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Deaths

WITH deep regret we record the deaths of the following members:

Hugh Charles Loudon Bloxam, on July 14th.
Christopher Rawson, on May 30th.

The Use of Thiocyanogen Values in the Determination of Linoleic and Linolenic Acids and their Glycerides

BY T. P. HILDITCH, D.Sc., F.I.C., AND K. S. MURTI, B.A., PH.D., A.I.C.

THE selective addition of thiocyanogen to linoleic and linolenic acids and their derivatives, in conjunction with their iodine values, was put forward by Kaufmann[1] in 1925 as a method for the determination of mixtures of oleic, linoleic and linolenic acids or their esters (including glycerides); it has since found considerable use in the analysis of fatty oils, especially in the hands of Kaufmann and his collaborators. Whereas halogens (*e.g.* iodine monochloride or monobromide) react completely and additively with each ethenoid linkage in oleic, linoleic or linolenic acids, thiocyanogen, according to Kaufmann, unites quantitatively with oleic acid, but with only one of the two ethenoid linkages in linoleic acid, and with two of the three ethenoid linkages in linolenic acid. Clearly, the validity of the thiocyanogen method of analysis depends upon two factors: (*a*) the degree of precision of the method—how far results are reproducible by the same or different analysts, and (*b*) the correctness of the fundamental assumption regarding the extent of the selective addition of thiocyanogen to linoleic and linolenic compounds.

Doubt has been expressed by some workers (van der Veen,[2] Gay,[3] Smith and Chibnall[4]) as to the possibility of obtaining reproducible results when addition of thiocyanogen is used as a quantitative method of analysis; but others (*e.g.* Waterman and Bertram,[5] Jamieson and Baughman,[6] Griffiths and Hilditch[7]) have found that the procedure can be made satisfactory in this respect, provided that most careful precautions are observed in the manipulative technique, especially in ensuring complete absence of moisture from all the reagents and apparatus, and in observing rigidly standardised conditions of procedure at all stages of the analysis. Admittedly, however, it is difficult to obtain, in the determination of thiocyanogen values, the same degree of accordance which characterises that of ordinary iodine values, but the disparity is not sufficiently great to interfere seriously with the usefulness of the method. Nevertheless, the time of contact of the thiocyanogen

reagent with the fatty compounds under examination is an important factor, to which further reference must be made below.

The main object of the present communication is to point out that Kaufmann's fundamental assumptions as to the "theoretical" thiocyanogen values of linoleic and linolenic acid appear to be ill-founded; with linoleic acid, thiocyanogen reacts to the extent of somewhat more than half the total unsaturation, whilst it reacts with considerably less than the assumed two-thirds of the total unsaturation in the triethenoid linolenic acid. We have had reason to suspect this for some time, and began a systematic investigation of the point more than a year ago. Pressure of other work prevented us from devoting full attention to this problem, and in the meantime other authors have published two communications (*v. infra*) which accord for the most part with our own observations. Since, however, we have approached the matter on somewhat different lines from either of the authors in question, an account of our results may be a useful further contribution to the discussion. The use of thiocyanogen values is not indispensable in the analysis of fats which contain only oleic and linoleic acids, but it is the only method, at present proposed, which affords a possibility of accurately determining oleic, linoleic and linolenic acids when all three are simultaneously present. Unfortunately, our results indicate that the thiocyanogen value of linolenic acid differs so much from that hitherto assumed by Kaufmann that calculations based on his value must be regarded as very uncertain.

We decided to prepare specimens of oleic, linoleic and linolenic acids, and of their methyl and ethyl esters, of as high a degree of purity as possible, and to examine the thiocyanogen values of the individual acids and esters, and also of various binary or ternary mixtures made up from the acids (or from the corresponding esters) in known proportions.

In the determination of the thiocyanogen value, a time of contact of exactly 24 hours was used, in accordance with previous custom in this laboratory and with the procedure adopted by most workers. Recently Riemenschneider and Wheeler[8] have advocated a contact time of three hours, on the grounds that after this period has elapsed the thiocyanogen value of methyl linoleate accords closely with Kaufmann's "theoretical" value (*i.e.* addition at exactly half of the total unsaturation), whilst that of methyl oleate is only fractionally below the theoretical value (*i.e.* 100 per cent. addition). These authors show that, after more than three hours' contact, methyl oleate undergoes a further very small increase in thiocyanogen value, finally reaching, but not exceeding, the value (85·8) corresponding with 100 per cent. addition of thiocyanogen; also, that the thiocyanogen value of methyl linoleate (having reached 50 per cent. addition of thiocyanogen in three hours) continues to increase, but more and more slowly, up to, and beyond, 24 hours. Our reasons for preferring the latter time of contact of the thiocyanogen reagent are as follows:

(i) Iodine values are based primarily on conditions of addition which show 100 per cent. addition of halogen to oleic acid or its esters, and it seems logical to adopt the same substance for calibration in thiocyanometric analysis. General experience, we believe, is in favour of the longer period of contact, to ensure 100 per cent. addition of thiocyanogen to oleic acid. (ii) Although addition of thiocyanogen to linoleic compounds has not ceased after 24 hours, the rate of addition at that period is much slower than at 3 hours (when it is still proceeding with moderate rapidity). Any error in timing would therefore have much greater effect after 3 hours' than after 24 hours' contact. (iii) The time factor in the addition of thiocyanogen to linolenic acid has not been explored in so much detail as for the other two acids, but the relatively low values observed in the case of linolenic acid and its esters (*v. infra*) suggest that addition is still incomplete even after 24 hours. (iv) In our experience the rates of addition of thiocyanogen to free fatty acids are liable to be slower than to their esters.

We have therefore continued to adhere, in the present work, to a time of contact of 24 hours in the thiocyanogen value determinations.

Experimental

Preparation of the Pure Fatty Acids and Esters.—The oleic acid and methyl oleate used were derived from accumulated fractions of almost pure C_{18} unsaturated esters which were fortunately available from ester-fractionation analyses of the "liquid" or mainly unsaturated acids of a group of beef fats. The latter contain only small proportions of linoleic acid, so that the ester-fractions employed already consisted almost wholly of methyl oleate.

Oleic Acid.—The acids (69 g.) from a portion of the combined methyl oleate fractions were first crystallised from acetone (690 ml.) at −20° C. for 2 hours, after which a crystalline deposit (about 9 g.) was removed; this contained a certain amount of palmitic acid. The portion in solution was crystallised from 720 ml. of acetone at −60° C. for 3½ hours, and the deposited crystals were recrystallised from acetone at −60° C. for 3 hours. The recrystallised oleic acid (36·7 g.; iod. val. 89·1) was then fractionally distilled in a vacuum through an electrically-heated and packed column, when a main fraction of 21 g. (iod. val. 89·7; CNS val. 89·0) was obtained. This material, which contained at most less than 1 per cent. each of palmitic and linoleic acids, was used in the tests described below.

Methyl Oleate.—A further portion (63 g.) of the combined methyl oleate fractions mentioned was crystallised from acetone (630 ml.) at −37° C. for 2 hours to remove traces of methyl palmitate as far as possible, the soluble fraction being further crystallised from 12 volumes of acetone at −60° C. for 3 hours. The deposited crystals (50·5 g.; iod. val. 84·8) were collected and fractionally distilled in a vacuum through the column mentioned, when three fractions of almost pure methyl oleate were obtained. The middle one of these fractions (12·0 g.; iod. val. 86·0; CNS val. 85·3) was employed in the present work.

Linoleic Acid and Methyl Linoleate.—These were prepared by debromination of pure crystalline tetrabromostearic acid, obtained from the unsaturated acids of cottonseed oil (which contains no linolenic acid). A large stock (340 g.) of the tetrabromostearic acid was prepared from refined cottonseed oil (800 g.) by brominating the unsaturated acids in light petroleum (b.p. 80–100° C.) and crystallising the product several times from light petroleum (b.p. 40–60° C.); it melted sharply at 115° C. (Br found 53·2; calc. 53·3 per cent.).

Linoleic Acid was prepared by debromination of the tetrabromostearic acid (40 g.) in pyridine solution with zinc by a modified form of Kaufmann and Mestern's method[9]; the acid (18·1 g.) so obtained was distilled in a vacuum, and the main fraction (15·5 g.; iod. val. 180·0) was used in the further experiments.

Methyl Linoleate was similarly prepared by Rollett's process[10] by debromination of tetrabromostearic acid (40 g.) with zinc and hydrogen chloride in methyl alcohol. The crude ester (19·5 g.) yielded on vacuum distillation 17·0 g. of methyl linoleate (iod. val. 172·9).

Linolenic Acid and Ethyl Linolenate.—These were similarly obtained from hexabromostearic acid, which was prepared by addition of bromine to the mixed fatty acids of linseed oil in ethereal solution. After repeated boiling of the crude product with ether, the purified hexabromostearic acid (235 g., from 520 g. of refined linseed oil) melted at 180·5–181° C. (Br found 62·9; calc. 63·3 per cent.).

Linolenic Acid was prepared by debromination of the hexabromostearic acid (27 g.) with zinc and pyridine; the crude acid (9·7 g.) gave on vacuum distillation 7·7 g. of slightly yellow-coloured linolenic acid (iod. val., found 267·4; calc. 274·1).

Ethyl Linolenate was prepared by Rollett's method from the hexabromostearic acid (25 g.) with zinc, hydrogen chloride and ethyl alcohol (the hexabromostearic acid is insufficiently soluble in boiling methyl alcohol to permit the ready

preparation of the methyl ester). The crude product (9·5 g.) yielded on distillation in a vacuum a colourless specimen of ethyl linolenate (7·8 g.; iod. val., found 246·8; calc. 249·0).

IODINE AND THIOCYANOGEN VALUES OF THE PURE INDIVIDUAL COMPOUNDS.—The following precautions were taken in connection with the preparation and use of the thiocyanogen reagent:—(*a*) Lead thiocyanate (AnalaR) was dried for at least a week in an evacuated exsiccator over phosphorus pentoxide. (*b*) Glacial acetic acid was refluxed with 15 per cent. of acetic anhydride for 2–3 hours, cooled, and kept for a few days before use in preparing the reagent. (*c*) A suspension of the dried lead thiocyanate (5 per cent.) in the prepared acetic acid was "aged" for about a week before use in the preparation of the actual reagent. (*d*) All apparatus and filter-paper employed were dried immediately before use, first in a steam oven and then at about 120° C. for at least an hour in an electrically-heated oven. (*e*) The reagent was always freshly prepared, by addition of bromine to the solution (*c*), immediately before use in determination of a batch of thiocyanogen values. Its strength was maintained close to $N/5$, and each batch of reagent was filtered twice to ensure an absolutely clear solution. (*f*) The amounts of acid or ester were so adjusted that the excess of reagent (20 ml.) was in every instance between 150 and 200 per cent. (*g*) The reagent (20 ml.) was left in contact with the fat (0·1–0·2 g. dissolved in 20 ml. of the prepared acetic acid) for 24 hours in the dark; 20 ml. of 20 per cent. aqueous potassium iodide solution were then added immediately prior to titration with standard thiosulphate solution.

The iodine and thiocyanogen values of the individual acids and esters used in the subsequent tests are given in Table I, together with the theoretical iodine values and the thiocyanogen values calculated according to Kaufmann's assumptions (addition to one of the double bonds in oleic and linoleic acids, and to two of three double bonds in linolenic acid).

TABLE I

Compound	Iodine value		Thiocyanogen value	
	Found	Calc.	Found	Calc. (Kaufmann)
Oleic acid	89·8	90·1	89·0	90·1
Methyl oleate	86·0	85·8	85·3	85·8
Linoleic acid	180·0	181·4	95·9	90·7
Methyl linoleate	172·9	172·8	91·8	86·4
Linolenic acid	267·4	274·1	162·5	182·7
Ethyl linolenate	246·8	249·0	146·6	166·0

IODINE AND THIOCYANOGEN VALUES OF BINARY AND TERNARY MIXTURES OF THE ACIDS OR ESTERS.—We proceed to report the rest of our experimental data before considering further the deviation between the observed thiocyanogen values of linoleic and linolenic acids and their esters and the values as calculated on Kaufmann's assumption. Five binary and three ternary mixtures of the acids, and also of the corresponding esters, were made up in the following proportions by weight:

	Acids				Esters		
Ref. No.	Oleic	Linoleic	Linolenic	Ref. No.	Methyl oleate	Methyl linoleate	Ethyl linolenate
A1	74·5	25·5	—	E1	76·0	24·0	—
A2	51·5	48·5	—	E2	48·0	52·0	—
A3	25·1	74·9	—	E3	33·0	67·0	—
A4	50·2	—	49·8	E4	49·8	—	50·2
A5	—	49·3	50·7	E5	—	50·3	49·7
A6	31·3	35·7	33·0	E6	32·4	35·7	31·9
A7	48·4	25·2	26·4	E7	48·2	26·7	25·1
A8	24·3	50·2	25·5	E8	24·1	50·5	25·4

The iodine values (Wijs) and thiocyanogen values of these mixtures are given in Table II, together with the values calculated numerically from the observed data in Table I. To illustrate the degree of reproducibility obtained, the individual determinations made are recorded, with the final mean value adopted; figures in brackets were not used for the calculation of the mean values.

TABLE II

OBSERVED IODINE AND THIOCYANOGEN VALUES OF THE MIXTURES OF ACIDS OR ESTERS

(i) *Iodine Values*

Acids				Esters			
Ref. No.		Mean	Calc.	Ref. No.		Mean	Calc.
A1	112·6, 112·8	112·7	112·8	E1	107·1, 106·7	106·9	106·7
A2	133·1, 133·3	133·2	133·5	E2	130·7, 130·7	130·7	131·1
A3	157·0, 156·9	157·0	157·3	E3	143·4, 143·3	143·4	144·1
A4	177·6, 177·1	177·4	178·5	E4	166·0, 166·6	166·3	166·8
A5	224·0, 224·7	224·4	224·3	E5	209·4, 209·1	209·3	209·6
A6	180·7, 180·7	180·7	180·6	E6	168·5, 168·5	168·5	168·2
A7	159·6, 159·4	159·5	159·4	E7	149·7, 149·6	149·7	149·6
A8	180·2, 180·6	180·4	180·3	E8	170·7, 170·5	170·6	170·7

(ii) *Thiocyanogen Values*

Acids			
Ref. No.		Mean	Calc.
A1	(89·2), 90·1, (88·7), 90·7	90·4	90·7
A2	91·5, 90·8, (90·4)	91·2	92·3
A3	92·8, 93·7, (91·9)	93·3	94·2
A4	(123·6), 122·3, 122·1	122·2	125·6
A5	127·2, 127·8, (125·7)	127·5	129·7
A6	(113·8), 112·8, 112·6	112·7	115·7
A7	108·7, 108·5, (106·9)	108·6	110·1
A8	109·1, 109·2, (108·0)	109·2	111·2
	Esters		
E1	86·6, 86·7	86·7	86·8
E2	88·8, 88·5	88·7	88·7
E3	90·1, 89·4	89·8	89·7
E4	117·1, 117·0	117·1	116·1
E5	120·8, 119·8, (116·6)	120·3	119·1
E6	107·7, 107·1	107·4	107·2
E7	102·7, 103·0	102·8	102·5
E8	104·5, 104·6	104·6	104·2

It will be seen from Table II that the observed iodine values show good reproducibility and also accordance with the calculated figures, but that the thiocyanogen data are not so accordant in either respect. The agreement between the individual determinations is not altogether satisfactory, and the mean values are sometimes more than one unit divergent from the calculated figures for the mixtures. This is more noticeable in the acid mixtures than in the ester mixtures, both reproducibility and accordance with the calculated figures being fairly satisfactory in the latter. Further, the discrepancies only become marked when linolenic acid or ester is a component of the mixture. It may also be remarked here that we have encountered similar difficulties with different preparations of the individual linoleic and linolenic compounds; preparations, made at an early stage of the work, which had practically the same iodine values as those recorded in Table I, occasionally gave thiocyanogen values from 3 to 5 units lower than those which we have finally accepted from our later work.

It remains to compare the percentage proportions of the components of the various mixtures which we have examined as determined (*a*) from the observed thiocyanogen values of the individual components recorded in Table I, and (*b*) from the equations based on the original assumptions of Kaufmann. These figures are given in Table III.

TABLE III

PERCENTAGE PROPORTIONS OF COMPONENTS OF THE MIXTURES

(*a*) Calculated from the observed thiocyanogen values in Table I.
(*b*) Calculated from the theoretical assumptions of Kaufmann.

Ref. No.	Oleic			Linoleic			Linolenic		
	Actual	Found		Actual	Found		Actual	Found	
		(*a*)	(*b*)		(*a*)	(*b*)		(*a*)	(*b*)
				Acids					
A1	74·5	73·5	75·4	25·5	26·5	24·6	—	—	—
A2	51·5	50·1	53·7	48·5	49·9	46·3	—	—	—
A3	25·1	24·3	29·8	74·9	75·7	70·2	—	—	—
A4	50·2	47·4	39·6	—	—	—	49·8	52·6	60·4
A5	—	—	—	49·3	60·3	66·5	50·7	39·7	33·5
A6	31·3	25·9	25·2	35·7	46·5	50·7	33·0	27·5	24·1
A7	48·4	45·2	44·1	25·2	31·8	36·2	26·4	23·0	19·7
A8	24·3	20·8	21·8	50·2	57·4	58·0	25·5	21·8	20·2
				Esters					
E1	76·0	75·1	76·6	24·0	24·9	23·4	—	—	—
E2	48·0	48·2	51·4	52·0	51·8	48·6	—	—	—
E3	33·0	33·9	38·0	67·0	66·1	62·0	—	—	—
E4	49·8	50·9	40·7	—	—	—	50·2	49·1	59·3
E5	—	—	—	50·3	41·4	62·3	49·7	58·6	37·7
E6	32·4	32·2	28·2	35·7	35·8	45·2	31·9	32·0	26·6
E7	48·2	48·3	45·0	26·7	26·2	33·9	25·1	25·5	21·1
E8	24·1	24·8	22·7	50·5	49·2	54·2	25·4	26·0	23·1

DISCUSSION.—The data in Table III point to two main conclusions:

(i) Calculations based on the theoretical assumptions of addition of thiocyanogen to exactly one double bond in linoleic compounds and to exactly two double bonds in linolenic compounds lead to results which, when the proportion of linoleic or linolenic compounds in the mixtures is at all considerable, are widely at variance with the actual proportions present; whereas employment of the actual thiocyanogen values observed for the individual compounds (Table I) gives figures which in general accord closely with the actual facts.

(ii) Calculations on the latter basis, however, in some instances (A5, A6, A7, A8, E5) fail to give figures in accordance with the facts. These are, of course, the instances in which unsatisfactory agreement was noted in Table II between the observed and calculated thiocyanogen values of the mixtures. As already stated, the agreement is in general satisfactory for the ester-mixtures, although even here the method appears to begin to give erratic results when the proportion of polyethenoid material is high, or when the content of linolenic acid exceeds about 25 per cent.; or, put in another way, when the iodine value of the mixture exceeds 170.

The information in Table III establishes, however, that (apart from the instances noted in the previous paragraph) the empirically determined thiocyanogen values of the pure compounds are operative in the mixtures, and should therefore be accepted in lieu of the formerly adopted "theoretical" thiocyanogen values for linoleic and linolenic compounds. It seems unfortunate, indeed, that so arbitrary an assumption as *exact* addition at one or at two double bonds, as the case may be, should have been accepted, apparently without adequate experimental verification. Kaufmann[1] observed a thiocyanogen value of 82·5 for a glyceride

"trilinolein" of iodine value 169·1, but seems not to have recorded a thiocyanogen value for pure linolenic acid (although Kaufmann and Keller[1] (p. 74) mention a specimen of linolenic acid prepared by Rollett's method[10] with an iodine value of 268·0). Other workers have recorded for individual compounds values which are not very dissimilar from our own, as follows (Table IV):

TABLE IV

THIOCYANOGEN VALUES RECORDED FOR LINOLEIC ACID, METHYL LINOLEATE AND LINOLENIC ACID

Observers	Linoleic acid	Methyl linoleate	Linolenic acid
Kimura[11]	—	89·9	—
Waterman, Bertram and van Westen[12]	92·9	—	—
Brown and Shinowara[13]	—	—	161·0
Riemenschneider and Wheeler[8] ..	—	89·0	—
Kass, Lundberg and Burr[14]	96·3	—	171·0
Present work	95·9	91·8	162·5

The figures in Table IV all refer to compounds prepared by debromination of crystalline bromo-adducts of the respective unsaturated acids, and it is possible to argue that the thiocyanogen values of the natural acids may be different; although it is now generally accepted that the product of debromination of the crystalline tetrabromostearic acid (formerly termed "α-linoleic acid") is identical with the natural product (Brown and Frankel,[15] Riemenschneider, Wheeler and Sando,[16] Hilditch and Jasperson[17]). There is, however, evidence in the studies of Brown and his co-workers, who have prepared highly concentrated forms of linoleic and linolenic acids by processes involving only the use of crystallisation from solvents at low temperatures, that the linolenic acid of seed fats has the same thiocyanogen value as that of the acid regenerated from crystalline hexabromostearic acid. Brown and Shinowara[13] have recorded the iodine and thiocyanogen values of four highly concentrated preparations of natural linolenic acid, which they obtained by repeated low-temperature crystallisation from solvents of the fatty acids from linseed or perilla oils (Table V). It may be taken for granted that the accompanying impurity in these specimens will be confined to linoleic acid (also present in the seed fats used), and in this instance the percentages of linolenic acid present can be determined from the iodine values, and then the thiocyanogen value of the linolenic acid can be calculated after allowance for that of the linoleic acid present. We have applied these calculations to Brown and Shinowara's data for the four concentrates of linolenic acid, employing for the thiocyanogen value of linoleic acid both the value observed by us in the present work and also the previously assumed "theoretical" value of 90·7 (Table V).

TABLE V

DEDUCED THIOCYANOGEN VALUES OF LINOLENIC ACID ISOLATED BY LOW-TEMPERATURE CRYSTALLISATION (BROWN AND SHINOWARA[13])

Concentrate	Iodine value	CNS value	Linolenic acid present		
			Per Cent. (calc.)	CNS value (*a*)	(*b*)
1	258·1	150·1	82·7	161·5	162·5
2	260·0	152·6	84·8	162·8	163·8
3	262·0	154·1	86·9	162·9	163·7
4	259·0	151·3	83·7	162·1	163·1
				(Mean: 162·3	163·3)

(*a*) Linoleic acid CNS value taken as 95·9.
(*b*) " " " " " " 90·7.

The calculated thiocyanogen value for natural linolenic acid is thus very close to that observed for the regenerated "α-linolenic acid" by Brown and Shinowara[13] (161·0) and by ourselves (162·5); Kimura[11] recorded that methyl linolenate (iod. val., found 258·6; calc. 261·9) showed a thiocyanogen value of 152·0, corresponding with 159·6 for the acid, whilst our value for ethyl linolenate (146·6) corresponds with 161·4 for the acid. It is evident from all these data that the actual thiocyanogen value of linolenic acid, natural or regenerated, is close to 162 and much lower than the figure of 182·7 which has hitherto been employed.

TABLE VI

ALTERATIONS IN OLEIC, LINOLEIC AND LINOLENIC ACID PERCENTAGES OF CERTAIN FATS BY THE ADOPTION OF THE REVISED THIOCYANOGEN VALUES FOR LINOLEIC AND LINOLENIC ACIDS

Fat	Observers	Fatty acid percentages calculated with CNS values: Linoleic 90·7, Linolenic 182·7			Linoleic 95·9, Linolenic 162·5		
		Oleic Per Cent.	Linoleic Per Cent.	Linolenic Per Cent.	Oleic Per Cent.	Linoleic Per Cent.	Linolenic Per Cent.
Linseed—							
Calcutta	Kaufmann and Keller[1]	12·5	34·1	42·1	14·3	29·2	45·2
La Plata	" "	8·0	46·7	36·3	16·1	30·9	44·0
" "	Griffiths and Hilditch[7]	9·6	42·6	38·1	18·8	24·2	47·3
Perilla	Kaufmann[18]	3·9	44·3	44·2	13·7	16·0	62·7
"	"	10·7	33·6	49·0	23·0	0·1	70·2
Stillingia seed—							
Chinese	Jamieson and McKinney[19]	11·1	52·8	26·8	15·8	45·5	29·4
American	" "	8·1	59·4	25·9	11·9	53·1	28·4
Candlenut	Jamieson and McKinney[20]	27·7	41·7	21·7	29·4	40·0	21·7
Wallflower seed	van Loon[21]	5·2	26·1	20·5	7·7	21·3	22·8
" "	Griffiths and Hilditch[7]	8·1	35·2	14·2	10·0	31·5	16·0
Hempseed	Kaufmann and Juschkewitsch[22]	12·6	53·0	24·3	16·0	45·8	28·1
"	Griffiths and Hilditch[7]	6·7	68·8	15·9	6·2	69·9	15·3
Walnut	Jamieson and McKinney[23]	36·4	50·0	7·7	34·7	56·7	2·7
"	Ueno and Nishikawa[24]	12·2	69·3	7·7	8·8	76·0	4·4
"	Griffiths and Hilditch[7]	19·1	65·9	6·9	15·6	72·6	3·6
Soya-bean	" "	26·1	54·7	5·8	23·3	60·3	3·0
"	Hilditch and Jasperson[25]	28·5	51·3	5·6	26·9	58·0	2·0
Grape-seed	Jamieson and McKinney[26]	33·8	54·6	2·4	30·8	60·0	—

Kass, Lundberg and Burr[14] have recently published work on similar lines to the present investigation in which they reach the conclusions that "the true thiocyanogen value of linoleic acid and the optimum conditions for determining it call for further consideration," and that "there can be little doubt that the thiocyanogen value of linoleic acid is an empirical value . . . which is appreciably higher than required by theory for half-saturation." They state, pending the result of further work*, that a preliminary investigation of a linolenic acid with iodine value 270·5 gave thiocyanogen values of 171 (24 hours' contact) and 175·6 (48 hours' contact); these figures, however, are higher than any of those to which we have just made reference. Kass *et al.* suggest the substitution of the empirical values for the hitherto accepted ones in the calculation of the proportions of unsaturated acids in fats.

* In a subsequent paper (*Oil and Soap*, 1940, **17**, 118), published while the present communication was in the press, Kass, Loeb, Norris and Burr report the thiocyanogen value of "α-linoleic acid" to be **167·3**, and formulate conclusions in close general agreement with those here put forward.

In the light of what has been pointed out in the present discussion, we are emphatically of the same opinion, provided that satisfactory agreement can be reached as to the true empirical thiocyanogen values of the two acids under accepted and rigidly standardised conditions of determination. The comparatively small difference between the observed and hitherto accepted thiocyanogen values of linoleic acid has a correspondingly small and perhaps not too serious effect on the calculated proportions of that acid in fats from which linolenic acid is absent (or present only in very small amounts). But the matter is widely different with fats of which linolenic acid is a major component—for which fats, as we have already pointed out, thiocyanometric analysis is most necessary and valuable. Here, the substantial difference in the values adopted for linolenic acid frequently has the result of altering in the same direction by several units per cent. both the percentages of oleic and linolenic acid, with a corresponding doubled effect in the opposite direction on the percentage of linoleic acid. In illustration of this point, we have collected in Table VI the results of typical analyses, as given by various workers, on some of the more unsaturated fatty oils in terms of the hitherto accepted thiocyanogen values of linoleic (90·7) and linolenic (182·7) acids, and have added thereto revised calculations based on our observed values of, respectively, 95·9 and 162·5. This table is for the time being merely illustrative; we consider that general agreement as to the values to be adopted must precede any final authoritative revision of previously published data.

SUMMARY.—The iodine and thiocyanogen values of carefully purified oleic, linoleic and linolenic acids, methyl oleate, methyl linoleate and ethyl linolenate have been determined. The thiocyanogen values (0·2 *N* reagent, 24 hours' contact, 150–200 per cent. excess) of linoleic and linolenic acids are respectively 95·9 and 162·5, corresponding values being observed for the respective esters. Both values differ from those originally postulated by Kaufmann[1] (respectively 90·7 and 182·7); the present results, especially for linolenic acid, accord well with recent data published by other workers.

Examination of binary and ternary mixtures of the pure acids or the pure esters shows that the observed values hold for the examination of mixtures of the compounds, subject to possible discrepancies when the unsaturation is high (iodine value above 170), especially with mixtures of the three acids.

It is recommended that agreed empirically determined values obtained under carefully prescribed conditions should replace the hitherto-accepted "theoretical" thiocyanogen values of linoleic and linolenic compounds; but that extensive revision of already published data should be deferred until general agreement has been reached as to the precise values and the conditions of determination.

Meantime, data obtained by thiocyanometric analysis for the component acids of fats which contain high proportions of linolenic and linoleic acids must be regarded as uncertain. Instances of the variations involved are quoted for a number of the more important liquid fats.

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DEPARTMENT OF INDUSTRIAL CHEMISTRY
THE UNIVERSITY, LIVERPOOL

May 23rd, 1940

The Determination of Aluminium, Magnesium or Beryllium in Nickel Alloys

(*Communication from the Staff of the Research Laboratories of The General Electric Company, Limited, Wembley, England*)

BY R. C. CHIRNSIDE, F.I.C., L. A. DAUNCEY, B.SC., AND P. M. C. PROFFITT

(*Read at the Meeting, April 3rd*, 1940)

IT is the purpose of this paper to describe the results of an investigation into the most suitable methods of analysis for certain alloys used in the manufacture of radio valves and other thermionic devices. Nickel is the metal most commonly used for the electrodes, and it is well known that impurities in the nickel have a considerable effect on the thermionic properties. The addition of certain reducing elements, for example, has been found beneficial and an alloy containing 2 per cent. of aluminium has been employed.

A note on a method for the determination of the aluminium has previously been published by one of us.[1] Briefly, that method consisted in pouring a solution of the nickel alloy, to which potassium cyanide had been added in excess to form the soluble nickelocyanide, into a dilute ammonia solution, the precipitated aluminium hydroxide being filtered off, ignited and weighed.

The method proved generally satisfactory, and it was later adapted, with suitable modification, to the determination of magnesium in nickel-magnesium alloys of which the magnesium-content was of the order of 0·3 per cent. However, difficulties were sometimes encountered in the analysis of the aluminium alloys, and doubts arose as to the accuracy of the results obtained. Continued experience of the method, particularly with alloys containing only 0·4 per cent. of aluminium, confirmed the doubts as to its accuracy. One serious difficulty was the occasional co-precipitation, with the aluminium hydroxide, of a flocculent brown organic nickel compound, but erratic results were sometimes obtained even in absence of the brown precipitate.

The factors that were thought to contribute to the variability of the results included the formation of alkali by hydrolysis of the cyanide with consequent solution of aluminium hydroxide, the time of standing before filtration, and the temperature of the solution. The greater variability of the results obtained on

the alloy containing 0·4 per cent. of aluminium was consistent with the relatively smaller amount of aluminium hydroxide involved in this instance. Several synthetic solutions were prepared to represent alloys containing 0·4 per cent. and 2 per cent. of aluminium, and the aluminium-content was determined by the cyanide method embodying various modifications designed to explore the effects of the various factors mentioned above. Some of the results obtained are given in Table I, and it will be seen that none of the variations made in the method resulted in an accurate determination of the aluminium-content of a solution representing the 0·4 per cent. alloy. The experiments are not described in detail, as the method was subsequently abandoned.

In further experiments on synthetic solutions the aluminium was precipitated directly with ammonia and ammonium chloride. A considerable excess of ammonia was required to form the soluble nickel complex, and this entailed a risk of losing aluminium hydroxide by solution. On the other hand, the precipitate was invariably contaminated with nickel, so that the accuracy of the final result depended on a fortuitous compensation of errors. Some results obtained by the use of this method are included in Table I.

TABLE I

ALUMINIUM IN SYNTHETIC SOLUTIONS

No.	Nickel added g.	Aluminium added mg.	Aluminium added per cent.	Aluminium found mg.	Aluminium found per cent.	Remarks
Cyanide method						
1	2·0	8·26	0·41	10·8	0·54	
2	2·0	7·96	0·40	5·5	0·28	
3	2·0	8·86	0·44	11·0	0·55	
4	2·0	8·63	0·43	10·5	0·53	
5	2·0	8·52	0·43	14·3	0·72	
6	2·0	40·0	2·00	42·6	2·13	
7	2·0	40·0	2·00	41·4	2·07	
Pptn. with ammonia						
8	2·0	8·48	0·42	11·4	0·57	One pptn.
9	2·0	8·70	0·44	8·8	0·44	One pptn.
10	2·0	8·52	0·43	8·5	0·43	Three pptns. Ppt. contained 0·05 mg. of NiO.
11	2·0	8·66	0·43	9·7	0·49	Three pptns. Ppt. contained 0·5 mg. of NiO.

Further experiments were carried out on samples of nickel-aluminium alloy with nominal 0·4 per cent. and 2·0 per cent. aluminium-contents. The aluminium was determined by the cyanide method, by precipitation with barium carbonate, by precipitation with sodium succinate, and by precipitation with ammonia after removal of the nickel by electrolysis. The last-named method proved to be most suitable and has been adopted for our work, but for purposes of comparison the results obtained by all the methods mentioned are given in Table II.

TABLE II

ALUMINIUM IN NICKEL-ALUMINIUM ALLOYS

No.	Aluminium found, per cent. Cyanide	Barium carbonate	Sodium succinate	Electrolysis
63	0·31, 0·27, 0·40	0·34	—	—
66	0·34, 0·38, 0·41, 0·41	0·45	—	0·40, 0·42
67	0·32, 0·32, 0·37, 0·41 0·34, 0·31, 0·72, 0·39 0·30, 0·40	0·35	—	0·34, 0·33
86	—	0·42, 0·38	0·38	0·35, 0·35
88	—	—	0·37, 0·38, 0·38	0·37, 0·37
87	—	—	—	1·91, 1·92

The results obtained with the electrolytic method were so encouraging that it was decided to examine the method in more detail, and for this purpose further experiments were carried out with synthetic solutions.

ELECTROLYSIS WITH A MERCURY CATHODE.—(i) *Preliminary Experiments on Synthetic Solutions.*—Fifty g. of Mond nickel pellets were dissolved in 400 ml. of nitric acid (1 : 1). The solution was filtered and made up to 500 ml., so that 20 ml. contained the equivalent of 2 g. of nickel. Weighed amounts of pure aluminium ribbon, to represent the 0·4 per cent. and 2·0 per cent. alloys, were dissolved in freshly-prepared sodium hydroxide solution and added to 20-ml. portions of the nickel solution.

The mixtures were evaporated to fuming with sulphuric acid, and the electrolysis and subsequent precipitation of the aluminium with ammonia were carried out as described under the heading "experimental procedure." A blank determination on 20 ml. of nickel solution yielded 0·6 mg. This was most probably derived from the reagents, glassware and filter-paper (*cf.* Etheridge, ANALYST, 1929, **54**, 142). The results, corrected for the blank, are given in Table III.

TABLE III

No.	Nickel added	Aluminium added		Aluminium found	
	g.	mg.	per cent.	mg.	per cent.
1	2·0	8·7	0·44	8·8	0·44
2	2·0	8·8	0·44	8·8	0·44
3	2·0	40·5	2·03	40·6	2·03
4	2·0	39·5	1·98	39·7	1·98

These experiments showed that the results obtained by the electrolysis of alloys and recorded in Table II were accurate as well as precise. It was therefore decided to develop a method for the routine determination of aluminium in nickel alloys by means of electrolysis over a mercury cathode.

(ii) *Development of the Method.*—Wolcott Gibbs[2] in 1883 first suggested the use of mercury as a negative electrode in electrolysis, and E. F. Smith[3] later suggested many applications of the process. Cain,[4] Lundell, Hoffman and Bright,[5] and Etheridge[6] have employed the method for the separation of vanadium from steel, and Brophy[7] and Etheridge[8] have used the method for the separation of aluminium from nickel-chromium alloys and steel respectively. B. S. Evans[9] has described an apparatus employing a moving mercury cathode, designed to overcome most of the disadvantages associated with this method of analysis.

In the method as originally conceived by Gibbs the metals deposited in the mercury were determined, but so many elements may be deposited that the method came to be used chiefly for the removal of interfering elements from solution. Lundell and Hoffman[10] give a table showing the elements quantitatively deposited in the mercury cathode, those which are quantitatively separated from the electrolyte but are not quantitatively deposited in the mercury, and those which are incompletely separated. Of the commoner elements, chromium, iron, cobalt, nickel, copper, zinc, cadmium, silver, tin and bismuth can be quantitatively separated from aluminium, magnesium, beryllium, titanium, zirconium and vanadium.

Manganese is said to be incompletely deposited in the mercury and on the anode. That this valuable and elegant method has found comparatively little use in analysis is due, in our opinion, to the belief that complicated and expensive apparatus is necessary. In devising an apparatus for our particular problem the main consideration were that it should be as simple as possible, and that a number of cells could be used at one time. In particular, the minimum number of parts was to be exclusive to this test, and special electrolysis stands, vessels and stirring devices were to be avoided if possible.

An electrode arrangement was constructed as in Fig. 1. A platinum anode was sealed into a glass tube, connection being made to it by means of a wire dipping into a small amount of mercury in the bottom of the tube. A short loop of stout platinum wire was sealed into a somewhat longer glass tube and a similar connection made to it. The two tubes were fastened by means of an elastic band to a grooved separator formed from a cork. The assembly was stood in a 250-ml. beaker, so that the loop rested on the bottom and near the side, and the lowest part of the anode was about 2 cm. from the bottom. The loop, which formed the connection to the cathode, was so shaped that it could be covered completely by 10 ml. of mercury in the bottom of the beaker. When the tubes rested in the lip of the beaker an ordinary watch-glass provided adequate protection against loss by spraying.

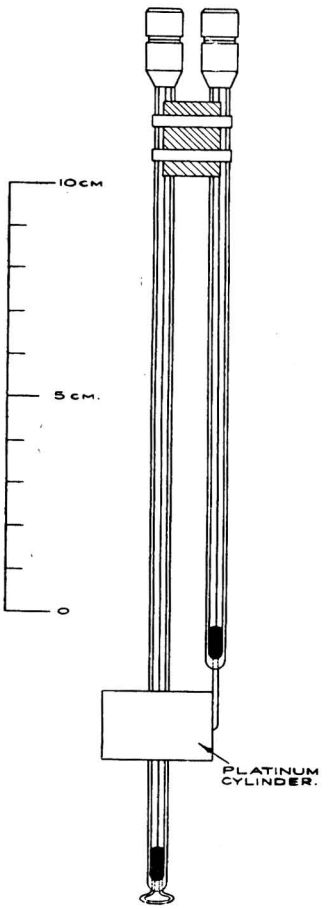

Fig. 1

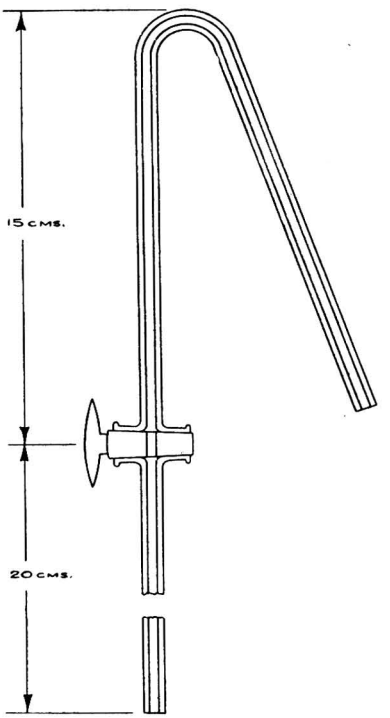

Fig. 2

The anode consisted of a cylinder made from platinum sheet, about 0·1 mm. thick, welded to a stout platinum wire lead. The cylinder, whose total surface area was approximately 30 sq.cm., was arranged to surround the lead to the cathode. The exact design of the anode is not important, and use could no doubt be made of other platinum ware which might be available. Carbon was tried in place of platinum for the anode, but the rods quickly disintegrated.

The only other special part of the apparatus was a siphon tube (Fig. 2), made of heavy-wall barometer tubing of 3 mm. bore and fitted with a capillary tap. The narrow bore of the tube, while not unduly restricting the flow, enabled a stable column of liquid to be maintained in the tube, even when the tap was closed, and the wide flat end of the tube made it possible for the liquid to be removed without any mercury being carried over.

The apparatus was arranged so that a number of electrolytic cells could be wired in series with a resistance to the 120-volt D.C. mains. There was a fall of 6–6·5 volts across each cell when a current of 8 amperes was flowing. No stirring arrangement was used, as the evolution of gas from the electrodes produced considerable agitation of the solution. Adjustment of the acidity of the solution during electrolysis was found to be unnecessary. At first the solutions were cooled during electrolysis, but it was found that if cooling was omitted the time for removal of 2 g. of nickel was reduced from 4 hours to about 1½ hours, and in the final procedure the time was further reduced to 1¼ hours by heating the solution to boiling prior to the electrolysis. The heat developed in the process maintained a temperature of about 90° C. when a current of 8 amperes was used. Another result of the heating was that no trace of nickel could be detected in the electrolyte after 1¼ hours, whereas complete removal of nickel was not achieved in 4 hours when cooling was employed.

A further reduction in the time of electrolysis from 1¼ hours to ¾ hour may be obtained by reducing the volume of the electrolyte to 60 ml. The electrolyte is then contained in a 100-ml. beaker and the amount of sulphuric acid is suitably reduced. Details of the procedure finally adopted are as follows:

Experimental Procedure.—Two g. of the sample are dissolved in 15 ml. of nitric acid (1 : 1). The solution is cooled, 10 ml. of conc. sulphuric acid are added, the solution is evaporated until fumes of sulphuric anhydride appear, and is then heated for a further 10 minutes. The solution is allowed to cool, 50 ml. of water are added, and the liquid is boiled gently until all soluble sulphates dissolve. The hot solution is filtered into a 250-ml. beaker, the paper and any silica being washed with hot water. Cold freshly-prepared sodium hydroxide solution (20 per cent.) is added to the filtrate until a permanent turbidity is produced. The turbidity is cleared by the addition of dilute sulphuric acid, and the solution is finally acidified with 1 ml. of sulphuric acid (1 : 1) and made up to a volume of about 150 ml. It is then heated to boiling, 10 ml. of clean mercury are poured in, the electrodes and cover-glass are placed in position, and a direct current of 8 amperes is passed through the solution for 75 minutes. The electrolyte is then run off through the siphon tube into a 400-ml. beaker. The electrodes and the sides of the beaker are washed down with water, the washings being added to the main solution before the circuit is broken. Three washes of about 15 ml. each are sufficient to remove the last traces of electrolyte. Any mercury which may be carried over accidentally should be filtered off before proceeding.

Two g. of ammonium chloride are added to the solution, which is then heated nearly to boiling. A few drops of methyl red solution are added and ammonia solution is added carefully until the yellow colour of the indicator appears. The solution is then boiled for not more than 1 minute (*cf.* Blum, *J. Amer. Chem. Soc.*, 1916, **38**, 1282), a little filter-paper pulp is stirred in, and the precipitate is collected on a Whatman No. 41 or equivalent paper. The precipitate is washed three times with hot ammonium nitrate solution (2 per cent.), and the paper and precipitate are returned to the beaker. Five ml. of hydrochloric acid are added, and the beaker is warmed on a water-bath for 5 minutes. One hundred ml. of hot water are added, and the aluminium is re-precipitated, the same procedure being used. When the aluminium-content of the sample exceeds 1 per cent., the second filtration may be carried out on a small Buchner funnel. The precipitate is washed 6 times with hot ammonium nitrate solution, dried and burnt off in a weighed platinum

crucible, with final ignition at 1200° C. for 30 minutes. The crucible is allowed to cool in a sulphuric acid desiccator, and the ignited precipitate is weighed rapidly as Al_2O_3.

EXTENSION OF THE METHOD TO OTHER ALLOYS.—(i) *Nickel-aluminium "king" alloy.*—A "king" alloy containing approximately 50 per cent. of aluminium was analysed by the same process. The results are given in Table IV.

(ii) *Nickel-magnesium.*—The method has been applied to the determination of magnesium in nickel-magnesium alloys, nominally containing 0·3 per cent. of magnesium. The alloy (3·0 g.) is dissolved in 20 ml. of nitric acid (1 : 1), the solution is evaporated to fuming with 10 ml. of sulphuric acid, and the same procedure is followed as that used in the removal of nickel from the nickel-aluminium alloys. The magnesium is then precipitated as magnesium ammonium phosphate, ignited, and weighed as $Mg_2P_2O_7$.

Synthetic solutions containing 2 g. of nickel with 0·29 per cent. of added magnesium were analysed by this procedure. In three determinations the results were 0·30, 0·28 and 0·29 per cent. of magnesium respectively. In the last two instances the magnesium ammonium phosphate was re-precipitated, but the results suggest that normally this should not be necessary.

A "king" alloy containing about 18 per cent. of magnesium was analysed by the same method. Some results are given in Table IV.

(iii) *Nickel-beryllium alloy.*—A nickel beryllium alloy containing approximately 0·5 per cent. of beryllium was analysed by the electrolytic method.

1·5 g. of the alloy were dissolved in nitric acid, and after evaporation with sulphuric acid the nickel was removed by electrolysis. The beryllium in the electrolyte was then precipitated by the addition of ammonia solution in slight excess, litmus being used as the indicator. The precipitate was filtered, washed with ammonium nitrate solution, ignited and weighed as BeO. The results of duplicate determinations are given in Table IV.

TABLE IV

Weight taken	Found		Time of electrolysis,
g.	g.	Per Cent.	minutes
Ni–Al	Al_2O_3	Al	
0·3	0·3046	$53·7_5$	30
0·3	0·3053	$53·8_6$	30
Ni–Mg	$Mg_2P_2O_7$	Mg	
3·0	0·0401	0·30 (0·29*)	100
0·5	0·4241	18·52 (18·45*)	25
Ni–Be	BeO	Be	
1·50	0·0244	0·59	60
1·51	0·0243	0·58	60

* By cyanide method.

Effect of Manganese.—The nickel alloys under consideration contained no manganese, but, as the literature suggested that this element might be incompletely separated, an experiment was made to investigate this point. Manganese sulphate, in amount equivalent to 0·1 per cent. of manganese, was added to 2 g. of a nickel-aluminium alloy, the aluminium-content of which had been previously found to be 0·42 per cent. The solution was electrolysed, and the aluminium was determined in the usual way. The result was again 0·42 per cent., and the ignited precipitate of Al_2O_3 was perfectly white. The nickel-mercury amalgam was shaken for a few minutes with 30 ml. of nitric acid (sp.gr. 1·135), and the dissolved manganese was determined by the bismuthate method. Sixty-five per cent. of the added manganese was recovered, and, as only a small amount of the nickel dissolved in this treatment, it is presumed that the remainder of the manganese would have been recovered by further extraction of the mercury.

No manganese was noticed on the anode, and it would seem that no interference is to be expected from quantities of this order.

SUMMARY.—An investigation has been made into methods for the determination of aluminium in nickel-aluminium alloys.

The following methods have been compared:

Precipitation with:—(i) Ammonia in presence of potassium cyanide; (ii) ammonia and ammonium chloride; (iii) barium carbonate; (iv) sodium succinate; (v) ammonia after the removal of the nickel by electrolysis over a mercury cathode.

The last method has been found to be most satisfactory, and has been applied to nickel-aluminium alloys containing from 0·3 to 50 per cent. of aluminium.

The method has been found suitable also for the determination of magnesium and beryllium in nickel-magnesium and nickel-beryllium alloys.

A simple form of apparatus for the electrolysis is described.

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RESEARCH LABORATORIES OF
THE GENERAL ELECTRIC COMPANY LIMITED,
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DISCUSSION

Mr. C. E. BARRS recalled a useful paper by Withey (cf. ANALYST, 1916, **41**, 181) on the determination of various impurities in aluminium. In that method, use was made of the fact that tartaric acid would prevent the precipitation of aluminium by ammonium sulphide, whilst zinc and nickel were precipitated quantitatively. An important point in the present paper was that the alumina was very strongly ignited; it was essential to do that to obtain a satisfactory final weight.

Mr. SAXBY asked if the method could be applied to alloys used in magnet steel. Had Mr. Chirnside any method of differentiating between metal and oxide?

Mr. PINDER asked if the authors had tried the colorimetric method for these alloys; also, had oxine titration been tried?

Dr. B. S. EVANS, in a written communication, suggested that the separation of manganese described by the authors might have been a "fluke," as there was a definite back reaction. Manganese was incompletely deposited in all forms of apparatus other than that described by him in THE ANALYST. In his apparatus the separation was complete because the circulating cathode mercury was continuously treated to remove the deposited manganese. Deposition on the anode was a question of anode density and could be avoided by having that high enough. He suspected that, in the authors' experiments, the excess manganese remained in the solution and was not carried down to any extent with the alumina; it was not, if oxidation could be avoided. Etheridge had found only traces of manganese in the alumina, and determined them colorimetrically. Was this done in the authors' experiments? Referring to the determination of magnesium, he thought that it was dangerous advice to eliminate re-precipitation of the magnesium ammonium phosphate. He would refer the authors to Epperson's work, described in the *J. Amer. Chem. Soc.* in 1928 (Abst. ANALYST, 1928, **53**, 239).

Mr. CHIRNSIDE, replying, said that the ignition of aluminium oxide, to which Mr. Barrs had referred, was an important point. Above 1000° C. the conversion of γ to α alumina took place, and at 1200° C. was complete in a comparatively short time. The change to the α form not only ensured the complete expulsion of moisture but also resulted in a non-hygroscopic form of oxide for the final weighing. Mr. Saxby had mentioned magnet steels. The use of alloys containing aluminium for this purpose was growing, and he thought the method might be applicable to these alloys. The differentiation between aluminium present as metal and as oxide was an important point, and an investigation was being made on alloys to which known amounts of alumina had been

added. In reply to Mr. Pinder, the quantities of aluminium under consideration were considered to be above the normal range of the colorimetric determinations. Separations of nickel and aluminium by means of oxine had been tried but they had met with little success. In the case of nickel-magnesium alloys, having separated the nickel, he believed it would be satisfactory to determine the magnesium by means of oxine.

Written reply to Dr. Evans.—Dr. Evans very kindly read through the MS. of this paper and questioned whether the apparatus separated manganese. The nickel alloys did not contain manganese but the work described in the section on manganese was subsequently carried out for its general interest. All that was claimed as a result of these experiments was that no interference was found from manganese of the order of 0·1 per cent. The authors were well aware, from an extensive experience of silicate analysis, that manganese in small amount was not co-precipitated with aluminium hydroxide; the alumina precipitate in the experiment described was not tested for manganese. No manganese was deposited on the anode; some of it might have remained in solution, but it was possible that the conditions obtaining in the apparatus, though not required to effect the separation of manganese, might yet have done so.

They had tried to determine aluminium in nichrome some years ago, using Dr. Evans's apparatus. In his paper (ANALYST, 1930, **60**, 393) Dr. Evans admitted that he had not satisfactorily solved the problem of the composition of purifying solutions for the mercury (except in the case of manganese) and their failure to do so led to the abandonment of his method. The composition of the solution for extracting manganese was not given.

They were aware of Miss Epperson's work, and it was their usual practice to make two precipitations. However, they considered that the accuracy obtainable with one precipitation justified the suggestion made. Since the paper was written a number of gravimetric determinations involving the use of oxine had been made. In general, the results were a little higher than those obtained by the use of phosphate. This was a further reply to Mr. Saxby's question concerning the use of oxine.

Antimony in Tin-Antimony Oxides

BY A. G. DUNBAR-POOLE

IN the investigation of the problem of the gravimetric determination of tin in brasses and bronzes,[1] it was found that when the procedure described was followed the final product consisted of the mixed oxides of tin and antimony present in the alloy.

The presence of antimony and, to some extent, its proportion in this mixture is indicated by the colour of the ignited mixed oxides. A precipitate in which the antimony-content is as little as one twenty-fifth of the tin present will give a definite pale blue colour. The intensity of this colour increases with rise in the proportion of antimony to tin, until when the tin/antimony ratio is about 1 : 10 the ignited mixture is bluish-black.

The ignited precipitate of tin and antimony oxides is practically insoluble in all single acids or mixtures of acids, and to determine the amount of antimony present it was found necessary to fuse the precipitate with caustic soda or Rose's mixture, to extract the melt and to precipitate the antimony as sodium antimonate, or to reduce it, in acidified solution, to the tervalent condition and determine it volumetrically.

Further experiments with this ignited precipitate have shown that it is possible to dissolve it by heating it in conc. sulphuric acid with addition of sodium thiosulphate. The antimony in the resulting solution will be in the tervalent condition and may be determined volumetrically by re-oxidation to the quinquevalent state—according to the method of Low.[2] The details of the procedure are as follows:

METHOD.—The ignited precipitate is transferred to a 400-ml. tall beaker, about 5 g. of sodium thiosulphate are added, and the mixture is heated on a hot plate until all the water of crystallisation has been expelled from the thiosulphate. During this process, when the salt is liquid, the beaker is rotated, so that intimate admixture of the oxides with the thiosulphate is effected. The beaker is then removed from the hot plate, 15 ml. of sulphuric acid (sp.gr. 1·84) are added, and

the beaker is replaced on the plate and heated until solution of oxides is complete. Heating for 20 to 30 minutes is generally sufficient to effect decomposition. The beaker is then removed and cooled, 100 ml. of cold water and 15 ml. of hydrochloric acid (sp.gr. 1·18) are added, and the whole is boiled for five minutes, after which 100 ml. of cold water are added and the solution is cooled by immersing the beaker in running tap-water.

When quite cold, the solution is titrated with $N/20$ potassium permanganate solution to a faint permanent tinge of pink (1 ml. $N/20$ $KMnO_4 \equiv$ 0·00305 g. of Sb.).

COMPOSITION OF TIN-ANTIMONY OXIDES.—Experiments were made to ascertain the nature of these ignited tin-antimony oxides. An alloy of tin and antimony was made by melting together, under charcoal, "Chempur" tin and pure antimony. The ratio of tin to antimony was roughly 10 : 1. The antimony-content of the finely-rasped alloy was found by repeated direct volumetric determination, by the method of Low[2], and by analysis of the sulphides obtained from a solution of the alloy in *aqua regia*. The results ranged from 9·10 to 9·18 per cent.; mean, 9·15 per cent.

A one-gram portion of the alloy was digested in boiling nitric acid (sp.gr. 1·42), water was added, and the precipitate was allowed to settle, collected on an "ashless" filter-paper, washed with dilute nitric acid, and ignited in an electrically-heated muffle furnace. No trace of tin or antimony could be detected in the filtrate.

The precipitate was ignited in successive stages of two hours each by advancing the crucible to hotter portions of the muffle, free access of air being allowed. The weights recorded were as follows:—After ignition at 400° C., 1·2850 g.; at 510° C., 1·2832 g.; at 700° C., 1·2815 g.; at 750° C., 1·2810 g.; at 800° C., 1·2810 g.

A further portion of the alloy was dissolved in *aqua regia*, the solution was rendered ammoniacal and then made acid with hydrochloric acid, and the sulphides of tin and antimony were precipitated with hydrogen sulphide gas. The sulphides were filtered off, washed, and ignited to oxides, which were finally roasted at about 750° C. The weight of oxides obtained was 1·280 g. per g. of the alloy, which is equivalent to 1·153 g. of SnO_2, calculated on the basis of 90·85 per cent. in the alloy. This amount of tin oxide, deducted from the weight of ignited mixed oxides obtained, *viz.* 1·281 g. per g. of the alloy, leaves 0·128 g. for the antimony oxide compound. As the amount of antimony present (see above) was 0·0915 g. in 1 g. of the alloy, a factor of 1·40 is required to convert this amount into 0·128 g. of antimony-oxide compound.

This factor is found to agree with that required to convert Sb_2 into $Sb_2O_5.H_2O$. (If the most recently published atomic weights are used, the factor is 1·4023.)

Conversely, if the antimony exists in the ignited mixed oxides as $Sb_2O_5.H_2O$, the factor for conversion to Sb_2 being 0·7131, a figure of 9·13 per cent. of antimony is arrived at, which is in agreement with the amount (9·15 per cent.) found.

If the antimony in the ignited oxides was present as Sb_2O_5, the factor for conversion into Sb_2 would be 0·7527 and would give a figure of 9·64 per cent. for the antimony content.

It is, seemingly, the opinion of many workers and authors that the antimony exists as Sb_2O_4. In a very recent publication (W. W. Scott's *Standard Methods of Chemical Analysis*, 1939), the A.S.T.M. Methods of Chemical Analysis of Metals are given, and in Vol. II, p. 1357, Note 4, it is stated that: "In alloys containing an appreciable amount of antimony and in the presence of a large excess of tin, the antimony as determined by the method given under 'Analysis of Bronze Bearing Metal' should be calculated to Sb_2O_4 and a corresponding amount deducted from the weight of the ignited SnO_2 before calculating to tin."

In the present instance, if the antimony existed in the ignited mixed oxides as Sb_2O_4 (the factor for converting Sb_2O_4 to Sb_2 being 0·7919) the figure for antimony would be 10·14 per cent., or 1 per cent. more than is known to be present.

Still further proof was sought by analysing 0·5 g. of a gun-metal alloy, the

tin-content of which was 10·25 per cent. and in which the absence of antimony had been proved. To this 0·0110 g. of pure antimony metal was added, both were dissolved in *aqua regia*, and the exact procedure given for the determination of tin in bronzes and brasses[1] was followed.

The final precipitate of tin and antimony was ignited at about 800° C., and when constant weighed 0·0805 g. Conversion of the antimony present into $Sb_2O_5.H_2O$ gives 0·01545 g. and leaves 0·06505 g. for SnO_2, which corresponds with 10·24 per cent. of tin.

The fact that these ignited mixed oxides are coloured tends to show that a definite compound is formed. Tin, in the form of metastannic acid or stannic sulphide, gives on ignition a white or grey-white oxide, SnO_2. Antimony sulphide can be oxidised with nitric acid and ignited to give white Sb_2O_4.

I prepared pure SnO_2 and pure Sb_2O_4, ground these white oxides together in a mortar and re-ignited the mixture at about 800° C. for several hours, but no change in colour or weight was observed at the end of this period.

The conclusions are that when antimony is precipitated with metastannic acid and the precipitate is ignited, or, when the mixed sulphides of tin and antimony are ignited, the tin being in large excess, it would appear that the antimony exists in the form of a compound having the empirical formula $SnO_2.Sb_2O_5.H_2O$; that is, an antimoniate of tin which retains 1 mol. of water at temperatures between 700° and 800° C.

Even at temperatures higher than 800° C. there seems to be no further loss in weight of the compound. It was not possible, however, to attain in the electrically-heated muffle furnace used in these experiments a temperature higher than about 800° C. Stress must be laid on the desirability of having free access of air during ignition of this compound, especially when a gas-heated muffle is used.

I wish to thank the Director of Scientific Research of the Admiralty for permission to publish this paper.

REFERENCES

1. A. G. Dunbar-Poole, ANALYST, 1939, **64**, 870.
2. A. H. Low, *J. Amer. Chem. Soc.*, 1907, **29**, 66; Abst., ANALYST, 1907, **32**, 101.

January, 1940

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.

SUCCINIC ACID IN BEER

ON examining a range of beers from a number of breweries, by alkalising 250 ml., evaporating to about 50 ml., acidifying, extracting with 250 ml. of ether and evaporating the extract, crystals appeared in three of these residues, which it was thought might be an unusual preservative. Larger quantities of the samples were extracted continuously with ether for 10 hours. The brownish extract contained masses of dark brown needles in small rosettes or clusters, the crystal form being quite distinct from those characteristc of salicylic or benzoic acid. The crystals were purified by recrystallisation from ether and washing with chloroform. They were then acidic, very soluble in water, less soluble in ether, and insoluble in chloroform, and melted at 183° C., which melting-point was not depressed on admixture with pure succinic acid. It was therefore concluded that the substance was succinic acid.

All the samples from which visible crystals separated were examined and found to contain succinic acid in amounts of the order of 0·002 to 0·008 per cent. w/v. It is to be expected that all beer contains succinic acid, but only occasionally is the amount sufficient to give visible crystals in an ethereal extract.

R. L. ANDREW
L. G. NEUBAUER

DOMINION LABORATORY
DEPT. OF SCIENTIFIC AND INDUSTRIAL RESEARCH
WELLINGTON, NEW ZEALAND

March 21st, 1940

A NEW METHOD FOR THE DETERMINATION OF FREE ACID IN SULPHATE OF ALUMINA, ALUM CAKE, ETC.

I HAVE pointed out (*Paper-maker*, 1940, **99**, 14; *Special Export Number*) defects of existing methods for this determination and have shown that a rapid method of sufficient accuracy for industrial purposes can be based on the detection of high acidity in an aqueous solution of the sample by means of an indicator solution and subsequent titration with standard alkali back to the "neutral" point, provided that a suitable indicator be found.

Before such a method can be evolved it is necessary *inter alia* to establish a standard of "neutrality." Owing to crystallisation difficulties, it appears to be extremely difficult to obtain supplies of sulphate of alumina of the exact composition $Al_2(SO_4)_3.18H_2O$. On the other hand, pure potash alum of the definite composition $K_2SO_4.Al_2(SO_4)_3.24H_2O$ is easily obtainable, and I have shown that a solution of that salt, having the same $Al_2(SO_4)_3$ content as the required aluminium sulphate solution will have the same *p*H value. A solution of potash alum of equal $Al_2(SO_4)_3$ content is therefore used as a standard of "neutrality."

The most convenient strengths for the solution of the sample and the standard alkali are selected so as to avoid dilution sufficient in itself to cause *p*H changes or, on the other hand, concentrations high enough to cause temporary local precipitation of alumina.

The most convenient strength for the solution of the sample requires a "neutral" point of *p*H 3·5 to be covered by the indicator. As no suitable single indicator is available, a mixture of methyl orange and Martius yellow is used to cover the end-point. The indicator solution is prepared by grinding together 0·025 g. of methyl orange and 0·050 g. of Martius yellow with 50 per cent. industrial spirit until solution is complete and diluting to 100 ml. with the same solvent.

In the method finally adopted, 1 g. of the sample is dissolved in 100 ml. of water and the solution is titrated with $N/4$ sodium hydroxide solution, 4 to 6 drops of the indicator solution being added. A solution of 1·425 g. of potash alum in 100 ml. of water, with exactly the same amount of indicator added, is used as a blank. Towards the end of the titration, up to 30 seconds is allowed for the colour-change to develop. The number of ml. of the alkali solution required by 1 g. of the sample gives the percentage of free acid as SO_3.

J. R. SIMMONS

AYLESFORD PAPER MILLS
LARKFIELD, KENT

June, 1940

Official Appointments

Erratum.—In the list of appointments on p. 411 (July issue) for "Westmorland County Council, Kendal Borough, W. H. Roberts" *read* "W. H. Roberts as a Public Analyst for that part of the County of Westmorland within the boundaries of the Borough of Kendal."

(C. J. H. Stock is the Public Analyst for the County of Westmorland.)

Ministry of Agriculture and Fisheries

CREAM CHEESES*

THIS Leaflet deals with the preparation and packing of cream cheeses. It is pointed out that the absence of legal standards of quality has resulted in a great variety of products, with a wide range of fat, being sold under the name of cream cheese.

The two main types sold in this country are:

DOUBLE CREAM CHEESE, which is made from cream containing about 50 per cent. of butter-fat, and

SINGLE CREAM CHEESE, which is usually made from cream containing 25 to 30 per cent. of butter-fat, and is thickened by adding rennet prior to drainage.

Methods of preparing these two types of cheese are described in detail.

Attention is directed to recent work (*J. Min. Agric.*, Sept., 1939), which has shown that cheese wrapped in close-fitting material (*e.g.* aluminium or coated tinfoil), keeps better than cheese packed in muslin or parchment paper; these promote the growth of mould.

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* Advisory Leaflet No. 222, 1940. H.M. Stationery Office, York House, Kingsway, London W.C.2. Price 1d. net per copy, or 9d. per dozen copies.

General Medical Council

SECOND ADDENDUM TO THE BRITISH PHARMACOPOEIA, 1932*

THE Second Addendum to the British Pharmacopoeia, 1932, was published on June 14th, 1940, and became official from that date. The following new monographs are included:—Emulsio Olei Morrhuae, Emulsio Olei Vitaminati, Extractum Malti cum Oleo Vitaminato, Liquor Vitamini A Concentratus, Liquor Vitamini D Concentratus, Liquor Vitaminorum A et D Concentratus, Oleum Amygdalae Volatile Purificatum, Oleum Hippoglossi, Oleum Vitaminatum, Toxinum Tetanicum Detoxicatum. Amended formulae are given for Linimentum Camphorae, Unguentum Acidi Tannici, Unguentum Aquosum, Unguentum Capsici, and Unguentum Hydrargyri Compositum.

There are five appendixes:—In IV.G the method of determining the ultra-violet absorption of cod-liver and halibut-liver oil at $328m\mu$, and of calciferol at $265m\mu$, is described.

Appendix X.C gives methods for determining iodine values (*a*) by the iodine monochloride method, (*b*) by the pyridine bromide method. It also describes the determination of the iodine value of the glycerides of halibut-liver oil.

In X.D. the S.P.A. method for the determination of unsaponifiable matter in fixed oils and fats is given.

In XI.C the determination of aldehydes in purified Volatile Oil of Bitter Almonds is described.

Appendix XV.O gives details for the assay of vitamin A by the spectrophotometric method at $328m\mu$. The factor declared by the Permanent Commission on Biological Standardisation of the League of Nations (at present accepted as 1600) is to be used for calculating the vitamin A content in Units per gram from the ultra-violet absorption figure.

Monographs of the British Pharmacopoeia, 1932, or of the Addendum, 1936, which are amended by this Addendum supersede, in their amended forms, the original monographs.

THE BRITISH PHARMACOPOEIA, 1932

ALTERATIONS AND AMENDMENTS

The Registrar of the General Council has sent us a notice to the effect that, in pursuance of Section 54 of the Medical Act, 1858, the General Council of Medical Education and Registration of the United Kingdom have caused to be altered and amended the British Pharmacopoeia, 1932, by modifying the list of medicines and compounds, and certain directions for preparing certain medicine and compounds, therein contained, as set forth in the following Schedule:

THE SCHEDULE

IPECACUANHA.—*Synonyms.*—Ipecacuanhae Radix: Ipecacuanha Root. British Pharmacopoeia, 1932, p. 237, line 4, "two-thirds" is changed to "three-fifths," so that the standard for alkaloidal content is amended to read:—"Not less than 2 per cent. of the total alkaloids of Ipecacuanha, calculated as emetine, of which not less than three-fifths consists of non-phenolic alkaloids, calculated as emetine."

EMPLASTRUM PLUMBI, Plaster of Lead.—*Synonyms.*—Lead Plaster; Diachylon Plaster; Diachylon.

INJECTIO HYDRARGYRI. Injection of Mercury. *Synonym.*—Mercurial Cream.

INJECTIO HYDRARGYRI SUBCHLORIDI. Injection of Mercurous Chloride. *Synonym.*—Calomel Injection.

UNGUENTUM HYDRARGYRI NITRATIS FORTE. Strong Ointment of Mercuric Nitrate. *Synonyms.*—Unguentum Hydrargyri Nitratis; Mercuric Nitrate Ointment.

Arachis Oil may be used, in place of Olive Oil, in making these four preparations.

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* Pp. 22. Published by Constable & Co., Ltd., for the General Medical Council. 1940. Price 2s.

Medical Research Council

THE CHEMICAL COMPOSITION OF FOODS*

THIS Report supplements, but does not supersede, the three Reports (Nos. 135, 187 and 213) previously issued by the Council. The earlier Reports contained sections dealing with analytical methods, the losses caused by cooking, and the value of hemicelluloses and celluloses in animal nutrition, and reference may be made to them for information on these points. The new feature of the present Report is its classification of recent analytical data obtained by a systematised procedure.

The foods have been divided into arbitrary groups under the following headings: cereals and cereal foods; dairy products; meat, poultry and game; fish; fruit; nuts; vegetables; sugars, preserves and sweetmeats; beverages; beers; condiments; vegetable fats; cakes and pastries; puddings; cooked dishes; sauces and soups. The figures for the cooked dishes were obtained by computation, not direct analysis. The cereal group includes starchy foods such as arrowroot and tapioca, and Bovril, Oxo, Marmite and Virol have been grouped with the beverages. The tables are given in two series, the first showing the composition of the foods per 100 grammes and the second the composition per ounce. Edible material only has been analysed, but for foods such as fish and stone fruits, which are usually served with waste, the amounts of the edible constituents that would have been obtained from 100 g. and from 1 oz. of the food as served are also given. Vitamins do not come within the scope of the report.

As in former Reports, protein nitrogen has been differentiated from non-protein nitrogen in meat and fish and in mushrooms. Since the nitrogen/sulphur ratio in meat and fish has been found to be very constant (Master and McCance, *Biochem. J.*, 1939, **33**, 1304), the sulphur in most of these foods has been calculated from the nitrogen figure.

The "available" phosphorus and "available" iron have been tabulated for a number of foodstuffs. By "available" phosphorus is meant the phosphorus not present as phytic acid (McCance and Widdowson, *Biochem. J.*, 1935, **29**, 2694), and "available" iron has been taken as the iron which reacts with $\alpha\alpha'$-dipyridyl (Shackleton and McCance, *Biochem. J.*, 1936, **30**, 582; McCance, *Chem. and Ind.*, 1939, **58**, 528; Abst., ANALYST, 1939, **64**, 335).

NOTES ON TECHNIQUE.—For the determination of fat in malted foods the Soxhlet method gives low results; also, with many cereals it gives results lower than those obtained by von Liebermann and Szekely's method (*Pflüg. Arch. ges. Physiol.*,1898, **72**, 360). On the other hand, with condiments higher results are obtained by the Soxhlet method.

INDIVIDUAL FINDINGS.—Bovril contained more potassium (3·59 per cent.) than any other food examined. Parmesan cheese contained the largest proportion of calcium (1·22 per cent.), Marmite was richest in phosphorus (1·89 per cent.) and carrageen moss in magnesium (0·63 per cent.) and sulphur (5·46 per cent.). Liver contained the most copper (5·8 mg. per 100 g.), and curry powder the most iron (75 mg. per 100 g.). Of all the foods analysed, Gruyère cheese was richest in nitrogen (5·9 per cent.).

Points not discussed in the previous reports include the following:

(1) The amounts of sodium and chlorine in packet cheese differ from those usually present in cheese.
(2) Fried fish tends to contain more calcium than the fresh fish, owing to some of the small bones being included in the edible material of the former.
(3) Glacé cherries contain much more iron than the raw fruit, probably owing to contamination during stoning.
(4) Golden syrup contains 7 times as much sodium as chlorine; in black treacle the ratio is reversed.

CHEMICAL COMPOSITION OF COOKED DISHES WITH THEIR RECIPES.—A section of 13 pages, by C. M. Verdon-Roe, gives a series of standard recipes for cooked dishes containing several ingredients. These comprise preserves and sweetmeats, beverages, cakes and pastry, meat and fish dishes, egg and cheese dishes, sauces and soups.

Since pooled samples of all the ingredients of these dishes had been analysed, it was only necessary to determine the loss or gain of water during the cooking process to enable an average composition for the made dish to be calculated. Details of the procedure are given.

BIBLIOGRAPHY AND INDEX.—The Report concludes with a list of 22 references to works cited in the text and an index of 7 pages, giving the places in the tables of every food mentioned.

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* Special Report Series, No. 235. By R. A. McCance and E. M. Widdowson. Pp. 150. H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1940. Price 4s. net.

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REPORT OF THE STATE CHEMIST FOR THE YEAR ENDED MARCH 31ST, 1940

IN his Report Dr. T. S. Wheeler gives an outline of the chemical work carried out in the State Laboratory for all Departments of the Government. The total number of samples examined was 37,843, as compared with 40,240 in the preceding year. The main decrease was in the number of Revenue samples. On the other hand, there were substantial increases in the numbers of samples examined for the Departments of (*a*) Agriculture and Fisheries, and (*b*) Local Government and Public Health.

DAIRY VOLUMETRIC GLASSWARE.—Under Part IV, Sec. 32, Sub-sec. (1) (*c*) of the Dairy Produce Act, 1924, it is provided that dairy volumetric glassware is to be tested and stamped at the State Laboratory or, alternatively, at the National Physical Laboratory, Teddington. The total number of instruments tested was 5719.

SEA-WATERS.—In connection with the work of the International Council for the Exploration of the Sea, the Department of Agriculture and Fisheries carries out an annual investigation of sea-water around the Irish coast. Among the objects of the investigation is the determination of the relation of salinity to fish life. The salinities are determined by a standard method, which has been adopted by all the countries taking part in the investigation. The number of samples, taken at various stations, was 209, and the salinities lay, in general, between 34 and 35 parts of salt in 1000 of sea-water.

COMMODITIES FOR LOCAL AUTHORITIES.—The Minister for Local Government and Public Health is empowered under the Local Authorities (Combined Purchasing) Act, 1925, to have commodities for local authorities tested. The 213 samples submitted included tars, soaps, disinfectants, oils and paints; 12 did not comply with the requirements of the specification.

SALE OF FOOD AND DRUGS ACTS, 1875–1936.—Under Section 22 three samples were forwarded to the State Laboratory by direction of District Justices in cases in which the defendants had appealed against the certificates of local analysts.

MILK.—Under the Milk and Dairies (Special Designations) Regulations, 1938 and 1939, the Laboratory received 404 samples, 197 for chemical and 207 for bacteriological examination.

Federated Malay States

ANNUAL REPORT OF THE INSTITUTE OF MEDICAL RESEARCH FOR THE YEAR 1938

THE Report of the Director, Dr. A. Neave Kingsbury, gives an outline of the work of the different Divisions of the Institute, including those of Bacteriology, Chemistry, Entomology, Malaria Research, Pathology, Rat Virus Enquiry and the Serological and Medico-Legal Section.

The Chemical Division is under the direction of Mr. J. Shelton, F.I.C. Of the 5758 samples examined, 4442 were for the medical and health services and 524 for the police. The Health Officers submitted 1040 samples of milk, of which 14·3 per cent. were condemned as adulterated. These included 36 samples which complied with the legal standards, but were shown, by means of the Hortvet cryoscope, to contain added water.

LEAD IN CANNED FOOD.—The Sale of Food and Drugs Rules, 1938, prohibit the sale or importation of food in cans which are so constructed as to allow the contents to come in contact with any solder except the small amount necessary to seal a vent hole. Since these rules were introduced the quality of the containers has noticeably improved. Several samples, however, gave evidence that the cans had been used a second time.

LEAD IN SAMSU.—Twenty samples of samsu taken from the distilleries were examined, and were found to contain lead in amounts up to 3 p.p.m. As samsu is often stored in jars which quite probably have a lead glaze, it would seem advisable to examine retail samples as well as bulk samples from the distilleries.

SIZE OF SHOT IN CARTRIDGE.—In a case in which the police wished to know what size of shot had been fired from a shot gun cartridge, it was found that the top wad had retained an impression of the shot. From the marks it was possible to give an approximate idea of the size of the shot.

FORMIC ACID POISONING.—Five cases were investigated. In one of these, acid equivalent to 43 g. of anhydrous formic acid was isolated from the stomach and its contents. Formic acid of about 95 per cent. strength is used as a coagulant on rubber estates.

CAUSTIC SODA POISONING.—Of the 52 cases in which poison was detected, caustic soda was found in 18. Prior to 1934 very few cases of this type of poisoning occurred, but since then they have continued to increase. Steps are being taken to include caustic soda in the schedule of poisons.

IRRITANT POISON IN WELL WATER.—Vegetable matter taken from a well was identified as the fruit of a species of palm, probably *Caryota mitis* Lour. According to Gimblette ("*Malay*

Poisons and Charm Cures") "The fruit of this palm is often put into wells with intent to cause annoyance. Bathing with well-water treated in this way gives rise to an intense itching of the skin and may cause an acute inflammation of the eyes." This is said to be due to numerous fine needles of silica in the pericarp of the fruit.

TRANSFERENCE OF REVENUE STAMP.—One of the document cases investigated involved the question whether a revenue stamp had been removed from one document and placed upon another. Microscopical examination of the back of the stamp showed the presence of fibres of a certain type of paper, which were not found in the questioned document, but agreed with those of paper similar to that from which the stamp was thought to have been removed.

"GROUPING" OF BLOOD STAINS.—With a view to the further refinement of routine tests for the "grouping" of blood stains, preliminary investigations with anti-"M" and "N" sera have been made. Sera have been made and adsorbed. The results with experimental stains with 0·02 ml. of blood were inconclusive, but with double that quantity the reactions were more definite. During the year the police submitted about 600 exhibits of blood stains. The "A" and "B" grouping was attempted on 62 of these and conclusive results were obtained with 49.

RAT VIRUS ENQUIRY REPORT*

THE Rat Virus Enquiry was instituted at the request of the United Planting Association of Malaya to investigate the local possibilities of a commercial rat "virus" imported by air from Europe. Rats are responsible for much loss on coconut plantations and oil palm and rubber estates and also for disease among the workers.

All the local rats examined were "black" rats (*Rattus rattus*). No "brown" rats (*Rattus norvegicus*) were seen. In Kuala Lumpur the prevailing species is *Rattus rattus diardi*, while on the plantations the common species is *Rattus rattus jalorensis*. A few specimens of *Rattus concolor*, which is a very small rat, were also taken.

EXPERIMENTS WITH "VIRUSES."—In order to ascertain if any of the known rat "viruses" could be effective against these local rats, "herd experiments" were undertaken. Rats were artificially inoculated with a particular organism and then introduced into a large "run" with a number of healthy rats. The artificial infection was effected in three ways: (*a*) intraperitoneal injection of the bacterial suspension; (*b*) injection into the stomach through a rubber tube; (*c*) feeding with milk in which the organism had been cultivated.

The organisms used in the experiments were:

(1) Three strains of *S. enteritidis*:—*S. enteritidis* "Medan," *S. enteritidis* "Liverpool" (from commercial "Liverpool Virus") and *S. enteritidis* "Ratin" (from a commercial bacterial preparation).

(2) Three organisms of the *Pasteurella* Group:—*P. muriseptica, P. cuniculiseptica, P. aviseptica.* These cause septicaemia in rats, if given in large doses, but are usually harmless to human beings.

From the results of the tests, which are described in detail, the conclusion was drawn that certain rat "viruses," if applied in a suitable manner, were effective in killing local rats. With few exceptions, however, uninfected rats, after contact, under favourable conditions for the spread of infection, with infected rats, failed to become infected. It was therefore inferred that there was little possibility of the intentional precipitation of widespread epidemics among local rats by the use of these rat "viruses."

EXPERIMENTS WITH ECTROMELIA VIRUS.—Ectromelia is a highly infectious disease of mice caused by a filtrable virus. This virus, obtained from the National Institute for Medical Research, Hampstead, proved pathogenic to local mice, but did not cause death, even when injected intraperitoneally in large amounts, into specimens of local *R. r. jalorensis*.

EXPERIMENTS WITH BACTERIAL TOXINS.—Sterile toxins of *B. dysenteriae, S. enteritidis* and *Cl. botulinum* were injected through stomach tubes into rats, but in no instance were pathological changes attributable to the respective toxins produced. The potency of the different toxins was checked by the inoculation of rabbits or guinea-pigs.

RATICIDAL VALUE OF COMMERCIAL VIRUSES AND CHEMICAL POISONS.—The results of inoculating or feeding rats with Liverpool Virus, New Liverpool Virus, Raxon, Ratinin, Vexterm Rat Biscuits, Ratbane and a number of chemical preparations are described in detail. Some of these poison baits proved effective. Bread soaked in Ratinin (which contains an extract of red squill) was readily eaten by rats when first offered, but was refused when subsequently supplied. A commercial phosphorus paste, containing 2 per cent. of phosphorus and 98 per cent. of inert ingredients (glucose, honey, flour) was readily eaten by rats, after it had been spread on cubes of bread, and proved effective. Ratbane, which consists of coarse, hard particles (possibly coarsely-ground corn), believed to be coated with zinc phosphide, proved very efficacious, although exposure diminished its attractiveness.

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* Bull. No. 1. 1939. The Institute for Medical Research. By J. T. Paranjothy. Kuala Lumpur, 1939.

NON-COMMERCIAL CHEMICAL BAITS.—Four poison baits were prepared according to formulae recommended by the Department of Agriculture, Straits Settlements and Federated Malay States. They contained respectively 0·4 per cent. of thallium sulphate, 10 per cent. of sodium arsenite, 2 per cent. of arsenious oxide and 20 per cent. of barium carbonate.

A dose of 2 g. of any of the four baits may be considered a fatal one for local rats, since from 80 to 100 per cent. of the rats that ingested that amount died.

RELATIVE ATTRACTIVENESS OF BAITS.—Thirty rats were placed in a pen and supplied with 30 g. of each of the following baits: Vexterm biscuits (containing red squill), commercial phosphorus paste, thallium sulphate bait, sodium arsenite bait, arsenious oxide bait, barium carbonate bait. In one series of tests the rats were first starved for 24 hours, and in another series they were not starved but supplied with protein food in addition to the baits. After 24 hours, the baits were removed and weighed. Bread cubes with phosphorus paste proved the most attractive, and arsenious oxide and barium carbonate baits in the form of flour and bran balls were the least attractive. Thallium sulphate bait came second in both series of tests.

Various poison baits were exposed for 5 days to atmospheric conditions, but not to direct sun or rain. Bread smeared with pastes became rapidly unattractive, but loose hard substances such as Ratbane, lost attractiveness much more slowly. Rolled oats with thallium sulphate occupied an intermediate position.

THE ANTINEURITIC VALUE OF PARBOILED RICE*

RICE is the chief staple food in Malaya, and is consumed principally in three forms: (i) undermilled or husked rice; (ii) overmilled or polished rice; (iii) parboiled rice, made by soaking the padi in water, boiling it until the grains burst, and drying it in the sun. When properly prepared, parboiled rice is nearly translucent and varies in colour from almost white to light yellow.

Vedder and Feliciano (*Philip. J. Sci.*, 1928, **35**, 351; Abst., ANALYST, 1928, **53**, 542) classified milled rice roughly, according to the amount of pericarp left on the grain, into (*a*) highly milled rice with 0 to 20 per cent. of external layers present; (*b*) medium-milled rice, with 21 to 49 per cent.; (*c*) undermilled rice, with 50 to 100 per cent. The danger of beri beri, resulting from the consumption of milled rice, largely depends on the amount of pericarp layers removed. When undermilled rice is used, beri beri does not occur: and with medium-milled rice, if cases occur at all, they are apt to be sporadic.

Typical samples (158 in all) of the forms of rice consumed by the rural Malay population were examined by Vedder's iodine test (*loc. cit.*) to determine the approximate percentage of pericarp remaining on the grains. Of these samples, 23 (15 per cent.) had between 50 and 100 per cent. of pericarp remaining (undermilled), 81 (51 per cent.) had between 21 and 49 per cent. (medium-milled), and 54 (34 per cent.) had 20 per cent. or less (overmilled).

In addition to vitamin B_1, the major portion of the fat, proteins and mineral salts (especially calcium and phosphorus) is also concentrated in the pericarp layers. Thus Sreenivasan (*Ind. Med. Gaz.*, 1939, **74**, 35) has shown that the outer envelope or bran and germ together contain from 50 to 75 per cent. of the mineral matter of the grain, more than 25 per cent. of the proteins, and practically the whole of the vitamins and fat.

It is now generally accepted that the antineuritic value of parboiled rice, although milled, is much greater than that of raw milled rice. It was suggested by Aykroyd (*J. Hyg.*, 1932, **32**, 184) that during the process of parboiling some of the vitamin B_1 (and possibly also mineral matter and protein) is dissolved out of the pericarp and absorbed by the endosperm, thus making the vitamin B_1 content of milled parboiled rice considerably less dependent on the amount of pericarp retained. This hypothesis was supported by the fact that the polishings from parboiled rice were considerably poorer in vitamin B_1 and phosphate than the corresponding polishings from raw rice.

More recently, Subrahmanyan, Sreenivasan and Das Gupta (*Ind. J. Agric. Sci.*, 1938, **8**, 459) have proved that this absorption of proteins and mineral salts by the endosperm at the expense of the integuments does, in fact, occur.

The fact that undermilled rice deteriorates rapidly on storage, developing an unpleasant odour and taste, has made it much less popular than the nutritionally inferior polished grain. Parboiled rice is in a different position. If properly prepared, it can be almost as white and palatable as polished rice. Unfortunately, however, the commercial article is frequently of bad colour and may have an objectionable flavour. These drawbacks are largely due to incorrect methods of preliminary soaking, which encourage the development of anaerobic bacteria. On the other hand, the steaming process is likely to sterilise the grain, and, provided that the final drying is sufficient, there is no reason why parboiled rice should not be capable of storage for long periods without serious deterioration.

The feeding experiments on rats, described in detail in the Report, show that the antineuritic values of parboiled rice, whether overmilled or undermilled, compare very favourably with those of undermilled raw rice.

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* Bull. No. 4. 1939. The Institute for Medical Research. By I. A. Simpson. Kuala Lumpur. 1940.

Investigation of Atmospheric Pollution

REPRESENTATIVES of local authorities and other bodies co-operating in the investigation of atmospheric pollution met, by courtesy of the London County Council, in conference at the County Hall on May 28th. Among others, representatives of Cardiff, Dagenham, Glasgow, London County, Halifax, Manchester, Newcastle, Salford, Sheffield, Rotherham, Westminster, the British Commercial Gas Association and Cadbury Brothers, were present.

The Conference, in considering its annual report to the co-operating bodies, unanimously agreed that while contribution to the war effort was the first duty and desire of every organisation, the need for vigilant attention to the purity of the atmosphere had by no means decreased since the outbreak of the war. The wasteful burning of fuel and the detriment which pollution caused to the nation's health were stressed as two aspects of the problem which must not be forgotten, particularly in wartime. The Conference therefore urged all local authorities to do whatever lay in their power to maintain the Investigation.

At the close of the meeting, Professor W. H. Roberts, M.Sc., F.I.C., of Liverpool, was unanimously elected Chairman of the Conference, in succession to Alderman Adams, M.P., of Newcastle, who had held the office for three years in succession.

Royal Agricultural Society of England

ANNUAL REPORT OF THE CONSULTING CHEMIST FOR 1939

AMONG subjects of interest to the farming community, commented upon by Mr. Eric Voelcker in his Report, are the following:

SOYA-BEAN HUSKS.—A sample of soya-bean husks, offered at £5 17s. 6d. per ton, gave the following analytical results:—moisture, 11·51; oil, 4·10; albuminoids, 15·87; carbohydrates, etc., 38·30; woody fibre, 25·20; mineral matter (ash), 5·02 per cent. The sample contained 2·54 per cent. of nitrogen, and the mineral matter included 0·55 per cent. of sand and siliceous matter. This sample was inferior to others examined because of the low percentage of oil and high fibre-content, and the price appeared excessive. One sample gave 8 per cent. of oil, 23 per cent. of albuminoids and 17 per cent. of fibre. A good sample of soya-bean husks is not equal to pea meal, but is better than undecorticated cotton-seed meal, and would make a useful addition to a feeding ration; with such a high fibre-content the material is not suitable for pig-feeding.

"OAT FEED."—A sample submitted contained, besides oat husk, some barley husk together with tapioca meal. As its fibre-content was 22·02 per cent., a more apt name for it would have been oat husk refuse. In this connection reference is made to a case in which a firm was convicted and fined for adding not less than 10 per cent. of oat shudes to ground oats. There is no statutory limitation to the amount of fibre in ground oats, and, although the Act defines Ground Oats as "the meal obtained by grinding commercially pure oats as grown," the defendant argued that, as only a product of the oat had been added, no offence had been committed. An average figure for the fibre-content of oats may be taken as about 10 per cent., and when one finds a figure considerably in excess of that proportion, it is reasonable to assume that an addition has been made. In this particular case the defendant admitted the addition of 2 cwt. of oat shudes to each ton of pure oats. Such adulteration is not apparent to the eye, and farmers should be on their guard against it.

REFUSE FROM A BACON FACTORY.—A sample submitted had the following composition:—moisture and organic matter, 74·98; phosphoric acid, 5·36; lime, 6·79; salt, 3·50; magnesia, iron oxide, etc., 4·05; sand and siliceous matter, 5·32 per cent. The amount of nitrogen in the moist organic matter was equivalent to 8·11 per cent. of ammonia and the oil therein was 8·54 per cent. Although the oil-content was fairly high, it did not appear to be excessive for manuring purposes, Such a material would be a useful source of organic matter when dug into the soil.

COMPARATIVE ANALYSES OF RED AND WHITE CARROTS.—The following percentage figures were obtained:

	Water	Oil (pet. spt. extract)	Albu-minoids	Sugar	Other sol. carbo-hydrates, etc.	Woody fibre	Mineral matter (ash)
Red carrot	87·79	0·16	1·26	3·00	5·88	0·81	1·10
White carrot	88·31	0·08	0·91	3·00	5·78	0·85	1·07

As the red carrot was little richer than the white, whilst the yield from the latter was three times that of the former, it was proposed by the member submitting the samples to grow only the white variety. Further examination of the two varieties, however, showed that the white carrots contained only 0·8 mg. of carotenoids per kilo. (not calculated on dry matter), whereas the red carrots contained 180 mg. per kilo. It would therefore seem inadvisable to replace the red by the white variety solely for the reason that the latter gives a much higher yield.

British Standards Institution

WAR EMERGENCY STANDARDS.—A communication from the Director points out that, owing to war conditions, the requirements of some existing British Standard Specifications cannot be strictly complied with by the manufacturers, who may in consequence be compelled to contract out of them. The British Standards Institution is meeting this situation by undertaking the revision of such Specifications and their issue as War Emergency Revisions, and the preparation of War Emergency Standards. These War Standards and Revisions are published on yellow paper to avoid confusion with the general B.S. standards, and it is made clear, wherever necessary, that they apply only to the home market and not to the export trade and can be modified again when peace comes. A number of such War Revisions have already been issued. They are put through with the minimum of delay—in some cases within a few days.

THE following British Standard Specification has been prepared by the Institution at the request of the Air Raid Precautions Department of the Ministry of Home Security.

BS/A.R.P. No. 40—1940. BLEACH OINTMENT (ANTI-GAS OINTMENT No. 1).*

The ointment shall consist of equal parts by weight of bleaching powder and white mineral jelly, and must be in the form of a uniform smooth paste, free from foreign matter and visible impurities. Undue heating must be avoided during mixing.

The bleaching powder used must be suitably stabilised, free from visible particles, and 99 per cent. must pass through a 60-mesh B.S. test sieve. It must contain not less than 30 per cent. of available chlorine and should not lose more than one-fortieth of its original chlorine-content after exposure for 2 hours at 100° C. in a specified manner.

The white mineral jelly shall comply with the following standards:—flash-point, not lower than 176·7° C.; drop-point, not lower than 40° C.; ash, not more than 0·03 per cent.; loss on heating for 6 hours at 100° C., not more than 1 per cent.; freedom from acidity, determined by boiling a mixture of 5 g. with 10 ml. of alcohol and testing with methyl orange. The jelly must also answer tests for freedom from reactive compounds (*e.g.* unsaturated hydrocarbons). Further tests include a check of the available chlorine in a freshly prepared sample of the ointment (not less than 14 per cent.); heating of the ointment for three hours at 57° C., when the temperature should not exceed 62° C., followed by a further check of the available chlorine, which should not be more than 2 per cent. below the original figure. Appendixes to the specification give the methods of determining (i) coarse particles in the ointment, (ii) available chlorine in the ointment, (iii) available chlorine in bleaching powder, (iv) stability of bleaching powder at 100° C., and (v) stability of the white mineral jelly.

The available chlorine in a freshly prepared sample of bleach ointment must not be less than 14 per cent. The labels and containers must be marked with the name "Bleach Ointment (Anti-gas Ointment No. 1)," the name of the maker, and the date of manufacture.

The following British Standard Specifications have also been published†:

No. 593—1940. GENERAL PURPOSE LABORATORY THERMOMETERS.

This is a revised Specification. It includes five series of thermometers for general purposes, the chief change in this revision being the inclusion of a series E, the thermometers in which are specially chosen to be suitable for use with distillation flasks specified in B.S. No. 571. The other series specified include thermometers for both Centigrade and Fahrenheit scales for partial and for complete immersion.

No. 611—1940. PETRI DISHES.

This Specification has recently been revised. The revision is mainly concerned with the tolerances, but the height and thickness of the top and bottom dishes have also been revised.

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* Copies of the full specification can be obtained from the British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2d. net.

† Obtainable from the Publications Department, 28, Victoria Street, London, S.W.1. Price 2s. net. Post free 2s. 2d. each.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Constitution of Banana Starch. E. G. E. Hawkins, J. K. N. Jones and G. T. Young. (*J. Chem. Soc.*, 1940, 390–394.)—Banana starch is best prepared by shaking minced, peeled unripe bananas in succession with alcohol (twice), and then with an aqueous 1 per cent. solution of sodium sulphite. If the fibrous matter is separated on a coarse muslin filter, the starch is deposited from the filtrate, and may be collected on a fine cloth filter or by flotation in alcohol. It forms a clear paste in hot water, which gives the deep-blue iodine reaction and does not reduce Fehling's solution. One preparation gave $[\alpha]_D^{20}$ + 152° in *N* sodium hydroxide solution; P_2O_5, 0·06; N, 0·15 per cent.; acidity equiv. to 0·6 ml. of 0·1 *N* alkali per g. Hydrolysis with taka-diastase left 5 per cent. of fibrous residue, and the reducing value of the residual solution corresponded with 98 per cent. of the theoretical amount of glucose. Distillation with 12 per cent. hydrochloric acid yielded no furfuraldehyde, and the amount of carbon dioxide evolved corresponded with the decomposition of hexose and, therefore, with the absence of uronic acids (*cf.* Campbell, Hirst and Young, *Nature*, 1938, **142**, 912). After hydrolysis with 2 per cent. sulphuric acid the reducing power was 97 per cent. of the value corresponding with quantitative hydrolysis to glucose, an 88 per cent. yield of crystalline glucose being obtained from this solution. In general appearance, granule size and paste-forming properties, banana starch, as thus prepared, resembles potato starch. The preparation of the fully-substituted acetyl and methyl derivatives is more difficult than for potato starch, but the properties of the corresponding derivatives of the two starches are similar. Methylated banana starch (prepared directly, or by methylation of the acetate) was shown by viscosimetric methods (*cf.* Hirst and Young, *id.*, 1939, 1471, 1475) to have a mol. wt. of about 200,000. Hydrolysis of these methyl derivatives resulted in 2.3.4.6-tetramethyl glucose, 2.3.6-trimethyl glucose and dimethyl glucoses only, in amounts corresponding with the presence of a repeating unit of about 24 glucose residues. The molecular structure of banana starch closely resembles that of rice starch in respect of the "disaggregation reactions" of the methyl derivatives, *i.e.* the hydrolysis (*e.g.* by 1 per cent. oxalic acid at 60° and 75° C.) of the bonds between repeating units to give products of lower mol. wt. but unchanged chain-length. Throughout this operation the proportion of end-group remains unchanged, the solution is non-reducing and the rotation is undiminished, as distinct from the formation of reducing dextrins and, ultimately, of glucose, which results from normal acid hydrolysis. Consideration of the kinetics of the disaggregation reaction shows that a normal glycosidic bond links the repeating units, so that under identical conditions the 1.6-fructofuranoside linkages in methyl inulin are hydrolysed about 7 times more rapidly than the bonds between the repeating units in methylated starches; this is illustrated graphically. Full experimental details of the methods of hydrolysis, methylation and disaggregation are given. J. G.

Determination of Amino-nitrogen in Malt Extracts. S. R. Snider. (*Cereal Chemistry*, 1940, **17**, 121; *J. Inst. Brewing*, 1940, **46**, 154–155.)—A method based on Pawlowski's modification of formol titration is as follows:—Sixty ml. of the wort or extract (12·5 per cent.) in a 100-ml. flask are kept in boiling water for 10 minutes, cooled, diluted to 100 ml. after addition of 10 ml. of 20 per cent. barium chloride solution and 5 ml. (7 ml. for proteolytic extracts) of saturated barium hydroxide solution, and filtered through a covered funnel after standing for 30 minutes. Four 20-ml. portions are measured into 125-ml. flasks, which are kept closed with rubber stoppers. Into flasks (1), (2), (3) and (4) are measured respectively 2 ml. of 0·02 per cent. phenol red solution, 2 ml. of water, and two 2-ml. portions of 0·04 per cent. thymol blue solution. The contents of flask (1) are then titrated with *N*/10 hydrochloric acid to a distinct, permanent yellow (*p*H 6·8). The same amount of acid is put into each of the remaining three flasks, followed by 10 ml. of 36–38 per cent. neutral formaldehyde (*p*H 5·6); cloudy or inferior grades should not be used. After titration of (3) with *N*/10 sodium hydroxide solution until it nearly matches a thymol blue *p*H 9 colour standard, and addition of an equal amount of the alkali to (2), the colours of (3) + water cell, and of (2) + thymol blue colour standard are compared in a colorimeter, a daylight lamp being preferable to daylight. If the matching is close, the titration of (3) is completed to an exact match after dilution of (2) and (3) to 40 ml. each. Flask (4) is used for a duplicate titration. Matching is more sensitive if colour standards are used on both sides of the titrated solution in the colorimeter; addition of 0·1 ml. of *N*/10 sodium hydroxide solution should make a matched solution perceptibly darker than the standard. A blank titration on the reagents is made, with water instead of wort or extract, while water cells replace the compensating wort solution in the colorimeter. If T and B represent the ml. required by the test solution and in the blank titration, and M the mg. of wort or extract in the 20 ml. titrated, the percentage of amino-nitrogen in the sample is 140 (T–B)/M. E. B. D.

Keeping Properties of *Hydnocarpus Wightiana* Oil and its Derivatives. U. P. Basu and A. Mazumdar. (*J. Indian Chem. Soc.*, 1940, **17**, 280.)—The inhibition of autoxidation of *Hydnocarpus Wightiana* oil, which can be brought about by addition of 7 per cent. of creosote (*Leprosy in India*, 1939, **11**, 53) is shown still to occur if the concentration of the creosote is reduced to 0·1–0·2 per cent. The unsaponifiable matter of the oil, about 0·02 per cent., is not pro-oxygenic in nature. A concentrate prepared by a slight modification of the method of Green and Hilditch (*J. Soc. Chem. Ind.*, 1937, **56**, 23T; Abst., ANALYST, 1937, **62**, 206), when dissolved in bicarbonate solution, reduced Fehling's solution, contained nitrogen and was insoluble in ether, but had no anti-oxygenic power. A sesame cake preparation, however, which was rich in nitrogen (6·1 per cent.), had a considerable anti-oxygenic effect. Thus the peroxide value (63·8 in terms of 0·01 *N* thiosulphate solution), obtained by heating an oil at 100° C. for 4½ hours, was reduced to about 2·6 when 0·5 per cent. of sesame concentrate was mixed with the oil prior to the heating. D. G. H.

Neem Oil. I. M. Qudrat-i-Khuda, S. K. Ghosh and A. Mukherjee. (*J. Indian Chem. Soc.*, 1940, **17**, 189–194.)—The oil was expressed from Birbhum neem seed (*Melia azadirachta*). Volatile substances were removed by prolonged steam-distillation of 30 lbs. of crude oil, the distillate consisting of the odoriferous constituent of the oil mixed with some solid material. On repeated distillation of the oil 15 g. of a colourless mobile oil with a penetrating, unpleasant odour were obtained; its probable molecular formula was $C_{15}H_{30}O_3S$, and it was termed "neemola." The residue of oil from the steam-distillation was extracted with several litres of water, and the bitter principle was isolated from the extract in the form of a solid substance termed "margosin," which, after purification, was found to be a glucoside with the formula $C_{28}H_{48}O_{10}$. The fatty oil remaining after removal of neemola and margosin was saponified and yielded a mixture of four acids which appeared to be different from those described by Roy and Dutt (*J. Soc. Chem. Ind.*, 1929, **48**, 333T; Abst., ANALYST, 1930, **55**, 50; and by Child and Ramanathan (*id.*, 1936, **55**, 124T; Abst., ANALYST, 1936, **61**, 498). One acid, m.p. 67° C., appeared to be an isomer of tetradecoic acid, $C_{14}H_{28}O_2$, and was called neem acid A. Another acid, neem acid B, regarded as a higher homologue of acid A (m.p. 55° C.), is described as an isomer of palmitic acid. After separation of these two solid acids a mixture of a solid and liquid oil was obtained on distillation under reduced pressure of the solid acidic substance remaining in the mother liquor. The methyl esters were fractionated into two distinct portions; the lower-boiling ester yielded neem acid C, a solid unsaturated acid ($C_{15}H_{28}O_2$) of the oleic acid series, and the higher-boiling ester produced neem acid D ($C_{18}H_{32}O_2$), semi-solid at ordinary temperature and apparently belonging to the cyclic acids. It is perhaps similar to hydnocarpus or chaulmoogric acid. D. G. H.

Determination of Indole by a Modification of Ehrlich's Reaction. L. H. Chernoff. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 273–274.)—Ehrlich's reaction (*Deut. Med. Woch.*, 1901, 1) depends upon the formation of a pink colour when indole is treated with dimethylaminobenzaldehyde in presence of hydrochloric or sulphuric acid. Separation by steam distillation of indole from products containing it is usually considered necessary, but the method to be described avoids steam distillation and appears to be conveniently applicable to food and biological material. It has been applied by Clarke *et al.* (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 475; Abst., ANALYST, 1937, **62**, 806) to butter and to distillates from butter. It is based primarily on the observation that when a solution of indole in chloroform is treated with dilute acid (up to about 12 per cent.) and Ehrlich's reagent the colour remains in the chloroform layer, but if the test is made with stronger HCl the colour is transferred to the aqueous phase. In the method described syrupy phosphoric acid is used instead of hydrochloric acid, because it is more easily separated from mixtures with chloroform and is less liable to promote interfering reactions with other substances. The reagent is prepared by dissolving 0·2 g. of purified dimethylaminobenzaldehyde in 100 ml. of 85 per cent. phosphoric acid and the test is made as follows: The reagent (5 ml.) is added to 50 ml. of chloroform containing from 1 to 10γ of indole in a separating funnel and, after the mixture has been shaken for 2 minutes, 25 ml. of glacial acetic acid are added. After further shaking the mixture is allowed to stand. The lower layer is transferred to a Nessler glass, and the chloroform is washed with 2·5 ml. of phosphoric acid, which is added to the first extract. The liquid is then diluted to 50 ml. with glacial acetic acid, and the colour produced is directly proportional to the amount of indole present. Standard comparison solutions from indole treated in this manner are stable for 1 or 2 days. The comparison may be made in a Clifford neutral wedge photometer (U.S. Food and Drug Administration, Food Control Statement, 1935, **41**, 1). The curve shows a maximum value in the neighbourhood of 570$m\mu$, and as little as 0·5γ of indole may be detected. The acetic acid used must be free from formaldehyde, and the chloroform should be washed free from alcohol. As indole is apparently polymerised by phosphoric acid, the dimethylaminobenzaldehyde reagent must be added first to the chloroform solution. Indole may be extracted with chloroform from slightly acid or slightly alkaline solutions. Biological material may be made slightly alkaline with dilute sodium hydroxide solution and extracted with a measured volume of chloroform. The separated chloroform layer is then washed with a little dilute hydrochloric acid, and an aliquot portion is treated in the

manner described. Emulsions formed during alkaline extractions may be broken by the addition of finely powdered ammonium sulphate, which also serves to remove formaldehyde. A. O. J.

Mesuol: The Bitter Principle of *Mesua ferrea*. P. Dutt, N. C. Deb and P. K. Bose. (*J. Indian Chem. Soc.*, 1940, **17**, 277–279.)—Nageshwar oil, expressed from the seeds of *Mesua ferrea* Linn., N. O. *Guttifereae*, deposits "stearine," which has been found to contain a crystalline substance soluble in aqueous alkali solutions to form a deep yellow solution; this is responsible for the yellow colour observed by Chatterjee and Gupta (*Oil and Colour Trades J.*, 1937, **91**, 1656), which is produced when the oil comes in contact with dilute alkali. Nearly 1 per cent. of pale yellow transparent prisms, m.p. 154° C., was isolated. This substance, called "mesuol," is neutral to litmus, has a somewhat bitter taste, and is soluble in 1 per cent. aqueous caustic alkali solution, in 10 per cent. ammonia and in hot sodium carbonate solution, but is insoluble in sodium bicarbonate solution. It is precipitated unchanged from alkaline solution by acids, and in alkaline medium gives a dirty green colour with ferric chloride; it is phenolic in character. It is optically inactive, free from methoxy- and methylenedioxy-groups, and is not a hydroxy-flavone. The analytical and molecular weight data allow of two formulae: $C_{23}H_{22}O_5$ or $C_{22}H_{20}O_5$, but in view of the analytical data for dimethylmesuol, the first is the more probable. Dimethylmesuol contains a lactone ring, but gives no colour with ferric chloride. D. G. H.

***Cannabis indica*. Isolation of Cannabidiol from Egyptian Hashish. Observations on the Structure of Cannabinol. A. Jacob and A. R. Todd.** (*J. Chem. Soc.*, 1940, 649–653.)—A fresh specimen of Egyptian hashish has been examined by the method used previously for Indian hashish (*Biochem. J.*, 1939, **33**, 123; Abst. ANALYST, 1939, **64**, 208), and cannabinol and cannabidiol (a typical constituent of American hemp resin) have been found to be present in approximately equal quantities. So far, cannabidiol has not been isolated from Indian resins, nor cannabinol from American resins. The experimental work supports the view of American authors (Adams and Clark, *J. Amer. Chem. Soc.*, 1940, **62**, 196) that cannabidiol is a double unsaturated derivative of menthylbenzene containing two OH-groups and one *n*-amyl group at positions in the benzene ring corresponding with those substituted in cannabinol. Both cannabinol and cannabidiol appear to be inactive in the Gayer test on rabbits. (*Arch. exp. Path. Pharm.*, 1928, 129, 312.) D. G. H.

Biochemical

Inertia of Highly Unsaturated Fatty Acids in the Animal, investigated with Deuterium. K. Bernhardi and R. Schoenheimer. (*J. Biol. Chem.*, 1940, **133**, 707–712.)—The manner in which doubly and trebly unsaturated fatty acids are formed in the body was studied by feeding mice on a fat-low diet of bread and heavy water. The saturated and total unsaturated fatty acids isolated from the animals were found to contain considerable amounts of deuterium, confirming the results of earlier experiments; the saturated acids contained more deuterium than the unsaturated acids. The unsaturated acid fraction yielded α-linolic acid as the tetrabromide, and a trebly unsaturated acid as the hexabromide. None of these highly unsaturated acids contained more deuterium than could be accounted for by the error of the analysis. It is concluded that such acids, unlike the saturated and less unsaturated acids, are not biochemically synthesised, but are derived directly from the diet. The results indicate, furthermore, that hydrogen of CH_3·, CH_2: and CH: groups is not exchangeable with the hydrogen of the water of the body fluids. F. A. R.

Biuret Reaction in the Estimation of Serum Proteins. I. A Study of the Conditions necessary for the Production of a Stable Colour which bears a Quantitative Relationship to the Protein Concentration. H. W. Robinson and C. G. Hogden. (*J. Biol. Chem.*, 1940, **133**, lxxxi–lxxxii.)—Absorption curves of the colour produced in the biuret reaction with serum proteins and varying concentrations of sodium hydroxide and copper sulphate were made, and the colour densities at wave-lengths of 560 and 700$m\mu$ were compared with the nitrogen contents of the solution. A colour that remained constant for at least 48 hours was obtained by the following method:—Serum is precipitated with trichloroacetic acid and centrifuged; the precipitate is dissolved in 3 per cent. sodium hydroxide solution, and the colour is developed with copper sulphate solution. Under these conditions the colour densities are proportional to the amounts of protein present. A wide variation in the concentration of copper had no influence on the colour. Rabbit serum diluted with saline was a more satisfactory standard than dog or human serum, and showed no loss of protein after being stored in the refrigerator for 6 months. By filtering the coloured solution a reduction in the intensity was obtained, but the amount of colour was still proportional to the nitrogen-content; it seems probable that the estimation can be carried out in a photoelectric colorimeter without the use of a standard. F. A. R.

Colorimetric Test for Methionine. M. X. Sullivan and T. E. McCarthy. (*J. Biol. Chem.*, 1940, **133**, c–ci.)—Five ml. of a solution containing 1 mg. of methionine in water or in 0·1 *N* hydrochloric acid are treated with 0·3 to 1·0 ml. of a 4 per cent. aqueous solution of sodium nitroprusside, and the solution is made alkaline with sodium hydroxide solution. After 5 minutes the yellow solution is acidified, and then becomes a pronounced red. Of the

ordinary amino acids, only histidine gives a red colour, and methods of overcoming interference from this source are being explored.
F. A. R.

Effect of the Oral Administration of Dimethylaminoazobenzene (Butter Yellow) on the Growth of the Rat. J. White. (*J. Biol. Chem.*, 1940, **133**, cviii.)—When 60 mg. of butter yellow per 100 g. of basal diet were added to the diet of young growing rats, the growth rate was reduced from 1·4–2·0 on the basal diet alone to 0·3–0·6 g. The normal growth rate was almost completely restored by the addition of *l*-cystine or *dl*-methionine (500 mg. per 100 g. of basal diet) to the diet.
F. A. R.

Behaviour of some Uramido-acids in the Nitrous Acid Method for the Determination of Amino-nitrogen. A. G. Gornall and A. Hunter. (*Biochem. J.*, 1940, **34**, 192–197.)—The behaviour of 14 uramido-acids in Van Slyke's method for the estimation of amino-nitrogen was examined by measuring the amount of nitrogen evolved after 3, 30 and 60 minutes and 2½ hours. The uramido-group was decomposed by nitrous acid much more slowly than the α- and ω-amino groups in an amino-acid, but the rate of evolution of nitrogen varied greatly from acid to acid. The uramido-acids could be arranged in 3 distinct, if not sharply delimited, groups according to the amount of nitrogen evolved in 2½ hours. Those in Group I yielded distinctly less than 1 atom, those in Group II between 1·2 and 1·6, and those in Group III exactly, or almost exactly, 2. Certain generalisations could be drawn concerning the constitution of the acids in each group. Thus all the ω-uramido-acids examined belonged to the first group, the α-uramido-acids with straight chains (with one exception) belonged to the second, and the α-uramido-acids with branched chains (with one exception) belonged to the third. The exceptions—α-uramidopropionic acid and α-uramido-isohexoic acid—yield less nitrogen than acids of analogous constitution.
F. A. R.

Histidine Detection and Estimation in Urine. E. Racker. (*Biochem. J.*, 1940, **34**, 89–96.)—Histidine can be detected by the Pauly diazo reaction, but this is not specific. The Knoop bromine reaction is more distinctive, and has now been made quantitative by the elimination of three sources of error. First, phosphates are removed with baryta because their precipitation in the test inhibits the development of colour; secondly, the urine is decolorised with charcoal because its pigmentation interferes with the measurement of colour; thirdly, an excess of sodium urate is added to eliminate variations in the action of certain substances (including sodium urate) normally present in urine, which intensify the colour in the bromine reaction. Six ml. of urine are pipetted into a test-tube, 3 ml. of saturated baryta solution are added, and the mixture is filtered. To the filtrate 3 ml. of *N* sulphuric acid and 100 mg. of decolorising charcoal are added, and the mixture is again filtered. Six ml. of the clear, colourless filtrate and 6 ml. of a standard solution of histidine hydrochloride (100 mg. in 1 litre of 0·1 *N* sulphuric acid) are treated with 2·5 ml. of a 5 per cent. suspension of sodium urate, and bromine in acetic acid solution (2 ml. in 100 ml. of glacial acetic acid diluted to 300 ml. with water) is then added in small portions until a faint yellow colour persists. After 10 minutes, with occasional shaking, the excess of bromine is removed by 1 or 2 drops of a saturated solution of arsenious oxide in 10 per cent. ammonia solution. The test-tubes are placed in boiling water for 5 to 7 minutes, and after a further 10 minutes the orange-red colours of the two solutions are compared in a colorimeter. The method will detect 1 part of histidine in 100,000 of urine, and the experimental error is about 10 per cent. with amounts between 10 and 20 mg. per 100 ml. After an examination of the behaviour of other substances, it was concluded that the test is not so distinctive as has previously been asserted. Some phenols (*e.g.* aminophenol), some alkaloids (*e.g.* morphine, tyrosine and tryptophane) react with bromine, but some of the colour can be extracted with amyl alcohol after addition of sodium carbonate; the colour due to histidine is not affected by this treatment. Histamine gives a colour that is much less intense and of a different shade. F. A. R.

Method for the Estimation of Acetone Bodies in Blood, applicable also to the Estimation of Small Amounts of Mercury. L. A. Crandall. (*J. Biol. Chem.*, 1940, **133**, 539–550.)—Into a 125-ml. Pyrex flask with a ground-glass joint are introduced 10 ml. of protein-free blood filtrate and 4 ml. of a modified Denigès reagent, prepared by dissolving 70 g. of mercuric sulphate in 6 *N* sulphuric acid and making up to 1 litre with 6 *N* sulphuric acid. The flask is fitted with a reflux condenser and the mixture is heated cautiously on a sand-bath, precautions being taken to avoid overheating. After a few minutes' boiling, 1·0 ml. of 5 per cent. potassium dichromate solution is added through the condenser and the heating is continued for a further 1½ hours. The solution is filtered through a sintered glass funnel while still warm, and the Denigès precipitate is thoroughly washed with water and then dissolved on the filter with 5 ml. of boiling conc. nitric acid, the solution being collected in a test-tube. The funnel is washed with water until the filtrate measures about 45 ml. Two ml. of 50 per cent. ferric nitrate solution are added, and the solution is diluted to 50 ml. with water. The concentration of mercury in this solution is estimated by adding 1 ml. of approximately 0·01 *N* potassium thiocyanate solution, and measuring the resulting colour in a photoelectric colorimeter. The mercury interferes with the colour formed when thiocyanate is added to an excess of ferric nitrate. The amount of mercury is calculated by

reference to a standard curve constructed with the aid of standard solutions of mercuric nitrate. The readings obtained in terms of mg. of mercury are converted into acetone bodies expressed as mg. of β-hydroxybutyric acid per 100 ml. of blood by multiplying by 15·4, or as mg. of acetone by multiplying by 6·33. The error of the method is less than ±5 per cent. with amounts of acetone bodies ranging from 15 to 20 mg. per 100 ml. F. A. R.

The Glycogen of *Helix pomatia*. E. Baldwin and D. J. Bell. (*Biochem. J.*, 1940, **34**, 139–143.)—The hepatopancreas ("liver") of *Helix* is very similar in its metabolic behaviour to the liver of mammals. The glycogen isolated from the hepatopancreas after previous removal of the albumin glands (which contain galactogen), was found to contain no galactogen, contrary to the observations of previous workers. It had a specific rotation of + 192°, and its chain length was estimated at 11 to 12 units, so that it is apparently identical with the glycogen of rabbit liver, fish liver, horse muscle, etc., but different from the only other molluscan glycogen (*Mytilus edulis* glycogen) that has been examined, for which a value of 18 units was found. F. A. R.

Manometric Estimation of Nitrite in Solution and in Tissues. J. Brooks and J. Pace. (*Biochem. J.*, 1940, **34**, 260–267.)—Baumgarten and Marggraff (*Ber.*, 1930, **63**, 1019) showed that nitrites can be estimated by measuring the amount of nitrogen liberated by the action of excess of amidosulphonic acid ($NH_2.SO_3H$), since the rate of reaction is rapid compared with the rate of decomposition of nitrous acid. The reagent is prepared by bubbling sulphur dioxide through a saturated solution of hydroxylamine hydrochloride for 48 hours at room temperature and allowing the mixture to stand at −10° C. for a further 3 to 4 days. The crystals of amidosulphonic acid are recrystallised from hot (50° C.) water by cooling to −10° C. The amount of nitrogen evolved can be measured either in a Warburg apparatus or in a Van Slyke apparatus. When a Warburg apparatus is used, 1 ml. of the sodium nitrite solution is introduced into the main compartment of the vessel and 0·4 ml. of 1·7 per cent. amidosulphonic acid solution into the side bulb; only a slight excess of the acid is required, but the same results are obtained with more concentrated solutions. When thermal equilibrium at 25° C. is reached, the contents of the side bulb are tipped into the main compartment; the pressure increase reaches a steady value in less than 10 minutes. With the Van Slyke apparatus, 2 ml. of the nitrite solution, a drop of octyl alcohol and 4·75 ml. of water are drawn into the gas chamber, the mixture is shaken *in vacuo* for 5 minutes, and the liberated gas is expelled. The chamber is evacuated until the solution is in the lower fourth, and 0·25 ml. of saturated amido-sulphonic acid solution are added through a mercury seal. The contents of the chamber are shaken, with the mercury meniscus at the 50-ml. mark, for 5 minutes and any traces of carbon dioxide are absorbed in the usual way by the addition of 1 ml. of air-free *N* sodium hydroxide solution. The gas is brought to a volume of 0·5 ml. (or 2·0 ml.) and the pressure, p_1, is read. The gas is ejected, the fluid meniscus is lowered to the 0·5 ml. (or 2·0 ml.) mark, and the pressure, p_2, is read. Then the volume of nitrogen per 100 ml. is equal to $f(p_1-p_2-c)$ where f is a factor tabulated by Peters and Van Slyke ("*Quantitative Clinical Chemistry*," 1932, p. 282) and c is a small correction obtained by a blank analysis in which 2 ml. of water are used in place of the sodium nitrite solution; $c = p_1 - p_2$. By either method, a concentration of 2×10^{-5} g. of sodium nitrite per ml. can be determined to within about 1 per cent. The quantitative evolution of nitrogen is not affected by the presence of sodium chloride, sodium nitrate, glucose, sucrose or tissue extractives. Nitrite in muscle can be estimated by the manometric analysis of an aqueous extract of the tissue, and, with certain limitations, by the direct action of amido-sulphonic acid on tissue contained in the Warburg apparatus. F. A. R.

Enzyme Activity in Frozen Vegetables: Asparagus. M. A. Joslyn and C. L. Bedford. (*Ind. Eng. Chem.*, 1940, **32**, 702–706.)—Samples of asparagus, cut in 1933, 1937 and 1938, had been blanched in water for different periods of time ranging from 1 to 20 minutes, and at various temperatures, and had then been packed in tins, which were sealed and stored at −17° C. The samples were all examined for catalase, peroxidase and ascorbic acid oxidase activity and aldehyde-content by methods already described in earlier publications (*Ind. Eng. Chem.*, 1936, **28**, 595; 1938, **30**, 1068; 1939, **31**, 751), the 1933 series after storage for 4·5 years, the 1937 after 15 months, and the 1938 after 3 months. In the 1933 series, maximum catalase activity was observed in the samples packed at 40° C., and maximum acetaldehyde-content in the samples packed at 60° C.; there was a fairly close correlation between the acetaldehyde-content and the catalase activity. Inactivation of catalase was most rapid above 75° C. The peroxidase activity of these samples, when measured in terms of pyrogallol-content, did not run parallel with catalase activity, though this also fell off markedly above 75° C. Asparagus packed in 1937 and 1938 had greater peroxidase activity, as measured colorimetrically with both guaiacum and benzidine, than the 1933 samples. The enzyme responsible for the guaiacum reaction was more thermolabile than that responsible for the benzidine reaction. The ascorbic acid oxidase activity of asparagus tissue was small. The presence of a weak oxidase, readily destroyed by heating, was established. The asparagus packed in 1933 was also examined periodically for colour and flavour. At first the flavour was good, but off-flavours developed

on storage, and after 4½ years all the samples had distinctly unpleasant flavours. Scalding in steam or boiling water for 2 to 5 minutes produced the most satisfactory flavour. The gum guaiac peroxidase reaction appeared to be more closely correlated with flavour retention than the other enzyme reactions. A similar correlation was observed with the 1937 and 1938 packs, and asparagus scalded for 3 minutes in boiling water retained its original flavour on storage for 15 months. Other factors beside enzyme inactivation appear to be involved in flavour retention, such as the length of time between cutting and processing.

F. A. R.

Carbonate Veronal Buffer Solution covering *p*H 7·5 to 10·7. E. J. King and G. E. Delory. (*Enzymologica*, 1940, **8**, 278–279.)—Most buffers are unsatisfactory for the study of the hydrolysis of phosphoric esters by mammalian phosphatases. For this, a combined Michaelis–Kolthoff buffer solution is proposed, which covers *p*H 6·8 to 9·6. It is prepared as follows:—25 ml. of *M*/10 sodium veronal are carefully pipetted on to *x* ml. of *N*/10 hydrochloric acid in a 100-ml. flask. After addition of 25 ml. of *N*/10 sodium carbonate solution and gently mixing, the solution is diluted to 100 ml. The following table gives the *p*H values of different mixtures. The determinations were made with the hydrogen electrode and the saturated calomel electrode, and the standard of reference was a sodium acetate and acetic acid buffer of *p*H 4·63 (*cf.* Sendroy, *Trans. Electrochem. Soc.*, 1934, **74**, 595).

x	*p*H at 22° C.	*p*H at 37° C.
2·5	10·7	10·4
7·5	10·3	10·1
12·5	9·95	9·79
20·0	9·44	9·27
25·0	9·00	8·83
30·0	8·44	8·34
40·0	7·96	7·87
50·0	7·48	7·45

When kept in well-closed, paraffin-waxed bottles, these mixtures showed no change in *p*H values for at least 10 months. E. B. D.

Use of Ascorbic Acid as a Substrate in Oxidase Measurements. B. D. Egell and F. Gerhardt. (*J. Agric. Res.*, 1940, **60**, 89–99.)—A study of the oxidative enzymes of fruit is of importance for an understanding of the changes that occur in stored fruit, and for this reason a more sensitive method of measuring small changes in enzyme activity is desirable. Guthrie (*J. Amer. Chem. Soc.*, 1930, **52**, 3614; *cf.* ANALYST, 1930, **55**, 709) determined oxidase activity iodimetrically, using as substrate a solution of glucose heated with dilute sodium hydroxide solution. Such a substrate has many disadvantages: (1) its composition is uncertain and variable, (2) it is usually coloured, and (3) it contains substances injurious to the enzyme. The use of ascorbic acid as substrate in place of the heated glucose solution has been investigated. Ascorbic acid has been found to be free from the disadvantages cited, and in addition it is readily oxidised, enabling smaller differences in enzyme activity to be detected. Twenty-five ml. of a 0·1 to 0·4 per cent. solution of ascorbic acid are introduced into a Van Slyke and Cullen aeration tube, and 1 to 10 ml. of the juice or extract containing the enzyme is added. A similar tube is filled with the substrate and a sample of the boiled juice or extract to serve as a blank. Air is drawn for 1 hour through the tubes, which are maintained at 25° C., and after aeration the solutions are transferred with 50 ml. of water to flasks containing 25 ml. of 10 per cent. trichloroacetic acid solution. About 20 ml. of 0·1 *N* potassium iodide solution are added, and after 30 minutes the solutions are titrated with 0·01 *N* sodium thiosulphate solution. The difference in the titration values of the boiled and unboiled samples is a measure of the oxidase activity. Preliminary experiments indicated that the optimal *p*H value for oxidase activity was approximately that of the original extract, *e.g.* 4·0 for apple juice and 6·2 for potato juice. Differences in the concentration of the substrate from 0·1 to 0·4 per cent. had little effect on the enzyme activity. The oxidation of ascorbic acid was certainly enzymic, the possibility of catalytic oxidation by traces of copper being excluded. F. A. R.

Vitamin A Destruction in Fish-liver Oils. E. J. Simons, L. O. Buxton and H. B. Colman. (*Ind. Eng. Chem.*, 1940, **32**, 706–708.)—Several different kinds of fish-liver oils were stored in the dark in small tubes open to the air at a temperature of 34·5 ± 0·5° C., and the peroxide values and vitamin A contents were determined at intervals. The peroxide values were measured by the methods of Wheeler* (*Oil and Soap*, 1932, **9**, 89), and the vitamin A contents spectrophotometrically, a factor of 2000 being used for converting $E^{1\%}_{1\,cm.}$ 328$m\mu$ into I.U. per g. When the percentage of vitamin A destroyed at any given time was plotted against the peroxide value at that time, the resulting curves fell into two distinct groups. With the more unsaturated oils, such as cod, pollack and the U.S.P. reference oil, the percentage of vitamin A oxidised was smaller at various peroxide values than in the less unsaturated oils, such as dog-fish, halibut and swordfish liver oils, at similar peroxide values. Within each of these two groups, the percentage of vitamin A oxidised was related to the peroxide value of the oil, and the higher the peroxide value the more vitamin

* One-gram samples of oil are dissolved in 25 ml. of a mixture (3 : 2) of glacial acetic acid and chloroform, 0·5 ml. of saturated potassium iodide solution is added, and the mixture is mixed gently for one minute. Fifty ml. of water are added, and the liberated iodine is titrated immediately with 0·02 *N* sodium thiosulphate solution, starch being used as indicator.

A was oxidised. The results are explained by assuming that two reactions occur, the first being the formation of peroxides and the second interaction between the peroxides and the vitamin. The ratio of rate of peroxide formation to rate of oxidation of vitamin A, is different for each of the two groups of oils. F. A. R.

Vitamin A Activity and Vitamin B_1 Content of Soya-beans and Cowpeas. J. O. Halverson and F. W. Sherwood. (*J. Agric. Res.*, 1940, **60**, 141–144.)—Nine varieties of soya-bean (*Soja max.*) and eight of cowpeas (*Vigna sinensis*) were assayed biologically for vitamin A activity and vitamin B_1 content. None of the samples contained appreciable amounts of vitamin A. The soya-beans contained 3·2 to 4·8 I.U. of vitamin B_1 per g., with an average value of 3·8, and the cowpeas 2·3 to 3·7, with an average of 3·0. F. A. R.

Observations on the Distribution of Vitamin B_1 in some Plant Families. M. Pyke. (*Biochem. J.*, 1940, **34**, 330–334.)—In continuation of work already published (*cf.* ANALYST, 1940, **65**, 180), a survey has been made, by the method previously described, of a large variety of fruit and vegetables. The following are the most important of the additional results now reported, the vitamin B_1 content being expressed in I.U. per 100 g. I. *Leaves and tops.*—New Zealand spinach, seakale, celery, 15 to 25. II. *Roots, etc.*—Beetroot, onions, 6 to 8; turnip, radish, 11 to 13; chicory, swede, 25; potato, parsnip, 30 to 38; leek, Jerusalem artichoke, 50 to 76. III. *Seeds and nuts.*—Butter-beans, 140; Barcelona nuts, 38; cob nuts, 76; Brazil nuts, 340. IV. *Fruit.*—Pineapple, cucumber, pear, peach, blackberry, lemon, currant, grape, 6 to 20; orange, 34; damson, 38; plum, greengage, 66. It is concluded that in general the vitamin B_1 content is highest in seeds, and that the amount in leaves is relatively constant irrespective of the botanical family. F. A. R.

Vitamin C Content of Honey. E. Becker and R. F. Kartos. (*Z. Unters. Lebensm.*, 1939, **78**, 305–308.)—The reducing substances in 12 samples of honey determined by titration with $N/100$ iodine solution, ranged from 3·5 to 89 mg. per 100 g. calculated as ascorbic acid. The amounts found in 4 samples by titration with 2-6-dichlorophenolindophenol ranged from 5·6 to 32·5 mg. Biological tests on guinea pigs, however, did not show any antiscorbutic action, and the authors therefore concluded that the honeys examined did not contain any vitamin C, but that an unknown reducing substance was present. D. A.

Bacteriological

Efficiency of the Wells Air Centrifuge as Determined by Air-washing Technique. K. MacDonald. (*Amer. J. Hyg.*, 1940, **31**, 85–87.)—The Wells Air Centrifuge technique has been accepted for the bacteriological analysis of air by most investigators in America and has been adopted by the American Public Health Association. It is not claimed by Wells that the instrument takes out all the bacteria, nor that it takes out the same proportion in every instance, and it was thought desirable to ascertain its average efficiency. The Palmer water spray sampler, which by means of an electrically driven fan aspirates air through a fountain spray curtain of water, retains 98 per cent., by actual test, of small particles of the same size as bacteria and spores. Parallel experiments were made with the Palmer apparatus and the Wells Air Centrifuge on air of an experimental room sprayed with 25 to 90 ml. of a 48-hour broth culture of *S. marcescens* per 10 cubic feet. Thirty minutes after the spraying of the air samples were taken, and again after every 15 minutes, until a series of 5 was completed, each sample consisting of 10 cubic feet of air and the sampling time being 5½ minutes. Thirty series of tests were made. Following each series the saline wash was plated out in agar and incubated, together with the contents of the corresponding Wells tube, at room temperature for 4 days. The results showed that the Wells Air Centrifuge has an efficiency of 96 per cent. in removing artificially inoculated droplet nuclei, but as the concentration of normal air-borne organisms increases, the average efficiency falls to 75 per cent. D. R. W.

Colouring Matters of *Penicillium carmino-violaceum* Biourge, with a Note on the Production of Ergosterol by this Mould. H. G. Hind. (*Biochem. J.*, 1940, **34**, 67–72.)—Cultures of *P. carmino-violaceum* grown on carbohydrate media are characterised by a colouring of the medium, yellow when acid and claret red when alkaline. The pigments responsible for these colour changes have now been isolated, and are given the names carviolacin and carviolin. The composition of carviolacin corresponds with the formula $C_{20}H_{16}O_7$ and that of carviolin with the formula $C_{16}H_{12}O_6$; both are monomethyl ethers of complex anthraquinone derivatives. Ergosterol was isolated from the mould mycelium. F. A. R.

Constitution of Carviolin: a Colouring Matter of *Penicillium Carmino-violaceum* Biourge. H. G. Hind. (*Biochem. J.*, 1940, **34**, 577–579).—Carviolin trimethyl ether was shown to be identical with the product obtained by methylating ω-hydroxyemodin, and carviolin $C_{16}H_{12}O_6$, which had previously been shown to contain one methoxy group, is therefore a monomethyl ether of ω-hydroxyemodin; the compound probably has a free β-hydroxyl group. F. A. R.

Studies on the Biochemistry of Micro-organisms. Emodic Acid and ω-Hydroxy-emodin, Metabolic Products of *Penicillium cyclopium* Westling. W. K. Anslow, J. Breen and H. Raistrick. (*Biochem. J.*, 1940, **34**, 159–168.)—The mycelium of a strain of

P. cyclopium yielded two derivatives of 2-methyl-anthraquinone, namely, emodic acid ($C_{15}H_8O_7$) in the form of orange needles, m.p. 363° to 365°, and ω-hydroxy-emodin ($C_{15}H_{10}O_6$), also as orange needles, m.p. 288° C. Emodic acid is 4 : 5 : 7-trihydroxyanthraquinone-2-carboxylic acid and ω-hydroxy-emodin is 4 : 5 : 7-trihydroxy-2-(hydroxymethyl) - anthraquinone. *Frangula* - emodin (4 : 5 : 7-trihydroxy-2-methylanthraquinone), ω-hydroxy-emodin and emodic acid, thus bear the same relationship to one another as do chrysophanic acid, aloe-emodin and rhein.

F. A. R.

Toxicological and Forensic

Detection of Chloralose in Urine. M. P. Cheramy. (*J. Pharm. Chim.*, 1940, [9], **1**, 233–234.)—Preparations of chloralose sold under names resembling those of the barbituric hypnotics have been used in attempted suicide. As the resulting coma resembles that produced by the barbiturates, large doses of strychnine are administered, and in one instance this treatment resulted in violent convulsions. Examination of the urine failed to reveal the presence of barbituric compounds, and after recovery the patient stated that he had taken a quantity of "somenal" corresponding with 2·25 g. of chloralose. A simple test for the presence of chloralose in urine is therefore required. The reaction described by Ross (*J. Biol. Chem.*, 1923, **58**, 641; Abst., ANALYST, 1924, **49**, 144), although neither delicate nor specific, serves for the detection of the moderately large amounts of chloralose that would be present in the urine of those attempting suicide with this drug. The test may be applied directly to the urine, but the following procedure is preferable:—The urine (20 ml.) is treated with 1 ml. of conc. sulphuric acid and 0·5 g. of activated carbon, and the mixture is boiled beneath a reflux condenser for 5 to 10 minutes. The cooled and filtered liquid is heated in a boiling water-bath with 2 or 3 ml. of pyridine and an equal volume of 30 per cent. sodium hydroxide solution for 1 or 2 minutes. In the presence of chloralose the pyridine layer is coloured rose to cherry-red, and the reaction will detect a concentration of 0·1 g. per litre. The reaction does not distinguish chloralose from other tri-halogenated products of methane (chloroform, chloral, bromoform, iodoform), but renders possible the rapid recognition of the type of hypnotic that has been taken. A. O. J.

Estimation of Barbiturates in Blood. G. A. Levvy. (*Biochem. J.*, 1940, **34**, 73–77.) None of the methods given in the literature for the estimation of the more stable barbituric acids can be applied to unstable barbiturates, such as evipan and pentothal. These compounds are insoluble in acid and neutral solution, and unstable in alkaline solution, rendering impossible the usual methods of extraction; they can, however, be isolated by drying the blood with anhydrous sodium sulphate and extracting the powder in a Soxhlet apparatus with a fat-solvent. After purification, the barbiturate is estimated by Koppanyi's colour reaction with cobalt acetate and isopropylamine in chloroform solution (Dille and Koppanyi, *J. Amer. Pharm. Ass.*, 1934, **23**, 1079). The method is applicable to the estimation of other barbiturates. For quantities of 1 mg. or more, the observed maximum error is 20 per cent., and for smaller amounts, the error is correspondingly greater. In a mortar (250 ml. capacity), 20 ml. of blood (coagulated or citrated) are mixed with 2 g. of sodium dihydrogen phosphate, and 40 g. of anhydrous sodium sulphate are added in small portions with constant grinding. The mortar is placed in a desiccator for 10 to 15 minutes to allow of complete drying, and the cake is then broken up and packed into a 100-ml. Soxhlet thimble. The solid is extracted for 3 hours at 50° C. with 80 ml. of a mixture (1 : 1) of petroleum spirit (b.p. 30° to 40° C.) and peroxide-free ether. At the end of the extraction the contents of the flask are shaken for a few minutes with 0·25 g. of a mixture (3 : 1) of charcoal (Merck's "Ultracarbon" washed with ether containing a few drops of glacial acetic acid, and then with ether) and magnesium oxide. The suspension is filtered, and the filtrate is distilled. The crystals of barbiturate that remain in the flask are taken up in a little chloroform and transferred to a 10-ml. graduated centrifuge tube and the solution is made up to a suitable volume. To 2 ml. of the solution are added 0·1 ml. of a 1 per cent. solution of cobalt acetate in methyl alcohol and 0·6 ml. of a 5 per cent. isopropylamine solution in methyl alcohol; the colour is compared with that given by 2 ml. of a standard solution similarly treated.

F. A. R.

Estimation of Carbon Monoxide in Blood. C. Scholten. (*D. Z. gericht. Med.*, 1939, **30**, 292–296; *Z. Unters. Lebensm.*, 1940, **79**, 296.)—An ammoniacal solution of silver oxide containing pyridine is mixed in a tube with a measured volume of fresh unclotted blood, and the tube is closed with a rubber stopper and left for 10 minutes in a water-bath at 70° C. The depth of the brown colour formed by reduction of the silver salt to colloidal silver is measured in a colorimeter. The degree of accuracy is about 5 per cent.

E. M. P.

Lead-content of Human Hair. K. N. Bagchi, H. D. Ganguly and J. N. Sirdar. (*Ind. J. Med. Res.*, 1940, **27**, 777–791.)—About 200 samples of hair from apparently healthy Europeans, Anglo-Indians and Indians of either sex and of various ages were examined. Contamination by extraneous lead compounds was eliminated by washing the samples, in bulk, successively with hot soap solution, ether, hot dilute sodium hydroxide solution, water, alcohol and ether. Attempts to reduce the number of stages were unsuccessful,

although further treatment (with alkali, acid, water, ammonium acetate solution, alcohol and ether, in succession) resulted in no further reduction in the lead content. The lead was determined by the dithizone method of Lynch, Slater and Osler (ANALYST, 1934, **59**, 787; 1935, **60**, 32), slightly modified, 2 g. of hair usually being taken. The values found varied widely, namely, from 3·0 to 508 p.p.m., and since women's black hair contained the largest amounts (170 to 508 p.p.m.), men, and women's grey hair the least (3·0 to 21·0 p.p.m.) and brown, auburn and other shades of hair intermediate quantities (9·0 to 16·5 p.p.m.), it is suggested that lead is a factor in the production of the characteristic hair pigmentation of different nationalities. The Bengalee Hindu married women use a cheap grade of "vermilion" (consisting of red lead mixed with a red synthetic dye and scented) in order to mark the thin line, about 1 inch long on the anterior end of the hair-parting, which is indicative of unwidowed married life, and the average lead-content of their hair (180 p.p.m.) is much higher than that of the Bengalee Mohammedan women (50·4 p.p.m.), who do not use it. The hair of children contains relatively less lead than that of their parents, unless there is evidence of abnormal exposure; girls seem to be more susceptible to such exposure, and absorb larger quantities of lead than boys. Thus in one family the hair of the son (7 years old) contained 9 p.p.m., and that of the daughter (3½ years old) 75 p.p.m. of lead. There is evidence that the use of vegetable hair oils (*e.g.* sesame oil) aids absorption of lead through the scalp in the same way that greasy cosmetics containing lead are absorbed through the skin (*cf.* Monier-Williams, "*Lead in Food*," 1938, p. 2; ANALYST, 1939, **64**, 32). The values found for the male population of the various Indian provinces, except Bengal, (20·0 to 22·7 p.p.m.) are of the same magnitude as that found for the average European of either sex, including Jews and Anglo-Indians (18·4 to 20·8 p.p.m.), and the hairs of European residents in Calcutta were similar in average lead-content. Hair from Bengalee Mohammedan males, however, gave a much higher figure (42·4 p.p.m.), although no reason for this has yet been found. Relatively large quantities of lead were found in the urine and faeces of some Hindu men and women and, since correspondingly high quantities were then found in the hair, it is considered that lead is absorbed into the general circulation and eliminated through the hair. Thus 0·04, 387·1 and 241·0 p.p.m. of lead were found in the urine, faeces and hair of a worker in a lead factory. In many instances a mild form of alopecia was associated with high lead-contents in the hair, and it is suggested that chronic lead intoxication may prevent access of nourishment to the follicles, with the result that the hair falls out. Lead is not always distributed uniformly in a hair; in one instance (female) the distal end contained 66 mg. and the proximal end 48 mg., whilst in another there was little difference between the ends. This was to be expected, since the excretion of lead through the hair varies from day to day, and it may prove of medico-legal importance, *e.g.* as an indication of the period of ingestion of a poison. The form in which the lead is present in hair is not yet known, but a combination with phosphorus is suspected. Other metals (*e.g.* cobalt, copper, zinc, and manganese) also occur in hair in relatively large quantities, and it is believed that the surplus metals which have served their purpose (*e.g.* as catalysts in the physiological system) are removed in this way (*cf.* ANALYST, 1939, **64**, 698). J. G.

Examination of Dusts from Lungs Produced by Mining and other Processes. D. G. Beadle. (*J. Chem. Met. Mining Soc. S. Africa*, 1940, **40**, 286–287.)—Methods of measurement of the size distributions of dust from silicotic lungs are discussed (*cf.* H. S. Patterson, *id.*, 1939, **39**, 229). In Jones's method (*J. Hyg.*, 1933, **33**, 309; and ANALYST, 1934, **59**, 124, 191) the lung is disintegrated with nitric acid, the resulting slime is filtered, and the residue is dried and ignited; the resulting deposit, however, is lumpy (probably because of the presence of phosphates which form glassy compounds on ignition), and is therefore unsuitable for size-distribution tests. It is preferable to use Fox's method, in which the tissue is boiled in a Kjeldahl flask with a mixture of nitric and sulphuric acids containing a crystal of copper sulphate. When the organic matter has been destroyed the residual siliceous dust may be separated by filtration and suspended in water, a drop of the suspension is allowed to evaporate on a microscope cover-glass, and the residual deposit is ignited and examined under the microscope. It was found that 22·5, 42·5 and 35·0 per cent. of the particles were less than 0·2, 0·2 to 0·8 and 1·2 to over 5·0 microns in size, respectively. In Simson's method the minced lung tissue is digested with papain in an incubator for 10 days at 54° C., the resulting mixture is diluted and centrifuged, and the deposit is washed by a combination of centrifuging and decantation. Phosphates are then removed by warming with hydrochloric acid for 30 mins. and the residue is again washed as described and mounted for examination. It was found that 48·1, 29·2, 5·2 and 17·5 per cent. of the particles were less than 0·2, 0·2 to 0·4, 0·8 and 1·2 to over 5·0 microns in size, respectively. The difference between the two methods probably arises from a loss of fine particles during filtration in the Fox method. J. G.

Active Principles of Leguminous Fish-poison Plants. IV. Isolation of Malaccol from *Derris malaccensis*. S. H. Harper. (*J. Chem. Soc.*, 1940, 309–314.)—The ethereal extract of the root of *Derris malaccensis* gives a gelatinous deposit (about 1·5 per cent. on the root). The substance is present in the root in a stabilised non-crystalline form, but when purified by crystallisation from benzene or

ethyl acetate yields bright yellow prisms or needles, m.p. 225° C., re-melting at 244° C. (the double m.p. is due to racemisation), and having $[\alpha]_D^{18} = +190°$ in chloroform, +67° in benzene. It was found to be identical with a substance isolated by Meyer and Koolhas from Sumatra derris root (*Rec. Trav. chim. Pays-Bas*, 1939, **58**, 207; Abst., ANALYST, 1939, **64**, 295), and was called "malaccol." Analytical data agreed with the formula $C_{20}H_{16}O_7$; this formula bears the same relationship to that of elliptone as does the formula of sumatrol to that of rotenone, and malaccol is thus isomeric with elliptolone (*J. Chem. Soc.*, 1939, 1424). Malaccol differs from other members of the group in giving a +rotation in benzene solution, but the introduction of a phenolic OH in position 15 in each instance gives a positive increment to the specific rotation, and malaccol is regarded as thus fitting into the *l*-series (rotenone—deguelin—elliptone—sumatrol—toxinol—malaccol). On maintaining the temperature of *l*-malaccol just above the lower m.p. a rapid loss of optical activity is observed and *l*-malaccol readily sublimes at 195° C. in a high vacuum to give a 75 per cent. racemised product. D. G. H.

Gas Analysis

Determination of Methylpropene by Means of a Modified Denigès Reagent. A. Newton and E. J. Buckler. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 251–254.)—An investigation of the reaction between methylpropene and Denigès' reagent (*Compt. rend.*, 1898, **126**, 1043) showed that the variation in the composition of the precipitate is due partly to the excessive acidity caused by the formation of nitric acid in the reaction and partly to the replacement of the nitrate radical by hydroxyl (or possibly water) during the washing of the precipitate. When the reagent is modified by addition of sufficient sodium hydroxide to convert the mercuric nitrate into the basic salt the total weight of the precipitate cannot be taken as a measure of the methylpropene absorbed, but the amount of mercury in the precipitate is equivalent to the methylpropene. The modified reagent is prepared as follows:—Mercuric oxide (100 g.) is mixed to a paste with 100 ml. of water and dissolved in the minimum amount (about 90 ml.) of 70 per cent. nitric acid. The solution is treated, drop by drop, with a solution of 10 g. of sodium hydroxide in about 15 ml. of water until a slight permanent precipitate of basic mercuric nitrate is formed. The mixture is then diluted with water to 2 litres, filtered and stored in a dark glass-stoppered bottle. The apparatus required for the determination consists essentially of a water-jacketed gas burette with a compensator and an absorption tube. The sample of gas, varying from 35 ml. for 20 per cent. methylpropene to 150 ml. for 1 per cent. methylpropene, is introduced into the burette and, after the lapse of 30 seconds, its volume and pressure are measured. The reagent (50 ml.) is drawn into the absorption tube which is then evacuated by means of a water-pump, closed and attached to the burette. The sample of gas is transferred to the absorption tube, which is then detached and shaken vigorously for 5 minutes and, after the admission of air, for a further 2 minutes. The liquid is run out from the absorption tube, which is rinsed, and the combined absorbent and washings are heated gently to 100° C. (but not allowed to boil). When cold the liquid is filtered through a No. 3 (or preferably No. 4) sintered glass crucible, and the precipitate is washed with cold water until the filtrate gives no precipitate with ammonium sulphide. The precipitate is dissolved by warming with about 10 ml. of 70 per cent. nitric acid, and the solution is oxidised by the addition of a saturated potassium permanganate solution until the pink colour persists. The excess of permanganate is destroyed by the addition of a slight excess of a 10 per cent. oxalic acid solution and, after dilution to 100 to 150 ml. and addition of 2 ml. of a saturated solution of ferric alum in 50 per cent. nitric acid, the liquid is titrated with 0·1 *N* potassium thiocyanate solution. Each ml. of 0·1 *N* potassium thiocyanate solution is equivalent to 0·01003 g. of mercury or 0·1601 ml. of methylpropene (at 0° C. and 760 mm.). Good results are obtained by the use of a volume of reagent equal to about 10 times the volume of methylpropene to be absorbed. Ethene, propene and 1, 3-butadiene were slowly absorbed by the reagent, but gave no precipitate when the solution was boiled. A mixture of 1- and 2-butenes prepared by the dehydration of secondary butanol was slowly absorbed, and yielded a faint turbidity corresponding with 0·37 per cent. of methylpropene in the gas. When the gas was shaken twice with 67 per cent. sulphuric acid the residue was slowly absorbed by the reagent but yielded no precipitate. Hurd and Goldsby (*J. Amer. Chem. Soc.*, 1934, **56**, 1812) report that 2-methyl-2-butene gives no precipitate with the acid Denigès reagent. With the modified reagent the mixture of pentenes obtained by dehydrating 2-methyl-2-butanol gave a heavy precipitate, and a C_5 fraction obtained from debutanised cracked gasoline behaved similarly. This was probably due to the presence of 2-methyl-1-butene in the samples. The possibility of applying the method to the determination of pentenes is being studied; 1- and 2-butenes neither give a precipitate with the reagent nor interfere with the determination of methylpropene. The method is entirely satisfactory in the presence of C_2, C_3 and C_4 olefines, but pentenes must be absent. A. O. J

Organic

Determination of Lactic and Pyruvic Acids by means of Periodic Acid. (Mlle) R. Boisson. (*J. Pharm. Chim.*, 1940, [9], **1**, 240–255.)—The behaviour of lactic and pyruvic

acids on oxidation with periodic acid (Boisson and Fleury, *J. Pharm. Chim.*, 1939, **30**, 145, 307) affords means for their analytical determination. It has been shown (*loc. cit.*) that when dilute solutions of lactic acid are oxidised at 100° C. with periodic acid, acetaldehyde and carbon dioxide are formed. The aldehyde, which must be removed as soon as it is formed, is passed by means of a current of air into alkaline iodomercurate solution, and the precipitated mercury is determined by a volumetric method. Ten ml. of an aqueous solution, containing 0·1 to 1·0 per cent. of lactic acid, are mixed with 10 ml. of 10 per cent. sodium periodate solution and 2 ml. of 10*N* sulphuric acid and heated in a flask provided with the means of leading an air current at the rate of 10 to 20 litres per hour through the liquid. The vapour is led through a reflux water-condenser into two absorption flasks in series containing the iodomercurate solution. Concentrated iodomercurate solution is prepared by dissolving 27 g. of mercuric chloride and 72 g. of potassium iodide in sufficient water to produce 250 ml. Ten ml. of this solution are mixed with 15 ml. of sodium hydroxide solution (sp.gr. 1·33), and 5 ml. of this mixture are placed in the second absorption flask and the remainder, with 5 ml. of a 20 per cent. suspension of barium sulphate in water, in the first. Distillation is allowed to proceed for 30 minutes. The combined liquids in the absorption flasks are acidified with dilute sulphuric acid, a known excess of *N*/10 iodine solution is added, and the mixture is allowed to stand with frequent shaking until all the precipitated mercury has dissolved. The residual iodine is then titrated with *N*/10 sodium thiosulphate solution. The factor to convert ml. of *N*/10 iodine solution into mg. of lactic acid is 4·5. With the following modifications the method may be used as a micro-method. Five ml. of lactic acid solution containing 0·5 to 1 mg. of lactic acid, 3 ml. of 10 per cent. sodium periodate solution and 1 ml. of 10*N* sulphuric acid are placed in the distillation flask. The first absorption flask contains 6 ml., and the second 1 ml., of alkaline iodomercurate solution. During the first 15 minutes water is not circulated through the condenser, and the volume of the reaction mixture is thereby reduced to about one-half. Water is then circulated, and the distillation is continued for a further 45 minutes, the air-current being maintained. The contents of the absorption flasks are acidified with 5 or 6 ml. of 10*N* sulphuric acid, and the determination is carried out as previously described, 0·02*N* iodine solution and 0·01*N* sodium thiosulphate solution being used. A control determination is made with 6 ml. of the iodomercurate solution. The application of the method to the determination of lactic acid in presence of glucose was studied. Methods depending upon the removal of glucose by chemical means were found unsuitable, and the method finally adopted was extraction of the lactic acid with ether from an aqueous solution saturated with ammonium sulphate. A simple form of extractor for this purpose is described. The lactic acid is then extracted from the ethereal solution with dilute alkali solution, and this extract is submitted to the process already described.

For the determination of pyruvic acid two methods are available. The solution containing 5 to 30 mg. of pyruvic acid is heated beneath a reflux air-condenser for one hour with 5 ml. of 0·1*M* sodium periodate solution in 30 per cent. (v/v) sulphuric acid. With 5 to 15 mg. of pyruvic acid the time may be reduced to 30 minutes. To the cooled mixture excess of sodium bicarbonate, 15 ml. of 0·1*M* arsenious anhydride solution and 1 ml. of 20 per cent. potassium iodide solution are added (*cf.* Abst., ANALYST, 1933, **58**, 307). After 10 minutes the residual arsenious anhydride is titrated with *N*/10 iodine solution. The result of a blank determination is deducted. The factor to convert ml. *N*/10 into mg. of pyruvic acid is 8·8. By the second method the acidity to thymolphthalein indicator is determined before and after the oxidation. Since pyruvic acid is oxidised to the equivalent amounts of acetic acid and carbon dioxide, the diminution of acidity to this indicator represents the amount of periodic acid reduced. The conditions of concentration and heating are the same as for the first method. The cooled liquid is titrated to the pale-blue end-point of the indicator with *N*/10 sodium hydroxide solution. The control determination is made with 5 ml. of sodium periodate solution and 5 ml. of the solution to be examined. The method is rapid, but less precise than the first. It was found impossible to determine lactic acid in mixtures of lactic and pyruvic acids by the methods described unless the molecular concentration of the lactic acid was at least equal to that of the pyruvic acid. A. O. J.

Identification of 2-Aminoethanol. B. Keiser. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 284.)—In aqueous solution 2-aminoethanol (monoethanolamine) can be identified readily by its reaction with phthalic acid to form 2-hydroxyethylphthalimide (m.p. 127° C.). The solution of 2-aminoethanol is treated with an equivalent amount of phthalic acid dissolved in hot water. The mixture is evaporated to dryness, and the residue is heated at 210° C. for 5 minutes. The phthalimide, which is formed quantitatively, is recrystallised from water, or, if inorganic impurities are present, from an anhydrous solvent such as benzene or absolute alcohol, and its m.p. is determined. Conversely, the reaction may be used for the identification of phthalic acid. The concentration of 2-aminoethanol in the sample is assumed, or determined by titration with acid, each ml. of *N* hydrochloric acid being approximately equivalent to 0·061 g. of the amine. 2-Aminoethanol can also be identified in aqueous solution by formation of its oxalate (m.p., 199° to 200° C. uncorr.; corr., + 3·8° C.). In addition, this salt may be

converted into N,N′-bis-(2-hydroxyethyl)-oxamide, which melts at 168° C. uncorr. (corr., + 2·4° C.). The solution of 2-aminoethanol is treated with an equivalent amount of an oxalic acid solution and evaporated to dryness. The residue is heated at 110° C. for 5 minutes and recrystallised from 70 per cent. alcohol and its m.p. is determined. On heating to about 222° C. brisk boiling occurs, with formation of the oxamide. The reaction may be used for the identification of oxalic acid. A. O. J.

Determination of Organic Peroxides. H. A. Liebhafsky and W. H. Sharkey. (*J. Amer. Chem. Soc.*, 1940, **62**, 190–192.)—Organic peroxides in *n*-butyl ether may be determined by iodimetric titration in glacial acetic acid. Satisfactory blank tests cannot be made by this method, but the need for a blank test is avoided by adding sodium bicarbonate to the reaction mixture to drive out air. To 25 ml. of glacial acetic acid and approximately 1·5 g. of sodium bicarbonate in a glass-stoppered flask, 1 ml. of potassium iodide solution (0·4 g. per ml.) is added. The faintly yellow mixture is titrated with *N*/100 thiosulphate solution, added two drops at a time, until the colour is the faintest perceptible to the eye. (Starch is an unsatisfactory indicator here.) As the reaction in glacial acetic acid does not appear to be instantaneous, the successive additions of thiosulphate should be made at intervals of about 10 seconds. The sample for analysis (usually 5 ml. of *n*-butyl ether) is then added, the flask is stoppered and kept in the dark for 5 minutes, and the mixture is titrated with *N*/100 thiosulphate solution. If, after 5 minutes more in the dark, no further liberation of iodine occurs, the titration is satisfactory. Experiments with test solutions showed the reaction to be complete in less than ten minutes, and accurate to within two drops of *N*/100 thiosulphate solution. A study of the formation and decomposition of the peroxides in *n*-butyl ether has shown that they are increased by exposure to ultra-violet radiation or to daylight, and still more rapidly by bubbling oxygen through the boiling ether, whilst they are destroyed by heating under reflux. Hydrogen peroxide or benzoyl peroxide in glacial acetic acid may also be determined accurately by this method. E. B. D.

Hemicelluloses of the Wood of English Oak. 5. Structure of Hemicellulose B. M. H. O'Dwyer. (*Biochem. J.*, 1940, **34**, 149–152.)—The hemicellulose B from oak sapwood, like hemicellulose A from the same source, contains anhydroglucose units, whereas the hemicellulose B (and hemicellulose A) from oak heartwood contains none. The anhydroglucose units of sapwood hemicellulose B account for its positive specific rotation. All the hemicelluloses contain xylose and uronic acid residues, and on hydrolysis with taka-diastase they yield xylose and a water-soluble polysaccharide with $[\alpha]_D^{20} = -51{\cdot}2°$. This is composed of 1 monomethylhexuronic acid residue and 6 xylose residues. F. A. R.

Examination of Damaged Cotton by the Congo Red Test: Further Developments and Applications. G. G. Clegg. (*J. Textile Inst.*, 1940, **31**, T. 49–68.)—Slight modifications of the original test (*cf.* Bright, ANALYST, 1926, **51**, 593) are described. The sample is (1) immersed for 3 minutes in the sodium hydroxide solution, which should contain a wetting-agent (*e.g.* 0·5 per cent. Shirlacrol); (2) washed in water; (3) placed in the Congo red reagent for 10 minutes; (4) washed; (5) immersed in 18 per cent. sodium hydroxide solution. The concentration of alkali used in stage (1) must be selected so as to produce a controlled degree of swelling; thus, if the fibres are already damaged so that the cuticle is ruptured and the secondary cellulose is exposed, a concentration of 9 per cent. is used. A concentration of 11 per cent. is required for examination of damage due to heat, light, chemicals or mildew, because this weakens the cuticle by splitting it, but without tearing it. Damage to the cuticle due to mild processing is slight, and therefore necessitates a concentration of 18 per cent., and this serves also for estimating the percentage of abnormally-thickened fibres. The investigations of Calvert and Summers (*J. Text. Inst.*, 1925, **16**, T. 233) on the mechanism of swelling by alkali are summarised, and a graph, reproduced from their paper, shows that as the concentration increases up to 13·5 per cent. the width of the fibre gradually increases, although with higher concentrations it remains constant on account of the constricting effect of the cuticle, the first influence of which is apparent at concentrations of 11 per cent. Similarly, stage (5) serves to swell the differentially-stained fibres and to accentuate colour contrasts. The examination should be made with a 2/3 inch objective and 10× eyepiece, with full daylight illumination. The mounts are only temporary, but will last a few days if sealed with a mixture of lanolin and colophony resin (1 : 4). The test is based on the different rates of diffusion of the dye into the exposed swollen secondary cellulose and cuticle of the fibre, with the result that the former is stained to a deeper shade; this diffusion depends on the nature and extent of the damage which the fibre has undergone, and is most critical at room temperature. The appearance of fibres which have been treated in various ways is described in detail and illustrated by photomicrographs. Mechanical damage may be evident from signs of surface bruising, deep cuts in the fibre wall, abrasion and broken fibre-ends. The test can also be used to indicate the nature and extent of the wear of finished goods, *e.g.* to distinguish between normal wear by frictional rubbing and contact with an abrasive surface. With heat tendering the cuticle breaks up, first into coarse spirals (*e.g.* after 24 hours at 95° C.), and then into finer spirals, until the constricting effect of the cuticle is no longer

exerted and it becomes almost completely detached; the fibres are then stained uniformly bright red (*e.g.* after 19 days at 95° C.). Singed fibre-ends are shown by a brownish-red tip, unless chlorides are present, when the tips concerned do not take the stain. Acid tendering and over-bleaching result in changes in the cuticle similar to those produced by heat, but the spirals are less distinct, and transverse cracks appear in the final stages; bright red local blotches are characteristic of local tendering by strong acid. The test usefully supplements fluidity tests for the amount of bleached stock in a yarn, especially when the sample is small, and when a proportion of fully-bleached cotton in the loose state has been introduced in order to whiten a yarn. The results are roughly quantitative, and those obtained by different observers are in good agreement. If the presence of stock which is not fully-bleached is suspected, an ash-content determination is used to decide whether a wet treatment has been used, and the Congo red test serves to indicate its severity. Tendering effects due to light are similar to those caused by acid tendering, but are more localised, and mercerisation increases the depth of shade of the cuticle. Mildew effects are difficult to distinguish from mechanical and chemical damage, but there is more evidence of disintegration, and the hyphae, if present, are stained bright red; fluidity tests in cuprammonium solution should be used to confirm the conclusions. Bacterial tendering varies with the nature of the organisms; some produce very characteristic effects (*e.g.* fuzzy fibre-contours), whilst others behave similarly to mildew. "Dead" cotton, due to attack by fungus while the fibres are growing on the boll, is stained bright red in the Congo red test, and can thereby be differentiated from fungus attack of other (*e.g.* genetic or physiological) origin which produces a pink stain. In the examination of yarn breaks (*cf.* Clegg, *id.*, 1926, **17**, T. 591) the number of broken fibres may be estimated by difference from the average numbers of fibres in the cross-section of the yarn, and of those which end naturally in the portion of the yarn in which the break occurs. A number of specific examples of applications of the test to the examination of defects in cotton goods, are described in detail and illustrated. J. G.

Use of Cheap Filter Paper for Analysing Tan Liquors. H. B. Merrill and G. C. Mueller. (*J. Amer. Leather Trades Chem.*, 1940, **35**, 289–290.)—The official A.L.C.A. methods for the analysis of tanning extracts and yard liquors specify the use of either Munktell No. 1F or S. & S. No. 590 filter-papers. As these are expensive and difficult to obtain in war-time, the use of a cheaper grade of paper for routine analyses of yard liquors has been considered; in the present instance the substitute was a Central Scientific Co. No. 13250 paper, but it is suggested that many other cheap grades would be found equally suitable. Duplicate determinations of the soluble and non-tannin matters and tannins in 14 representative yard liquors with the C.S. paper, as compared with the 1F paper, gave maximum differences of −0·06, −0·04 and −0·05 and average differences of ±0·021, 0·014 and 0·018 g. per 100 ml., respectively. These are regarded as negligible for routine purposes. Filtration with the cheaper paper was somewhat slower, although the yard liquors in question were relatively free from insoluble matter. J. G.

Inorganic

Titration of Nickel with Dimethylglyoxime with the Aid of the Dropping Mercury Electrode as Indicator Electrode. I. M. Kolthoff and A. Langer. (*J. Amer. Chem. Soc.*, 1940, **62**, 211–218.)—The "amperometric" titration of nickel with dimethylglyoxime can yield accurate results and is applicable to dilute nickel solutions. Delicate electrical apparatus is required and the titration requires to be carried out in absence of air. Numerous other ions interfere. S. G. C.

Determination of Lead in Tin Coatings. P. Foerster. (*Ann. Chim. anal.*, 1940, **22**, 93–94.)—The coating is dissolved off the specimen with hot water to which portions of sodium peroxide are added. The liquid is boiled to destroy peroxide, and the lead, together with small amounts of copper and iron, is precipitated as sulphide by the addition of sodium sulphide. The precipitate is filtered off, washed with dilute sodium sulphide solution, and dissolved in hydrochloric acid containing bromine; after removal of bromine by heating, the lead is re-precipitated as sulphide from alkaline solution in presence of potassium cyanide to keep copper and iron in solution. The lead sulphide precipitate is filtered off and dissolved, and the lead is determined by the chromate colorimetric method. S. G. C.

Improved Form of the Formaldoxime Colorimetric Method for Manganese. C. P. Sideris. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 307.)—The author's formaldoxime colorimetric method for the determination of manganese (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 445; Abst., ANALYST, 1937, **62**, 831) was found inadequate by Wiese and Johnson (*J. Biol. Chem.*, 1939, **127**, 203; Abst., ANALYST, 1939, **64**, 459), and, in more recent studies by the author, for biological material of high phosphate-content. The interference of phosphates can be eliminated by precipitation with lead acetate in acetic acid solutions, and the original method may then be employed. An aliquot portion (10 ml.) of the solution of ashed biological material in dilute hydrochloric acid is neutralised with *N* sodium hydroxide solution, the amount of alkali required being ascertained by titration of another aliquot portion with methyl red as indicator. The solution is then acidified with 2 ml. of 20 per cent. acetic acid, which dissolves the manganic phosphate but not the ferric phosphate precipitate. Excessive phosphate, *e.g.* with plant

tissues, is removed by the addition of 0·5 ml. of a 5 per cent. solution of lead acetate. The mixture is agitated and allowed to stand for 10 minutes, and excess of lead salt is removed by the addition of 1 ml. of a 20 per cent. sodium sulphate solution. After 30 minutes the mixture is filtered or centrifuged. An aliquot portion (10 ml.) of the filtrate is neutralised with 40 per cent. sodium hydroxide solution, 3 to 4 drops of the formaldoxime reagent (Sideris, *loc. cit.*) are added and then more of the 40 per cent. sodium hydroxide solution until the colour develops. The addition of sodium cyanide, as prescribed in the original publication (*loc. cit.*), is not necessary. Ferric chloride need not be added to the comparison standard solution if the removal of iron from the sample solution was complete. The final volume of the sample and comparison solutions is made up to 15 or 20 ml. In 10-ml. portions of sample containing from 0·005 to 0·01 mg. of manganese in presence of 0·010 to 0·100 mg. of phosphate (PO_4) the average error was 2 per cent. A. O. J.

Volumetric Determination of Small Quantities of Barium and Sulphate with Barium Rhodizonate as Indicator. C. C. Miller. (*J. Chem. Soc.*, 1940, 401–406.)—Advantages are offered by the use of a suspension of the scarlet modification of barium rhodizonate as indicator; 40 mg. of sodium rhodizonate are dissolved in 20 ml. of water and treated with 0·1 g. of barium chloride dissolved in a little water. The flocculent brown precipitate is centrifuged, washed with a little water and then with ethyl alcohol; 5 ml. of ethyl alcohol, containing 0·1 ml. of conc. hydrochloric acid, are added to the precipitate, and the tube is placed in hot water to convert the complex into the scarlet form. The precipitate is centrifuged off and suspended in 250 ml. of alcohol. The suspension keeps well in a stoppered bottle; it is shaken before use. *Titration of Barium.*—The solution (10 ml., equivalent to 2 to 20 mg. of sulphate and containing 0·2 to 1 ml. of 2 *N* hydrochloric acid) is treated with 0·5 ml. of indicator suspension, and alcohol equivalent to the volume of the solution, less 5 ml., is added. The mechanically stirred liquid is titrated, drop by drop, with a 0·02 *M* solution of ammonium sulphate in 50 per cent. alcohol until the pink colour disappears. A very slow rate of titration (1 drop in 10 seconds) is advisable near the end-point, and the temperature is preferably 25° C. Occasionally a pale pink colour persists beyond the end-point, owing to adsorption on the barium sulphate. The most consistent results were obtained with solutions containing 0·5 ml. of 2 *N* hydrochloric acid in a final volume of 18 to 27 ml. *Determination of Sulphate.*—Direct titration of sulphate is impracticable. The following indirect method was devised:—Ten ml. of the sulphate solution, containing 2 to 20 mg. of sulphate and 0·5 to 1 ml. of 2 *N* hydrochloric acid, are titrated at 90° C., at the rate of 1 ml. per minute, with 0·02 *M* barium chloride solution until an excess of 1 to 2 ml. is present. The precipitate is digested at 90° C. for 10 minutes, and the liquid is then cooled. Alcohol equivalent to the total volume, less 5 ml., is added, followed by 0·5 ml. of indicator suspension, and the liquid is titrated with 0·02 *M* ammonium sulphate solution in 50 per cent. alcohol, as in titrating barium. *Notes.*—The required degree of acidity for the titration was conveniently obtained by the use of "brilliant cresyl blue" indicator. The indicator solution, as supplied by the British Drug Houses, was diluted tenfold with alcohol, and 0·1 ml. of the dilute solution was added to the solution to be titrated. Sufficient 2 *N* hydrochloric acid was added until the blue colour was just discharged; this corresponds to the addition of about 1 ml. of the acid to a neutral solution. For solutions initially too acid, the acidity was conveniently reduced by addition of magnesium acetate solution until the blue colour appeared and then just discharging it with 2 *N* hydrochloric acid. The addition of alcohol causes the blue colour to return. In association with the scarlet barium rhodizonate the blue produces a violet colour changing at the equivalence point to a pure blue. The change-point was sharper than in absence of the blue indicator. The accuracy of the determination was within about 1 per cent. of the theoretical amount. The only ions found to have any appreciable interfering action were ferric, cupric, lead, calcium and phosphate. Reduction with hydroxylamine hydrochloride or aluminium powder overcame the interference of ferric and copper salts. Sodium rhodizonate costs 5s. per g., but 40 mg. converted into barium rhodizonate suspension suffices for 500 titrations. S. G. C.

Removal of Phosphoric Acid from Hydrogen Peroxide. S. R. Dickman and R. H. Bray. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 279.)—Phosphoric acid present in hydrogen peroxide as a stabiliser, may be removed, if objectionable, by the following process:—Ten ml. of 2 per cent. ferric chloride solution and 5 g. of calcium carbonate are added to a 100-ml. sample, and the mixture is stirred and filtered on a Buchner funnel. The hydrogen peroxide solution is then acidified with an alternative acid for stabilisation. S. G. C.

Microchemical

Colorimetric Determination of Silver. C. G. Makris and R. Menaché. (*Ann. Chim. anal.*, 1940, **22**, 117–120.)—The method is based on reduction with tannin in presence of small amounts of alkalis and a solution of sodium albuminate. The test substance should first be converted into nitrate and then dissolved in 2 ml. of water in a small colorimeter tube. Three different amounts (0·25, 0·5 and 1 ml.) of a standard 0·01 per cent. silver nitrate solution are measured into other tubes, and each is made up to 2 ml. Into each tube are introduced 4 ml. of a freshly prepared 0·5 per

cent. solution of tannin and 0·18 ml. of 0·1 *N* sodium hydroxide solution, and then, after shaking, 2 drops of sodium albuminate (5 ml. of fresh egg-white in 100 ml. of 0·1 *N* sodium hydroxide solution). After 5 minutes the tubes are examined, the unknown being compared with the standard solution most approximating to its colour intensity. Lead, if present in large proportion, should be removed as sulphate before determining the silver. The average error is ± 5 per cent. J. W. M.

Colorimetric Determination of Magnesium. C. P. Sideris. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 232–233.)—The method is devised for the determination of magnesium in dried plant tissues. The material (2 g.) is ashed in a platinum or porcelain crucible, and the ash is dissolved in 5 ml. of 18·5 per cent. warm hydrochloric acid. After dilution to a suitable volume (100 ml.) any insoluble matter is removed by filtering or centrifuging. An aliquot part is transferred to a 50-ml. centrifuge tube, treated with 1 ml. of 1 per cent. lead acetate solution to precipitate phosphate, and centrifuged. The excess of lead is precipitated with 1 ml. of 1 per cent. sulphuric acid and separated by centrifuging. The filtrate is transferred to a 125-ml. conical flask and neutralised with *N* sodium hydroxide solution, methyl red being used as indicator. The calcium is precipitated with 2 ml. of 20 per cent. acetic acid and 5 ml. of 4 per cent. ammonium oxalate. After standing 4 to 6 hours the mixture is filtered through asbestos, and the residue is washed with water. If required, the calcium may be determined, after solution, by titration with permanganate. To the filtrate are added 2 ml. of 20 per cent. acetic acid and 3 ml. of a 5 per cent. alcoholic solution of 8-hydroxyquinoline. If a precipitate forms (copper or nickel hydroxyquinolinate) the mixture is centrifuged and the precipitate is filtered off and discarded. To the clear solution 5 ml. of conc. ammonium hydroxide (28–29 per cent.) are added, and the mixture is heated over a water-bath for 30 minutes. It is then cooled and treated with about 5 ml. of chloroform to dissolve the hydroxyquinolinates of iron, manganese, aluminium, etc. After an hour the mixture is filtered through a G4 Jena sintered glass filter, which is rinsed with at least 5 ml. of a 10 per cent. aqueous solution of ammonium hydroxide and 2 ml. of chloroform. The magnesium hydroxyquinolinate is dissolved in 5 ml. of 18 per cent. hydrochloric acid and made up to a known volume. An aliquot amount (10 ml.) is buffered with 3 ml. of a 50 per cent. solution of sodium acetate, and 3 ml. of a 1 per cent. solution of ferric chloride hexahydrate are added. The green-black pigment is extracted with chloroform (3–4 times), made up to volume with butyl alcohol (to retard volatilisation), and compared in a colorimeter with a standard solution, prepared in the same way, containing 10 to 20γ per ml. Results were excellent with amounts of magnesium ranging from 1 to 0·1 mg. J. W. M.

Test for Iodide and Nitrite. C. L. Wilson. (*Chem. and Ind.*, 1940, **59**, 378–379.)—Several brands of special paper sold for spot tests contain enough starch to enable the usual iodide test to be carried out without any specially-prepared starch solution. In making the test a drop of 2*N* acetic acid is placed on the paper, and the test drop is run in from a capillary and followed by a drop of 0·1*N* potassium nitrite solution for the oxidation. *Limit of identification:* 0·025γ of iodide; *concentration limit:* 1 : 2,000,000. In absence of other oxidising agents the test may be used reciprocally for nitrite. *Limit of identification:* 0·005γ of NO'_2; *concentration limit:* 1 : 10,000,000. J. W. M.

Microgram and Millimicrogram. (*Ind. Eng. Chem., News Ed.*, 1940, **18**, 491.)—The Committee of the American Chemical Society on Nomenclature, Spelling, and Pronunciation has approved the following recommendation of the Division of Microchemistry:—For 0·001 milligram the term "microgram," designated by the symbol γ (the word "gamma" should not be used as a substitute for microgram). For 0·001 microgram, the term "millimicrogram," designated by the symbol mγ (the term "milligamma" is not to be used).

Determination of Sodium in Biological Fluids. M. C. Darnell, Jr., and B. S. Walker. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 242–244.)—Either 0·1 ml. of material wet-ashed by means of nitric and sulphuric acids and hydrogen peroxide, or an equivalent amount of the trichloroacetic acid filtrate are analysed, the total volume by either method being 1 ml.; this is placed in a 15-ml. conical centrifuge tube. To the sample solution 5 ml. of freshly filtered zinc uranyl acetate reagent are added (for preparation, see Wembach, *J. Biol. Chem.*, 1935, **110**, 95) and then at 5-minute intervals seven 0·3-ml. portions of 95 per cent. ethyl alcohol, with careful tapping of the bottom and thorough rotatory mixing. The last two additions are allowed to remain on top, and the tube is centrifuged at 2000 r.p.m. for 10 minutes, and, after decantation of the liquid, is inverted, allowed to drain, and treated with 2 ml. of wash liquid (300 ml. of ethyl acetate of analytical reagent quality, diluted to 1 litre with glacial acetic acid); this process is repeated. Finally, 5 ml. of ether are used for washing, 5 minutes being allowed for centrifuging and 1 minute for draining. *Blood* and *cerebrospinal fluid.*—The dried precipitate is dissolved in 4 to 5 ml. of water, and the solution is transferred to a 100-ml. flask. It is then diluted to about 70 ml., and 4 ml. of 5 per cent. sulphosalicylic acid, 4 ml. of a 10 per cent. solution of sodium acetate trihydrate, and water to make 100 ml. are added. The colour is determined photometrically by means of an Evelyn colorimeter tube and a 440mμ filter. The instrument is set to read 100 with a tube containing 4 ml. each of 5 per cent. sulphosalicylic acid solution and 10 per cent. sodium

acetate solution in 100 ml. The sodium-content of a blank similarly treated must be subtracted. *Urine.*—The precipitate is dissolved in 10 ml. of water. Any uranyl phosphate present remains in the form of a gelatinous precipitate. The tube is centrifuged for 10 minutes at 2000 r.p.m., and 5 ml. of the supernatant liquid are transferred to a 50-ml. graduated flask, diluted to 35 ml., and treated with half the quantities of the reagents used for blood and cerebrospinal fluid, and the readings are taken as before. The maximum error in the authors' determinations did not exceed 1 per cent. J. W. M.

Reviews

MELLOR'S MODERN INORGANIC CHEMISTRY. 9th Edition. Revised and edited by G. D. PARKES, M.A., D.Phil., in collaboration with J. W. MELLOR, D.Sc., F.R.S. Pp. xix + 915. Longmans, Green & Co., Ltd. 1939. Price 12s. 6d.

On reading this book one is immediately impressed with two things. The first is its surprisingly low price, when the ground it covers is taken into consideration; the second is the profound yet delicate historical sense of its authors. This may seem a strange quality to select first in a criticism of a scientific textbook, but in point of fact it has done more than provide a brief historical introduction, a good deal of interesting and out-of-the-way information concerning the many minerals mentioned, and arresting quotations, drawn from many sources and ages, at the headings of the chapters; it has made of the whole of the first section of the book a veritable *tour de force.* This first section (of 250 pp.) deals with the theories of chemistry and, maintaining the historical sequence, presents them in a logical and clear manner which is masterly; where the facts on which theories are based seem to make possible some other explanation, this is stated, concrete examples of actual weights, volumes and so forth are given, and the reader finds himself in touch with the authors in a somewhat unusual manner. The next 287 pages deal with the elements hydrogen, oxygen, carbon, nitrogen, sulphur and the halogens and then follow the remaining elements in their periodic groups, including excellent discussions of family relationships at the end of each. In this descriptive part the high inspiration of the earlier chapters seems to "fade" somewhat "into the light of common day" of the ordinary textbook—perhaps this is inevitable, and in any event the standard remains good. Possibly the defects of the historical sense are here making themselves felt, and the criticism is one, indeed, that applies to a very large proportion of textbooks; but one cannot help wondering whether the time is not ripe for the consignment of any detailed discussion of, for example, the hardness of water (with its pendant jewel, Clark's soap test) to more specialised textbooks. Whether or no this is so, the proper place for the discussion of hardness is surely not under water *considered as a compound of hydrogen.* Other changes in traditional presentment also suggest themselves; is it not also time that details of ore smelting and like processes, which are primarily the concern of metallurgical students, should largely be left to them, and, in any event, why give processes which are outworn when those processes are of no special chemical interest? The fault lies probably not with these or any other authors, but with examiners, for whose demands they have to cater and who do not seem to realise that inorganic chemistry has grown to huge proportions and that the padding of an earlier day should now be stripped from it. The times are changing, and many an element which was a "chemical curiosity" a few decades ago has become an important factor in the life of nations and so demands far more than the few lines of small type that is all that subjects such as hardness of water, the Leblanc process and various methods of steel-making now allow for it. As so often happens with textbooks, among the least satisfactory portions are those devoted to analytical chemistry; they are short and make no pretence to be exhaustive and so little harm

is done; but it is not provocative of confidence to be told (p. 796) that *heating* a solution of steel in nitric acid with sodium bismuthate oxidises all the manganese to permanganate—this being the one thing you must not do with it. One curious omission must be recorded: the pardonable enthusiasm of the authors in describing the discovery and separation of the rare earths has led them to forget to give any description of cerium at all.

At the end of the Group VIII elements there is an account of Werner's valency theory, which reverts to the clarity of the beginning of the book; the same may also be said of the account of radio-activity in the final chapter. The book ends with a series of questions drawn from English-speaking universities of many lands, and (an unusual feature) answers to these where they may be given briefly. The volume is well produced and bound, but is not entirely free from misprints, proof-reading slips and misuse of words; these, however, are relatively unimportant. Such criticism as has been made is very slight in comparison with the outstanding merit of the book; its eight predecessors have shown by their unexampled success how adequately they filled a gap, and one can pay no higher tribute to this, the ninth edition, than to express the sincere belief that it will carry that success to still higher peaks. One can but regret that one of the authors has not lived to see it.

B. S. EVANS

PHOTOGRAPHY BY INFRA-RED: ITS PRINCIPLES AND APPLICATIONS. By W. CLARK, Ph.D., F.I.C. Pp. xi + 389. London: Chapman & Hall. 1940. Price 25s. net.

There is an extensive and ever-growing literature on ultra-violet rays and their applications, but, with the exception of a few small practical handbooks, there has hitherto been no complete textbook on the rays just beyond the other end of the visible spectrum. Although nearly 140 years have passed since Herschel discovered infra-red rays, the difficulty of studying them stood in the way of their general scientific application. Even after Higgs, in 1891, had prepared an emulsion sensitive to the extreme red, photography by infra-red rays remained in the experimental stage. It was not until the discovery of the use of dicyanine as a sensitiser (since replaced by kryptocyanine and neocyanine) that it became practicable to apply the method in special investigations. Since 1934 the introduction of tetra- and penta-carbocyanines as sensitisers has made it possible to produce plates sensitive up to 13,000Å, but for most practical purposes a sensitivity between 9500 and 10,800Å has proved sufficient.

In this book theory and practice go hand in hand. Dr. Clark first gives an outline of the theory and development of infra-red photography, including a valuable description of the evolution of sensitisers, with practical directions for sensitising plates. He next discusses the Herschel effect and indirect methods of infra-red photography, and then (Chapter VII) gives a full and practical account of the sources of infra-red radiation. These general chapters are followed by detailed descriptions of methods for the examination and differentiation of materials by means of infra-red rays. Among the subjects dealt with and illustrated in this chapter are the examination of textiles, paintings, inks and pigments, and documentary photography, including the deciphering of charred papers and erased writing.

Chapter IX gives a full description of the application of infra-red photography to medicine, and includes the study of the superficial venous system and the transmission and reflection of the rays by skin and tissue. Chapter X deals with botany and palaeontology, and Chapter XI with infra-red photomicrography. Chapter XII, which describes special applications of infra-red photography, is perhaps the most striking from the popular point of view; it includes general landscape photography, photographic survey from land and air, fog penetration, and the photography of hot objects. The last three chapters have for their subjects

the measurement of infra-red radiation, the penetration of radiation through the atmosphere, and the optical characteristics of materials.

After each chapter there is a full bibliography containing, in all, some hundreds of references, and the book concludes with good name- and subject-indexes. The numerous illustrations are excellent, and the printing is clear and easy to read.

It would be difficult to overpraise this book. It is much more than a compilation of the work of others, for it is imbued throughout with the author's own knowledge and experience. It can be warmly recommended as a standard textbook on a fascinating subject about which there is still much to learn. EDITOR

STARCH AND ITS DERIVATIVES. By J. A. RADLEY, M.Sc., A.I.C. Pp. 346, with 61 photomicrographs and 28 figures. London: Chapman & Hall, Ltd. 1940. Price 22s. net.

This volume is the eleventh in the series of monographs on applied chemistry, produced under the editorship of Dr. E. Howard Tripp. Its contents have been divided into four parts. The first of these is a very interesting one dealing with the structure of the starch molecule, the physical chemistry of starch, the reaction of starch with iodine, and starch esters. A survey of the history of starch and dextrin is included, from which it is amusing to learn from well-authenticated reports that the discovery of dextrin was made by a method similar to that which led to the Chinese discovery of roast pork. Particular attention has been devoted to the physical properties of starch, because these have considerable importance in industry. Part II deals with the manufacture of various root and cereal starches, with modified starches, and with some starch derivatives—glucose, maltose, ethyl alcohol and dextrin. Part III is of more particular interest to the manufacturer. The field covered is large; in addition to an account of adhesives made from starch and dextrin, the uses of starch in the paper and textile industries are discussed and a useful section on enzymes used in the starch industry is included. Part IV is the one that should be of most use to the analytical chemist. It opens with a discussion on the general examination of starches, deals with the determination of starch and the analysis of dextrin, and concludes with methods of determining the activity of enzyme preparations.

Particular praise is due for the admirable series of photomicrographs, all but a few of which are in duplicate, showing the same field under ordinary and polarised light. The reproduction of these is as good as may be found anywhere and reflects much credit on both printer and publisher. The proof-reading also has been excellent, for there are very few errors and those which have been detected are innocuous.

The book concludes with a subject index and a name index, both of which seem adequate. In the latter there is some confusion between brothers, the work of H. R. Nanji being indexed under the name of D. R. Nanji, though in the references in the body of the book both names are correctly coupled with the two authors' contributions to the literature of starch, except in two places where, in mention of the work of J. J. Chinoy, F. W. Edwards and H. R. Nanji, the last name is omitted.

The value of this book to chemists, research workers and manufacturers lies mainly in its wealth of references. No important contribution to science appears to have been omitted, and they constitute an invaluable guide not only to those parts of the subject already adequately covered but to those in which there is much need for further research.

This volume, like its companions in the series, is much more than one of the "Recent Progress" order, but even if it is viewed merely in that light, it can be warmly commended to all interested in the chemistry of starch and allied substances. F. W. EDWARDS

BREWING SCIENCE AND PRACTICE. VOL. II., BREWING PROCESSES. By H. LLOYD HIND, B.Sc., F.I.C. Pp. xiv + 514 with 157 illustrations. London: Chapman and Hall. 1940. Price 56s.

The first volume of this comprehensive work was reviewed in THE ANALYST (1939, **64**, 149), and the second volume has now appeared after some delay due to war conditions. The original intention of the author was that the book should be completed in two volumes, but the inclusion of the results of recent investigations of considerable importance has necessitated the production of a third, which will deal with bottling, cleaning, brewery by-products and analysis.

The contents of the present treatise comprise descriptions of the construction and care of the many varieties of plant used throughout the brewing process from the grinding of the malt to the racking of the finished beer into casks. Each stage of the process, together with the selection of the water, malt, hops and yeast used for the production of different types of beer, is dealt with, and the effects upon the composition of the worts and beers of modifying the various conditions are discussed in considerable detail. The more scientific sections of the work include the biochemical or physical changes occurring during mashing, boiling, cooling and fermentation, the microbiology of deleterious organisms such as "wild" yeasts, moulds and bacteria (including an excellent chapter written by Dr. J. L. Shimwell on beer bacteria, based largely upon his own valuable researches during recent years) the nutrition and respiration of yeast, the redox potential of beer and its determination, and finally the causes of non-biological turbidities of beer. The numerous illustrations add considerable value to the volume, for whether, as in the form of plates, they depict photographs of brewery plant or photomicrographs by visible and ultraviolet light of yeast or other organisms, or appear as line blocks in the text, they are well selected and admirably reproduced, with perhaps one exception, Fig. 220, in which loss of detail has eliminated many spectrum lines. The experience of the author, both as brewer and chemist, has enabled him to summarise the whole available knowledge in an extensive field of industry with wide ramifications in detail, and the present volume shows the many admirable qualities of its predecessor. Numerous results of scientific research, which are here published in book form for the first time, will be welcomed by brewing chemists and others interested in the physical, chemical and biochemical sciences underlying a great industry.

To the brewer this volume will naturally appeal to a greater extent than the previous one, and its sound and comprehensive character will ensure it a position in the brewing room library, where it will serve as a valuable and up-to-date book of reference on all matters pertaining to the art of beer production. T. J. WARD