values for the proportion of elaeostearic acid in Chinese wood oil.



Absorption of halogen by Chinese wood oil.

DETERMINATION OF TRUE IODINE VALUE OF OIL.—Böeseken (*Rec. Trav. Chim.*, 1927, **46**, 619) has observed that the four outer unsaturated carbon atoms, in the conjugated system in elaeostearic acid, are saturated with halogen by means of Wijs solution within 15 minutes, whereas the remaining two unsaturated atoms in this conjugated system become saturated only after many hours' contact with the reagent.

This observation would appear to indicate that the iodine value corresponding to the absorption of 4 atoms of halogen per molecule of elaeostearic acid could be obtained by limiting the action of the Wijs reagent to a very short period, say, less than 5 minutes. We have found such a method to give satisfactory figures in the case of some specimens of Chinese wood oil, but, with others, consistent results are obtainable only when absorption is allowed to proceed for 20 minutes: figures so obtained are near enough to the true figure for practical purposes, though, admittedly, they are distinctly high.

By allowing Chinese wood oil to absorb halogen from both Wijs solution and pyridine sulphate bromide solution for varying periods of time, we have found that the first rapid stage is almost complete within five minutes, that most of the absorption is instantaneous, and that, during the second slow stage, absorption proceeds at a regular speed. This is shown in Fig. I, in which are plotted typical figures obtained by the action of the two reagents upon one specimen of the oil; the actual experimental results from which the curves are drawn are shown in Table I. In Fig. I it will be seen that the second slow stage is represented by a straight line, indicating that the increase in the apparent iodine value, during any

given period of time, is constant for a given halogenating solution under the usual conditions of the determination. Since this increase is due to the slow saturation of the last two carbon atoms of each elaeostearic acid molecule, and such saturation begins as soon as the reagent comes into contact with the oil, it follows that the actual turning point of the curve may be measured by extrapolation to zero time of the straight line representing the second stage of absorption.

TABLE I.

ABSORPTION OF HALOGEN BY A CHINESE WOOD OIL.

Reagent.	Time of contact of oil and reagent. Hours.	Apparent iodine value.
Wijs iodine monochloride	0·5	164·5
	1·0	169·0
	3·0	185·0
Pyridine sulphate bromide.. ..	0·5	163·5
	1·75	166·0
	2·5	168·0

In the case illustrated the turning point occurs at an iodine value of 160·8 with Wijs solution and 161·2 with pyridine sulphate bromide, and is thus the same, within the error of experiment, for both reagents. We find that this case is typical of all absorptions of halogen from these two reagents, the slope of the line representing the slow absorption varying from oil to oil and being dependent on the reagent used, while the turning point is constant and independent of the reagent. This we consider affords very strong evidence that at this turning point the oil has absorbed a proportion of halogen corresponding to 4 atoms per molecule of elaeostearic acid.

The instantaneous iodine value may best be determined graphically from the iodine values obtained after absorption has proceeded for 30 minutes and for 3 hours, or by calculation from these two quantities by means of the expression:

$$\text{"Instantaneous" iodine value} = \text{I.V.}_{30\text{ min.}} - \tfrac{1}{5}\left[\text{I.V.}_{3\text{ hrs.}} - \text{I.V.}_{30\text{ min.}}\right]$$

in which:

$\text{I.V.}_{30\text{ min.}}$ is the Wijs iodine value obtained after 30 minutes' absorption.

$\text{I.V.}_{3\text{ hrs.}}$ is the Wijs iodine value obtained with the same solution after 3 hours' absorption.*

* Since this paper was read, Dr. Mitchell has drawn our attention to a thesis presented by van Loon, in 1929, to the University of Delft, in which the abnormal iodine values of fatty oils containing a conjugated system of double bonds is discussed. In our paper we have termed the iodine value given by Wijs solution an "apparent" iodine value, and we notice that the same phrase is used by van Loon, who approaches the problem of iodine values in a very ingenious manner and on distinctly different lines from those of our present communication.

PROPORTION OF ELAEOSTEARIC ACID IN CHINESE WOOD OIL.—The bromine value of elaeostearin corresponding to saturation of all three double bonds of the acid, is 164·8, or, calculated in terms of iodine, 261·7; and the true iodine value corresponding to the absorption of 4 atoms of halogen per molecule of the acid is 174·5; the difference between the two values, expressed in terms of iodine, is, therefore, 87·2. Since the amount of iodine monochloride absorbed by all other constitutents of Chinese wood oil is exactly equivalent to that of bromine, it follows that the proportion of glyceride of elaeostearic acid present in the oil may be obtained by dividing the difference between the bromine value and the true, or instantaneous, iodine value by 87·2 and multiplying the result by 100.

We have used the above method to determine the proportion of elaeostearic acid glyceride in a number of specimens of Chinese wood oil in which we have also determined the proportion of polymerisable matter by the method previously described (ANALYST, 1926, **51**, 335).

In Table II we have set out the results of these determinations, and it will be seen that the amounts of polymerisable matter and of the glyceride of elaeostearic acid are the same, within a small experimental error. This being so, we feel that we are justified in the assumption that the polymerisable matter consists entirely of the glyceride of elaeostearic acid, and, consequently, we suggest that our original method of determining the polymerisable matter in Chinese wood oil determines the glyceride of elaeostearic acid.

TABLE II.

PROPORTIONS OF ELAEOSTEARIC ACID AND POLYMERISABLE MATTER IN CHINESE WOOD (TUNG) OIL.

		Iodine value.			Bromine value. Toms' method.	Glyceride of elaeostearic acid, calc. from bromine and iodine values. Per Cent.	Polymerisable matter (Bolton and Williams' method). Per Cent.
		Half-hour.	Three hours.	Instantaneous. value.			
Pure Oils:	1.	168·5	175·5	167·1	229·0	71·0	70·4
	2.	165·4	175·7	163·3	226·2	72·2	71·5
	3.	162·0	169·2	160·6	223·8	72·5	71·8
	4.	166·5	176·2	164·6	228·2	73·0	73·0
	5.	169·7	174·8	168·7	233·2	74·0	73·0
	6.	166·6	178·1	164·3	228·5	73·6	74·7
Adulterated oil containing approx. 15 per cent. soya bean oil ..		161·6	169·0	160·1	211·2	58·7	58·1

The method which we have described in this communication requires very careful manipulation, particularly with regard to the weighing of the brominated compound, and for this reason we feel that it is less simple to operate than the determination of the polymerisable matter.

CONCLUSIONS.—From the results put forward above, the following conclusions may be drawn:

(1) Elaeostearic acid glyceride may be determined in Chinese wood oil by the separation of the polymerisable matter previously described by us (ANALYST, **1926, 51**, 335).

(2) If the iodine value of elaeostearic acid is to be defined as the percentage of halogen in terms of iodine absorbed by exactly four of the unsaturated carbon atoms—the absorption by the remaining two being entirely excluded—then this figure may be obtained with sufficient accuracy for practical purposes by an absorption limited to 20 minutes, or, where great accuracy is required, it may be obtained by the more elaborate method described in this communication.

Our thanks are due to Mr. W. J. Newman for his assistance in the analytical work.

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DISCUSSION.

Mr. CHASTON CHAPMAN congratulated the authors on this useful addition to their previous communication. He had had very considerable experience of the examination of wood oil, and had, he believed, supplied one of the first sets of figures for authentic specimens. It was interesting to him to see that the figures he put forward so many years ago were those which were generally accepted to-day.

In regard to the graph which had been shown as representing the rate of iodine absorption he was rather surprised to find that it proceeded in a straight line. He would rather have supposed that there would have been an increase up to a point and then a decrease.

Referring to Mr. Bolton's earlier paper on the estimation of foreign oils by the polymerisation method, he (Mr. Chaston Chapman) felt that Mr. Bolton would confer a boon on all his colleagues who were interested in the examination of this oil if he would specify in detail the exact procedure to be followed between the point at which the oil strings and the weighing out of the 2 grms. for the estimation of unpolymerised matter. He had, himself, tried this method, following as closely as he could the procedure given in the paper, but he had not obtained very good results. It might be that he had omitted some little point to which Mr. Bolton attached importance. He also thought that the amount of oil required for the test, namely, 150 grms., was an objection in cases where a sample of small size was submitted, and where the Worstall test was not required. He (Mr. Chaston Chapman) only carried out, as a matter of fact, the Worstall test when he was actually asked to do so.

Mr. Bolton had thrown on the screen a set of numbers for "genuine" wood oil showing 70 to 75 per cent. of polymerisable matter. It was obvious, therefore, that an oil of really good polymerising properties could be adulterated with, say, 5 per cent. of some other oil and yet come within the limits of genuineness. By this test, therefore, one could not safely certify to adulteration unless a result of at least 8 per cent. had been obtained. The proposed method was of such importance that he felt it would be necessary to have a considerable body of confirmation concerning oils of known origin from all parts of the world. If, as the result of this, 70 per cent. was found to be, in fact, the absolute minimum of

polymerisable matter, and if chemists could carry out the method in such a way as to be able to agree within one or two per cent., then, of course, a very definite opinion as to adulteration could be expressed. Regarded as an addition to existing methods, Mr. Bolton's polymerisation method was very useful, but he felt that a good deal more work was necessary before it could be regarded as in any way superseding those methods.

Dr. C. A. MITCHELL added his congratulations to the authors on having given a further proof of the value of the differential halogen absorption of oils and fats. He thought that the term "true iodine value" applied to the result of a partial absorption of iodine chloride was not altogether happy. Was the accepted Wijs value for croton oil also the "true" iodine value? Since with tung oil the authors were measuring a two-thirds absorption, he suggested the use of the term "sesqui-iodine value" as somewhat more suitable than "true" iodine value.

Mr. WILLIAMS, in reply to Mr. Chaston Chapman, suggested that the complete line representing the second stage of absorption of halogen would almost certainly be curved. This stage, however, occupied about five or six days, and the authors had studied only the first few hours, or about one-fiftieth of the whole period. The curvature of the line over so short a fraction of its total length would be so slight that the line would appear straight.

The authors had not examined samples of tung oil from parts of the world other than China sufficiently large for the polymerisable matter to be determined. They looked forward to making such determinations in the near future.

Miss Lewkowitsch had asked whether he had applied Kaufmann's modified bromine solutions to Chinese wood oil. The authors had not used this method, but consideration of Kaufmann's published results for the proportion of elaeostearic acid, obtained by its use, showed that it had been assumed that linolic acid was not present in the oil; and that without such an assumption it was not possible to obtain the required proportion. The validity of this assumption was, in his opinion, open to grave doubt, more especially as Kaufmann's figures were so much higher than those yielded by the author's experiments.

The authors themselves disliked the term "true" iodine values, and had replaced it wherever possible by "instantaneous" iodine value. He was therefore interested in Dr. Mitchell's suggestion of the term sesqui-iodine value. Unfortunately, he felt that this was a misdescription, since such a term would imply an absorption of 3 molecules of iodine by every 2 of elaeostearic acid, and had not the meaning suggested by Dr. Mitchell.

In accordance with the request made by Mr. Chaston Chapman during the discussion, the authors would reconsider the original description of their method and would amend it so as to deal more fully with such details of manipulation as they felt required amplification (*vide infra*).

Mr. BOLTON, in replying to Mr. Chapman, said that an oil of really good polymerising properties could be adulterated with about 4 per cent. of foreign oil before the proportion of polymerisable matter was reduced sufficiently to come outside the lower limit found by the authors, but this was not true for all oils. In fact, an addition of 2 per cent. to the majority of oils would bring the proportion of polymerisable matter down to 70 per cent. This being so, he felt that, in general, adulteration to the extent of 5 per cent. was readily detectable by the method, and this was the amount the authors claimed. He would like to add that, as far as he was aware, the authors' proposed limits had not been disputed, and, that, in fact, confirmation of their figures by analysts in this and other countries had been received; the authors themselves had examined a very large number of samples since the publication of the original paper.

DETERMINATION OF POLYMERISABLE MATTER IN CHINESE WOOD OIL.

About 150 grms. of the oil, contained in a stout aluminium beaker, exactly 3 inches in diameter and approximately 4 inches in height, are heated by means of a Bunsen burner so as to reach a temperature of 285° C. in approximately 4 minutes, the oil being vigorously stirred by means of the thermometer during the operation.

As soon as the temperature of the oil has reached 285° C. a stop-watch is started, and the temperature of the oil is thereafter maintained as nearly as possible at 285° C., the stirring being continued all the time. Polymerisation sets in suddenly after heating has taken place for some minutes. Its approach is first indicated by a thickening of the oil, and this is followed by the setting of the oil to a jelly. The time is noted when, just prior to complete solidification, the oil just fails to drop from the thermometer if this is raised from the bath.

Genuine tung oils reach this point after from 8 to 8½ minutes' heating at 285° C.

The temperature of the oil is maintained above 280° C. for about one minute after complete solidification has taken place and the vessel and contents are then allowed to cool spontaneously.

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

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

A portion of approximately 2 grms. is taken from the centre of the cold polymerised mass, cut into small pieces, and weighed into a mortar to which are added about 3 grms. of dry "silver" sand and 2 ml. of petroleum spirit. The mixture contained in the mortar is allowed to stand for a few minutes, and is then ground until the petroleum spirit has, for the most part, evaporated and the polymerised mass and sand are thoroughly mixed. The mixture is now transferred to an extractor, the mortar thoroughly washed with petroleum spirit into the extractor and extraction carried on in the usual manner. In these circumstances tung oils are found to give an extract of 28 per cent., with a variation not exceeding 2 per cent. on either side.

The proportion of polymerisable matter is obtained by subtracting the proportion of extract or unpolymerisable matter from 100.

The following communications on this paper have been received:—

Mr. W. H. SIMMONS writes:—"The authors of the paper appear to have established a close connection between the amounts of elaeostearin, and of polymerisable matter, as determined by their process, in China wood oil, and to this extent they are to be congratulated; they have not yet adduced any evidence, however, in support of their hypothesis that the amount of polymerisable matter is a measure of the commercial value of the oil; indeed, from my experience of the use of China wood oil in the paint and varnish industry, it would appear extremely unlikely that there should be any such definite relationship."

Dr. L. A. JORDAN writes:—"Fundamentally it may be rather difficult to establish the true connection between the chemical properties of the drying oils (in so far as they can be quantitatively determined) and the properties for which the oil is utilised in industry, but in the case of tung oil the matter is quite clear, for the oil is undoubtedly bought because of its capacity for rapid gelation, and if that capacity is not normal, the oil is invariably rejected.

"One instance may be cited which is of interest as illustrating these matters, namely, the saponification rate of tung oil in comparison with other drying oils. McBain has definitely reported upon the saponification rates of raw linseed oil and raw tung oil, as approximately 3: 1. It is true that he worked with a linseed oil of low acid value and a tung oil of rather high acid value, which variations do affect the rate; it may well be that on a basis of equivalent molecular acidity, which after all is the only basis upon which the matter should be considered, the

ratio would have been something very much higher, perhaps even of the order of 10:1.

"Further, it is well known to workers on this subject that the saponification rate of thickened oils falls rapidly with the increase of viscosity or degree of thickening, and this is much more apparent in the case of tung oil than in the case of thickened linseed oil. There is good reason to suppose that the ratio of the saponification rates between thickened tung oil and thickened linseed oil, as used industrially, is of the order of 50: 1, at least. Much of the industrial value of tung oil films depends upon the high resistance to saponification.

"In passing, one might mention that the rate of increase of viscosity has some connection with the triply unsaturated glycerides, of which tung oil contains up to 90 per cent. and linseed oil 25–30 per cent. At the same time it is quite certain that there is a direct parallel between the drop in saponification rate and the polymerisation of tung oil, which establishes, or so it seems to me, the intimate connection between the technical purpose for which the oil is used and the polymerisable capacity. I would submit that the work of the immediate future in connection with tung oil is to provide a means of evaluating in a proper manner what the industrial user is really buying, namely, the capacity for gelation."

A Solubility Method of Classifying Acid Caseins.

By W. R. MUMMERY, F.I.C., and F. BISHOP.

(*Read at the Meeting, November 6th*, 1929.)

The solubility of acid caseins in a solution of borax has for long been employed as a laboratory test of their suitability for commercial uses. The three methods most generally known are those of Reuter (*Seifensied. Ztg.* and *Revue Augsberg*, 1907; *Papier Ztg.*, 1907, **32**, 3286, 3374; Dahlberg, *U.S. Dept. of Agr. Bull.*, 661, 1918; and Zoller, *J. Ind. Eng. Chem.*, 1920, 11, 71). The following table indicates the wide variation in conditions laid down in these three tests:—

	Reuter.	Dahlberg.	Zoller.
Casein ..	100 grms.	100 grms.	100 grms.
Borax	10 grms.	15 grms.	50 grms.
Water	400 ml.	600 ml.	670 ml. (approx.)
Temperature ..	60–70° C.	65° C.	30° C.
Time allowance ..	60 minutes	10 minutes	*30 minutes
Mesh of casein ..	—	20 mesh	40 mesh

* Vigorous stirring every 5 minutes.

In our experience no one of these three methods is suitable for the classification of commercial casein which has been carefully manufactured under modern conditions, because insufficient information is afforded as to the readiness of solubility; further, the conditions of the tests are not sufficiently stringent. The method which we have employed, particulars of which are given below, has been used by us both for classifying the raw casein curd and also in the examination of

the finished article. It is not so much a measure of the gross insolubility of casein, for such gross insolubility does not occur in well prepared caseins, as of the quantity of alkali (borax) required for its complete solution.

The following solutions should be prepared:—*Borax Solution.*—20·833 grms. of $Na_2B_4O_7 10H_2O$ dissolved in water and made up to one litre. *Bromthymol Blue Indicator.*—One decigram of the powder macerated in a mortar with 3·2 ml. of *N*/20 sodium hydroxide solution and made up to 250 ml. with distilled water. *Standard Buffer Solution.*—Made according to Clark and Lubs' formula, with potassium dihydrogen phosphate and caustic soda (*J. Biol. Chem.*, 1916, **25**, 479). *Distilled Water, p*H 6·0.—For the purpose of this determination, it is necessary to work with distilled water of a constant *p*H value. It is found that freshly boiled distilled water, *p*H 7·0, gradually absorbs carbon dioxide, with a consequent fall in *p*H. A point of equilibrium is attained in the vicinity of *p*H 6·0; very slight adjustment is necessary when the *p*H value of the water is above or below this figure.

METHOD.—Two grms. of lactic acid casein, ground if necessary to pass a 30-mesh sieve (opening 0·0223 inch), are placed in a ¾ inch test tube, 12 ml. of borax solution are added, and the test tube placed in a water bath at 70° C. The casein is stirred thoroughly and at frequent intervals for threequarters of an hour. *If the casein is not fully dissolved after forty-five minutes, incomplete solubility is demonstrated.*

When the casein is dissolved, the solution is made up to 100 ml. with distilled water, and 1 ml. is pipetted into another test tube, together with 10 ml. of distilled water. To the diluted solution of casein in borax are added 5 drops of bromthymol blue indicator, and the colour is compared with that of the standard buffer solution. The requisite turbidity of the buffer solution may be produced with a few drops of a suspension of colloidal silica, or a comparator can be employed.

The *p*H of the solution after dilution, which we term the solubility index, indicates the ease of solubility of the casein.

Solubility index.	*p*H value.	Colour.
Very good	Above 6·8	Blue
Good	6·8–6·4	Green
Passable	Below 6·4	Yellow

We have found that caseins which do not completely dissolve when submitted to the procedure described above give a *p*H of 6, or lower if the undissolved particles consist of casein. In some cases, where the undissolved particles have proved to be albumin, the *p*H has been 6·4 or higher.

When the test is used for the evaluation of the freshly prepared moist casein curd, the samples can be dried on canvas trays at a temperature of 70° C.

Before publishing the method, we have proved its utility on some hundreds of samples of casein; Zoller's test was used simultaneously, and, apart from disclosing albumin and foreign matter, failed to distinguish between the samples.

We append a few typical analyses of caseins to illustrate the manner in which our method makes distinction.

Nitrogen (on anhydrous substance). Per Cent.	Ash (on anhydrous substance). Per Cent.	Solubility index. Per Cent.
14·56	0·91	6·6
14·43	1·24	Incomplete
14·61	0·99	6·4
14·64	0·64	6·9
14·36	1·31	6·7
14·42	1·29	6·6
14·89	0·62	6·5
14·65	0·66	6·5
14·70	0·88	6·4
14·80	0·93	6·7
14·02	0·75	Incomplete
—	1·12	6·3
—	1·42	6·0

Examples taken from analyses of lactic acid casein produced in other countries.

Country of origin.	Ash (on anhydrous substance). Per Cent.	Solubility index. Per Cent.
France	1·71	6·9
,,	2·51	6·5
,,	1·32	7·0
,,	3·11	6·3
India	4·72	Incomplete
,,	4·15	6·9
,,	5·30	6·8
Argentina	2·47	6·4
,,	3·88	Incomplete
,,	3·82	Incomplete
,,	2·61	6·4

The summary of determinations on 230 samples, representing 2400 tons of lactic acid casein, shows:—

				Solubility Index.
12 samples,	equivalent to	5·2	of total ..	6·5
87 ,,	,,	37·8	,, ,, ..	6·6
96 ,,	,,	41·7	,, ,, ..	6·7
31 ,,	,,	13·5	,, ,, ..	6·8
3 ,,	,,	1·3	,, ,, ..	6·9
1 ,,	,,	0·5	,, ,, ..	7·0

The solubility is only one item or feature in the analytical record of a casein. Any solubility test must be judged as such and not on its ability to disclose other characteristics which are ascertained by other determinations.

In conclusion, we wish to express our thanks to the New Zealand Casein Co., Ltd., for permission to publish this paper.

WANGANUI, N.Z.

Notes on the Thiocyanate Method of Estimating Iron. Influence of Different Classes of Phosphates.

By GEOFFREY WINTHROP LEEPER, M.Sc.

(*Read at the Meeting, February* 5, 1930.)

There are various statements in the literature (*cf.* Elvehjem and Hart, *J. Biol. Chem.*, 1926, **67**, 43) as to the interference caused by phosphates in the formation of the colour of ferric thiocyanate. Other reagents, such as ferrocyanide (Walker, Analyst, 1925, **50**, 279) and thioglycollic acid (Lyons, *J. Amer. Chem. Soc.*, 1927, **49**, 1906), have been recommended, as giving colours with iron, that are unaffected by phosphates. In order to avoid this interference by phosphates, Elvehjem and Hart (*loc. cit.*) use a lengthy process involving the precipitation of phosphates by means of ammonium molybdate, followed by the precipitation of the iron as ferric hydroxide from the filtrate, and the formation of the ferric thiocyanate colour from a solution of this hydroxide in hydrochloric acid.

It appears, however, that the danger of orthophosphate interference has been exaggerated. Effects put down to orthophosphates may often have been due to the salts of dehydrated phosphoric acids—mainly, that is, to pyrophosphates. Both pyro- and meta-phosphates are several hundred times as effective as orthophosphates in destroying the colour of ferric thiocyanate. Pyrophosphates must inevitably be formed in the process of ashing biological material, and subsequent methods of extracting the ash with acids may well fail to convert all the pyrophosphoric acid into orthophosphoric, since pyrophosphoric acid is not immediately decomposed by strong acids, even on the water-bath.

As far as orthophosphates are concerned, the problem appears to be mainly one of pushing the equilibrium

$$FePO_4 + 3CNS' \rightleftharpoons Fe(CNS)_3 + PO_4'''$$

as far as possible to the right. One should, therefore, use a high concentration of thiocyanate and work with 50 c.c. of solution rather than with 100 c.c.

Working with a solution containing 10 c.c. of 2*N*-sulphuric acid, 1 c.c. of *M*/2000 ferric sulphate solution (or 0·028 mgrm. of iron), and 5 c.c. of 2·5 *M*-ammonium thiocyanate, the whole being made up to 50 c.c. with water, it is possible to add orthophosphates up to the equivalent of 100 mgrm. of phosphoric anhydride before interference sets in. Higher concentrations of phosphate turn the red colour progressively towards a straw yellow, which cannot be matched in tint with phosphate-free solution.

Tests have been made on solutions of the above composition with various types of phosphates, to determine in each case the minimum amount (in terms of P_2O_5)

which produces interference with the colour matching. The following are the results:

Type of phosphate.	Amount of P_2O_5 present. Mgrm.
$NaPO_3$	0·08
$Na_4P_2O_7$	0·40
H_3PO_4, Na_2HPO_4, KH_2PO_4	100–120

However, one sample of anhydrous disodium hydrogen phosphate (A.R reagent) gave an interference when present to an amount equivalent to 2 mgrms. of phosphoric anhydride. This sample, on testing, was found to contain an appreciable quantity of pyrophosphate.

The figure 100 mgrms. of P_2O_5, in the form of orthophosphate, is found, as above, to be the limit of safety in order to avoid interference. Walker (*loc. cit.*), however, quotes 35 mgrms. of P_2O_5 as the limit. He used a lower concentration of acid and of thiocyanate, and diluted to 100 c.c. for matching. All these differences in method lead to a lower level of toleration of phosphate. His statement that different levels of phosphate are tolerated, according to whether solution is made in hydrochloric or nitric acid, has not been confirmed in the present work, which, rather, has indicated that the acid used, whether hydrochloric, nitric or sulphuric, is immaterial so far as interference by phosphates is concerned. The colours given in sulphuric acid are always less intense than in nitric acid, but this causes no inaccuracy, as the same acid is naturally used both in the unknown and in the standard solution. Sulphuric acid has been used here in order to admit of a method of estimating both manganese and iron from aliquot portions of a solution made up from the same ash.

Since a quantity of 0·02 mgrm. of iron may be conveniently determined in this way, so long as the amount of phosphoric anhydride present in the Nessler tube does not exceed 100 mgrms., it follows that it is safe to use the thiocyanate method in cases where the ratio of phosphoric anhydride to iron is of this order, provided that all the precautions referred to above, are observed, and that, in the extraction of the ashed material with acid, due time is allowed during the digestion for any pyrophosphate to be reconverted into orthophosphate. Care must, of course, be taken that all pyrophosphate is destroyed. The method is thus sufficient for all biological material with the possible exception of milk. In the case of milk, when the iron content is high, the method described by Marriott and Wolf (*J. Biol. Chem.*, 1906, **1**, 451) may be applied. This involves the use of a mixture of acetone and water as solvent, and this solvent is far more immune from phosphate interference than any aqueous solution can be.

I desire to acknowledge my indebtedness to Mr. W. Godden, in whose Department the work was done.

THE ROWETT RESEARCH INSTITUTE,
ABERDEEN.

Drinking Waters for Cattle.

By T. McLACHLAN, F.I.C.

(*Read at the Meeting of the North of England Section, February* 15, 1930.)

THE subject of drinking waters for cattle is one on which much has been written in the veterinary press, which has been dealt with by more than one Act of Parliament, and one which is frequently the prime or a subsidiary cause of litigation.

The Milk and Dairies Order, 1926, (1) stipulates that "the water supply used for the watering of cows shall, as far as reasonably possible, be protected against contamination caused by the drainage of foul water."

It is a fact that cattle prefer to drink water containing what is known as sewage (whether this be derived from human or other animal sources) to rain water, and that they prefer rain water, which has been collected in a field, to water which has been drawn from a tap. When cattle are drinking, they usually stand with their front feet in the water and drop their pads and urine on the edge of the pond or stream, or into the water itself, thereby, in any case, contaminating the supply.

Prof. Wooldridge (*Private Communication*) states that a series of tests has been carried out on animals at the Royal Veterinary College, London, animals being given water deliberately contaminated with known amounts of human or cattle sewage. Many experiments have been made on the effects of feeding cattle for prolonged periods on sewage farms; as a general rule these have shown no deleterious effect whatever on the animals. Wooldridge has come to the conclusion that there is little likelihood of sewage having any harmful results, unless it is present in such an amount as to have a distinct effect on the total protein intake of food, in which case there is the possibility of poisoning by protein degradation products, as in excessive contamination by too heavy concentration on irrigation farms.

It is well known that animals kept on a vitamin-free diet, or a diet deficient in vitamins, will eat their own faeces in order to obtain that vitamin. If such animals are allowed to continue this practice, they require a much longer period to be affected by the vitamin deficiency in their food, than other animals kept on a grid to prevent them devouring their own excrement. If the bacteria or toxins in such faeces were very harmful, the animals swallowing them should suffer more than those which cannot do so.

Levie (*Veterinary Record*, 1925, 5, 692), on the other hand, holds that the presence of sewage in water gives rise to very definite symptoms in animals, namely, loss of appetite and condition, "unthriftiness," drowsiness, weariness, scouring and sometimes vomiting. He maintains that such animals can be cured only by changing them to fresh pasture for a period of three to six months, and supplying them with fresh water. He states that cattle drinking sewage water are more susceptible to tuberculosis, Johne's disease and contagious abortion than those kept on pure water. Although he mentions that these animals must be

taken to a fresh pasture, he does not state whether he has kept them on the same land and prevented them from drinking the contaminated water by fencing it off and watering systematically from a tap. Most diseases, in fact all known diseases, which can be carried by water from sewage, could be contracted by the cattle from the grass on which infected animals have been dropping their pads for a considerable period. Presumably the object of moving the cattle to a fresh pasture is to give them better grass, but it cannot be denied that a certain amount of sewage improves the growth of the pasture, and, therefore, there is no object in moving them to fresh pasture to change the water. The symptoms, which Levie ascribes to the toxins of sewage, are very similar to those of the diseases to which he says that the animals become susceptible, and in any case it is known that cattle suffering from these diseases may be improved considerably by removing them to fresh pasture. Levie proposes to determine the toxicity of waters by counting the number of *B. coli* present in the sample; then, since there is a much greater *B. coli* count in human sewage than in that of cattle, he thinks that the former is more liable to cause disease in cattle than is sewage caused by their own excrement. This argument is unsound, since *B. coli*, as such, are not known to cause any disease in man or other animals, apart from minor or secondary infections, where the bacillus has been able to enter a lesion. On the other hand, it is known that numerous diseases may be transferred from one animal to another of the same species by means of excrement, and it is because *B. coli* are indicative of sewage pollution, with the possibility of the presence of members of the typhoid group, not for any other reason, that they are regarded with suspicion when present in water required for human consumption.

S. Rideal, in his book on "Water Supplies," states that, although pathogenic bacteria are readily destroyed, especially in the presence of a large excess of non-pathogenic bacteria, they may leave poisonous toxins in the water, and that some of these toxins have been isolated. Although some toxins have been concentrated from special cultures, I am unable to find any reference to the isolation of toxins from sewage water, remembering that proof of the presence of a toxin requires that it shall be capable of producing the symptoms of a specific disease.

EXPERIMENTAL.—In order to ascertain what kind of water is being drunk by perfectly healthy cattle, I obtained samples from five ponds (11, 12, 13, 18, and 19) in a certain district, the water from which has, to my knowledge, been used for years. I have classified in a table the results of the examination of these waters with those from fourteen other waters.

The figures for organic matter were not determined in every case and, although indicative of the amount of organic matter present, they cannot be considered trustworthy. Owing to the presence of hydrogen sulphide in samples Nos. 17 and 18, the chlorides were determined after precipitation with zinc sulphate, as recommended by Thresh and Beale (*The Examination of Waters*).

The first thirteen could, in my opinion, be considered satisfactory, unless there was distinct evidence, calling for further investigation, that they were harmful

for some reason or other. Sample No. 14 would be passed, normally, as satisfactory, but there was a complaint that the animals drinking it showed definite signs of alkaloidal poisoning. I, therefore, concentrated 400 c.c. with a few drops of acetic acid to about 3 c.c. on a water-bath, and injected 1 c.c. into each of two frogs, which died in a few minutes. Control experiments, made under the same conditions from tap water, caused no inconvenience to frogs. The tests for alkaloids were quite indefinite, and the poison might have been arsenic, due to sheep dip, or an alkaloid derived from weeds in the field. Unfortunately, the client was quite satisfied with the preliminary report, and failed to supply a further sample, when requested. Sample No. 16 has obviously been highly chlorinated, and it was found, on further investigation, that no weeds or grass were growing on the side of the stream along which it was running; it contained the effluent from a hospital.

Waters Nos. 14–19 cannot be considered as satisfactory for cattle drinking, although, from the evidence at our disposal, we are unable to say in some cases, that they could cause harm, and, as mentioned above, I know that Nos. 18 and 19 are being drunk by cattle. On the other hand, if there should be any disease, capable of being water-borne, present in the herd, waters Nos. 15, 17, 18, and 19 would contain a large number of pathogenic bacteria, in all probability, owing to the fact that the proportion of sewage is high and that the water is not changed quickly enough by current, or purified by bulk. Two further samples of water were submitted for examination, but these were condemned on account of the high content of hydrogen sulphide. Investigation showed that whereas the pasture in the fields was previously good, it had suddenly become sluggish and rotten. The cause of the trouble was that water was being pumped out of a mine on to the fields in question. When it has been discovered that any member of a herd of cattle is suffering from any disease, such as contagious abortion or Johne's disease, it is obviously important to pay attention to the water which they are drinking, but it must be remembered, at the same time, that they will eat the grass which is being contaminated by the pads of the affected animals.

SUMMARY.—It is not safe to condemn water to be used by cattle for drinking on the results of chemical analysis, except when it can be shown that some definite chemical poison is present in the water.

Such poisons may be due to sheep dips, minerals introduced from the surrounding neighbourhoods, an excess of certain decomposition products such as hydrogen sulphide, free chlorine caused by recent high chlorination of sewage, or possibly certain weeds.

Although it is inadvisable to recommend waters for cattle drinking purposes with an oxygen absorbed figure of more than 1 part per 100,000 in three hours, it has been shown that a water with a figure of 7·8 may be perfectly safe.

A water should only be condemned on the results of bacteriological examination when bacteria, known to be pathogenic to cattle, can be isolated from it.

In cases where a herd is affected by some contagious disease, which may be water borne, the supply should be very good, or the cattle should be watered regularly and not allowed to drink surface water in the neighbourhood.

	1	2	3	4	5	6	7	8	9	10
Total solids	35	21	28	31	25	51	51	56	87	53
Organic matter						11	6	6	10	14
Chlorine as chlorides ..	3·0	3·4	4·6	2·3	1·9	4·1	4·6	3·8	5·7	4·5
Nitrogen as nitrites ..	P	A	T	A	A	A	P	A	T	A
Nitrogen as nitrates ..	A	0·25	0·44	0·5	0·4	T	A	A	A	A
Free and saline ammonia	0·04	0·005	0·007	0·006	0·004	0·11	0·05	0·03	0·06	0·05
Albuminoid ammonia ..	0·07	0·02	0·02	0·01	0·01	0·14	0·08	0·14	0·05	0·06
Oxygen abs. in 15 mins. ..	0·24	0·07	0·07	0·08	0·02	0·80	0·53	1·25	0·23	0·37
Oxygen abs. in 3 hrs. ..	0·37	0·13	0·13	0·12	0·13	1·29	0·86	1·95	0·40	0·59

	11	12	13	14	15	16	17	18	19
Total solids	51	58	35	49	57	63	70	237	23
Organic matter	15	6	8	16	30	13	8	54	13
Chlorine as chlorides ..	5·1	5·0	1·0	2·2	4·4	11	5·4	54	2·8
Nitrogen as nitrites ..	P	A	T	P	P	T	A	A	A
Nitrogen as nitrates ..	A	A	0·8	0·4	P	A	A	A	A
Free and saline ammonia	0·04	0·06	0·06	0·004	0·80	0·10	2·4	0·28	0·14
Albuminoid ammonia ..	0·06	0·08	0·08	0·01	0·76	0·24	0·16	0·84	0·22
Oxygen abs. in 15 mins. ..	0·20	0·35	0·08	0·05	3·6	0·48	0·79	6·2	0·83
Oxygen abs. in 3 hrs. ..	0·38	0·65	0·14	0·09	4·8	0·80	2·3	7·8	2·1

All results expressed in parts per 100,000.

A indicates absent, T indicates trace, P indicates present, but not sufficient to warrant a determination.

I must thank Prof. Wooldridge for giving me information about his observations privately, Mr. Shaw for assistance with part of the work, and Messrs. Evans, Sons, Lescher & Webb, Ltd., for permission to publish the figures.

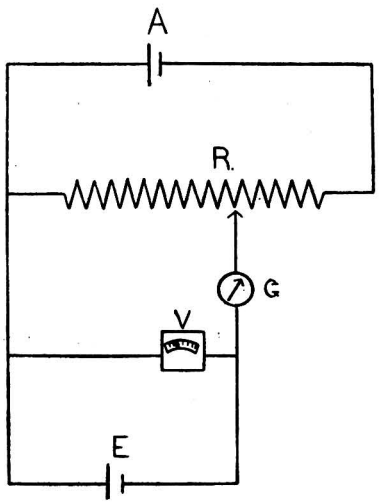
Electrometric Determination of Copper.

III. APPLICATION OF BI-METALLIC ELECTRODES.

BY MARJORIE E. PRING, M.Sc., AND
JAMES F. SPENCER, Ph.D., D.Sc., F.I.C.

IT was shown by Osterheld and Honegger (*Helv. Chim. Acta*, 1919, **2**, 238) that copper may be determined electrometrically by treatment of the solution with potassium iodide in the presence of sulphuric acid and titration of the iodine set free with standard sodium thiosulphate solution. The method, although accurate, suffers from the disadvantage that the potential at and near the end-point becomes steady only after some time. Since it is known that bi-metallic electrode systems, when applicable, give sharp end-points very rapidly, it was decided to examine the above-mentioned method, using a bimetallic electrode system to indicate the end-point.

The bimetallic electrode system, as recommended for the titration of iodine by sodium thiosulphate (Foulk and Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045) was found to be most suitable for the present purpose. Stated briefly, this consists in immersing two small platinum electrodes E (Fig. 1) in a well-stirred solution of iodine. A difference of potential of about 15 milli-volts (that is a potential of the same order as the electromotive force of polarisation), is maintained between



these electrodes by means of a small battery, A, and a variable resistance, R. The potential is measured by the milli-voltmeter, V. On adding successive quantities of sodium thiosulphate the needle of a sensitive galvanometer, G, approaches the zero position, and reaches it when all the iodine has reacted. Further addition of thiosulphate has no influence on the galvanometer. The process requires for its success that at least one of the chief reactants must be an efficient depolariser, whilst the products of the reaction must have no depolarising action.

The suitability of the bimetallic electrode system for the determination of copper was established by a few preliminary titrations, carried out with a 0·2 *N* solution of copper sulphate. The end-point was found to be very sharp; a single drop of 0·1 *N* sodium thiosulphate solution was sufficient to bring the galvanometer reading from a measurable value to zero. It was further established that a potential difference of 10–30 millivolts between the electrodes was the best value to use, although the titration may be performed with voltages up to 60 millivolts, but above this value the results are inaccurate.

Effect of Dilution on the End-point.—Several series of titrations were carried out with solutions of copper sulphate of concentrations varying from 0·2 *N* to 0·002 *N*, to which appropriate quantities of acetic acid and potassium iodide were added. The electrometric titration, carried out by means of the bi-metallic electrode system, was compared in all cases with a corresponding

titration in which starch was used as indicator. Sodium thiosulphate solutions of normality approximately equivalent to that of the copper sulphate solution were used in the titrations. The results of six series of titrations are recorded in the tables below:

Indicator.	20 c.c. 0·2 *N* $CuSO_4$ +25 c.c. 0·2 *N* KI.		20 c.c. 0·05 *N* $CuSO_4$ +10 c.c. 0·5 *N* KI.		20 c.c. 0·02 *N* $CuSO_4$ +20 c.c. 0·5 *N* KI.	
	Starch. c.c.	Electrometric. c.c.	Starch. c.c.	Electrometric. c.c.	Starch. c.c.	Electrometric. c.c.
$Na_2S_2O_3$ used	20·15	20·20	21·10	21·14	20·45	20·49
,, ,,	20·14	20·20	21·06	21·17	20·46	20·51
,, ,,	20·16	20·21	21·09	21·12	20·41	20·50
,, ,,	20·17	20·20	21·09	21·11	20·42	20·49
Average	20·16	20·20	21·09	21·14	20·45	20·50

Indicator.	20 c.c. 0·01 *N* $CuSO_4$ +10 c.c. *N* KI.		20 c.c. 0·004 *N* $CuSO_4$ +1 grm. KI.		20 c.c. 0·002 *N* $CuSO_4$ +1 grm. KI.	
	Starch. c.c.	Electrometric. c.c.	Starch. c.c.	Electrometric. c.c.	Starch.	Electrometric. c.c.
$Na_2S_2O_3$ used	19·47	19·47	20·90	20·99	No end-point distinguishable.	19·13
,, ,,	19·45	19·51	20·90	20·97		19·12
,, ,,	19·46	19·50	20·88	20·99		19·13
,, ,,	19·44	19·51	20·90	20·99		19·13
	19·45	19·50	20·90	20·99	—	19·13

The end-point is easily distinguishable with all concentrations down to 0·004 *N*, and results may be obtained with 0·002 *N*, although the end-point is a little difficult to find. As the solution becomes more dilute it is found that the galvanometer needle reaches the zero point more slowly. The results show that a more dilute solution may be determined by using the electrometric method than by starch indication of the end-point. The end-point of the electrometric titration is seen to be about 0·05 c.c. higher with the more concentrated solutions than it is with starch, and the value is a little more divergent with the more dilute solutions. This result is confirmatory of that obtained by Foulk and Bawden (*loc. cit.*) for the titration of iodine with thiosulphate. They concluded that the electrometric indication is sharper and more sensitive, and consequently more accurate, than the starch indication. To test this point 19·98 c.c. of a solution containing 12·425 grms. of $CuSO_4 5H_2O$ per litre was titrated electrometrically, as above, with a solution of sodium thiosulphate which had been freshly standardised with pure iodine. The volume of thiosulphate required in 4 successive titrations was 19·00, 19·01, 19·89, 19·01 c.c., whilst the calculated titre is 19·00 c.c. This shows that the end-point, as determined by electrometric indication, is more accurate than that obtained by starch indication.

Effect of the Acid and Iodide Concentration.—A series of titrations was carried out in which (i) the amount of acetic acid was varied, and (ii) the

amount of potassium iodide was varied, the other constituents of the titration solution being kept constant. The tables below give the values obtained:

20 c.c. 0·2 *N* $CuSO_4$ + 25 c.c. 0·2 *N* KI.

Vol. of 0·2 *N* acetic.	0·00 c.c.	10·0 c.c.	20·0 c.c.	50·0 c.c.
	c.c.	c.c.	c.c.	c.c.
Vol. $Na_2S_2O_3$ used	20·22	20·20	20·22	20·18
,, ,, ,,	20·17	20·18	20·20	20·21
,, ,, ,,	20·20	20·19	20·18	20·20
,, ,, ,,	20·20	20·20	20·19	20·20
Average	20·20	20·19	20·20	20·20

20 c.c. 0·01 *N* $CuSO_4$ + a few drops glacial acetic acid.

Amt. of KI added.	10 c.c. 0·04 *N*.	10 c.c. *N*.	10 c.c. 2 *N*.
	c.c.	c.c.	c.c.
Vol. $Na_2S_2O_3$ used	19·98	20·01	19·98
,, ,, ,,	19·99	20·00	20·00
,, ,, ,,	20·00	20·03	19·99
,, ,, ,,	19·99	20·00	19·99
Average	19·99	20·01	19·99

These results show that the concentration of both acetic acid and potassium iodide may be varied over a wide range without any material effect on the result of the titration.

INFLUENCE OF OTHER METALS ON THE TITRATION.—The end-point of this method of determining copper is so sharp and the accuracy so little dependent on conditions, that it appeared advisable to ascertain whether the presence of other metals, which occur with copper either naturally or in commercial products, has an effect on the accuracy. Consequently a series of titrations was carried out with an approximately 0·05 *N* solution of copper sulphate to which had been added an equal volume of a 0·05 *N* solution of a salt of the metal in question. The sulphates of aluminium, nickel and zinc, the nitrates of bismuth and silver, stannic chloride and lead acetate were used. In the case of lead a solution of copper nitrate was substituted for copper sulphate.

20 c.c. 0·05 $CuSO_4$ + 3 grms. KI + acetic acid + 20 c.c. 0·05 *N* metallic salt.

Salt added.	None.	$NiSO_4$.	$SnCl_4$.	$Bi(NO_3)_3$.	$Al_2(SO)_4)_3$.	$ZnSO_4$.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Vol. $Na_2S_2O_3$ used	19·90	19·90	19·89	19·92	19·92	19·91
,, ,, ,,	19·91	19·91	19·90	19·89	19·92	19·92
,, ,, ,,	19·92	19·90	19·89	19·91	19·91	19·92
,, ,, ,,	19·91	19·91	19·89	19·90	19·90	19·93
,, ,, ,,	19·91	19·91	19·90	19·91	19·90	19·92
Average	19·91	19·91	19·89	19·91	19·91	19·92

20 c.c. 0·05 *N* $CuSO_4$+3 grms. KI+acetic acid+20 c.c. 0·05 *N* metallic salt.

	$CuSO_4$(II)+H_2O.	$CuSO_4$(II)+$AgNO_3$.	$Cu(NO_3)_2$+H_2O.	$Cu(NO_3)_2$+PbA_2
	c.c.	c.c.	c.c.	c.c.
Vol. $Na_2S_2O_3$ used	19·59	19·58	20·03	20·03
,, ,, ,,	19·58	19·58	20·01	20·04
,, ,, ,,	19·59	19·57	20·02	20·05
,, ,, ,,	19·60	19·58	20·01	20·03
Average	19·59	19·58	20·02	20·04

The titration values given in the above tables show clearly that copper may be determined electrometrically in the presence of nickel, bismuth, aluminium, zinc, silver, lead, and stannic tin, as sharply and accurately as in their absence. In the case of bismuth and lead the electrometric method has a distinct advantage over the ordinary method where starch is used as indicator, because the deep yellow colour of the lead and bismuth iodides makes the end-point very difficult to determine with starch, but this has obviously no effect on the electrometric method.

Determination of Copper in the Presence of Iron.—In addition to the metals mentioned above, copper frequently occurs along with iron. Should the iron be present in solution in the ferrous condition, there appears to be no reason why the titration should not be made directly, as in the case of the metals described above; but should the iron be present in the ferric condition the addition of potassium iodide will reduce the ferric salt, with the liberation of iodine, as shown by the equation—$Fe_2(SO_4)_3+6KI=2FeI_2+I_2+3K_2SO_4$.

Two methods have been proposed for the determination of copper in the presence of iron: (i) Hahn and Windisch (*Ber.*, **1923**, **56**, 598) propose to titrate the total iodine liberated by the cupric and ferric ions and to follow this by a determination of the ferric ion; whilst (ii) Moser (*Z. anal. Chem.*, **1904**, **43**, 597) adds a sufficient excess of sodium pyrophosphate to the solution to precipitate and to redissolve the iron. The solution is then treated with acetic acid and potassium iodide, when iodine is liberated by the cupric ion, but not by the iron, for this is now present as a complex iron pyrophosphate anion. The process is complete after 20 minutes, and the iodine may then be titrated with sodium thiosulphate. Both these methods have been examined, using the bi-metallic electrode system described above.

Determination of Copper in the Presence of Ferrous Salts.—Parallel titrations were carried out with a 0·1 *N* solution of copper sulphate and a similar solution, to which has been added an equal volume of 0·1 *N* ferrous ammonium sulphate. The titrations were carried out exactly as described above, and the results of a series are recorded in the table below :

	20 c.c. 0·1 *N* $CuSO_4$+20 c.c. H_2O +1 grm. KI+acetic acid.	20 c.c. 0·1 *N* $CuSO_4$+20 c.c. 0·1 *N* $FeSO_4$+2 grm. KI+acetic acid.
	c.c.	c.c.
Vol. $Na_2S_2O_3$ used	20·19	20·18
,, ,, ,,	20·17	20·19
,, ,, ,,	20·15	20·21
,, ,, ,,	20·15	20·21
Average	20·17	20·20

The titre is slightly higher when the ferrous salt is present; this is probably due to the trace of a ferric salt in the solution or to atmospheric oxidation during the titration. The amount of the difference is hardly sufficient to prevent the method being used to determine copper in the presence of ferrous salts.

DETERMINATION OF COPPER IN THE PRESENCE OF FERRIC SALTS.—For this series of titrations accurate standard solutions were prepared. A solution of copper sulphate containing 12·50 grms. of $CuSO_4,5H_2O$ was prepared from the pure salt, and the concentration of the solution checked electrolytically. A solution of sodium thiosulphate was standardised against the copper sulphate, and the relationship was found to be 19·98 c.c. of $CuSO_4$ solution = 19·32 c.c. thiosulphate solution. A solution of ferric alum was standardised gravimetrically and found to contain 3·960 grms. of Fe_2O_3 per litre.

A mixture of 19·89 c.c. of ferric alum solution and 19·98 c.c. of copper sulphate solution was treated with 3 grms. of potassium iodide and titrated with sodium thiosulphate, when 37·42 c.c. of this solution were required. Theoretically, 38·41 c.c. should have been necessary to react with the iodine set free, which means that the titre is 2·60 per cent. too low. The experiment was repeated in the presence of acetic acid, when a mean titre of 37·90 c.c. was obtained, which shows an error of 1·35 per cent.

These results show that the amount of iodine liberated from potassium iodide by a mixture of ferric and cupric salts always falls short of the calculated quantity; the amount is less if acetic acid is present, but the error is still so large as to make the suggestion of Hahn and Windisch impracticable.

The proposal of Moser (*loc. cit.*) was next investigated. Twenty c.c. of 0·1 *N* copper sulphate solution mixed with 20 c.c. of a 0·1 *N* solution of ferric alum are treated with powdered sodium pyrophosphate, and the solution gently warmed until the whole of the precipitate first formed has redissolved, more pyrophosphate being added, if necessary. The solution thus obtained has a clear blue colour; it is acidified strongly with glacial acetic acid, and 5 grms. of potassium iodide are added. The whole is left to stand for 20 minutes, after which the free iodine is titrated with thiosulphate, using the bi-metallic electrode system. It was found that as the end-point is approached the thiosulphate must be added slowly, and, in consequence, the end-point is a little difficult to define. The following table gives the results of a series of titrations:

	20 c.c. of 0·1 *N* $CuSO_4$. c.c.	20 c.c. 0·1 *N* $CuSO_4$ + 20 c.c. $Fe_2(SO_4)_3$. c.c.
Vol. $Na_2S_2O_3$ used	19·32	19·33
,, ,, ,,	19·31	19·33
,, ,, ,,	19·32	19·28
,, ,, ,,	19·32	19·30
Average	19·32	19·31

These figures show that the method permits the accurate determination of copper; it has a slight drawback in the difficulty of defining the end-point. Despite the drawback, the method is thoroughly practicable.

TITRATION OF THE LIBERATED IODINE WITH SODIUM ARSENITE SOLUTION.—Foulk and Bowden (*loc. cit.*) state that the titration of iodine by means of sodium arsenite gives a sharper end-point than that obtained with sodium thiosulphate. Preliminary experiments show that sodium arsenite may be used to titrate the iodine liberated from potassium iodide by cupric salts, provided that a neutral solution is used and that an excess of sodium bicarbonate is present. In such circumstances the end-point is very sharp, whilst, in the presence of acetic acid, the reaction is slow and no definite end-point could be found.

A number of experiments were made to ascertain the accuracy of the method. A solution of copper sulphate containing 14·425 grms. of $CuSO_4,5H_2O$ per litre was used, and this was titrated with a solution of sodium arsenite, prepared from re-sublimed arsenious oxide, containing 2·450 grms. of As_4O_6 per litre. The titration was carried out with the bi-metallic electrode system as indicator. The results of the series are recorded in the following table:

	19·98 c.c. $CuSO_4$ + 3 grms. KI. c.c.
Vol. of arsenite used	20·09
,, ,, ,, ,,	20·08
,, ,, ,, ,,	20·07
,, ,, ,, ,,	20·08
Average	20·08

The volume of arsenite solution theoretically necessary to reduce the iodine liberated is 20·10 c.c.

To ascertain how dilute a solution of copper may be determined by this method, each of the solutions used in the foregoing titrations was diluted exactly ten times, thus making the copper sulphate solution approximately 0·01 *N*. The titration was repeated with the diluted solutions, and an average titre of 20·08 c.c. was again obtained, but in this case the end-point was not so well-defined as with the more concentrated solution. Solutions more dilute than 0·01 *N* could not be determined in this way.

Osterheld and Honegger's method (*loc. cit.*) has been repeated using the conditions employed by them. It was found that the end-point was sharper the more dilute the sulphuric acid, further, with excess of sulphuric acid, the titre is too low, whilst with dilute acid the titre is too high. The substitution of acetic acid for sulphuric acid improved the method, and correct titres were obtained for a wide range of acid concentration, but the end-point is obtained only slowly.

Amongst other methods investigated, the direct titration of cupric salts with potassium thiosulphate, potassium cyanide and potassium iodide may be mentioned. In the case of potassium thiosulphate it was found that cupric sulphate

is not completely reduced to cuprous sulphide even when an excess of thiosulphate is present and the solution is boiled. Similarly an excess of potassium iodide must be added to copper sulphate to reduce it (completely) to cuprous iodide, whilst in the case of potassium cyanide the reaction with copper sulphate becomes too slow as one approaches the end-point.

The titration of copper salts with stannous chloride solution appeared to be a possible method of estimation, particularly as Weil (*Ann. Chim. Phys.*, 1872, [4], **25**, 109) has stated that from observation of the colour change copper sulphate may be estimated by titration with this reagent. Experiment shows that even with electrometric indication of the end-point this method cannot be recommended. It was found that the end-point can only be obtained rapidly if the titration is carried out at 70° C., and further, that the value of the titre depends on the concentration of the hydrochloric acid present. With a large excess of hydrochloric acid (40 c.c. of conc. acid to 25 c.c. $N/10$ Cu SO_4) a value 2·63 per cent. too high is obtained, whilst with 20 c.c. of acid the error drops to 0·53 per cent. The end-point in the latter case is unsatisfactory. These results are confirmatory of those of Buchrer and Schupp (*Ind. Eng. Chem.*, 1926, **18**, 121), and at variance with those of Weil (*loc. cit.*). The high titre is attributed by Buchrer and Schupp to the fact that stannous chloride is not a sufficiently powerful reducing agent to reduce the cupric ion completely unless a slight excess of the reagent is present. A further reason for the high results may, however, be advanced. S. W. Young (*J. Amer. Chem. Soc.*, 1901, **23**, 21) has shown from conductivity measurements that in concentrated solutions of hydrochloric acid, stannous chloride tends to form complex acids of the type $HSnCl_3$, H_2SnCl_4. Hence, since some of the stannous chloride goes to form these complexes, which are not likely to act as reducing agents, the amount of stannous chloride used in a titration must be too great.

Conclusions.—The titration of iodine liberated by the action of cupric salts on potassium iodide can be carried out accurately by means of the bi-metallic electrode system of Foulk and Bawden, using either sodium thiosulphate or sodium arsenite. With the former a good end-point can be obtained with solutions of copper sulphate as dilute as 0·004 N, but with the latter the dilution must not exceed 0·01 N. Variation of the amount of acetic acid and potassium iodide is without effect on the end-point. Copper can be determined by titration with sodium thiosulphate in the presence of zinc, silver, lead, bismuth, aluminium, nickel, stannic tin and ferrous iron. It can also be determined in the presence of ferric iron in the presence of sufficient sodium pyrophosphate to convert the ferric ion into a complex ferric pyrophosphate anion, but titration of the total iodine liberated from potassium iodide by a mixture of ferric and cupric salts yields low results and the method is not to be advocated.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research, which enabled one of us (M. E. P.) to take part in the work.

Dept. of Inorganic and Physical Chemistry,
Bedford College, Regent's Park, N.W.1.

Official Appointments.

THE Minister of Health has confirmed the following appointments:

F. MAUDSLEY, B.Sc., F.I.C., as Public Analyst for the County Borough of Burnley (April 26th, 1930).

ALAN WEST STEWART, D.Sc. (Brux.), A.I.C., as Public Analyst for the Metropolitan Borough of Islington (April 4th, 1930).

MARTIN PRIEST, F.I.C., as Public Analyst for the Metropolitan Borough of Camberwell (May 22nd, 1930).

RICHARD WILLIAM SUTTON, F.I.C., as Additional Public Analyst for the County Borough of Leeds (May 22nd, 1930).

ARTHUR FRANK LERRIGO, F.I.C., as Additional Public Analyst for the County Borough of Birmingham (May 20th, 1930).

ARCHIBALD PRIDEAUX DAVSON, A.R.C.S., F.I.C., as Public Analyst for the County of Southampton (to date from July 1st, 1930).

HARRI HEAP, M.Sc., F.I.C., as Public Analyst for the Borough of Lancaster (May 28th, 1930).

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.

AIR-FREE WATER FOR SULPHUR DIOXIDE DETERMINATIONS IN FOODS.

THE Committee's* method (ANALYST, 1928, **53**, 122) and the method of Magnus Herd (ANALYST, 1930, 36) for the determination of sulphur dioxide stipulate the use of air-free water in their respective procedures.

Where occasional tests are made by these methods, it is necessary to de-aerate water freshly each time, unless suitable means are available for storage.

A convenient means of storage has been found in the use of a "Sparklet" syphon and charging bulbs. The syphon is completely filled with cooled de-aerated distilled water, and a wash-bottle syphon fitting inserted in the neck with the shorter limb of the syphon at the level of the red line round the body of the "Sparklet." The water is displaced to this level by carbon dioxide from a generator or cylinder. The wash-bottle fitting is quickly removed, and the components of the "Sparklet" assembled rapidly, after which the water is charged with carbon dioxide from a bulb.

Water stored under this condition has been found to yield results in sulphur dioxide determinations in agreement with those in which freshly de-aerated water is used.

D. M. FREELAND.

THE LABORATORY,
MACFARLANE, LANG & CO., LTD.

* The Preservatives Determination Committee of the Chemists of the Manufacturing Confectioners' Alliance and of the Food Manufacturers' Federation.

A SIMPLE POLARIMETRIC TEST FOR SUGARS IN JAMS.

(*Read at the Meeting, March* 5, 1930.)

ALTHOUGH several communications have been published on the detection and determination of glucose in fruit juice products by taking the specific rotation of the inverted extract, the method has not attracted much attention in this country. The process was first introduced by Juckenack and Pasternack (*Z. Unters. Nahr. Genussm.*, 1904, **8**, 10), who found that the specific rotation of the inverted extract of all fruit juices is approximately −20°, and gave a table showing the extent to which this figure is raised, eventually becoming a plus rotation, on addition of increasing quantities of commercial glucose syrup. Juckenack and Prause (*Z. Unters. Nahr. Genussm.*, 1904, **8**, 26) applied the method to the determination of glucose in marmalades and jams, and modifications of the process and its applications were subsequently published in papers by the following:—Matthes and Müller (*Z. Nahr. Genussm.*, 1906, **11**, 73); Ewers (*Z. Offentl. Chem.*, 1905, **11**, 374); Härtel and Sölling (*Z. Nahr. Genussm.*, 1910, **20**, 19; 1911, **21**, 168); Beythien and Simmich (*Id.*, 1910, **20**, 241); Grünhut (*Z. anal. Chem.*, 1910, **49**, 743); Beythien (*Z. Nahr. Genussm.*, 1911, **21**, 271); Härtel (*Id.*, 1919, **37**, 65).

Using the test as a rapid method for sorting out some jams, the results proved so satisfactory that the general usefulness of the method ought to be recognised.

The test is made as follows: Stir well 25 grms. of the jam with 120 c.c. of water during one minute in a beaker, being careful *not* to break up the fruit of the jam. Strain the mixture through double muslin into a flask. Add two grms. of citric acid and keep in boiling water for 30 to 35 minutes; cool. Add just sufficient (about 12 c.c.) of a strong solution of lead sub-acetate, shake, leave for 5 minutes, filter, and so produce the inverted sugar solution, which should be lead free and nearly citric acid free; the somewhat variable lead solution should be balanced against the citric acid, and a minimal excess of citric acid allowed. Test for lead by sodium sulphate, when nothing more than a faint turbidity should appear. Polarise at 20° C. and determine the total solids in 5 c.c. of the solution, dried at 100° C. (that is after all acetic acid, as well as water, has been eliminated). Then determine the acidity of these total solids and calculate it as citric acid, and deduct the weight of this acid from the solids. This will give the weight of the "saccharine solids," = w. Then calculate the specific rotation by the following formula:

$$[\alpha] = \frac{100\alpha;}{w20.1}$$ that is, 5.α/w. for a 100 mm. tube, or 2·5 α/w for a 200 mm. tube.

$[\alpha]_D$ should approximate the $[\alpha]_D$ for invert sugar.

The following nine results refer to as many different jams:—Raspberry, −21·8, −20·8, −21·6, −22·9, −22·0; strawberry, −20·5, −20·8; stoneless plum, −22·4, −21·9; stoneless plum after having had mixed into it 10 per cent. of glucose, +1·21.

These figures are those obtained in the original series of experiments, and they suffice both to define the process and indicate its possibilities. A wide range of precise observations would probably reveal a still closer regularity with the several jams, such that the test might prove useful beyond the mere question of sugars; but there is little doubt that it will be effective in the ordinary way in discovering even so little as one per cent. of glucose.

S. JUDD LEWIS.

THE SOLUBILITY OF SULPHUR.

THE extent of the solubility of sulphur in solvents other than carbon disulphide may not generally be realised. In fact, a method has been given in which the percentage of sulphur in sulphur ointment is determined by extracting a weighed quantity of the ointment with petroleum spirit and weighing the residual sulphur.

In the following experiments weighed quantities of sublimed sulphur and precipitated sulphur were placed in filter paper packets over a cotton wool plug and extracted in a continuous extractor (Type X, ANALYST, 1928, **53**, 380), a rapid flow of the solvent being maintained.

(1) Two grms. of each kind of sulphur were extracted with methylated ether.

	Sublimed sulphur dissolved. Grm.		Precipitated sulphur dissolved. Grm.
6 hours	0·973	6 hours	0·747
6 ,,	0·392	6 ,,	0·564
6 ,,	0·166	6 ,,	0·435
11 ,,	0·120	6 ,,	0·176
6 ,,	0·020	6 ,,	0·078
Undissolved residue	0·329 = 16·45 per cent.		———
	———		2·000
	2·000		

(2) One grm. of each kind of sulphur was extracted with petroleum spirit (boiling range under 40° C.).

	Sublimed sulphur dissolved. Grm.		Precipitated sulphur dissolved. Grm.
6 hours	0·803	6 hours	0·882
4 ,,	0·021	4 ,,	0·097
4 ,,	0·002	4 ,,	0·021
Undissolved residue	0·174 = 17·40 per cent.		———
	———		1·000
	1·000		

(3) One grm. of sublimed sulphur was extracted with carbon disulphide.

	Sublimed sulphur dissolved. Grm.
3 hours ..	0·831
2 ,, ..	0·004
Undissolved residue	0·165 = 16·50 per cent.
	———
	1·000

Precipitated sulphur is easily soluble in carbon disulphide, and, as shown above, dissolves slowly but completely in methylated ether and petroleum spirit, whereas sublimed sulphur is slowly soluble to the extent (in the particular sample used) of about 83 per cent. in all three solvents. The samples extracted contained only slight traces of mineral matter.

Two grms. of sulphur ointment, extracted for 2 hours with petroleum spirit in a continuous extractor, showed 3·75 per cent. of residual sulphur. The actual content of sulphur in this sample was 10·2 per cent.

DOUGLAS HENVILLE.

STEPNEY BOROUGH LABORATORY,
43, WHITE HORSE STREET, E.1.

Seventh Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods.

THE DETERMINATION OF SOLUBILITIES.

THE Essential Oil Sub-Committee makes the following recommendations in connection with the solubility tests for essential oils.

Unless otherwise stated, tests should be carried out at 15·5° C.

The strengths of the alcohol used should be stated as per cent. by volume (v/v).

While it is not considered necessary to specify any particular method for carrying out these tests, it seems desirable to define the meaning of the terms used for describing the solubility of oils.

(1) *Soluble, or completely soluble,* means that the oil forms a clear and bright solution in the proportions stated.

(2) *Soluble with opalescence* means that the solution formed is not perfectly clear and bright, but is similar in appearance to solutions of standard opalescence prepared as described below.

(3) *Soluble with turbidity* means that the solution formed is not clear, but is similar in appearance to solutions of standard turbidity prepared as described below.

OPALESCENCE.—Prepare three solutions by diluting 0·25 c.c., 0·5 c.c., and 1·0 c.c. of *N*/50 sodium chloride solution to 50 c.c. with distilled water; then add 0·5 c.c. of *N*/10 silver nitrate solution, stir and view against a dark background, comparing the opalescence with that of the solution of the oil through equal thicknesses of liquid. The resulting effects are described as:

0·25 c.c.	Faintly opalescent.
0·5 c.c.	Slightly opalescent.
1·0 c.c.	Distinctly opalescent.

TURBIDITY.—Prepare three solutions by diluting 0·25 c.c., 0·5 c.c. and 1·0 c.c. of *N*/10 sulphuric acid to 50 c.c. with cold distilled water; then add 0·2 c.c. of approximately *N*/1 barium chloride solution; stir and allow to stand for 5 minutes at room temperature, and compare the turbidity with that of the solution of the oil through equal thicknesses of liquid. The resulting effects are described as:

0·25 c.c.	Faintly turbid.
0·5 c.c.	Slightly turbid.
1·0 c.c.	Distinctly turbid.

(*Signed*)

John Allan (Chairman), C. T. Bennett, S. W. Bradley, E. Theodore Brewis, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, C. Edwd. Sage, W. H. Simmons, and T. Tusting Cocking (Hon. Secretary).

MARCH 26TH, 1930.

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.

COUNTY OF ABERDEEN.

ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1929.

THE total number of samples analysed was 8175. Of the 254 formal samples received, 17 were found to be adulterated, deficient or doubtful. Of the 83 samples of whole milk, 8 contained less than 8·5 per cent. of solids-not-fat.

SULPHUR DIOXIDE IN MINCE, SAUSAGES, ETC.—Thirty-one samples of mince, etc., were tested for preservatives. One sample of mince (with 40·6 parts of sulphur dioxide per million) and one of sausage mince (with 487 parts) were returned as adulterated. Sulphur dioxide up to 450 parts per million is permitted in mince during the months of June, July, August, and September, whereas the first sample mentioned was analysed in the period October to May. The samples of sausages, with regard to which there is no restriction as to the period of the year, contained from *nil* to 440 parts per million.

BYRE ("APPEAL-TO-THE-COW") SAMPLES TAKEN IN CONNECTION WITH FORMAL SAMPLES FOUND DEFICIENT.—Six of the 47 byre samples were found to be below the prescribed presumptive limit for fat, 15 for solids-not-fat, and 6 for both fat and solids-not-fat.

There is no change in the unsatisfactory state of the law relating to the sale of milk, notwithstanding the overwhelming proof that the law does not discriminate between the fraudulent seller and the seller of milk of poor quality. Instead of the present law, which presumes, until the contrary is proved, that milk containing less than 3 per cent. butter fat and less than 8·5 per cent. solids-not-fat is adulterated, it is my view that the law should provide that the seller must give a warranty as to the quality of his milk. This is what is provided for and given under the Fertilisers and Feeding Stuffs Act, 1926. A civil claim would then be made if the sample did not conform to the warranty. On the other hand, if a seller was fraudulent—if he added water or otherwise adulterated his milk—then he would be brought into Court on a criminal charge. Any further change in the law should also provide the empowering of officers of Local Authorities to enter the registered premises of a seller of milk in order to test the warranty given by that seller. A claim would be made for any deficiency found, provided the sample was taken with all the necessary formalities. Adulteration would thus be detected at its likely source, and the abstraction of butter fat or the addition of water or skimmed milk would be made extremely difficult.

J. F. TOCHER.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1930.

THE number of samples examined was 1335, of which 106 were bought formally; 82 of the total samples were adulterated or incorrect.

SULPHUR DIOXIDE IN SAUSAGES.—As, in spite of the fact that a number of vendors have been cautioned within the last year or two for offences against the

Preservatives Regulations, the practice of the addition of preservative without declaration has not diminished, it was thought advisable to issue summonses against seven vendors who had sold sausages without notice that they contained preservative, and the cases were the first under the Preservative Regulations to be taken in Birmingham. Each vendor was fined 10s., the chairman of the magistrates remarking that any future offenders would be more severely dealt with.

PREPARED HONEY.—A sample of prepared honey sold under a trade name was labelled, "Made from honey but better than honey." As a matter of fact, it was found to contain a large proportion of commercial invert sugar which, although consisting of the same kinds of sugars as honey, cannot be described as honey, any more than patent spirit can be described as whisky.

The manufacturers gave an undertaking to sell the product in future labelled with the declaration, "This is sold as a mixture of honey and invert sugar."

In fairness to the makers it should be stated that the product was perfectly wholesome, and contained vitamin *D* in the form of ostelin. This, of course, is not present in ordinary honey, and its addition increases its value as a foodstuff.

TEA.—On the label of a sample of tea appeared the statement: "Contains the maximum of theine with the minimum of tannin," and other matter indicating that its value was greater than that of other teas. As a matter of fact, analysis showed that both these constituents were present in about the usual proportions, and from this point of view, therefore, the tea had no advantage over any other tea at a similar price. Such statements as the above are untrue and misleading, and are naturally taken by the purchaser to mean that he is getting something better than the ordinary article. This is unfair to the purchaser, and also to the other traders who are trying to sell similar articles without the use of such advertisements. The packers were communicated with, and undertook to have new cartons printed on which the offending statement should not appear. They were given permission to use up the remaining stocks of the old cartons.

INFANTS' FOOD.—A sample of malted food for infant feeding was labelled in a very unsatisfactory way. The label stated that, made with milk and water, the food would closely resemble, in chemical composition, mother's milk, and that it was the best substitute for mother's milk. The directions for mixing the food were extremely vague and read as follows: "Mix one tea-spoonful to one table-spoonful into a thin paste with a little cold milk and water, and pour on gradually half-a-pint of milk and water. . . ."

The tendency on the part of the user of such a food would be to use as little milk as possible, and it is desirable that the proportions of the preparation and of the milk and water to be used for mixing with such a food should be stated more clearly.

I calculated that, if one table-spoonful of the food were mixed with half-a-pint of equal parts of average milk and water, the resulting mixture would be seriously deficient in fat and milk sugar, as compared with mother's milk, and that it would also contain, in addition, several constituents, for example, cane sugar, starch and dextrin, which are not found in human milk at all. If less milk were used, the deficiencies in fat and sugar would, of course, be proportionately greater. The proprietors were written to, and have agreed to revise the label and to delete the statements referred to.

LABELLING OF BEEF SUET.—The label of one sample bore the statement "1 lb. goes considerably farther than 1 lb. of raw suet." In view of the fact that the sample contained only 79 per cent. of fat, against an average of about 95 per cent. of available fat for raw suet, this seems rather a large claim to make. No action has yet been taken in the matter.

The label on another sample stated that "1½ lb. goes as far as 2 lb. of raw suet," which again seems to be over-stating the fact, since only 86 per cent. of fat was present. A sample of this firm's product was taken last year, on the label of which similar wording appeared, with the addition of the phrase, "Purer and richer in fat than raw suet." This was deleted at the request of the Medical Officer.

The label on a third sample was to the effect that "Only three-quarters of the quantity is required to replace the full measure of raw suet, margarine or lard. Purer and richer in fat." The sample contained 91 per cent. of fat and was, therefore, certainly not richer in fat than raw suet or lard, the latter of course, being practically pure fat. The makers have been asked to omit this statement from the description.

Another sample consisting of 100 per cent. of beef fat was labelled that "¾ lb. is equal to 1 lb. of butcher's or shredded suet." This manufacturer would, evidently, have us believe that butcher's suet and shredded suet are equal in value, contrary to the opinion of the makers of shredded suet.

BORAX HONEY.—The article should consist, according to the B.P., of 10 per cent. of borax, 5 per cent. of glycerin, and 85 per cent. of honey. It is used in children's throat and mouth affections. An informal sample from a drug store contained no honey and consisted of a mixture of 32 per cent. of borax and 68 per cent. of glycerin. The formal sample was of very similar composition, containing 40 per cent. of borax and 60 per cent. of glycerin. Honey was again absent. This mixture obviously bore no resemblance in composition to genuine borax honey, and was four times as strong in borax as it should have been. The Inspector, on going into the shop for the sample, was told by the woman that she had no honey at the moment, and asked him to come again in an hour's time. It could not, therefore, be stated that the mixture was sold in error, and the substitution was evidently deliberately made. The vendor was prosecuted and fined 10s.

CAMPHORATED OIL.—A sample contained an ingredient entirely foreign to camphorated oil, namely, 1·6 per cent. of the B.P. 10 per cent. solution of ammonia. The smell of the camphor was completely masked. It is not suggested that there was anything harmful about the sample, but it showed gross carelessness on the part of the pharmacist concerned. Probably he had used for filling the Inspector's bottle a measure or vessel previously used for ammonia, without taking the trouble to wash it out. What happened with camphorated oil might very easily happen with things of more importance, and the vendor was strongly cautioned by the Medical Officer.

GLAUBER'S SALT.—In this case Epsom salt was sold in error instead of the article asked for. The action of the two salts is similar, and this was probably a case of a genuine mistake. The vendor was cautioned.

H. H. BAGNALL.

Dominion of Canada.

REPORT OF THE DOMINION CHEMIST FOR THE YEAR ENDING MARCH 31ST, 1929.

IN his Annual Report, Dr. F. Shutt states that 4263 samples were analysed during the year, of which 1852 were from the Meat and Canned Food Division. The chemical service for farmers has been steadily maintained, and in the course of the year farmers submitted 617 samples of soils, manures, waters, etc., for analysis and advice. In addition a large amount of work has been done in investigations connected with agriculture.

COMPOSITION OF GRASS AS INFLUENCED BY CUTTING.—Full details are given of the results obtained during two seasons. There is evidence to show that the yield of dry matter per unit acre decreases with frequency of cutting. The close-grazing scheme appears to be essentially one productive of herbage rich in protein and of high digestibility.

INFLUENCE OF LIGHT CONDITIONS ON THE CONSTITUENTS OF BONE.—Detailed analytical data are given of the analyses of the bones of two breeds of chicks, as influenced by light from various sources and by the addition to the meal ration of cod-liver oil. It was found that high water content (poor bone development) is associated with low fat and low phosphate of lime, whilst good bone development is associated with a high percentage of fat and phosphate of lime. The pens of chicks could be grouped in the following order of bone development:—*Group I.* Direct sunlight through open window. *Group II.* Ultra-violet ray treatment; sunlight through vita-glass; irradiated mash (Leghorns); cod-liver oil supplement (Plymouth Rocks). *Group III.* Sunlight through common glass; diffused sunlight (dull, dim light); irradiated mash (Plymouth Rocks); cod-liver oil supplement (Leghorns).

IODINE IN "IODISED" SALT AND FISH MEAL.—Since the normal daily ration of live stock generally contains very little iodine, it has been recommended that small amounts of this element should be supplied in the form of an iodide. This may be easily accomplished by the use of "iodised" salt, that is, salt to which potassium iodide has been added by the manufacturer. The following table presents some determinations made by the Division of Chemistry of the iodine content of various salts:—

IODINE CONTENT OF "IODISED" SALT.

No.	Source.	Description.	Iodine per cent.
80508	Canadian Salt Co., Windsor, Ont. ..	Pressed block	0·0003
80509	Canadian Salt Co., Windsor, Ont. ..	Granular	0·0003
91426	Century Salt	.. ..	0·0074
91427	Century Salt	.. ..	0·0034
91428	Dominion Salt Co., Sarnia ..	.. ..	0·0120
91429	.. ..	.. ..	0·0038
91661	Canadian Salt Co., Windsor, Ont. ..	.. ..	0·0007
93070	Windsor Salt Co.	Crescent Brand	0·0001 (approximately)

In the manufacture of "iodised salt" for live stock, sufficient iodide is added to give, theoretically, 0·02 per cent. of potassium iodide (0·0152 per cent. of iodine) in the finished product. The figures of the above table show that there is considerable variation in this percentage. This may be due in part to loss of iodine from the "iodised" salt during storage, and in part to the difficulty in the process of manufacture of obtaining a uniform percentage of iodine throughout the whole product. A sample from one part of a shipment may contain only traces, while that from another part may contain a fairly high percentage of this element. In the above table, for instance, the samples reported under Lab. Nos. 91426 and 91428 contain amounts which approach the order of the theoretical. On the other hand, the iodine content of the samples reported under Lab. Nos. 80508, 80509, 91661, and 93070, is extremely low.

Fish Meal.—Besides "iodised" salt, fish meal may also be used to supply iodine to the daily ration. This concentrate is produced in considerable quantity on the Atlantic and Pacific coasts from fish and fish wastes. The whole fresh fish

and fish wastes are subjected to a process of reduction by steam cooking, the larger proportion of the oil is skimmed off, and the residue is dried and ground. Among the fish used are mackerel, pilchard, cod and dog fish. Some attempt has been made, also, to utilise the salmon and salmon wastes from the canning industry in British Columbia.

In a bulletin of the Division of Chemistry*, a number of chemical analyses of fish meals are reported; the following table presents the determinations of iodine in certain of these fish meals:—

IODINE CONTENT OF FISH MEALS.

No	Source.	Description.	Iodine in parts per 100,000.
67443	Todd's Cannery, Esquimalt, B.C. ..	.. .. ..	0·07
80594	W. R. Beatty & Co., Vancouver, B.C.	Hiuskookum meal	0·37
80595	Marine Products, Prince Rupert, B.C.	Salmon meal ..	0·15
95396	National Fish Co., Halifax, N.S. ..	Fish meal ..	0·90
95397	City Renderer's, Montreal	Fish meal ..	0·84
98272	Magdalen Islands	Cod's head and bones	1·22
98273	,, ,, ...	Mackerel meal ..	0·56
98408	,, ,, ...	Seal meat and bones	0·04
98409	,, ,, ...	Seal meat ..	0·03
101215	City Renderer's, Montreal	Fish meal ..	1·30

These figures show that there is a distinct variation in the iodine content of different fish meals depending upon the nature of the materials used and, probably, upon the process of manufacture. The samples reported under laboratory Nos. 80595, 95396, 95397, 98272, 98273, and 101215 contain sufficient iodine to make them comparable to "iodised" salt as a source of iodine for live stock. One pound of fish meal and one-tenth of a pound of salt are approximately the quantities which would be given in the ration per animal per day. The one sample listed under laboratory No. 67443 is low in iodine, and must be considered as an exception, rather than the general rule. The samples produced from seal meat must not be classified as fish meals proper.

Fish meal is a valuable concentrate not only on account of its high protein content, but also because of its calcium and phosphorus content. It may possess an additional value as a source of iodine. In co-operation with the Division of Animal Husbandry some experimental work preliminary to a more complete investigation of the subject has been conducted wherein fish meal was fed to milch cows in the concentrate ration at the rate of one pound per animal per day. During the period in which the fish meal was fed, the "iodised" salt generally furnished to the cattle was replaced by ordinary stock salt containing no iodine. The Division of Chemistry took the opportunity of determining the iodine content of the milk after the feeding of "iodised" salt and after the feeding of fish meal. The results are summarised in the following table:—

IODINE CONTENT OF MILK AFTER FEEDING WITH "IODISED" SALT AND WITH FISH MEAL.

Source of iodine.	Per cent. iodine	Pounds given per animal per day.	Grms. iodine furnished.	Iodine in milk, parts per billion (10^9).
Iodised salt	0·009	0·1	0·0041	40
Fish meal	0·0009	1·0	0·0041	55

* Meat and Bone By-Products. Bulletin No. 49—New Series.

The apparent difference in the iodine content of the two milks is not significant, since the amounts are extremely small. Milk from herds not receiving any additional iodine in the ration has been reported as containing iodine to the order of ten parts per billion. The feeding of "iodised" salt tends to raise the level of the iodine content of the milk. Feeding with fish meal will maintain the iodine content at approximately the same level as the feeding with "iodised" salt.

The results of this preliminary experiment, together with the analyses reported of fish meals, suggest that fish meal, already recognised as a valuable protein concentrate, may occupy a place of still greater importance in the daily ration.

Sea Weed.—The suggestion has been advanced that sea weed might be added to or incorporated in the concentrate ration to furnish iodine. Certainly sea weeds are very high, comparatively speaking, in iodine, as the table below will reveal.

IODINE CONTENT OF SEA WEEDS.

Kind of seaweed.	Iodine per cent.
Fucus vesiculosus and nodosus	0·070
Fucus vesiculosus	0·013
Potwrack	0·050
*Laminaria	0·175
*Costaria	0·029
*Alaria	0·027

* Furnished by Dr. A. T. Cameron of the University of Manitoba, who has made an extensive survey of the iodine content of sea weeds.

Whether or not a high iodine ration is beneficial or desirable is debatable. It has been shown that the small quantity of iodine in "iodised" salt has been sufficient to prevent the occurrence of gôitre in regions where this malady has not assumed too serious proportions. In regions, however, where gôitre is serious it is possible that the amount of iodine in salt may not prove sufficient, and a supplemental addition of sea weed might, in this case, be indicated.

ANALYSES OF PRESERVED FRUITS AND JAMS.—Of the 219 samples of canned and preserved fruits and vegetables examined, 36 were jams and marmalades made in Canada. The analyses of 16 samples of pure strawberry jams and 12 samples of pure raspberry jams were as follows:

SUMMARY OF RESULTS OF ANALYSES OF PURE STRAWBERRY AND RASPBERRY JAMS MADE IN CANADA.

Fruit.		Total solids. Per Cent.	Water insoluble solids. Per Cent.	Pectin (calcium pectate). Per Cent.	Ash. Per Cent.
Strawberry ..	Ave. ..	73·93	1·12	0·28	0·22
	Max. ..	77·82	1·66	0·33	0·28
	Min. ..	64·42	0·69	0·23	0·15
Raspberry ..	Ave. ..	75·42	1·98	0·27	0·19
	Max. ..	78·93	2·98	0·33	0·30
	Min. ..	68·69	1·02	0·21	0·13

The average, maximum and minimum percentages of glucose in thirty-seven samples of glacè cherries were 48·1, 72·1 and 22·5 respectively.

One sample of canned peaches, which was intended for use as a diabetic food, was found to contain 20 per cent. of sucrose and 11 per cent. of invert sugar.

One sample of apple juice imported from Holland contained 1340 parts per million of sulphur dioxide.

Government of Bihar and Orissa.

ANNUAL REPORT OF CHEMICAL ANALYST FOR THE YEAR 1929.

THE Chemical Analyst for Bihar and Orissa, Dr. K. N. Bagchi, reports that during the year 1186 samples of foods, drugs and waters received from 18 of the 21 districts of the province, were examined.

GHEE.—Of the 182 samples analysed, 50 were found adulterated or below the standard prescribed by the Bihar and Orissa Food Adulteration Act. The maximum Reichert–Wollny figure obtained with a genuine sample was 36·5. The samples of bazaar ghee are usually made of mixed milk-fat from the cow and buffalo.

RAPE OIL.—This is popularly known as mustard oil.—Of the 129 samples examined, 69 were found adulterated or below standard. The usual adulterants are linseed oil, niger seed oil (*Guizotia abyssinica*) and paka oil or kusum oil (*Cassambium spinosum* or *Schleichera trijuga*). Linseed oil was detected in 37·5 per cent. of the total samples. Paka oil was detected in only 3 samples which were sent by the Purulia Municipality. As this oil contains hydrocyanic acid, one of the samples produced symptoms of poisoning when used in the preparation of food.

SWEETS.—Seventy-two samples of sweets were examined. They are made of sugar, ghee or rape oil, and flour (of peas or of wheat and other cereals), and the object of analysis was to detect the adulteration, if any, of ghee or oil extracted from them. Twenty-three samples were found to have been made with bad ghee or oil.

Sale of Medicated Spirituous Preparations.

THE Commissioners of Customs and Excise have issued instructions to their officers to the effect that *bona fide* medicated spirituous preparations may be sold without an Excise Licence being held, subject to the following conditions:—

1. The preparation must contain a medicinal substance in such proportion as in the opinion of the Commissioners gives it a distinct medicinal character and makes it unsuitable or unpalatable for use as a beverage; and

2. The directions as to dose, etc., on the labels of the bottles or other containers must indicate to the satisfaction of the Commissioners that the preparation is intended for use as a medicine and not as a beverage.

The effect of this ruling is that unlicensed grocers may sell the spirituous preparations of the B.P., such as quinine wine, tincture of iodine, ipecacuanha wine, Friar's balsam, spirit of peppermint, sal volatile, sweet spirit of nitre (*cf.* ANALYST, 1926, **51**, 186).

Ministry of Health.

DAMAGED TEA.

(CIRCULAR 1059.)

THE following circular has been issued to authorities administering the Food and Drugs Act.

FOOD AND DRUGS (ADULTERATION) ACT, 1928

1. I am directed by the Minister of Health to request that a copy of the Report of the Public Analyst for the fourth quarter of the present year may be transmitted to this Department during the month of January.

2. The Minister has been informed by the Commissioners of Customs and Excise that in consequence of the abolition of the tea duty it is no longer possible for their officers to exercise the same control as heretofore in preventing the delivery of damaged tea and tea sweepings. The attention of the appropriate Port and Riparian Sanitary Authorities has already been drawn to the matter with a view to the exercise of their powers under the Public Health (Imported Food) Regulations, 1925, but the Minister thinks that Food and Drugs Authorities should also be aware of the possibility of the relaxation of Customs control resulting in a slight increase in the quantity of contaminated tea offered for sale.

3. Copies of this Circular are being sent to the Medical Officer of Health and the Public Analyst.

December 28th, 1929.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Cholesterol as a Measure of Egg Yolk in Milk Products. L. M. Lampert. (*Ind. Eng. Chem.* (*Anal. Edition*), 1930, **2**, 159–162.)—The sample is extracted by Mojonnier's modification of the Röse-Gottlieb method, and the residue, after evaporation of the extract, is saponified by boiling for about 10 minutes with 15 c.c. of 95 per cent. alcohol and 1 c.c. of 100 per cent. potassium hydroxide solution, the solution being extracted with four 30 c.c. portions of ether. The ethereal extracts are washed with distilled water till neutral, and the residue left on evaporation is dissolved in 50 c.c. of chloroform. The colour produced after 15 minutes by 10 c.c. of this extract, 2 c.c. of acetic anhydride and 0·2 c.c. of concentrated sulphuric acid is matched against that of a solution containing 0·5 mgrm. of cholesterol per litre. The method is satisfactory for egg and milk products, a mean cholesterol content of 1·36 per cent. being found for whole fresh egg-yolk. The following formula may be used to calculate the percentage of egg-yolk in ice-cream and other milk products:—$73{\cdot}5\ (a-bc)/(1-16{\cdot}9c)$, where a and b are the percentages of cholesterol and fat, respectively, and c a factor which varies approximately linearly from 0·00377 for 9 per cent. to 0·00240 for 16 per cent. of cream. The error is normally less than 0·1 per cent. J. G.

Detection of Small Quantities of Chlorine in Flour. D. W. Kent-Jones and C. W. Herd. (*J. Soc. Chem. Ind.*, 1930, **49**, 223–226T.)—For the detection of the minute quantities of chlorine introduced into flour by the nitrogen trichloride bleaching process, 500 grms. of the flour are shaken intermittently during 30 minutes with 700 c.c. of petroleum spirit (b.pt. 40–60° C.) and, after standing overnight, the mixture is filtered, the filtrate distilled, and the residue hydrolysed with 20 c.c. of 4 per cent. alcoholic sodium hydroxide solution (prepared from metallic sodium), being taken down to dryness on a water-bath. The residue is either placed in a platinum bowl in a muffle furnace at about 500° C., or just charred over a flame, cooled, and 20 c.c. of nitric acid (1 : 1), free from chlorine, added. The extraction is repeated once with acid and three times with 20 c.c. of water, the extracts filtered successively, and paper and bowl dried at 100° C., the paper

ignited, and the ash dissolved in a few drops of nitric acid and added to the extracts. The extracts and washings are evaporated to 30–40 c.c., and 5 c.c. of sodium chloride solution (1·65 grm. per litre), and 10 c.c. of silver nitrate solution are added. The silver chloride is coagulated by boiling, and is filtered off on paper which has been washed with nitric acid, or is thrown down by centrifuging, and to the clear solution 2 c.c. of ferric-indicator are added, and the excess of silver nitrate titrated with ammonium thiocyanate solution (2·14 grms. per litre). Flours known to have been treated with nitrogen chloride or chlorine in any form have always given less than 1 part per million of chlorine; anything over 2 parts per million was a clear indication that the flour had been treated with chlorine. D. G. H.

Properties of Arachin and Conarachin and the Proportionate Occurrence of these Proteins in the Arachis Nut. D. B. Jones and M. J. Horn. (*J. Agric. Research*, 1930, **40**, 673–682.)—Oil-free meal obtained by successive extractions with petroleum spirit and ether of raw, shelled Virginia arachis nuts was found to contain 7·36 per cent. of nitrogen, equivalent to 40·48 per cent. of protein. The factor $N \times 5{\cdot}5$ was used, since arachin and conarachin both contain 18·29 per cent. of nitrogen, and together represent over 80 per cent. of the total nitrogen present. A fresh extract obtained by extraction of the oil-free meal with 10 per cent. sodium chloride solution in the centrifuge contained 6·41 per cent. of nitrogen. Heat-coagulation tests on the extract and fractional precipitations with ammonium sulphate indicated that arachin and conarachin are the only two globulins present, and occur to the extents of 25 and 8 per cent., respectively. Precipitated arachin, dehydrated by alcohol and ether, is a fine white powder, $[\alpha]^{20}_{D}$–39·5° (in 10 per cent. sodium chloride solution). Solutions in 10 per cent. saline are stable at the b.pt., but are precipitated when treated with ammonium sulphate to the extent of 40 per cent. Conarachin, $[\alpha]^{20}_{D}$–42·7°, coagulates at 80° C. or at 85 per cent. saturation with ammonium sulphate. Arachis solutions are precipitated by trichloracetic, tannic or tungstic acid, and may thus be separated from amino acids, and, in the case of trichloracetic acid, from peptone, but the two latter reagents precipitate 39·13 and 44·66 per cent. of the peptone nitrogen, respectively. Albumin, prolamin and glutelin were shown to be absent from arachis nuts. In the determination of arachin (1) 500 c.c. of fresh, clear saline extract are treated with ammonium sulphate to the extent of 40 per cent., centrifuged, and the deposit of arachin redissolved, re-precipitated and finally purified by precipitation from salt solution with 10 volumes of water, and dehydrated and weighed. (2) Conarachin is obtained by slowly raising 10 c.c. of extract to 85° C., the coagulum being filtered off and washed with salt solution. (3) If the refractive indices of the original and supernatant liquids are found, their difference gives the refraction due to conarachin, and the percentage of either protein (c) may be found from Robertson's formula, $n-n'=0{\cdot}00236\ c$, where n is the refractive index of the solution of the protein concerned, and n' that of the solvent. (4) If arachin is removed by method (1) conarachin may be precipitated by trichloracetic acid. The four methods give concordant results. J. G.

Component Glycerides of Borneo (Illipé) Tallow. T. P. Hilditch and J. Priestman. (*J. Soc. Chem. Ind.*, 1930, **49**, 196–200T.)—The Borneo tallow examined (from trees of the genus *Shorea*, mainly *Stenoptera, Dipterocarpaceae*) had m.pt. 36–36·5° C., solidification pt. 28·8° C., saponification equivalent 290·7, iodine value 32·3, and contained 0·74 per cent. of unsaponifiable matter. The methods of analysis used were as for cocoa butter (ANALYST, 1929, **54**, 242), and the composition of the mixed fatty acids was: Myristic, 1·5; palmitic, 21·5; stearic, 39·0; and oleic acid, 38·0 per cent. Oxidation of the tallow with potassium permanganate in acetone solution showed the presence of 4·5 per cent. of fully saturated glycerides containing 6 per cent. of unsaponifiable matter, and the fatty acids consisted approximately of 57 per cent. of palmitic and 43 per cent. of stearic acid; as with cocoa butter, the palmitic acid appears to be relatively concentrated in the fully saturated glycerides in spite of the preponderance of stearic acid in the total fatty acids. The deduced component glyceride structure of the tallow showed that 95·5 per cent. of the fat consisted of mixed saturated-unsaturated glycerides, with saturated and unsaturated acids in the molecular ratio of 1·55: 1. Mono-oleo-glycerides must form at least 78 per cent. of the fat, which cannot contain more than 17·5 per cent. of dioleoglycerides or more than 8·5 per cent. of triolein, and this was confirmed by experimental examination of the acidic products of oxidation of the tallow. A possible approximate composition of the tallow is: Palmito-stearins 4·5, mono-oleodisaturated glycerides (mainly oleopalmitostearin) 85; dioleomonosaturated glycerides 6·5, and triolein 4 per cent. Slightly more fully saturated glycerides and definitely more mono-oleo-glycerides are present than in cocoa butter, and there is also probably more oleodistearin. These slight differences account for the somewhat higher m.pt. and tendency to granulation shown by Borneo tallow, but the results bring out the similar features of glyceride structure which render the two fats specially suitable for confectionery purposes.

D. G. H.

Determination of Citric Acid in Fruits and Fruit Products. B. G. Hartmann and F. Hillig. (*J. Assoc. Off. Agric. Chem.*, 1930, **13**, 99–103.)—The citric acid is isolated as the lead salt. This is decomposed with hydrogen sulphide and the liberated acid determined as pentabromacetone, pectin and organic acids being previously removed. The sample is prepared as described in *Methods of Analysis*, A.O.A.C., 1925, 209, or for fruit juices a quantity of material is taken containing not more than 200 mgrms. of citric acid. The titratable acidity is determined, in terms of normal acid, the volume adjusted to 35 c.c., 3 c.c. of *N* sulphuric acid added, the liquid heated to 50° C., transferred with 15 c.c. of warm water to a 250 c.c. flask, made up to the volume with 95 per cent. alcohol, shaken and filtered. To 200 c.c. of filtrate in a centrifuge bottle is added lead acetate solution (70 grms. dissolved in water, 1 c.c. of glacial acetic acid added, and the volume made up to 250 c.c.) equivalent to 0·8 times the titratable acidity plus 3 (as found above). (In the case of products containing alcohol where saponification is necessary, the volume of the portion taken is adjusted to 35 c.c., 3 c.c. of *N* potassium hydroxide in excess of that required for neutralisation added, the

mixture boiled, left overnight, and *N* sulphuric acid added equal to the total quantity of *N* alkali, with 3 c.c. in excess, and the solution transferred to the 250 c.c. flask; the acidity is then the number of c.c. of *N* sulphuric acid added plus the titratable acidity of the material). The mixture is shaken for 2 minutes, centrifuged for 15 minutes, the liquid decanted, and 150 c.c. of 80 per cent. alcohol are added to the sediment, and, after shaking, centrifuging is repeated. The salts are transferred to a 400 c.c. beaker with 150 of water, and hydrogen sulphide passed into the warm liquid with frequent stirring until cool. The liquid is made up to 250 c.c. and filtered, and 225 c.c. of the filtrate evaporated to about 75 c.c., and after the addition of 10 c.c. of 1 : 1 sulphuric acid and 5 c.c. of potassium bromide solution (15 grms. in 140 c.c. water), the mixture is maintained at 48–50° C. for 5 minutes, 50 c.c. of 5 per cent. potassium permanganate solution added, and the stoppered flask shaken vigorously and left 4 minutes. More potassium permanganate may be added if necessary during the precipitation of the manganese dioxide, which is removed with about 20 c.c. of ferrous sulphate solution (40 grms. in 100 c.c. water containing 1 c.c. of concentrated sulphuric acid). The solution is cooled, left overnight in a refrigerator, filtered quickly, the volume of filtrate noted, and the precipitate transferred to a Gooch crucible. The contents of the crucible are washed with ice-cold water, dried and weighed, and the pentabromacetone removed with 3 portions of 20 c.c. each of alcohol and 3 portions of ether. The residue is again dried and weighed, and the difference is the weight of pentabromacetone, from which the citric acid is calculated. Malic, tartaric and *iso*citric acids do not interfere with the reaction. Percentages of recovery for pure solutions of citric acid were, on the average, 95 per cent. D. G. H.

Determination of Tartaric Acid in Fruits and Fruit Products. B. G. Hartmann and F. Hillig. (*J. Assoc. Off. Agric. Chem.*, 1930, **13**, 103–112.)—Tartaric acid in fruits and fruit juices may be determined either (1) by the acid potassium tartrate method, and this method is preferable, or (2) by the calcium racemate method. The preliminary treatment in either case requires the removal of pectin and isolation of the lead-precipitated acids.

(1) The same procedure is followed as for citric acid to the point of having passed the hydrogen sulphide. The solution is then made up to 250 c.c., and 225 c.c. evaporated to about 20 c.c., neutralised with N potassium hydroxide to phenolphthalein, 3 drops excess alkali added, followed by slow addition, with stirring, of 2 c.c. of glacial acetic acid and 80 c.c. of 95 per cent. alcohol. After standing in a refrigerator overnight the supernatant liquid is decanted on to a Gooch crucible with a removable bottom, leaving about 25 c.c. in the beaker, to which are added 0·3 grm. of dry asbestos. Three portions of 15 c.c. of ice-cold 80 per cent. alcohol are used to transfer this liquid to the crucible, and 3 more portions are used to wash the contents of the crucible, and the pad of asbestos and precipitate are then removed with about 100 c.c. of hot water, boiled, and the liquid titrated with 0·1 *N* alkali, with phenolphthalein as indicator. The number of c.c. of 0·1 *N* alkali,

multiplied by 0·015, gives the quantity of tartaric acid. Malic and citric acids do not interfere.

(2) When *l*-tartaric acid is added to a solution of *d*- acid in the presence of a soluble calcium salt, equal weights of the two modifications combine to form the very much less soluble calcium racemate and calcium tartrate, *l* or *d*-. Proceeding from the same point as in (1), 200 c.c. of clear filtrate from the lead sulphide filtration are evaporated to about 100 c.c., made up to 150 c.c., and 15 c.c. of diammonium citrate added (29 grms. of citric acid in about 200 c.c. of water neutralised with ammonium hydroxide to methyl red, 14·5 grms. of citric acid added, and the solution made up to 1 litre); 25 c.c. of ammonium *l*-tartrate (3·2 grms. diluted to 200 c.c. with the addition of 1 c.c. of formalin), and 20 c.c. of calcium acetate solution (16 grms. of calcium carbonate in 120 c.c. of glacial acetate acid diluted with water to 1 litre and filtered). The mixture is stirred until precipitation begins, and left overnight. After decanting, the precipitate is transferred to a Gooch crucible with part of the filtrate, and after washing 5 times with water the precipitate and asbestos are treated with 20 c.c. of concentrated hydrochloric acid (34 c.c. diluted to one litre). The solution is made up to 150 c.c. with water, and 50 c.c. of calcium carbonate solution added (5 grms. in 20 grms. of acetic acid with 100 grms. of sodium acetate, made up to 1 litre and filtered), brought to 80° C., cooled, left at least 4 hours, with occasional stirring, filtered and washed, as in the first operation. The pad and precipitate are transferred with 150 c.c. water to a casserole, 50 c.c. of 10 per cent. (by vol.) sulphuric acid added, the liquid brought to 80° C., and immediately standard potassium permanganate is run in until excess is indicated (6·9745 grms. per litre standardised against a solution of tartaric acid as in the final titration; 1 c.c. equals nearly 0·005 grm. of tartaric acid). After heating to 80° C., 5 c.c. more potassium permanganate are added, and after 1 minute's standing and heating again to 80° C., 10 c.c. of standard oxalic solution are added (13·8793 grms. per litre titrated against the permanganate solution) and titrated back with permanganate. The weight of total tartaric acid, divided by 2, represents the weight present. When extreme accuracy is not required the removal of the pectin and precipitation of the acid with lead may be omitted, the volume being adjusted to 150 c.c., and the tartaric acid determined as above. D. G. H.

Determination of Phenol [Carbolic Acid] in Pharmaceutical Preparations. J. Rae. (*Pharm. J.*, 1930, **124**, 239–240.)—To 1 c.c. of a solution of 5 c.c. of *glycerin of carbolic acid* diluted to 100 c.c., is added 1 c.c. of a 10 per cent. solution of sodium nitrite and 1 c.c. of diluted sulphuric acid (B.P.), and after 10 minutes the mixture is diluted to 50 c.c. in a Nessler cylinder. The colour should match that obtained with 1 c.c. of a 1 per cent. solution of carbolic acid similarly treated. For *trochiscus acidi carbolici* 1 lozenge is ground up with water and made up to 30 c.c., and, after shaking, 10 c.c. are filtered off, and the filtrate treated as above, the standard solution being similarly diluted to 10 c.c. before addition of nitrite. *Carbolic acid pills* are digested for half-an-hour with 25 c.c. of water, and filtered, the residue washed, and 10 c.c. of the filtrate and washings (30 c.c.) diluted to

50 c.c. The colour of the liquorice is matched in the standard by adding a dilute solution of burnt sugar, and the procedure is the same as for lozenges. When 0·5 grm. of phenol was present in the pills 47 c.c. of the diluted standard matched 50 c.c. of the pill solution. This test can also be used for the determination of sodium phenolate solutions. D. G. H.

Quality of Commercial Ether. H. Leffmann and C. C. Pines. (*Amer. J. Pharm.*, 1930, **102**, 58–62.)—Aldehydes may be present even in the best grades of anæsthetic ether, and tin containers appear to favour their development. Schiff's reagent, (magenta decolorised with sulphurous acid), which is best prepared by Fincke's formula, *Amer. J. Pharm.*, 1927, **99**, 289) is a very delicate reagent for aldehydes, and for practical purposes a toleration limit may be desirable. Peroxides are not often present; they are satisfactorily tested for with chromic acid, which should be poured through the sample (1 c.c. of a solution containing 1 grm. of potassium dichromate and 5 c.c. of concentrated sulphuric acid in 100 c.c. of water, dropped into 1 c.c. of ether). D. G. H.

Biochemical.

Iodine Metabolism. C. Newcomb and G. Sankaran. (*Trans. F.E.A.T.M. Seventh Congress, India*, December, 1927, 329–334.)—By a modification of Fellenberg's method, it is found possible to determine the amount of iodine in 50 c.c. of urine to within 0·5γ ($\gamma = 10^{-6}$ grm.), and to obtain a recovery of added iodine within this figure. Investigations on a person on a constant and adequate diet showed that, in general, the rate of excretion of iodine per litre of urine is remarkably constant and, excepting on two days of total starvation, always within the experimental error of 50γ per litre. The daily total excretion was, however, dependent on the amount of urine, and could be raised above its normal limit by increasing the flow of urine, but the body appears to resist an attempt to reduce it much below the normal by starvation. When extra iodine was administered, the percentage of the amount added that was recovered was 56 in one experiment and 68 in another. T. H. P.

Analysis of Small Urinary Calculi. C. Newcomb. (*Ind. J. Med. Res.*, 1930, **17**, 1–13.)—The whole of the material is powdered in an agate mortar and dried in an oven at 100–105° C. by day, and in a vacuum desiccator over sulphuric acid by night. Of the dry powder, 0·005–0·02 grm. is heated in a hard glass tube with 1 grm. of potassium sulphate, exactly 1·6 c.c. of nitrogen-free sulphuric acid, and one drop of 5 per cent. copper sulphate solution until dissolved, the solution being made up to 50 c.c. The phosphate is determined colorimetrically by Kuttner and Cohen's method (*J. Biol. Chem.*, 1927, **75**, 517) on 5 c.c. of the solution. The total nitrogen is determined by direct Nesslerisation on 5 c.c. of the liquid, but if phosphates are present in sufficient quantity to give an appreciable precipitate in the alkaline solution, 10 c.c. of the liquid are made alkaline with sodium hydroxide and, after the phosphate precipitate has formed, the whole is centrifuged;

5 c.c. of the clear liquid are then used for the nitrogen determination. Calcium is determined on 10 c.c. of the liquid and is precipitated as oxalate, which is filtered off, washed with dilute ammonia solution, dissolved in *N*-sulphuric acid, and titrated with 0·01 *N*-permanganate; a blank determination is made with the sulphuric acid alone, and the result applied as a correction. Magnesium is determined in the filtrate from the calcium oxalate, by precipitation as magnesium ammonium phosphate and application to this of the colorimetric method. Oxalates are determined by heating 0·01–0·02 grm. of the dry powdered material with 10 c.c. of *N*-sulphuric acid, centrifuging, treating the undissolved residue with a further quantity of the sulphuric acid, again centrifuging, and precipitating as calcium oxalate, which is titrated with permanganate. Carbonates are determined by measuring the gas liberated on treatment of 0·01 grm. of the powder with hydrochloric acid. Qualitative tests for cholesterol, urates, creatinine, creatine, and cystine are described. T. H. P.

Solubility of Glycogen. M. Kerly. (*Biochem. J.*, 1930, **24**, 67–76.)—Glycogen from mussels, prepared without boiling with alkali, was found to take from 3 to 4 days to reach saturation in water, whereas a similar sample boiled for 2½ hours with 60 per cent. potassium hydroxide, reaches a slightly higher value within a few hours. Glycogen has now been prepared from several sources, without boiling with potassium hydroxide, and the solubilities of the products obtained have been determined. In the course of the work it was found necessary to revise the method used for the determination of glycogen, and, in order to do this, the solubility of glycogen in aqueous alcohol was investigated. Three sources of glycogen were used, mussel (whole body), frog (skeletal muscle), and rabbit (liver). The method of preparation employed varied slightly in each case. The solubility in water of mussel glycogen, not boiled with potassium hydroxide, at 0° C. is 16 per cent., at 20° C. is 17·7 per cent., and at 37° C. at least 40 per cent. Glycogen from skeletal muscle of frogs has a solubility in water of 14·9 per cent. at 20° C., and that from rabbit liver has a solubility of 21 per cent. at 20° C. Glycogen is slightly soluble in aqueous alcohol, the concentration and nature of any electrolyte present having an influence on the value. Curves show the decreasing solubility of glycogen with increasing concentration of alcohol in the presence of potassium acetate, potassium trichloroacetate, potassium chloride, potassium hydroxide and trichloroacetic acid. A micro-modification of the method of Pflüger (*Pflüger's Arch.*, 1904, **103**, 169) for the determination of glycogen, based on the results of the experiments on the solubility of glycogen in aqueous alcohol, and employing a correction for this solubility, is described. When glycogen prepared from mussels is precipitated with alcohol, after two precipitations the nitrogen content of the preparation increases, the phosphorus content remaining nearly constant. P. H. P.

Antirachitic Value of Irradiated Yeast. S. K. Kon and M. Mayzner. (*Lancet*, 1930, April 12, 794–796.)—During a visit to the United States one of the authors discussed the therapeutic possibilities of irradiated yeast with Hess,

and was encouraged by him to try the yeast in Poland. Reliability, low price and ease of preparation are essential if an antirachitic product is to gain access to those classes of the Polish population where rickets is common, and irradiated yeast seems to fulfil these requirements to a remarkable degree. A co-operative investigation was therefore started by the State Institute of Hygiene in Warsaw in order to gather reliable experimental information on the practical value of this and other antirachitic preparations, and a preliminary account is given of the results obtained so far. Pure baker's yeast was used. It was irradiated and tested on rachitic children. Those receiving it were compared with controls on non-irradiated yeast and untreated controls. The results show that the daily administration of 0·75 grm. of irradiated yeast to rachitic infants brings about a disappearance of the symptoms in the course of six to eight weeks. A commercial preparation of irradiated yeast has lately been widely advertised in America, in the hope that with the addition of the antirachitic vitamin *D* this particular brand of yeast "will play an increasingly important part in the American dietary." The authors doubt whether the inclusion of such a potent preparation in the daily menu would be wise or advisable. The recent work on hypervitaminosis, and especially the important findings of Heilitz, Jundell and Wahlgren (*Acta Paed.*, 1929, **8**, 443) should sound a serious warning against the indiscriminate use of irradiated preparations and foods by the general public. The authors consider that antirachitic medication and prophylaxis must be left in the hands of physicians. P. H. P.

Chemistry of Vitamin *A*. [Action of Chemical Agents.] O. H. Cady and J. M. Luck. (*J. Biol. Chem.*, 1930, **86**, 743–754.)—Cod-liver oil, butter, and a concentrated extract of alfalfa were treated with sulphur dioxide. At room temperature there was a marked loss of growth-promoting and anti-xerophthalmic activity in the cod-liver oil after 15 minutes, and at 100° C. destruction of activity was complete. The destruction of activity in the alfalfa was negligible, and butter occupied an intermediate position. Neither alfalfa nor spinach, treated with sulphur dioxide when green or dry, suffered any loss of activity. The active principle of cod-liver oil was destroyed by phosphorus pentachloride, chlorine, acetyl chloride, nitrous fumes, and Benedict's alkaline copper reagent, and also by prolonged treatment with sodium bisulphite. Hydrogen peroxide caused a partial loss, formaldehyde a negligible one, and hydrogen sulphide, ethylene, ammonia, and neutralised Benedict's solution had no effect. The vitamin *A* potency of inactivated oils could not be restored. Vitamin *A* activity is regarded as a property of a specific atomic grouping rather than of a specific molecule, and the active principle of cod-liver oil is either different from that of alfalfa, or protective substances may be present in the latter. The active principle of cod-liver oil has aldehydic properties. D. G. H.

Absorption Spectra in Relation to Vitamin *A*. R. A. Morton, I. M. Heilbron and F. S. Spring. (*Biochem. J.*, 1930, **24**, 136–140.)—The criticism of Rosenheim and Webster (*Biochem. J.*, 1929, **23**, 633; ANALYST, 1929, **54**, 764)

that the selective absorption in the ultra-violet (broad band, maximum 328$\mu\mu$) of liver oils, in itself, cannot be taken as a criterion of vitamin *A*, is contested on general grounds. The statement that dehydroergosterol exhibits an absorption band in the ultra-violet similar to that of vitamin *A* of liver oils is also contested. In comparing the absorption curve for dehydroergosterol and vitamin *A*, Rosenheim and Webster neglected the intensity factor. The authors have conducted a very careful re-investigation of dehydroergosterol, and have found that the general shapes of the respective curves for vitamin *A* and dehydroergosterol are entirely different, and that dehydroergosterol exhibits four narrow bands, *viz.* three distinct bands at 342, 326 and 311$\mu\mu$, and an inflexion at about 297$\mu\mu$. The only similarity between the ultra-violet absorption spectra of dehydroergosterol and vitamin *A* is that they absorb in approximately the same region. Further, the intensity of absorption of dehydroergosterol is not greater than one-sixth of that shown by the absorbing constituent of liver oils. P. H. P.

Colour Reactions and Absorption Spectra of Sterols in Relation to Structure. I. M. Heilbron and F. S. Spring. (*Biochem. J.*, 1930, **24**, 133–135.) —Häussler and Brauchli (*Helv. Chim. Acta*, 1929, **12**, 187) have stated that the green coloration produced by the Tortelli-Jaffé reaction is specific for the detection of ergosterol or its derivatives (dehydroergosterol and *iso*ergosteryl acetate), but they purposely did not alter the standardised method of carrying out the reaction, with which the colour only develops slowly (in about 10 minutes), and is only just discernible with 0·5 mgrm. ergosterol. The authors find that by the use of the following modification the reaction can be rendered both instantaneous and more sensitive:—A crystal of ergosterol is dissolved in glacial acetic acid (5 c.c.) and 1 c.c. of a 2 per cent. solution of bromine in chloroform is introduced down the side of the tube by means of a pipette; a green ring appears at the surface of contact of the two solutions. Under these conditions, 0·02 mgrm. ergosterol can be detected immediately. The reaction is of peculiar importance, as the appearance of colour occurs in hydrogenated derivatives of ergosterol which do not respond to either the Rosenheim (trichloroacetic acid) or antimony trichloride reagent. Whereas the compounds responding to the Rosenheim reaction are characterised by the presence of the $\triangle^{1:13}$ (or $\triangle^{1:2}$) double bond, it is evident that the appearance of colour in the bromine reaction is dependent upon some other ethenoid linkage. From the results obtained the reagent appears to be specific for sterol derivatives which contain an "inert" (as applied to hydrogenation) linkage, possibly in position $\triangle^{10:19}$. Heilbron, Morton and Sexton (*J. Chem. Soc.*, 1928, 47) suggested that the power of selectively absorbing in the ultra-violet is only shown by sterol derivatives containing at least two double bonds in the molecule. It is now shown that, of the sterol derivatives examined, only those show selective absorption which contain not only two double bonds, but give positive colour reactions with trichloroacetic acid or antimony trichloride. Therefore, selective absorption of sterols is conditioned by the presence of two ethenoid linkages in the molecule, one of which must apparently be in the $\triangle^{1:13}$ (or $\triangle^{1:2}$) position. A table shows the

results obtained with trichloroacetic acid, antimony trichloride, bromine and absorption spectra tests on different sterol compounds. P. H. P.

Relative Vitamin *A* Value of the Body and Liver Oils of Certain Fish. B. Ahmad and J. C. Drummond. (*Biochem. J.*, 1930, **24**, 27–36.)—Schmidt-Nielsen (*Kon. Norsk. Videnskab.*, 1928, **1**, No. 15; No. 29; No. 63; 1929, **2**, No. 13), on the basis of a comparative colorimetric and biological assay for vitamin *A* of a number of fish oils, has claimed that there is no relation between the results obtained by the two methods, and consequently concluded that the blue colour reaction with arsenic trichloride or antimony trichloride is not specific for vitamin *A*. An investigation was undertaken by the authors for the purpose of examining the claims of Schmidt–Nielsen. While it was in progress Norris and Danielson (*J. Biol. Chem.*, 1929, **83**, 469; ANALYST, 1929, **54**, 612) published data concerning colorimetric and biological tests of the vitamin *A* values of some Pacific coast salmon-body oils. They concluded that the results of the colorimetric assays agreed within reasonable limits with those obtained from the biological method. However, both their colorimetric and biological values (3–10 units, United States Pharmacopoeia) are so low that in the opinion of the authors, their significance is not great. Six samples of fish-body and fish-liver oils, including two samples supplied by Schmidt–Nielsen, have been examined both colorimetrically and biologically for vitamin *A*. The results of animal tests are shown to agree within reasonable limits with those of the colorimetric method, although no claim is made that the colour reaction is specific. The disagreement between Schmidt–Nielsen's results and those of the authors is due possibly to differences of technique, and to the fact that he attempted to express the results of the biological test, which is liable to wide variations, in terms of the units proposed by the United States Pharmacopoeia. This is especially liable to lead to erroneous results when oils of low vitamin *A* content are examined. In view of the errors associated with the colorimetric assay, to which attention is drawn, and those of very much more serious dimensions that are almost inseparable from the biological test, unless very large numbers of animals are used, it seems unreasonable to seek an exact quantitative relation between the two methods. P. H. P.

Concentration of Vitamin B_2. B. T. Narayanan and J. C. Drummond. (*Biochem. J.*, 1930, **24**, 19–26.)—A considerable amount of work has been done to elucidate the chemical nature of vitamin *B*, but as yet few observations of a similar character have been recorded regarding the more recently discovered vitamin B_2. Several investigators have stated that it is sparingly soluble in alcohol of greater concentration than 80 per cent.; it has also been recorded that it is adsorbed by fuller's earth and silica gel. The most potent concentrate recorded in the literature appears to be that obtained by Levene (*J. Biol. Chem.*, 1928, **79**, 465; ANALYST, 1928, **53**, 666) by means of adsorption on silica gel. This preparation supplied the requirements of the young rat in doses of only 2 mgrms. of organic matter daily. Levene observed that the activity was destroyed by treatment with nitrous acid. Narayanan (*Biochem. J.*, 1930, **24**, 6) describes an investigation

on the chemical nature of "bios" in the earlier part of which it was uncertain whether the yeast stimulant was identical with the factor known as B_2 or not, but precipitation of the baryta-hydrolysates of yeast extracts with lead acetate effected a separation of the two substances. The vitamin B_2 is precipitated by lead acetate, and the "bios" remains in the filtrate. The authors now describe the efforts that were made to separate the factor B_2 from the materials precipitated by lead acetate. An attempt to concentrate the vitamin B_2 by means of adsorption on fuller's earth is described. Adsorption was complete at the extreme acid range of pH (0·05 to 0·10), but great difficulty was encountered in removing the adsorbed active factor. It was found that "norite" charcoal is not an efficient adsorbent of the active factor. In view of the failure of the efforts to concentrate vitamin B_2 by adsorption methods, it was decided to attempt fractionation by alcohol. The results show that the active factor is relatively insoluble in alcohol of greater concentration than 70 per cent. by volume. By this process a concentrate has been obtained, of which the daily dose which supplies the requirements of the young rat contains 6 mgrms. of organic matter. Further fractionation of this concentrate is in progress. The general finding that the active factor is stable to heat, acids and alkalis is confirmed; it is also found that vitamin B_2 is not destroyed by hydrogen peroxide. In contradiction of Levene's statement, and in confirmation of the more recent observation of Chick (*Biochem. J.*, 1929, **23**, 514), no appreciable destruction of the active factor was observed when treated with nitrous acid. Vitamin B_2 is not appreciably soluble in butyl alcohol. P. H. P.

Colour Reaction of Ergosterol; Differentiation of Ergosterol and Irradiated Ergosterol. R. Meesemaecker. (*J. Pharm. Chim.*, 1930, **122**, 380–384.)—If 0·01 grm. of ergosterol is dissolved in 5 c.c. of chloroform, 2 c.c. of acetic anhydride and an excess (about 2 grms.) of anhydrous zinc chloride added, and the mixture shaken, a pink colour forms in a few seconds, turning yellow and then green, and the intensity of the green is at a maximum in less than 30 minutes. The colour is stable for several days, gradually turning yellow. Addition of water to the filtered reaction mixture causes the green colour to disappear, and a yellow coloration to appear in the chloroform solution, but if the chloroform solution is again shaken with zinc chloride the green colour reappears. Other suitable solvents are tetrachlorethane, trichlorethylene, carbon tetrachloride, petroleum spirit, ethyl ether, benzene, toluene, xylene, ethyl acetate, etc. A reaction may still be obtained with 0·01 mgrm. of ergosterol. The addition of zinc chloride alone to a chloroform solution of ergosterol produces a rose colour with a fresh solution or one kept in the dark, and a green colour with a solution exposed to the light or to ultra-violet rays. With ethereal solutions a green colour is always formed, but with benzene and petroleum spirit there is no coloration. D. G. H.

Influence of Ultra-Violet Irradiation on the Nutritive Value of Hardened Oils. S. Ueno, M. Yamashita, and Y. Ota. (*J. Soc. Chem. Ind., Japan*, 1930, **33**, 61B.)—Sardine, herring and cod-liver oils, after hydrogenation in the presence of nickel at 120° C., were irradiated by the mercury vapour lamp.

The iodine values of the hydrogenated oils were 75·1, 60·5 and 69·3, respectively. The sp. gr., refractive index, acid value, saponification value and iodine value of the hardened oils all showed little change after irradiation. The antirachitic properties, as shown by feeding tests, were in all cases found to be better after irradiation. R. F. I.

Toxicological and Forensic.

Microchemical, Microspectroscopical and Quantitative Examination of Blood. M. Wagenaar. (*Pharm. Weekblad*, 1930, **67**, 415–437.)—In the author's modification of Teichmann's test for blood a trace of the blood and a grain of sodium salicylate are mixed on a watch-glass, gently warmed, a drop of glacial acetic acid containing a little dissolved sodium chloride added, and the mixture again warmed. Crystals of haematin chloride are produced from 0·005 mgrm. of blood, corresponding with 0·0003 mgrm. of haemin. The haemochromogen test, which is considered preferable, in that it gives reliable results for old blood stains, and is not affected by the presence of soluble substances removed from materials during extraction of the stains, has also been modified and rendered quantitative. A circular portion of the stained material, 1·5 cm. in diameter, is macerated with about 5 c.c. of a mixture of 10 c.c. of 5 per cent. sodium thiosulphate solution, 10 c.c. of 10 per cent. sodium hydroxide solution, 50 c.c. of distilled water, 15 c.c. of pyridine and 15 c.c. of glycerin, under a layer of paraffin wax for 5 minutes at about 90° C. (*cf.* Van Eck, ANALYST, 1922, **47**, 528). This serves the double purpose of extraction and reduction of the blood, and the colour so produced is stable in the absence of air. When the process is complete it may be matched against the colours produced from known amounts of blood placed on an unstained portion of the same material of the same area, and extracted under the same condition. It is usually considered that the test fails if the blood has been heated to 180° C., but the author's experience is that after 5 minutes at 200° C. no marked effect is produced. At a temperature of about 240° C. the spectroscopic method begins to fail. The technique of the micro-spectroscopical examination of blood is also discussed, and it is pointed out that the absorption spectrum of the colouring matter of blood may be simulated by other colouring materials (*e.g.* indigo carmine has a similar spectrum to that of alkaline blood). A yellow-red luminescence in ultra-violet light is produced in blood in the presence of sulphuric acid, and this is changed to carmine red on removal of the acid by concentrated ammonia. The protein and iron contents of samples of blood from a number of animals vary from 17·9 to 20·9 per cent., and from 0·040 to 0·058 per cent., respectively, and indicate a mean value of approximately 360: 1 for the protein: iron ratio. A sample of blood from a tomb dating back to 1300 B.C. was examined by the author's methods, and the value 320: 1 obtained for this ratio. J. G.

Spectrographic Study of Carbon Monoxide Haemoglobin. A. K. Boor and A. Bachem. (*J. Biol. Chem.*, 1930, **85**, 743–749.)—It has recently been shown by immunological methods by Boor and Hektoen (*J. Infect. Dis.*, 7930, **46**,

1) that carbon monoxide haemoglobin is species-specific. This specificity may be due to differences in the prosthetic group of the molecule of this conjugated protein, in the histone (globin) fraction, or in both the prosthetic group and the globin. The antigenic differences suggest, but do not conclusively prove, that the globin fraction is the chemically species-specific part of the compound, since this is the protein part and the largest portion of the molecule. It is presumed that the visible absorption spectrum of the carbon monoxide haemoglobin is due primarily to the effect of the coloured prosthetic group. Since pure carbon monoxide haemoglobin was available, a study of spectra of this material presented itself, with the possibility that the species-specific portion of the molecule might be made evident. The oxyhaemoglobin and carbon monoxide haemoglobin studied spectrographically were prepared by the method described by Boor and Hektoen. A figure shows the approximate transmission curve of carbon monoxide haemoglobin spectrum, sheep carbon monoxide being taken as an example. The absorption bands appear as follows: the far ultra-violet end absorption occurs at 240$\mu\mu$, the far ultra-violet absorption at 280$\mu\mu$, and the violet at approximately 400$\mu\mu$. Visible absorption also occurs at about 540 and 570$\mu\mu$. Evidence of the purity of the carbon monoxide haemoglobin, made by the method described, is given in a figure. No difference is indicated between spectra of uncrystallised and crystallised carbon monoxide haemoglobin made by this method. Spectra of carbon monoxide haemoglobin from different species (human, sheep, hog and ox) are shown to be alike. The relative stability of carbon monoxide haemoglobin and oxyhaemoglobin was also investigated. An aqueous solution of oxyhaemoglobin is shown to change upon standing; in time methaemoglobin is formed, probably with another modification of oxyhaemoglobin. Carbon monoxide haemoglobin seems very stable in this respect. P. H. P.

Agricultural.

Determination of Total Nitrogen of Plant Extracts in Presence of Nitrates. G. W. Pucher, C. S. Leavenworth and H. B. Vickery. (*J. Ind. Eng. Chem.* (*Anal. Edition*), 1930, **2**, 191–193.)—The conclusions of Ranker (ANALYST, 1927, **54**, 555, 556) as to the inaccuracy of the salicylic acid and zinc method are confirmed, and a modification of Olsen's method (*Compt. rend. Trav. Lab. Carlsberg*, 1927, **17**, 1) for soils is shown to give accurate results for plant extracts. The sample is diluted to 40 c.c., shaken for 10 minutes with 10 c.c. of 1: 1 sulphuric acid and 3 ($\pm$0·3) grms. of reduced iron powder, and then boiled for 5 minutes, cooled, and 30 c.c. of concentrated acid, 0·5 grm. of mercury and 5 grms. of sodium sulphate added. The water is evaporated and the acid mixture heated for 2 hours. A few crystals of potassium permanganate are then added to the hot acid, which is diluted to 300 c.c. and distilled, as in the Kjeldahl process, in the presence of 5 grms. of sodium thiosulphate, an excess of sodium hydroxide, and a little zinc. Check analyses on dry tobacco and mixtures of solutions of potassium nitrate and hydrolysed edestin showed that the method gives accurate results so

long as the prescribed quantities of water, acid and iron powder are taken, but blank determinations on the reagents must be made (*cf.* Vickery and Pucher, ANALYST, 1929, **54**, 608). J. G.

Tests of various Aliphatic Compounds as Fumigants. R. C. Roark and R. T. Cotton. (*U.S. Dep. of Agric., Tech. Bull No.* 162, March, 1929, 1–52.)—Of 309 aliphatic compounds tested against the rice weevil in ½-litre Erlenmeyer flasks half filled with wheat, 66 proved lethal after 24 hours in doses less than 0·1 grm. per litre, 18 being lethal in the minimum dose tried, 0·02 c.c. per litre. The greatest toxicity was shown by iodides, bromides, mercaptans, thiocyanates, isothiocyanates, disulphides, oxides, epichlorhydrin, halogenated ethers, halogenated esters, and formates. No apparent relation exists between the boiling points and relative toxicities, except that compounds boiling above about 150° C. have vapour pressures too low at ordinary temperature to give toxic concentrations. Compounds with branched chain radicals are more toxic than those with straight chain radicals, and compounds inert chemically show little toxicity. Certain chemically reactive compounds do not kill weevils in wheat, probably because they are absorbed by the wheat and fail to reach the insects.

Germination tests with wheat show that chlorides, formates, sulphides, disulphides, thiocyanates, isothiocyanates and mercaptans in more than lethal doses do not affect germination. The iodides, halogenated alcohols, epichlorhydrin, halogenated ethers, oxides, and esters of halogenated fatty acids are injurious to germination and should be used with caution. Of 17 compounds showing promise of commercial value tested in a 500 cubic foot fumigation vault, ethylene oxide and methyl monochlooacetate proved slightly more toxic than carbon disulphide, being lethal with a dose of 1 lb. per 1000 c.ft. Ethyl and isopropyl monochlooacetates were somewhat less toxic. A mixture of ethylene dichloride (3 vols.) with carbon tetrachloride (1 vol.) at 6 lbs. per 1000 c.ft. proved lethal and, owing to its low cost, its effectiveness, and its being non-inflammable and non-toxic to human beings, ethylene dichloride should be a useful fumigant. T. H. P.

Organic Analysis.

Ferric Chloride as Indicator in the Titration of Potassium Ferrocyanide with Zinc Sulphate. P. F. Felkers. (*Chem. Weekblad*, 1930, **27**, 209–210.)—An approximately 0·05 *M* solution of potassium ferrocyanide free from chloride, sulphate and carbonate, was standardised against a 0·1 *N* solution of potassium permanganate, 25 c.c. added to 100 c.c. of water and 10 c.c. of 0·1 *N* sulphuric acid, and titrated with a 0·1 *M* solution of recrystallised zinc sulphate with a 1 per cent. solution of ferric chloride as external indicator. It is shown that if a titration-figure of about 17 c.c. is obtained and a blank of 0·12 c.c. is added to it for undetermined ferrocyanide, the agreement with the theoretical value is exact to within 0·04 c.c. Ferric chloride is more sensitive than uranium nitrate as indicator for this titration, and may be used satisfactorily at room temperature and in artificial light. In the presence of 10 c.c. of 10 per cent. acid

the results are 1·85 per cent. too high, but they are not affected by the presence of 25 c.c. of 20 per cent. potassium or ammonium chloride solutions, though 10 c.c. of 2·8 per cent. sodium chloride solution gives results 0·4 per cent. too low. J. G.

Determination of Hydroquinone with Ceric Sulphate. N. H. Furman and J. H. Wallace, Jnr. (*J. Amer. Chem. Soc.*, 1930, **52**, 1443–1447.)—The volumetric determination of hydroquinone with ceric sulphate was found to be preferable in several respects to the published processes. The reaction is rapid at ordinary temperature: $2CeO_2+C_6H_4(OH)_2=Ce_2O_3+C_6H_4O_2+H_2O$; it proceeds directly without the need for a back-titration. The end-point may be ascertained potentiometrically: a platinum wire and a normal calomel half-cell compose the electrodes. The cold hydroquinone solution acidified with hydrochloric or sulphuric acid (up to 2·5 *N*) is titrated with 0·1 *N* ceric solution until a sudden rise in the voltage (of the order of 0·3 volt for one drop of 0·1 *N* solution) marks the completion of the oxidation. Instead, the colour change of diphenylamine may be used, with the same degree of accuracy. One drop of a 1 per cent. solution of the base in sulphuric acid is added; the end-point is revealed by the sudden appearance of a blue coloration. W. R. S.

Method of Analysis of Cellulose Formate by Oxidation. G. Tocco and A. Nyssens. (*Giorn. Chim. Ind. Appl.*, 1930, **12**, 124–126.)—This method depends on the complete oxidation of the cellulose ester to carbon dioxide and water by means of standard permanganate or dichromate solution and is applicable only to the formates, since with the acetates the proportions of oxygen required for the oxidation of the cellulose and acetic acid are too nearly equal to allow of accurate results being obtained. One grm. of the finely divided ester, rendered absolutely dry by heating at 100–105° C. for 2 hours, or at a lower temperature in a vacuum, is treated with 135–150 c.c. of *N*-potassium dichromate and, slowly and with cooling, with 40 c.c. of sulphuric acid, the evolution of carbon dioxide being moderated by cooling the liquid. After the lapse of 30 minutes the flask is left for 8 hours in a boiling water-bath, and the excess of dichromate solution, which should be at least 10 c.c., determined by titration either with ferrous sulphate solution or iodometrically. The volumes of *N*-dichromate required for oxidising 1 grm. of cellulose mono-, di-, and tri-formate are 148·14, 136·78, 128·43, and 121·95 c.c. respectively.

This procedure, which may be applied also to the analysis of other formic esters, such as those of starch, may be used for the control of the hydrolysis of formic esters by alkali. Of the finely powdered product, 1 grm. is dissolved in 40 per cent. potassium thiocyanate solution (pyridine is unsuitable as it gives a very compact coagulum), and treated for 3 hours with excess (40 c.c.) of cold *N*-sodium hydroxide, the excess of which is determined by titration: 5·26, 9·18, or 12·19 c.c. of *N*-alkali is required for the hydrolysis of 1 grm. of the mono-, di-, or tri-formate of cellulose. If the ester is not finely divided, the hydrolysis requires heat. For formic esters which are not readily attacked by *N*-sodium hydroxide, or are not readily soluble in thiocyanates, or are of very abnormal composition, the oxidation method is recommended. T. H. P.

Chemical Structure of *iso*-Oleic Acid produced during the Hydrogenation of Oleic Acid. S. Ueno and N. Kusei. (*J. Soc. Chem. Ind. Japan*, 1930, **33**, 62B.)—The mixed fatty acids prepared from tsubaki oil were hydrogenated in the presence of 0·5 per cent. of nickel at 180° C. for 75 minutes. The product (iodine value 42·0) was separated into solid and liquid fatty acids by the lead soap and ether process, and the solid acids were fractionally crystallised. The *iso*-oleic acid thus obtained had an iodine value of 41·3. Examination of the ozonide showed that it was a mixture of a considerable amount of $\triangle 9:10$ oleic acid and a small amount of other solid oleic acids ($\triangle 10:11$ and $\triangle 11:12$ acids). R. F. I.

Bull Frog Oil. Y. Iwamoto and M. Kisegawa. (*J. Soc. Chem. Ind., Japan*, 1930, **33**, 66B.)—A preliminary experiment showed that, of the various parts of the bull frog, that part most suitable for frog oil manufacture was the oil sac and work was confined to the oil from this source. It was a pale yellow liquid depositing a small amount of solid at 15° C., and having an odour of chrysalis oil, probably originating in the diet. It had sp. gr. at 15°/4° 0·9216; n_D^{15}, 1·4733; iodine value, 135·6; unsaponifiable matter, 0·87 per cent.; and solidification point, −5°. The mixed fatty acids solidified at 29·5° C., and yielded 24·38 per cent. of ether-insoluble hexabromides, which melted at 180·5° C., and contained 63·2 per cent. bromine, thus indicating a high content of linolenic acid. The filtrate from the hexabromides was shown to contain linolic acid. The mixed fatty acids consisted of 18 per cent. of solid, and 78·7 per cent. of liquid fatty acids. Oxidation of the latter with alkaline permanganate proved the presence of dihydroxystearic, sativic and linusic acids. The m.pt. and neutralisation value of the solid fatty acids indicated that they consisted of 12 per cent. of palmitic and 88 per cent. of stearic acid. R. F. I.

Composition of the Saturated Fatty Acids of Japanese Great Herring Oil. S. Ueno and H. Ikuta. (*J. Soc. Chem. Ind. Japan*, 1930, **33**, 62B.)—An exhaustive analysis of Japanese great herring oil (Ō-Nishin oil) was carried out on the original oil, on its mixed fatty acids, and on the separated solid fatty acids. The methyl esters of the latter were fractionally distilled *in vacuo*. From the results the authors concluded that the saturated fatty acids (15 per cent. of the mixed fatty acids) consisted chiefly of palmitic acid, some stearic and myristic acids, and small quantities of arachidic and behenic acids. They also detected the presence of small quantities of a water-soluble fatty acid resembling butyric or valeric acid. R. F. I.

Inorganic Analysis.

New Separation Methods for Thallium. L. Moser and W. Reif. (*Monatsh. Chem.*, 1929, **52**, 343–350.)—*From aluminium, chromium, and ferric iron.*—Instead of the precipitation of thallium chromate from a solution containing sulphosalicylic acid (ANALYST, 1928, **53**, 459), hydrolysis by ammonium nitrite (*id.*, 402) may be used to precipitate the trivalent metals first. The acid sulphate

solution is approximately neutralised with sodium carbonate, treated with 20 c.c. of 7 per cent. ammonium nitrite solution at 40° C., followed by 20 c.c. of methyl alcohol, and boiled gently for 20 minutes. Complete precipitation is ascertained by a small further addition of the reagents and short boiling. The precipitate, after settling, is collected and washed with dilute ammonium nitrate solution, dried, and ignited. The filtrate is evaporated to 100 or 200 c.c., made ammoniacal, boiled, and the thallium precipitated with enough potassium chromate to furnish a 2 per cent. solution (*vide supra*).

From thorium, zirconium, and titanium.—Ammonium nitrite is added to the *cold* solution, which is slowly heated, and treated with methyl alcohol only when part of the precipitate has formed; other details as above.

From cerium.—The precipitation by nitrite is not quite complete, hence precipitation by oxalic acid is employed. The almost neutral sulphate solution is treated at 60° C. with a moderate excess of oxalic acid. The precipitate becomes crystalline after standing for 12 hours; it is ignited to, and weighed as, CeO_2. The filtrate, concentrated to approximately 200 c.c., is made ammoniacal, and the thallium precipitated as chromate.

From molybdenum and tungsten.—Thallium is precipitated from the ammoniacal molybdate (tungstate) solution as chromate. W. R. S.

Gravimetric Determination of Ruthenium. R. Gilchrist. (*Research Paper* 125, *U.S. Bureau of Standards.*)—The weakly acid chloride solution is boiled and treated with 10 per cent. sodium bicarbonate solution till the precipitate formed suddenly coagulates. A few drops of bromcresol purple are added, and more bicarbonate solution until a faint purple colour forms. After 5 minutes' boiling the solution is filtered at once, the beaker and rod wiped with a small piece of filter paper, and the precipitate washed with 1 per cent. ammonium sulphate solution. The last washes are given with a 2·5 per cent. solution of the same salt. The precipitate is heated very gently in a porcelain crucible; the charring of the dry paper continues without further application of heat. The precipitate has a tendency to deflagrate, which is lessened by the ammonium sulphate remaining from the washing. After complete removal of carbonaceous matter by stronger heating, the crucible is covered with a Rose lid and the precipitate reduced and cooled in a current of hydrogen. The metallic ruthenium is weighed.

W. R. S.

Determination of Titanium Dioxide in Titanium White. G. Agamennone. (*Giorn. Chim. Ind. Appl.*, 1930, **12**, 123–124.)—In this method, the titanium dioxide is dissolved as sulphate, reduced to the titanous state by means of zinc amalgam, and titrated with ferric alum in presence of thiocyanate as indicator. The reduction may be carried out in a burette, 60 cm. high and 3 cm. wide, provided with a stopcock and with a discharge tube 17 cm. long, this passing through a two-holed rubber stopper into a pump flask of 750 c.c. capacity. Through the stopper passes also a short tube used later for introducing carbon dioxide, but now closed

with rubber tube and clip. The burette is charged (about four-fifths) with amalgamated zinc in granules able to pass a 30–40 sieve. The 0·1 *N* ferric alum solution is standardised by reduction to the ferrous state by stannous chloride, followed by titration with permanganate solution. The pigment (0·5 grm.) is completely dissolved in 25 c.c. of concentrated sulphuric acid and 8–9 grms. of anhydrous sodium sulphate, the liquid being heated gently at first and more strongly later. If complete solution cannot be effected in this way, the pigment should be fused with potassium hydrogen sulphate. The cooled solution is mixed with 150 c.c. of water and heated for a few moments to boiling, the precipitated barium sulphate and silica being filtered off and washed with 5 per cent. sulphuric acid solution, and then with water. The filtrate and washings are made up to 250 c.c., and 100 c.c. of this solution diluted with 100 c.c. of water and heated to 50° C. Meanwhile 150 c.c. of 5 per cent. sulphuric acid are poured into the burette, suction being applied and the acid drawn into the pump flask at the rate of 30 c.c. per minute. The titanium solution is similarly introduced and is followed successively by 150 c.c. of 5 per cent. sulphuric acid and 150 c.c. of water, both used to rinse out the beaker, which is finally washed out into the burette. The air in the flask is displaced by a current of carbon dioxide, the flask being then detached and the contents titrated with 0·1 *N* ferric alum solution, after addition of 10 c.c. of 25 per cent. ammonium thiocyanate solution, until a slight reddish-yellow colour persists for a minute; 1 c.c. of the ferric alum solution corresponds with 0·00801 grm. of TiO_2. T. H. P.

Determination of Molybdenum in Alloy Steels. W. Hertz. (*Z. anal. Chem.*, 1930, **80**, 109–112.)—(1) For steels containing 0·15 to 0·35 per cent., 5 grms. of drillings are dissolved in 40 c.c. of hydrochloric acid, which is evaporated. The residue is heated for a short time at 130° C. and dissolved in 30 c.c. of hydrochloric and 10 c.c. of nitric (1 : 1) acids. The silica is filtered off, the filtrate evaporated to small bulk and strongly diluted. It is poured boiling hot into a boiling solution of 70 grms. of sodium hydroxide in 300 c.c. of water in a 750 c.c. flask. The liquid is boiled, cooled, made up to volume, and 600 c.c. filtered off. The filtrate is neutralised against methyl red with nitric acid (one drop excess), and boiled for half-an-hour with 10 to 15 c.c. of 10 per cent. lead nitrate solution. The precipitated lead molybdate is treated as usual and weighed. (2) For steels containing tungsten, the solution of the drillings in hydrochloric acid is oxidised with nitric acid, boiled down somewhat, and poured into caustic soda as above. A measured portion of filtrate is treated with 6 grms. of tartaric acid, a slight excess of sulphuric acid, then a slight excess of ammonia, and boiled for some time, when silica and alumina are precipitated. The precipitate is filtered off, the filtrate treated with 50 c.c. of ammonium sulphide and, when near the boiling point, with 50 c.c. of sulphuric acid (1 : 1). The liquid is left to stand hot for 2 hours; the precipitate is collected and washed with dilute sulphuric acid, then with dilute alcohol, after which it is converted into MoO_3 by gentle ignition. After weighing, this is treated with a few c.c. of 10 per cent. caustic soda, the solution diluted, and filtered. The small precipitate of impurities is well washed with hot water, ignited,

and its weight subtracted from the first weight. (3) For ferromolybdenum, 1 grm. of fine powder is fused with 10 grms. of sodium hydroxide in a nickel crucible for 20 minutes. The product is dissolved in hot water, and the solution filtered into a 500 c.c. flask and made up to the mark. One hundred c.c. are transferred to a 750 c.c. conical flask and acidified with nitric acid against methyl red as under (1); the determination as lead molybdate is completed as there described, 50 c.c. of lead nitrate solution being used as the precipitant. W. R. S.

Volumetric Determination of Sodium. E. C. Caley. (*J. Amer. Chem. Soc.*, 1930, **52**, 1349–1353.)—The method consists in the precipitation of sodium as sodium magnesium uranyl acetate (*J. Amer. Chem. Soc.*, 1929, **51**, 1664). The precipitate, washed with alcohol, is left for a few minutes on the suction pump to remove most of the alcohol. It is then transferred to a beaker and dissolved in 2 c.c. of glacial acetic acid and 40 to 50 c.c. of hot water. The solution is titrated at 90° C. with sodium phosphate solution, potassium ferrocyanide paper being used as external indicator. This procedure is an old-established one for the determination of uranium; it is not highly accurate, but the ratio U: Na=31·07 is so high that the sodium errors are almost negligible. The phosphate solution is standardised against pure sodium chloride, the quantity of which should be approximately the same as that in the assay. For the spot tests, only the clear liquor should be taken, as the uranium precipitate reacts with ferrocyanide after a few seconds. W. R. S.

Microchemical.

Microchemical Reactions of Pilocarpine. M. Wagenaar. (*Pharm. Weekblad*, 1930, **67**, 285–287.)—Pilocarpine is normally a colourless viscous liquid, very soluble in water, alcohol or chloroform, and almost insoluble in ether. It produces an amorphous sublimate, and may be recognised by the following reactions: (1) A 2 per cent. solution of the hydrochloride is precipitated by excess of sodium carbonate as oily droplets, which crystallise in small, negatively doubly-refractive needles. (2) A 1 per cent. solution of the hydrochloride gives flat crystals with platinum and sodium chlorides; (3) crystals, 500μ in length, with platinum chloride and sodium bromide; (4) dichroic crystals, 100μ in length, and having a dull metallic lustre, with warm platinum chloride solution and sodium iodide. In the presence of hydrochloric acid: (5) gold chloride gives yellow needles 1 mm. long; (6) gold bromide, brown-red star-shaped groups of needles; (7) gold iodide, branched needles; (8) Picric acid gives star-shaped groups of negatively doubly-refractive prisms. (9) With iodine, yellow, negatively doubly-refractive crystals grouped in the form of an outer margin of crystals 300μ long, and an inner layer of crystals 40μ long, are slowly produced, the actual proportions depending on the amount of iodine present. Except where stated otherwise, all the crystals are *d*-rotatory and positively doubly-refractive, and are produced for the following minimum quantities and dilutions of pilocarpine, respectively:—(2) 10μ grm., 1: 100; (3) 5μ grm., 1: 200; (4) 2μ grm., 1: 1000; (5) 1μ grm., 1: 2000; (6) 2μ grm., 1: 1000; (7) 10μ grm., 1: 100; (8) and (9) 5μ grm., 1: 500. (See also Rosenthaler, *Apoth. Ztg.*, 1929.) J. G.

Microchemical Reactions of Veratrine. M. Wagenaar. (*Pharm. Weekblad*, 1930, 67, 393–394.)—Veratrine is a strong base and may be crystalline (when it has the composition $C_{32}H_{49}NO_9$, m.pt. 205° C., and refractive indices 1·52 and 1·55), or amorphous. Its solubility is low in water, but high in alcohol, ether and chloroform. An amorphous deposit is obtained on sublimation, and the precipitate from a solution in a mineral acid does not form well-defined crystals, or at the best is micro-crystalline. Solutions of the hydrochloride (1 per cent.) give diamond-shaped and square-shaped crystals with platinum chloride in the presence of a crystal of sodium iodide, and fine crystalline precipitates with a 1 per cent. solution of picric acid and with a crystal of potassium dichromate. The limiting concentrations of these reactions are 1: 100, 1: 200 and 1: 200, and the smallest quantities detectable are 10, 5 and 5μ grms., respectively. J. G.

Simple Micro Analytical Separation of Chlorine and Bromine. L. Moser. (*Mikrochemie. Pregl-Festschrift.*, 1929, 293–295.)—The method depends on the difference in thermal dissociation values of hydrogen chloride, bromide and iodide. The silver chloride or bromide, or mixture of both, is precipitated in the usual way, and filtered with the use of a micro Gooch Neubauer crucible, washed in the cold and dried at 150° C. The silver chloride is then converted into silver bromide, or the silver chloride and bromide into iodide by admixture with about 6 times the weight of either pure ammonium bromide or ammonium iodide, and then heating, first covered, then open, in the muffle at 250°–300° C., until all the ammonium salts are driven off, and the weight is constant. The method can also be used to test the purity of silver chloride or bromide. In a typical result 2·960 mgrms. of silver chloride, and 1·628 mgrm. of silver bromide were used, and the weight of silver iodide found was 6·884 mgrms., as compared with the calculated 6·900 mgrms. J. W. B.

Micro Determination of Iodine in Organic Substances. T. Leipert. (*Mikrochemie. Pregl-Festschrift*, 1929, 265–271.)—A titrimetric determination of iodine is described, to be used instead of a gravimetric method after oxidation of the organic matter in the Pregl method. To the product of oxidation in the Erlenmeyer flask a drop of methyl orange is added, and the solution accurately neutralised with 2 *N* sulphuric acid, and then a further 3 drops of acid are added, and the solution diluted with water to a volume of 50–60 c.c. The iodine is oxidised to iodate with 2 c.c. of bromine water, and then a rapid current of steam is passed through and continued for 7 minutes after the solution boils. After cooling, 1 grm. of potassium iodide, dissolved in a little water, is added, and the solution titrated against freshly diluted 0·01 *N* thiosulphate, starch being used as indicator. For amounts of iodine of 1·5–3 mgrms., in pure compounds, the results were 0·1–0·2 per cent. lower than theory. J. W. B.

Micro-determination of Iodine. I. Ashing. II. Titration of small amounts of Iodine. III. Quantitative Determination of Organic and Inorganic Iodine in the presence of each other. G. Lunde, K. Closs, and J. Böe. (*Mikrochemie. Pregl-Festschrift.*, 1929, 272–295.)—I. The methods are

adapted from Fellenberg's. (*a*) *Solution of material.*—In order to get a representative sample a larger amount of the material is dissolved than is to be ashed. The weighed sample is mixed with 25–30 per cent. of its weight of potassium hydroxide, a little water, and heated over a water bath to dissolve; a little alcohol hastens the solution. More alcohol is used for material rich in fat, and the oils and fats are saponified with the alcoholic potash. With protein-rich material as much as 4 times its weight of potassium hydroxide is used to prevent the formation of excess carbon and to destroy hydrocyanic acid and ammonia. Cellulose and similar substances are melted with caustic alkali; the substance decomposes with evolution of gas and will then dissolve in water. Materials rich in silicic acid are treated similarly. Substances rich in lime are treated first with alkali, then hydrochloric acid, or, better, with hydrochloric acid beneath a reflux condenser, and then with alkali (see under). (*b*) *Ashing.*—A proportional part of the dissolved material (equivalent to about 1 grm. of fresh material) is treated with 1–2 c.cm. of 50 per cent. potassium hydroxide in an iron crucible (Krupp's V2A steel), and evaporated as far as possible on the water bath. It is then heated very carefully over a free flame, and finally for about 10 minutes at 450–500° C., until there is little or no smell. After cooling, the contents are treated with a little water, and any lumps of carbon broken with a rod. If a hard crust has been formed the material must again be mixed with 1–2 c.c. of potassium hydroxide solution and treated as before. If, after the third burning, the carbon is still unoxidised, about 50 c.c. of water are added, and, after standing, the solution is sucked through a micro-filter, the carbon washed twice with 10 c.c. of water. The carbon is then washed back into the crucible, dried, and burned off at a low red heat. The filtrate is returned to the crucible, evaporated to dryness, and heated again until the disappearance of smell. Soaps from animal fats and oils ignite with difficulty, and sometimes the separation from carbon must be repeated, and finally an oxidising substance, such as sodium nitrate, or caustic potash, is added. The ash should finally be colourless, or, if iron is present, light red, but never grey. (*c*) *Alcohol extraction.*—The contents of the crucible are treated with 2–3 c.c. of 96 per cent. alcohol and a few drops of water; after standing covered for 10 minutes the mixture is stirred with an agate pestle until it is an even viscous mass. The alcohol is decanted into a platinum or gold dish of 5 cm. diameter. The extraction is repeated at least 3 times. (*d*) *First ignition in platinum dish.*—About 5 drops of 50 per cent. potassium hydroxide solution and enough water to make the mixture homogeneous are added, the mixture is evaporated to dryness, and then carefully and evenly heated over a naked flame. After cooling, 2 drops of water are added, and the mixture dried and heated as before. This process is repeated until the residue is white and evenly spread over the dish bottom. (*e*) *Second alcohol extraction.*—The residue is extracted as before with 2 c.c. of 96 per cent. alcohol into a second platinum dish, and evaporated to dryness with a little water. (*f*) *Second ignition in platinum dish.*—The dish is carefully heated in a strong Bunsen flame, but the salts must not be heated to melting point, otherwise loss will occur. If organic matter is still present, the ash must be treated

with potash, extracted, and heated again. (*g*) *Treatment of substances rich in lime.*—Substances rich in lime give results by the above methods that may be as much as 80 per cent. too low. It is shown that in this case, after ashing most of the iodine is in an alcohol-insoluble form. Therefore, after the ashing in the iron crucible, water is added to the contents, the crucible is heated on the water bath, and the insoluble calcium carbonate filtered off and thoroughly washed with hot water. The calcium carbonate is then dissolved in acid, re-precipitated and filtered, so that all the iodine is obtained in the combined filtrate. The filtrate is evaporated to dryness, and the residue heated, and extracted with alcohol as above. The disturbing effect of lime is probably due to the presence of the somewhat insoluble calcium iodate, which was either originally present, or formed in the presence of the oxidising medium.

II. When more than 1γ of iodine is present it is estimated volumetrically, by oxidising it to iodate with chlorine water and titrating with $N/250$ sodium thiosulphate after adding a crystal of pure potassium iodide. The titration method of Schulek and Stasiak (*Pharm. Zentralhalle*, 1928, **69**, 113, 513), suitable for amounts of iodine of 50γ or more, is discussed; this method does not require such careful ashing.

III. The material is exhaustively extracted with water (alcohol or acetone). From the solution made slightly acid, the iodine fat compounds are extracted with ether. In the aqueous solution (slightly acid with acetic acid) the inorganic iodine is liberated by treatment with nitrite or hydrogen peroxide, and it can then be removed with ether. Larger amounts of inorganic iodine can be precipitated by palladium chloride in weak acid solution. Protein iodine is precipitated by the usual reagents. The residue from the first extraction is heated with hydrochloric acid beneath a reflux condenser, to dissolve the more insoluble inorganic iodine compounds (alkaline earth iodates), and also the iodine compounds of the complex carbohydrates of cell walls. J. W. B.

Determination of Small Amounts of Iodine in Organic Material rich in Iron. K. Wülfert. (*Mikrochemie*, 1930, **8**, 100–105.)—Unreliable results are often due to the material not being completely moistened throughout in the first treatment. The form in which the iron is present (such as colloidal iron hydroxide) rather than the total amount may cause low results. Good results are obtained when the material is mixed with 4–5 times its weight of ground potassium hydroxide, and 10 c.c. of water in a 50 c.c. Erlenmeyer flask, and heated on the water bath until the material is completely decomposed and the iron hydroxide flocculates. When larger amounts of material are used carbon dioxide should then be passed through, otherwise too much potassium hydroxide is taken up in the alcohol extraction. For small amounts enough carbon dioxide is taken up from the air during heating. The material is then poured into an iron crucible and treated in the usual way (*see previous abstract, Lunde, Closs and Böe*). Typical results gave percentages of iodine found 2·01, calculated 2·06; found, 1·07, calculated 1·02; found 2·2, found 2·35. J. W. B.

Physical Methods, Apparatus, etc.

Electrolytic Cell for Use with the Mercury Cathode. A. D. Melaven. (*Ind. Eng. Chem.* (*Anal. Edition*), 1930, **2**, 180.)—The difficulty experienced in removing the electrolyte from the mercury cathode in the electrolytic-amalgam method of separation of metals (*e.g.* of aluminium or magnesium from iron) without resolution of the amalgam, is overcome by the use, as electrolytic cell, of a cylindrical glass vessel with a conical base fitted with a 2-way cock. This cock is connected by rubber tubing filled with mercury with a levelling bulb in which connection is made with the rest of the circuit by means of a copper wire, while the other outlet is constricted in the form of a burette tip. In operation, the area of the mercury cathode is adjusted by raising or lowering the levelling tube, the solution added, the anode inserted and the circuit closed. When electrolysis is complete, the mercury surface is lowered to the top of the stop-cock and the electrolyte drained off through the other outlet, care being taken that the anode is always below the surface of the electrolyte, so that the circuit remains closed. J. G.

Mounting Media for Microscopic Work. J. M. Preston. (*Nature*, 1930, **125**, 563.)—A medium giving a refractive index of 1·42 when liquid, rising to 1·47 when hard, which is very useful for unstained cellulose materials (n=1·52 to 1·54), has the following composition:—Cellulose nitrate (extra low viscosity type—Nobel's H.X.2), 25; triacetin, 25; methyl ethyl ketone, 50 per cent. The medium is applied in the same manner as Canada balsam and allowed to harden either with or without heat. During the hardening process the ketone evaporates, and the refractive index rises from the lower to the upper value. Other media containing various plasticisers in place of triacetin may be used in special cases, and give an extended range.

	Refractive Index.	
	Liquid.	Hardened.
Cellulose nitrate, methyl ethyl ketone and		
Triacetin	1·417	1·471
Resorcinol diacetate	1·435	1·517
Benzyl alcohol	1·442	1·525
Tricresyl phosphate	1·448	1·545
Benzophenone	1·461	1·573
Euparal	1·481	1·525
Canada balsam	1·530	1·545

Cellulose acetate may be used in place of cellulose nitrate, and is found to give somewhat lower values of the refractive index with the same plasticiser. To obtain a sufficiently fluid medium more dilute solutions must be used than with the nitrate.

Mountants for Biological Tissues. W. Marshall. (*Nature*, 1930, **125**, 564.)—The mountant of highest refractive index that can conveniently be used is a saturated solution of sulphur and arsenious sulphide in methylene iodide. It is of a canary yellow colour and has refractive index 1·804. It appears to be stable, but the mounts in this medium need ringing. A higher refractive index (1·87) is obtained with a solution of phosphorus in methylene iodide, but the golden yellow liquid soon becomes cloudy on exposure to air.

Reviews.

ELEMENTARY QUALITATIVE ANALYSIS. By C. J. ENGELDER, Ph.D. Pp. vi+211. London: Chapman & Hall. Price 11s.

The text of this volume is based on notes used during the last five years by the author in his classes and is intended for the use of students beginning the study of qualitative inorganic analysis. In order to develop the invaluable faculty of logical independent thought, the fundamental principles of chemistry are lucidly dealt with, and their application to practical qualitative work is emphasised throughout the book.

The text is divided into four parts dealing respectively with the fundamental principles, analysis of the cations, analysis of the anions and the systematic analysis of mixtures of salts, alloys, silicates and technical products. At the end of each chapter is a series of questions admirably designed to test the student's knowledge, both theoretical and practical, of the experimental work he has carried out, and an appendix at the end provides the usual table of atomic weights, preparation of test solutions and reagents, and a somewhat extensive list of apparatus required by each student.

The volume has been carefully prepared, and is well adapted to its intended purpose, being thoroughly coherent, lucid and commendably free from inaccuracies. Throughout the text there is practically nothing deserving adverse criticism, but the statement on p. 68, to the effect that "Many of the salts of silver are colored," appears somewhat curious when one considers that several other metals show the same characteristic. In the list of reagents on p. 204, under the heading of sodium hypochlorite, the student is told to "use a solution of bleaching powder," although this is certainly not a sodium salt.

In every way the volume is an admirable production, being well arranged, with legible type, an accurate and comprehensive index, and with durable binding well adapted to withstand the arduous usage to which students' manuals are often subjected. This textbook will undoubtedly achieve an extensive reputation when its many merits become known, and will be highly appreciated by both demonstrators and students.

T. J. WARD.

INTERMEDIATE INORGANIC CHEMISTRY. By J. W. MELLOR, D.Sc., F.R.S. Pp. xx+690, with illustrations. London: Longmans, Green & Co. 1930. Price 7s. 6d.

This book is a revised and remodelled version of the author's *Introduction to Modern Inorganic Chemistry*, which was written to suit students who want to start with a rather simpler book than the well-known *Modern Inorganic Chemistry*. The book is remarkable in several respects, chiefly in the way in which the salient

facts of chemistry are assembled, and the main generalisations drawn from them after impartial and stimulating discussion. A feature of the book is the historical perspective in which most of the material is viewed. The author's vigorous and characteristic style does much to render the text attractive.

The subject matter is treated with great thoroughness in thirty-eight chapters, the arrangement being similar to that adopted in *Modern Inorganic Chemistry*; these chapters are in the form of connected essays and conclude with a list of questions, many of which are drawn from papers set at recent Matriculation and Higher School Certificate examinations. An interesting feature is the inclusion of biographical notes of a number of famous chemists. No themes of importance from the point of view of an introductory course are missed; even such a recent important topic as U. R. Evans's work on the electrical currents set up by the differential aeration of metals is introduced, but apparently the time is not considered ripe for a mention of the electron, although the student will have to be acquainted with this before he goes very far in chemistry.

The writer of a text-book on elementary chemistry must find himself sometimes in a quandary, since a number of generalisations have to be presented which cannot always be discussed as fully as desirable. Dr. Mellor is able to meet such difficulties more happily than most authors. He is somewhat free, however, in the use of graphic formulae, representing in the same manner the attachment of potassium and iodine in potassium iodide and the bonds joining the hydrogen atoms with the carbon atom of methane, and representing sulphurous acid as a mixture of two isomeric forms in equilibrium containing, respectively, sulphur in the quadrivalent and sexavalent states, although no evidence in favour of the existence of the latter form is mentioned. The "electro-chemical series" of the elements is made to look far too simple and free from anomaly.

The reader is led to believe that the artificial production of diamonds is an accepted fact. This is far from being the case, since Sir Charles Parsons and others have repeated the experiments of workers who have claimed to have produced diamonds by artificial processes, but in every case the results have been negative.

Misprints are very rare in the volume; a few have been noted, such as the omission of an oxygen atom in the graphic formula of perchloric acid (p. 279), the formula of *m*-phenylenediamine being given as $C_2H_4(NH_2)_2$ (p. 510), Mn_2O_2 for manganese heptoxide (p. 625), and H_2Fe for H_2Te (p. 611). The product of the action of hot concentrated sulphuric acid upon tin is stannic sulphate, not stannous sulphate, as stated on p. 480, and the statement (p. 326), that *iron* precipitates tin quantitatively from a solution of tin chloride acidified with hydrochloric acid is possibly a misprint.

The price is low for this valuable and admirably produced book, which is clearly printed on good paper and has a full index. The volume should certainly occupy a foremost place among textbooks of similar scope.

S. G. CLARKE.

A HANDBOOK FOR CANE-SUGAR MANUFACTURERS AND THEIR CHEMISTS. By the late GUILFORD L. SPENCER, D.Sc. Seventh Edition, revised, re-written and enlarged by GEORGE P. MEADE, B.S., Ch.E. Pp. xix+560. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1929. Price 30s. net.

About 40 years ago the late Dr. Guilford Spencer published, in the form of a little pocket book, a concise description of the methods used in the control of cane-sugar manufacture. This book up to 1917 went through six editions, in each of which its scope was extended, and it has now been revised and further enlarged by Mr. G. P. Meade, who worked under Dr. Spencer for many years. It is still concise, and still a book for the pocket, but its contents have grown prodigiously; which is a measure of the expansion of methods of control in the period.

The growth has been natural and healthy; a large portion of the present edition has been re-written, and embodies much of the recent work on manufacture and analysis. As with most healthy growth, some of the material in earlier editions has become superfluous; although pruning has been vigorous, it has missed a dead patch here and there.

There is first given a full account of the manufacturing and refining plant and processes, an adequate knowledge of which is essential for efficient control by the chemist. Useful new chapters have been added on Economic Phases of the Sugar Industry, and on Keeping and Refining Qualities of Raw Sugars, while the sections on evaporation and pressure filtration have been much extended.

In the second part, dealing with analytical and chemical control, the new chapters are on Hydrogen-Ion Control, Colour Determination, and Fermentation and Micro-Organisms in Sugar Manufacture (this last by Mr. W. L. Owen). It is in connection with the older branches of analysis that one regrets the retention in some places of descriptions of earlier methods at the expense of newer material.

The description of optical methods would have been made clearer by an explanation of the meaning of polarisation and of the mutual relations of polariser and analyser, with an account of the circular-scale polarimeter before the description of quartz-wedge compensation. An elucidation in cold print of the connection between specific rotation and sugar-scale degrees, always somewhat confusing, would have been welcome.

The discussion on the volume of lead precipitate and on the influence of subacetate of lead and other substances on polarisations should have been brought up to date; especially by including the quantitative data of Jackson and Gillis on salt and acid effects.

Much space is devoted to the Herzfeld modification of the Clerget method, although the more accurate one of Jackson and Gillis is also given, and it is admitted that this has now become widely used. In regard to the latter, it should be noted that the table of divisors (p. 524) given by those workers has been shown to be

slightly in error, owing to a false assumption as to the effect of sugar concentration. Satisfactory divisors can, however, readily be obtained from their basic data.

The Herzfeld gravimetric copper method, with several subsidiary methods for estimating precipitated copper, might also have been curtailed, and the cumbersome Soxhlet volumetric method omitted entirely, in view of the convenience and accuracy of the Eynon-Lane method (which is fully described). No mention is made of the newer methods for estimating copper reduction without separation of the precipitate, or of the careful study by Quisumbing and Thomas of the gravimetric process. It is stated that the volumetric method requires checking against a standard invert sugar solution. This excellent advice might well be extended to gravimetric methods; variations in details of manipulation are likely to cause errors quite as large as variations in the composition of Fehling's solution.

The refractometer, though well described, is hardly given its due as a means of determining total solids. Recent work has thrown light on the relation between its results and those by density and drying; and its advantages for many purposes are unquestionable.

The account of electrometric ash determinations would have been improved by a definition of the units in which specific conductivity is expressed. To the reviewer, the problem of the varying relation between conductivity and direct ash determinations seems an artificial one. Incineration results are essentially empirical, and the conductivity figure itself might well serve as a suitable measure of dissolved salts without reference to the ash.

A full description of colorimetric methods is given under Hydrogen-Ion Control, but more should have been said about electrometric methods, especially with the quinhydrone electrode. A diagram here shows a calomel half-cell dipping directly into the test solution, which is not altogether desirable.

In a chapter on special reagents, the description of alkaline tartrate solution (without any tartrate), on p. 411, might mislead the tyro.

A large collection of handy tables is supplied at the end. Those for conversion of measures and temperatures, and some of the others, are particularly well displayed. A few, however, require bringing up to date. In Table 2, which is a partial list of atomic weights presumably for sugar chemists, the inclusion of radium provokes speculative surprise; while the 14 pages of Table 51, a classified index of substances that are or have been used for purifying, clarifying, etc., saccharine solutions, is an amazing lexicon of hope and ingenuity. The presence in the list of such articles as hay, soap, milk, kerosene and gin, besides all the more obvious chemicals, suggests that investigators have sometimes tried the nearest thing at hand!

The perusal of this book leads to an uncomfortable feeling that we are a long way from finding in any of the manufacturing processes which use sugar such a rigid analytical control as in those concerned with its production. This is a matter, however, capable of remedy, and many of the analytical methods and

manufacturing details described here can be readily adapted to the requirements of the sugar-using industries.

The book is admirably clear and readable in style, is furnished with numerous figures and diagrams and with copious references to original papers, and is well printed. In the newer portions a sprinkling of misprints is excusable, but a few which have come through from earlier editions are not so.

Durably bound in limp cloth, the book is well fitted to be a constant companion of the sugar chemist. Mr. Meade is to be congratulated on the fit of Dr. Spencer's mantle.

C. L. HINTON.

COLLOID SYMPOSIUM ANNUAL. Volume VII. Edited by HARRY BOYER WEISER. Pp. viii+300. New York: J. Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1930. 22s. 6d. net.

The Seventh Colloid Symposium was held at the Johns Hopkins University, June 20, 21, 22, 1929, and twenty-three papers were read. These have been edited by Professor Weiser and published with a subject index. The former title of Colloid Symposium Monograph (blue binding) has been replaced by that of Colloid Symposium Annual (red binding), with a change in publishers.

The first paper was presented by Professor F. G. Donnan, the Guest of Honour. He describes work carried out in his laboratory by Krishnamurti on the scattering of light in sols and gels, the data having "considerable interest in their bearing on the nature of the sol-gel and gel-sol transformations." Agar sols and gels were studied, and the results "are of considerable assistance in the determination of the bulk and shape of the colloid particles" contained therein.

Sheppard and McNally present an excellent paper on "The Structure of Gelatin Sols and Gels." Gelation is treated as an incomplete crystallisation "in which the aggregation or *condensation* process is ahead of the *orientation* process." The hydration of gelatin and the relation of this to swelling is described by Neville and Theis. Although all the papers are full of interest, and describe original investigations, it is permissible to refer specially to:—Frumkin, "Significance of the Electrocapillary Curve"; McBain and Williams, "Determination of the Number of Free Electric Charges on Air Bubbles and Oil Droplets Dispersed in Water containing a Small amount of Cetyl Sulphonic Acid"; Patrick, "The Adsorption of Vapours"; Bingham and Lowe, "The Nature of Flow"; Weiser, "Adsorption and Permeability of Membranes."

Papers of interest to technologists deal with adsorption, flotation, dyeing, soils, and fat solvents, whilst the physiologist and pathologist will read the papers dealing with bacteria, human blood serum, and gall stones.

The high standard set in the former monographs is still maintained, and the excellent printing and binding make the reading a pleasure. All advanced students of colloid physics will add this volume to their shelves.

WILLIAM CLAYTON.

DIE UNSICHTBAREN STRAHLEN IM DIENSTE DER KRIMINALISTIK. By G. KÖGEL. Pp. 181. Graz: Ulr. Mosers Buchhandlung (J. Meyerhoff). Price, Marks 16.70.

The first attempt to use ultra-violet light in the examination of documents was made in 1914, when it was shown that graphite reflects ultra-violet rays, and that it is possible by this means to detect an erasure of pencil writing. The next important work on the subject was a communication to this journal (ANALYST, 1922, **47**, 206) by Kitching, who showed that many substances may be differentiated by the fluorescent effects of ultra-violet light, and that various kinds of paper may thus be distinguished from one another. Since then several types of apparatus have been devised, and the principles of the method have found application in many directions, and in particular for the examination of oils and for the differentiation of materials used in tanning.

As the process has established its value for deciphering obliterated writing, it has now become a recognised weapon in the armoury of the criminologist, and there was room for a book to summarise the available means of using invisible rays for this particular purpose, and especially to deal with the methods of recording the visual effects by photography. The author rightly lays stress upon the point that no evidence based solely upon personal observation of what has been seen in ultra-violet light should be accepted by a Court ("No photographic proof—no judgment," is his dictum), for, as he points out, it is possible for transmitted red rays to make the visual image deceptive. The difficulty is to obtain a satisfactory photograph of a fluorescing substance, since the long-wave ultra-violet rays, which are simultaneously reflected, act more rapidly upon the plate than the fluorescing rays. Hence, if an attempt is made to photograph, *e.g.* secret writing in quinine sulphate by means of ultra-violet light, the result is a failure unless a suitable filter which will absorb the long-wave ultra-violet rays is interposed between the object and the photographic plate. Of the various solutions tried for this purpose, the most satisfactory was found to be a solution of triphenylmethane in absolute alcohol; all the glass filters tried were found to give poor results.

The various types of ultra-violet lamps and appliances are described in detail, and a full description is given of the methods of using them to obtain photographic records of the appearance of an object when submitted to the various kinds of rays, including *X*-rays and infra-red rays.

The objects which have been made the subject of examination include erasures, typing inks, pencil markings, paste, etc. In this connection it is interesting to note that the author's experiments on saliva writing confirm my conclusion (ANALYST, 1920, **45**, 256) that the action of saliva in darkening the iron constituent of ink is a chemical, not a physical process.

The book concludes with an interesting series of plates of photographs obtained by reflected ultra-violet rays and by fluorescent rays, but it is a pity that it is so difficult to find any reference to these in the text. One would have liked to know more about the significance of the fluorescent footprints shown in Figure 37. Another defect of an otherwise excellent book is the absence of an index.

EDITOR.