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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

INAUGURAL MEETING OF THE PHYSICAL METHODS GROUP

THIS was held at the Chemical Society's Rooms, Burlington House, Piccadilly, London, W.1, at 3 p.m. on Wednesday, February 7th, 1945. The President of the Society, Mr. S. E. Melling, was in the chair.

Mr. R. C. Chirnside was elected Chairman of the Group and took over the chair from the President. The following other officers were then elected—*Vice-Chairman*, Dr. J. G. A. Griffiths. *Hon. Secretary*, Dr. F. Wokes.* *Committee*, Mr. B. S. Cooper, Dr. J. H. Hamence, Dr. S. Judd Lewis, Mr. G. F. Lothian, Dr. J. E. Page, Mr. N. Strafford.

A letter was read from Mr. W. G. Marskell offering the co-operation of a group formed in Scotland for studying spectroscopic and absorptiometric methods as applied to chemical analysis. The Chairman welcomed this offer and pointed out that meetings of the Group would not necessarily be confined to London.

Mr. Chirnside then delivered an address on "Physics and the Analyst"†, the meeting being opened to members of the Society generally.

The President thanked Mr. Chirnside for his stimulating address. Physical methods were developing rapidly, and it was essential that the analyst should take every opportunity of learning more about their possibilities. Dr. Monier-Williams endorsed the President's remarks.

The meeting of the Physical Methods Group then closed and was followed immediately by a short

ORDINARY MEETING OF THE SOCIETY

under the chairmanship of the President.

The President drew attention to the fact that this was the 70th anniversary of the foundation of the Society and also of the membership of Dr. Bernard Dyer, who was elected an Associate Member at the first General Meeting of the Society, on February 5th, 1875. The President was authorised to send to Dr. Dyer, from the meeting, a telegram and a letter conveying the Society's greetings and most cordial good wishes.

The following paper was read and discussed:—"Some Examples of the Use of the X-ray Powder Diffraction Method in Quantitative Analysis: the Determination of Small Amounts of (*a*) Calcium Oxide in Magnesium Oxide, (*b*) Zinc Oxide in Zinc Sulphide," by H. P. Rooksby, B.Sc., F.Inst.P.

NORTH OF ENGLAND SECTION

A MEETING of the Section was held in Manchester on Saturday, November 11th, 1944. The Chairman (Mr. W. Gordon Carey) presided over an attendance of thirty-seven, including the President (Mr. S. E. Melling). The following papers were read and discussed: "The Analysis of Diethylamine," by H. N. Wilson, F.R.I.C., and A. E. Heron, A.R.I.C.; "A Note on the Determination of Ephedrine," by N. A. Hurt, A.M.C.T., F.R.I.C.

NEW MEMBERS OF THE SOCIETY

Jack Dennis Allen‡; James Ashley-Jones, A.R.I.C.‡; Charles Lancelot Cleveland Bourne, A.R.I.C.; John Herbert Campbell, B.Sc. (Lond.); Donald William Grover, B.Sc. (Lond.), F.R.I.C.; James Gordon Hay, F.R.I.C.; Harold Hamilton Hutt, A.R.I.C.‡; John Terrence George Johnson; Arnold Edward Martin, B.Sc., F.R.I.C.; William Martin, B.Sc. (Lond.); Miss Ettie Winifred Mercer, B.Sc. (Lond.)‡; Robert Lyell Mitchell, B.Sc., Ph.D.§; Hugh Bryan Nisbet, Ph.D., D.Sc. (Edin.), F.R.I.C.; Albert Norton, M.A., B.Sc.(Oxon), A.R.I.C.; Eric Ackerley O'Brien, B.Sc.Tech. (Manc.), A.R.I.C.‡; James Parkes, A.C.T.C. (Birm.), A.R.I.C.; Miss Stella Jean Patterson, B.Sc. (Lond.), A.R.I.C.; John Herbert Pennington, B.Sc. (Lond.), A.R.I.C.; Adam Tait, F.R.I.C.†; George Weatherston, A.R.I.C.‡; Robert Louis Wickens, A.R.I.C.; Joseph Vivian High Wredden.

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* Address: Ovaltine Research Laboratories, King's Langley, Herts.

† This will be published in a later issue of THE ANALYST.

‡ Through the North of England Section. § Through the Scottish Section.

DEATHS

We regret to have to record the deaths of

George Davidson Elsdon
Lewis Sidney Fraser

The Spectrographic Determination of Linoleic, Linolenic and Elaeostearic Acids

By T. P. HILDITCH, R. A. MORTON and J. P. RILEY

Saturated aliphatic substances are transparent, except in the far ultra-violet region amenable to study only with a vacuum spectrograph. The presence of an ethylenic linkage results in a displacement of the selective absorption in the direction of longer wavelengths, but the maximum remains below 215$m\mu$ in most cases. Two *conjugated* double bonds bring about a shift of the maximum to 230–235 $m\mu$, and three conjugated double bonds to 265–275 $m\mu$. If the absorbing molecule contains two or more unconjugated double bonds, λ max. will be unaffected but ϵ max. will increase approximately linearly with the number of ethylenic linkages. If a carboxyl group is isolated by CH_2 from the conjugated system its chromophoric rôle is negligible; thus, *e.g.*, (*cf.* Smakula[1]).

	λ max.
$CH_3CH_2(CH{=}CH)_2CH_2.COOH$	228 $m\mu$
$CH_3CH_2CH_2(CH{=}CH)_2.COOH$	260 ,,
$CH_3CH_2(CH{=}CH)_3.CH_2.COOH$	265 ,,

A high degree of unsaturation in a fat is not normally accompanied by selective absorption in the region 200–400 $m\mu$. Thus, cod-liver oil with a high proportion of polyethylenic acids only displays selective absorption due to a small amount of vitamin A with its conjugated double bonds. Heilbron, Morton *et al.*[2] observed (1931) that the mixed acids recovered from cod-liver oil after thorough alkaline saponification are more strongly absorbing and exhibit a large number of well-defined narrow bands, and also found that the appearance of these bands is not confined to cod-liver oil, but may also occur during similar treatment of unsaturated seed oils. These workers considered that the absorbing acids were produced during the saponification process, but believed that they were not ordinary fatty acids, whereas it is now known that the specific absorption arises from molecular rearrangements of the latter which take place in an alkali medium at elevated temperatures, whereby unconjugated acids are in part isomerised to conjugated acids. Dann and Moore[3] (1933) were the first to observe that the development of selective absorption depends upon the prolongation of alkaline hydrolysis in boiling alcohol, and Moore[3] (1937) found that linoleic and linolenic acids are respectively isomerised to conjugated dienoic, and to a mixture of conjugated dienoic and trienoic acids by prolonged boiling with alcoholic potash. Kass, Miller and Burr[4] in 1939 showed that this change was effected much more rapidly at higher temperatures (*e.g.*, by use of a solution of potassium hydroxide in ethylene glycol at 180° C.), and could be used to determine the proportion of linoleic acid in a mixture of the latter with saturated acids and oleic acid. Later, Mitchell, Kraybill and Zscheile[5] proposed a method whereby the proportions of saturated, oleic, linoleic and linolenic acids in a mixture can be at once determined from the iodine value of the mixed acids together with the extinction coefficients for ultra-violet absorption at 234 $m\mu$ and 268 $m\mu$ after isomerisation under standardised conditions (180° C. for 25 min.) with potassium hydroxide in solution in ethylene glycol.

Whilst this method leads to the approximate determination of linoleic and/or linolenic acids in a single analytical operation with probably greater precision and facility than thiocyanometric analysis, and should thus be of great value in the rapid technical evaluation of drying oils, we have formed the opinion that it is not possible to obtain values of the greatest accuracy for the proportions of both linolenic and linoleic acids by a single isomerisation carried out at a given temperature for a given time, for reasons which are briefly as follows. Linolenic acid is rapidly isomerised in presence of alkali from about 160° C. upwards, and at 180° C. the max. amount of di- and tri-ethenoid conjugation is already reached in 10 min.; thereafter the amount of both conjugated forms declines, evidently owing to progressive

thermal polymerisation. This polymerisation is fairly rapid at 180° C. and at 170° C., as will be seen from the following values of $E^{1\%}_{1cm}$ for linolenic acid (*cf.* Fig. 2):—

Time of isomerisation (min.)	$E^{1\%}_{1cm}$ 268 $m\mu$		$E^{1\%}_{1cm}$ 234 $m\mu$	
	15	60	15	60
170° C.	532	490	622	594
180° C.	512	482	610	569

On the other hand, linoleic acid is converted to conjugated diene forms relatively slowly at 170° C., and at 180° C., in our experience, the maximum value of $E^{1\%}_{1cm}$ at 234 $m\mu$ is not reached until heating has continued for about 60 min.; thereafter a slow decline due to polymerisation sets in (Fig. 2).

We therefore prefer not to employ one isomerisation at 180° C. for such a time (*e.g.*, 25 min.) that a compromise has to be effected between (i) loss of conjugated isomerisation from linolenic acid due to thermal polymerisation and (ii) failure to reach maximum conjugated diene formation from linoleic acid, but prefer to make two separate determinations:

1. From the value of $E^{1\%}_{1cm}$ at 268 $m\mu$ after isomerisation at 170° C. for 15 min. the amount of linolenic acid is determined.

2. From the value of $E^{1\%}_{1cm}$ at 234 $m\mu$ after isomerisation at 180° C. for 60 min. the amount of linoleic acid is determined. When both acids are present, the increment of $E^{1\%}_{1cm}$ at 234 $m\mu$ due to conjugated dienes produced from linolenic acid must be allowed for; this is based on the observation that pure linolenic acid isomerised at 180° C. for 60 min. shows a value of $E^{1\%}_{1cm}$ at 234 $m\mu$ of 569 (*cf.* table above).

The observations on which these proposals rest are discussed below, with other data which confirm the findings of Mitchell *et al.*[5] that mixtures of linoleic and linolenic acids or esters behave additively so far as the isomerisation data are concerned. We have also found that the method can be applied to the determination of linolenic and/or linoleic acid in presence of elaeostearic acid, and we have illustrated the proposed application of the technique to sunflower seed oil, niger seed oil, linseed oil, tung oil, and a mixture of the two last-named oils.

Experimental

PREPARATION OF FATTY ACIDS AND ESTERS—(1) *Methyl linoleate*—Tetrabromostearic acid (m.p. 114–115° C.), prepared from the unsaturated acids of cottonseed oil, was debrominated in methyl alcohol with activated zinc dust and hydrochloric acid (Rollett[6]), and the methyl linoleate obtained was fractionated in a vacuum through an electrically-heated and packed column. The main fraction had iodine value 172·5 (calc. 172·8) and thiocyanogen value 91·8 (*cf.* Hilditch and Murti[7]).

(2) *Methyl linolenate*—Hexabromostearic acid (m.p. 180–181° C.), prepared from the acids of linseed oil, was debrominated in pyridine solution with activated zinc dust (Kaufmann and Mestern[8]). The crude linolenic acid obtained was esterified with methyl alcohol in presence of 0·5% of sulphuric acid, and the methyl ester was distilled as above. The purest fraction of methyl linolenate had iodine value 255·3 (calc. 260·8) and thiocyanogen value 152·2 (Hilditch and Murti,[7] 154·5).

(3) *α-Elaeostearic acid*—Tung oil (50 g) was saponified with alcoholic potash and the mixed fatty acids were liberated and crystallised, first from light petroleum (b.p. 40–60° C.) and thereafter several times from alcohol. The α-elaeostearic acid melted at 46–46·5 C.*

(4) *β-Elaeostearic acid*—Tung oil (30 g) was mixed with flowers of sulphur (10 mg) and allowed to stand in daylight for 4 days. It was then hydrolysed, and the liberated mixed fatty acids were crystallised successively from light petroleum and from alcohol, when β-elaeostearic acid, m.p. 70·6–71·2° C., was obtained.

REAGENTS—(1) *Alkaline glycol solution*—Dissolve 7·5 g of potassium hydroxide A.R. (assaying at least 85% KOH) in 100 ml of ethylene glycol (which has been purified by fractional distillation under reduced pressure); heat the solution at 190° C. for 2 min., cool, and store in a stoppered flask.

(2) *Absolute alcohol*—Heat abs. alcohol (1000 ml) under reflux for 1 hr. with zinc dust (20 g) and potassium hydroxide (20 g) and then distil the purified alcohol.

* It is essential to avoid the use of rubber corks during the isolation or storage of α-elaeostearic acid, otherwise some isomerisation to the β-acid is liable to occur. The pure α-elaeostearic acid does not keep well, even when stored in evacuated vessels.

METHOD OF ISOMERISATION—This was essentially as described by Mitchell *et al.*,[5] except for variations in the temperature and times of heating. Fatty acids, methyl esters or fats were employed (the necessary correction being made in the latter cases to obtain the equiv. weight of fatty acids present). Difficulty was at times encountered in obtaining accordant results during alkali-glycol treatment at 170° C. for 15 min. when fats were directly employed (especially in cases of high linolenic acid content). It is recommended that, at least for the isomerisations at 170° C. and 15 minutes, the mixed fatty acids should be first prepared from the fat, and used in the determinations. Methyl esters of fatty acids, however, gave no difficulty.

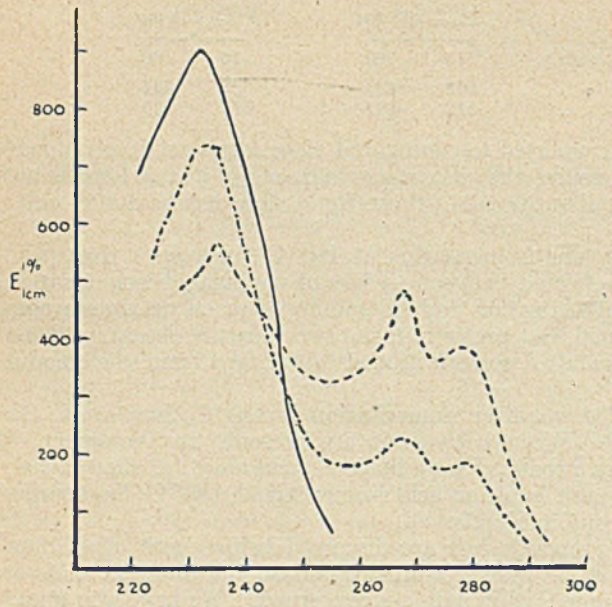

Fig. 1*a*. Linolcate (————), linolenate (--------); mixture of 49% of linoleate with 51% of linolenate (-·-·-·-·-); all isomerised at 180° C. for 60 min.

Weigh the fatty acids, esters or fat (*ca.* 0·1 g) accurately into a small capsule, and drop the latter into a loosely-stoppered Pyrex test-tube (6 in. × 1 in.), containing the glycol reagent (10 ml), and maintained in an electrically heated oil bath at the desired temperature (±0·3° C.). At the end of the required time, cool the tube quickly, and transfer its contents quantitatively to a 250-ml graduated flask, and make up to 250 ml with abs. alcohol. After standing at 0° C. overnight, filter the soln. and dilute with abs. alcohol to an appropriate concn. for spectrographic examination.

Make a blank determination with the alkaline glycol soln. in exactly similar conditions throughout, and use the final soln., diluted with alcohol to the same degree as the soln. containing the alkali-isomerised product, in the compensator cell of the spectrograph, making duplicate determinations in all cases.

The final values adopted as standards for the different individual acids represent the mean of four or more separate accordant determinations.

The apparatus employed was a Hilger E3 Quartz Spectrograph with sector photometer and an iron-nickel arc. War-time conditions have thus far not permitted us to use a photoelectric method, but we hope soon to obtain a Beckmann spectrophotometer as employed by Mitchell *et al.*,[5] which will simplify, and enhance the accuracy of, determination of the extinction-coefficients. It is estimated that the limits of experimental error in the determination of $E^{1\%}_{1cm}$ with the apparatus used in the present work are ±2%.

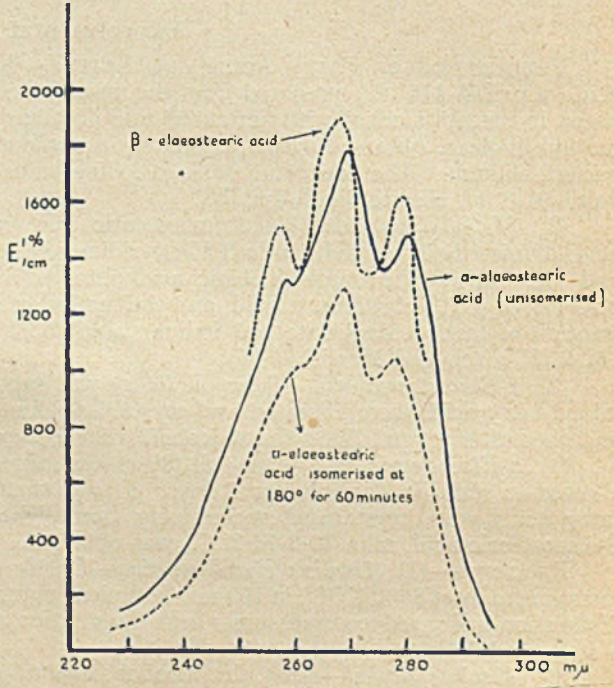

Fig. 1*b*.

The extinction-coefficients ($E^{1\%}_{1cm}$) were determined for the bands with heads at 234 $m\mu$ (conjugated diene) and 268 $m\mu$ (conjugated triene). A second band characteristic of conjugated triene systems in long-chain aliphatic compounds occurs at 278 $m\mu$, but this is less well-defined in character and it has not been necessary to use it in the present work.

Typical absorption curves for some of the individual acids are shown in Fig. 1*a* (linoleic and linolenic acids, and a mixture of these acids, isomerised at 180° C. for 60 min.) and Fig. 1*b* (α- and β-elaeostearic acids).

Influence of Temperature on Isomerisation—*Linolenic Acid*—Methyl linolenate was isomerised, and the standard conditions described were followed at 160° C., 165° C., 170° C. and 180° C. for various periods. The mean results for each time and temp., expressed as $E^{1\%}_{1cm}$ for the linolenic acid present after hydrolysis, are given in Table I.

Linoleic Acid—Methyl linoleate was similarly isomerised at 170° C. and 180° C., with the mean results given in Table II.

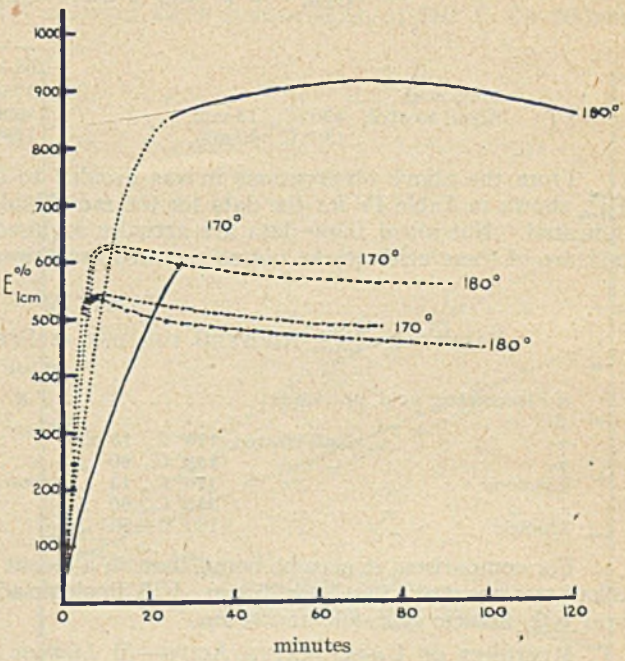

Fig. 2. Linoleate at 234 $m\mu$ (————); linolenate at 234 $m\mu$ (--------); linolenate at 268 $m\mu$ (·· ·· ··).

Table I

$E^{1\%}_{1cm}$ for Linolenic Acid after Alkali-isomerisation

Time	Wavelength 268 $m\mu$				Wavelength 234 $m\mu$			
(Min.)	160° C.	165° C.	170° C.	180° C.	160° C.	165° C.	170° C.	180° C.
10				529				620
15	308	473	532	512	466	578	622	610
25				492				596
30	362	510	517		523	600	613	590
45	458	505	492	476	575	594	596	573
60	512	496	490	483	599	585	594	569
90				447				545

Table II

$E^{1\%}_{1cm}$ for Linoleic Acid after Alkali-isomerisation

Time	Wavelength 234 $m\mu$	
(min.)	170° C.	180° C.
15	415	
25	564	852
45		863
60		906
80		923
90		863
100		899
120		859

The variation of $E^{1\%}_{1cm}$ for both wavelengths in the cases of linoleic and linolenic acids isomerised at 170° C. and 180° C. is shown graphically in Fig. 2.

Elaeostearic Acids—The extinction coefficients of these acids were measured for the pure compounds, and also after the latter had been heated with alkaline glycol under the standard conditions respectively at 170° C. for 15 min., and at 180° C. for 60 min. (Table III).

TABLE III

$E^{1\%}_{1\,cm}$ FOR α- AND β-ELAEOSTEARIC ACIDS

	α-Acid		β-Acid
	268 mμ	234 mμ	268 mμ
Pure acid	1780	208	1870
Alkali-treated, 170° C., 15 min.	1690	237	1830
,, 180° C., 60 min.	1290	197	1550

From the above observations it was decided to adopt for the present the values for $E^{1\%}_{1\,cm}$ shown in Table IV for the data for the individual acids after receiving the treatment indicated. Not all of these data are actually required in evaluating the components of a mixture of these acids (those not so required are shown in brackets).

TABLE IV

VALUES OF $E^{1\%}_{1\,cm}$ ADOPTED FOR USE IN SPECTROGRAPHIC ANALYSES

	268 mμ	234 mμ
α-Elaeostearic acid, untreated	1780	(208)
β- ,, ,, ,, ...	(1870)	
α- ,, ,, alkali-treated, 170° C., 15 min.	1690	(237)
α- ,, ,, ,, 180° C., 60 ,, ...	(1290)	197
Linolenic ,, ,, 170° C., 15 ,, ...	532	(622)
,, ,, ,, 180° C., 60 ,, ...	(483)	569
Linoleic ,, ,, 180° C., 60 ,, ...	—	906

For comparison, it may be noted that, in a recent paper, Beadle and Kraybill[5] give, for alkali-treatment at 180° C. for 25 min., $E^{1\%}_{1\,cm}$ linolenic acid 532 at 268 mμ and 609 at 234 mμ, and $E^{1\%}_{1\,cm}$ linoleic acid, 860 at 234 mμ.

MIXTURES OF UNSATURATED ACIDS—(i) *Linoleic and linolenic acids*—Six mixtures of methyl linoleate and methyl linolenate of known composition were made up and their composition was determined by the spectrographic method as described above. The resulting data are shown graphically in Fig. 3, in which the circles round the experimental points indicate the probable max. experimental error of the spectrographic determinations. It is seen that the data approximate to the linear relationships indicated by the straight lines drawn between the respective values for pure linoleic and pure linolenic acid (*firm lines*: isomerisation at 180° C. for 60 min.; *broken lines*: isomerisation at 170° C. for 15 min.).

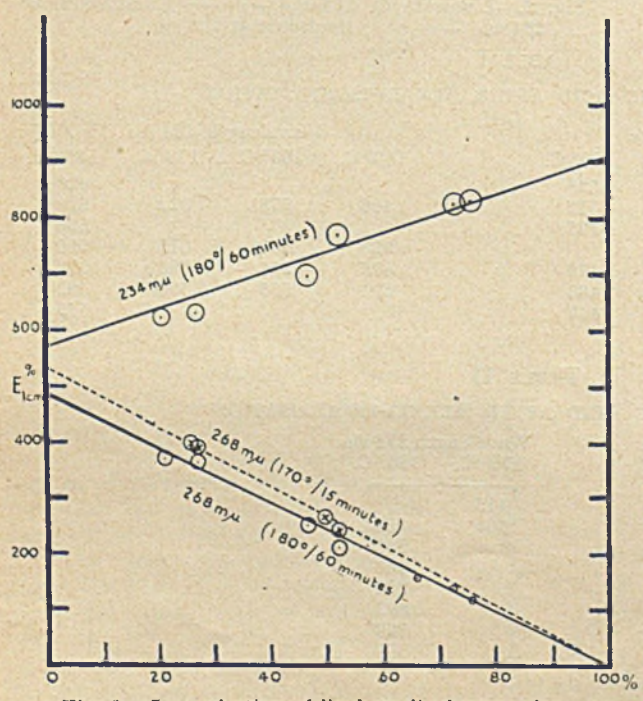

Fig. 3. Isomerisation of linoleate-linolenate mixtures.

(ii) *Linolenic and α-elaeostearic acids*—Similar determinations were made with mixtures of α-elaeostearic acid and methyl linolenate of known, but varying, composition, with results shown graphically in Fig. 4. In these instances, of course, the extinction-coefficients for 100% α-elaeostearic acid are taken from the observed values after heating with alkaline glycol under the standard conditions, respectively, at 170° C. for 15 min. (1690 at 268 mμ and 237 at 234 mμ) and at 180° for 60 min. (1290 at 268 mμ and 197 at 234 mμ). The relationship is again linear, within the limits of error of the method.

ILLUSTRATIONS OF THE METHOD—(i) *Fats containing saturated, oleic and linoleic acids only*—If linolenic acid is shown to be absent from a fat, determination of the iodine value and of the extinction-coefficient at 234 $m\mu$ after alkali isomerisation at 180° C. for 60 min. gives the proportions of saturated, oleic and linoleic acids. This is illustrated by the analysis of specimens of sunflower seed and niger seed oils (Table V); analyses by ester-fractionation had been made earlier on the same specimen of each oil, and the results of these (quoted in Table V) indicate reasonable accordance between the two methods.

(ii) *Fats containing saturated, oleic, linoleic and linolenic acids*—In this case the proportion of linolenic acid is determined from the value of $E^{1\%}_{1cm}$ at 268 $m\mu$ after alkali treatment at 170° C. for 15 min. The proportion of linoleic acid is then obtained from $E^{1\%}_{1cm}$ at 234 $m\mu$ after alkali treatment at 180° C. for 60 min., after deducting the increment of this $E^{1\%}_{1cm}$ due to the observed proportion of linolenic acid ($E^{1\%}_{1cm}$ at 234 $m\mu$ for 100% linolenic acid after alkali treatment at 180° C. for 60 min. being 569, *cf.* Tables I and IV). The oleic acid is then determined from the iodine value of the mixed fatty acids in the oil, after allowing for that due to the observed proportions of linolenic and linoleic acids. The saturated acids (with any unsaponifiable matter) are obtained by difference.

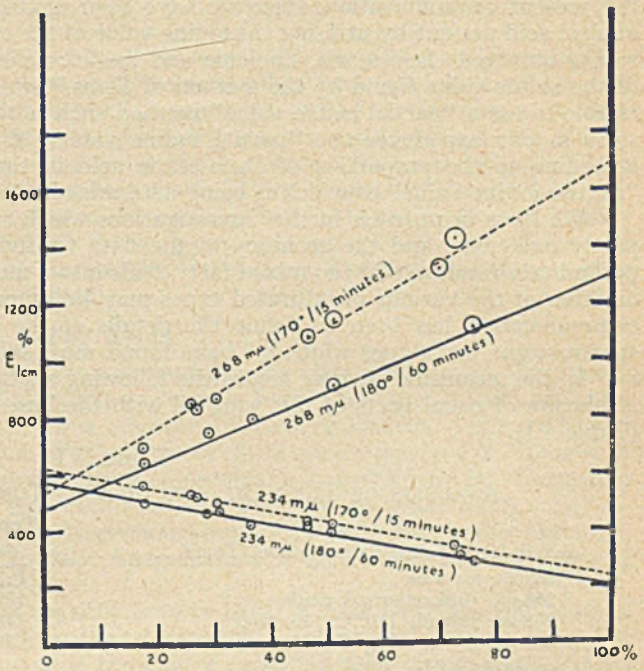

Fig. 4. Isomerisation of linolenate-α-elaeostearic acid mixtures.

TABLE V

COMPONENT ACIDS OF SUNFLOWER SEED AND NIGER SEED OILS

	Sunflower seed oil		Niger seed oil	
Saponification equiv.	290·6		293·3	
Iodine value	135·9		138·7	
	Present method	By ester fractionation[9]	Present method	By ester-fractionation[10]
$E^{1\%}_{1cm}$ (after alkali glycol treatment at 180° C. for 60 min.)	615	—	653	
Component acids				
Saturated (+ unsaponifiable)	11·1†	9·5	11·6†	12·7
Oleic	21·0*	24·8	16·3*	16·8
Linoleic	67·9	65·7	72·1	70·5

* Calculated from iodine value, after allowing for observed linoleic acid. † By difference.

A sample of linseed oil (saponification equiv. 290·6, iodine val. 182·2) was hydrolysed, and its mixed fatty acids were isolated (iodine val. 191·3). The mixed acids were submitted to the standard alkali-glycol treatment, and the following values of $E^{1\%}_{1cm}$ were found:

Alkali-treatment at 170° C. for 15 min., $E^{1\%}_{1cm}$ at 268 $m\mu$ 301
" " " 180° C. " 60 " $E^{1\%}_{1cm}$ " 234 $m\mu$ 437

The component acids of the linseed oil, from these data, were calculated to be saturated (+ unsaponifiable) 16·2, oleic 14·4, linoleic 12·8, and linolenic 56·6% (wt.).

(iii) *Fats containing saturated, oleic, linoleic, linolenic and elaeostearic acids*—Here the proportion of α-elaeostearic acid is first determined spectroscopically from the extinction coefficient at 268 $m\mu$ of the mixed fatty acids of the oil (without isomerisation). The

elaeostearic acid found has then to be taken into account in calculating the % of linolenic and linoleic acids from, respectively, $E^{1\%}_{1cm}$ at 268 $m\mu$ after alkali-glycol treatment at 170° C. for 15 min., and $E^{1\%}_{1cm}$ at 234 $m\mu$ after alkali-glycol treatment at 180° C. for 60 min.

The proportions of oleic and saturated acids are given together in these instances in the present communication, since we have been unable to determine the small proportion of oleic acid present by utilising the iodine value of the oil. The calculated iodine values due to the observed elaeostearic, linolenic and linoleic acids were together somewhat in excess of the iodine value found by the method of Toms,[11] whilst, on the other hand, we have been unable to use a "partial iodine value" method such as that described by von Mikusch *et al*,[12] since in our experience the "partial iodine value" of elaeostearic acid varies too widely according to the proportion of elaeostearic acid in the total unsaturated fatty acids, the "partial iodine value" of which is being determined.

We have in progress further investigations which suggest that these difficulties may be partly overcome, and the accuracy of the data for individual acids improved, by suitable preliminary resolution of the mixed fatty acids into a number of groups, in each of which one or other of the various unsaturated types may be concentrated. Our object in the present communication has been to define the details of the alkali-isomerisation and subsequent spectroscopic techniques which we have found most suitable up to the present time.

In the meantime we may record the following analyses of a specimen of tung oil, and of a mixture of equal parts of this tung oil with the linseed oil used in the preceding analysis (Table VI).

TABLE VI

ANALYSIS OF TUNG OIL AND OF 50% TUNG + 50% LINSEED OIL

	Tung oil	Tung-linseed oil	
Mixed fatty acids, iodine value (Toms)	242·0	214·0	
Spectroscopic data	$E^{1\%}_{1cm}$	$E^{1\%}_{1cm}$	
268 $m\mu$ (unisomerised acids)	1370	700	
268 $m\mu$ (alkali, 170° C., 15 min.)	1400	855	
234 $m\mu$ (,, 180° C., 60 ,,)	267	375	
Component acids			Calc.*
Saturated and oleic (+ unsaponifiable) ..	3·4	14·6	17·0
Linoleic	1·0	10·4	6·9
Linolenic	18·6	35·7	37·6
α-Elaeostearic	77·0	39·3	38·5

* *i.e.*, mean of observed values for the tung oil and the linseed oil.

We desire to thank the Colonial Products Research Council for permission to publish these results and for a grant to one of us (J. P. R.), and to acknowledge the assistance given by Mr. R. H. Creed in connection with many of the spectrographic measurements.

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Spot-tests for the Detection of Alloying Elements in Steel*

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The original intention of this research was to provide one or two simple tests to discriminate between plain-carbon and alloy steels, also to detect high-alloy steels used as coatings. As the work proceeded, however, it was found possible to include almost all elements at present used for alloying steel, and consequently the following scheme should provide an almost complete qualitative analysis without destroying the specimen. In view of the minute amounts used for alloying, no attempt has been made to find a spot-test for boron.

Apparatus—The only apparatus required, beyond that in normal use, is (*a*) short lengths of narrow glass tubing drawn out into rather fine long jets,—these are for the transference of drops,—and (*b*) short cut-off lengths of glass tubing (10 mm. × 8 mm. dia.),—these are to contain small filters (*vide sec.* XII, Vanadium).

The Tests

The tests given below cover the detection of the following elements—nickel, chromium, manganese, molybdenum, tungsten, aluminium, copper, lead, titanium, cobalt, selenium and vanadium. Each test was tried on a number of steel specimens, both with and without the element in question, and a collection of these steels was made, somewhat laboriously, to the end that all elements likely to be present in a steel should be represented in a variety of concentrations and surroundings. Our aim was to make every test unambiguous, and no test was accepted that was given or simulated by any of the other elements, or that was ever noted, inexplicably, to fail. Compositions of these trial steels are given in the appendix.

For each test the surface to which the drop is to be applied must be thoroughly cleaned with emery paper; in one instance (lead) further treatment is required, and this is given in the account of the test. The numbers given at the end of each test refer to the table of trial steels (*vide* Appendix).

(I) Nickel—*Reagents*—(*a*) Bromine water. (*b*) Dil. nitric acid (sp.gr. 1·2), 1 vol.; citric acid soln. (50%), 2 vols.; dilute phosphoric acid (5 ml of "syrupy" in 100 ml), 2 vols. (*c*) Diluted ammonia (1 + 1), 2 vols; dimethyl glyoxime (sat. soln. in alcohol), 1 vol.

Method—Place 1 drop of (*a*) on the surface of the steel and leave it to become decolorised. Add 4 drops of (*b*) and leave for 10 min.; add 6 drops of (*c*), or sufficient to make the drop permanently red, stir and leave for a further 2 to 3 min. If there is a fair amount of nickel present (*e.g.*, down to 1·5%), the red nickel ppt. can now be seen floating in the drop. Place a disc of fairly close-grained filter-paper on the mouth of a beaker; remove the liquid from the steel by laying the open capillary end of a rather long drawn-out jet tube almost or quite horizontally in the middle of the drop and allow the liquid so removed to fall on the centre of the paper, letting each drop spread before adding the next. Repeat, if necessary, until all the liquid and ppt. are transferred. Finally, wash the ppt. once by running 3 or 4 drops of cold water on to the centre of the paper. A scarlet spot indicates nickel.

Tried on: Samples Nos. 18, 93, 63, 64, 65, 15, 13, 60, 34, 61, 29, 62, 16, 10, 53, 2—Nickel present; all gave positive results.

No. 14—Nickel absent; result negative.

No. 53 containing 0·1% of Ni gave a weak reaction, and No. 2, with 0·01% of Ni, a very slight indication; the reactions with Nos. 15, 13 and 60 (4·84, 3·10, 3·10%) were very strong.

(II) Chromium—*Reagents*—(*a*) Hydrochloric acid (conc.), 1 vol.; hydrogen peroxide (20 vol.), 1 vol. (*b*) Sodium hydroxide soln. (20%), 1 vol.; hydrogen peroxide (20 vol.), 1 vol. (*c*) Diphenyl carbazide soln. (1·0% in glacial acetic acid),† 1 vol; diluted sulphuric acid (1 + 3), 1 vol.

Method—Place 2 drops of (*a*) on the steel surface and leave for about 10 min. (an almost immediate green coloration of the drop is a good indication of chromium; it might be used

* Communication from the Armament Research Department (formerly the Research Department, Woolwich).

† The carbazide solution slowly loses strength; it must not be more than a fortnight old.

as a sorting test). Transfer the drop to a watchglass, add 3 to 4 drops of (*b*), stir well (the mixed soln. *must* be alkaline), and leave for 1 min. Transfer the drop to the centre of a piece of close-grained filter-paper placed on the open mouth of a beaker, allow the drop to finish spreading and then add a succession of single drops of (*c*) round the edge of the wet patch. If chromium is present, bands of purple colour are produced at the points where the reagent (*c*) penetrates into the steel solution. Scarlet patches are due to local alkalinity and are to be ignored.

Tried on: Samples Nos. 17, 87, 93, 86, 84, 88, 65, 67, 83, 64, 16, 26, 15, 13, 12, 62, 85, 29, 34, 81, 89, 10, 90, 49, 92—Chromium present; all results positive.
Nos. 14, 91, 9, 7, 56—Chromium absent; all results negative.

The lower limit of detection appears to be about 0·1% for the full test.

(III) MANGANESE—*Reagents*—(*a*) Bromine water (saturated). (*b*) Diluted nitric acid (sp.gr. 1·2). (*c*) Sodium bismuthate.

Method—Place 1 drop of (*a*) on the surface of the steel, and leave it to become decolorised. Add 2 drops of (*b*) and leave for 2 to 3 min. Remove (as given under Nickel) the drop to a white tile and place a minute amount of (*c*) in the centre of the drop. A purple colour indicates manganese. All steels contain manganese, say, up to 1·5%, but, whilst the colour produced with an ordinary steel will never be intense but of varying shades of mauve, a "Hadfield" manganese steel with, say, 14% of Mn, will produce a very intense purple coloration. The earlier test[7] does not reveal manganese below, say, 1·5%. This test gives a faint indication with 0·09%.

Tried on: Samples Nos. 18, 10, 17, 27, 28, 29, 12, 16, 15, 13, 26, 30, 31, 32, 33—Manganese present; all gave positive results.

(IV) MOLYBDENUM[1,2]—*Reagents*—(*a*) Bromine (sat. soln.) in hydrochloric acid. (*b*) Distilled water. (*c*) Potassium ethyl xanthate in water (2·5% soln.).* (*d*) Hydrochloric acid (5·0% soln.). (*e*) *Iso*propyl alcohol. Subsequent work, however, has shown that if the papers are treated with the soln. and allowed to dry they will keep for at least 3 months.

Method—Run 4 drops of (*c*) on to a filter-paper disc and cause them to spread as evenly as possible. Place 2 drops of (*a*) on the surface of the steel and leave to become decolorised. Add 3 drops of (*b*) and then transfer (as given under Nickel) the liquid to the centre of the prepared paper. Wash 3 or 4 times with 3 drops of (*d*) added to the centre of the paper. Run 3 drops of (*e*) into the centre of the spot, allow almost to dry, then repeat. Molybdenum is indicated by a pale pink (generally rather narrow) ring slowly moving out from the centre while the alcohol is spreading. Orange crystals (due to Ni) in the centre dissolve in reagent (*e*). Steels with only a trace of molybdenum gave a very slight reaction; a 3·45% steel gave a very strong reaction and 0·3 to 0·6% a strong one. The molybdenum ring fades slowly after about 20 minutes, and the paper cannot be kept for comparison.

Tried on: Samples Nos. 17, 93, 13, 34, 35, 36, 37, 38, 39, 16, 26, 40, 15, 41, 42, 43, 44, 45—Molybdenum present; all gave positive results.
Nos. 46, 47, 48, 14, 18, 27—Molybdenum absent; all results were negative.

(V) TUNGSTEN—*Reagents*—(*a*) Bromine water (saturated). (*b*) Sat. soln. of ammonium persulphate and oxalic acid, 1 vol.; diluted sulphuric acid (1 + 3), 1 vol.

Method—Place a drop of (*a*) on the steel surface and leave it to become decolorised. Add 2 drops of (*b*), stir and leave until the liquid has almost or quite dried. When the drop is almost dry a blue band round (generally outside) the edges indicates tungsten; if the amount of tungsten is so small as not to be readily visible, it can sometimes be made to appear by re-treating the dry spot with another drop of (*b*). This test is neither so sensitive nor so easily observed as the other tests in this series; the coloured ring is best observed with the naked eye from directly above. Care must be taken not to confuse with the tungsten band the narrow diffraction fringe liable to occur round the edge of a drop. Tungsten steels containing 0·1% were detectable.

Tried on: Samples Nos. 68, 78, 95, 104, 99, 49, 94, 12, 56, 76, 96, 70, 75, 97, 74—Tungsten present; all gave positive results.
Nos. 17, 18, 11, 7, 66, 10, 8, 9, 29, 13—Tungsten absent; all results were negative.

Tungsten in "18 : 8" *Austenitic steels*—The above method does not work with "18 : 8" Austenitic steels owing to their non-reactive character. The following modification has been

* Made up fresh daily.

found to give the desired result with these steels—immediately after the rubbing down (which must be very thorough) and without allowing the specimen to stand longer than can be helped, place on it a drop of dil. (5%) hydrochloric acid and drop into the centre of this, from the point of a knife, *ca.* 15 mg of a mixture of equal parts of oxalic acid and potassium persulphate ground together in a mortar. Stir the mixture into the drop with a pointed rod and spread the drop out until it is fairly flat; leave for about 30 min. A dark greenish-blue line at the edge of the drop indicates tungsten; with high tungsten this is fairly conclusive, but if there is no tungsten at all, dark green patches of chromium salts may form and largely mask the blue of low tungsten. Make a small heap of oxalic acid in the centre of the drop and into the centre of the heap run 2 drops of 5% hydrochloric acid; after a further 30 min. add 2 more drops of 5% hydrochloric acid and again leave. In absence of tungsten the chromium colour should be bleached almost entirely, but any tungsten blue remains (probably still tinged with green to an olive colour). The tungsten blue sometimes deposits on the metal surface and is then less visible; it can be made more characteristic by clearing a space in the centre of the drop with a rod, filling this with solid potassium persulphate and dropping on the latter 3 or 4 drops of diluted sulphuric acid (1 + 3); the film slowly detaches from the metal in the centre and moves outward as a more identifiable ring.

Tried on six "18 : 8" Austenitic steels, containing respectively nil, 0·1, 0·4, 0·6, 1·4 and 2·0% of tungsten; the test showed tungsten in this order.

(VI) Aluminium—*Reagents*—(*a*) Saturated soln. of bromine in conc. hydrochloric acid. (*b*) Sodium hydroxide soln. (20%). (*c*) Potassium cyanide soln. (10%). (*d*) Soln. of aurine tricarboxylic acid in alcohol (0·1%). (*e*) Ammonium chloride soln. (20%). (*f*) Acetone.

Method—Prepare a disc of fairly close-grained filter-paper by running on to it 1 ml of (*d*), causing the liquid to spread as evenly as possible and allowing to dry; lay the prepared paper on the open mouth of a beaker. Place a drop of (*a*) on the surface of the steel, which in this instance must be very thoroughly cleaned immediately before, and allow it to become decolorised. Run in 2 or 3 drops of (*b*) with continuous stirring until the iron seems completely pptd., then add 4 or 5 drops of (*c*) and again stir thoroughly. Transfer the liquid (as given under Nickel) to the centre of the paper, being careful not to add one drop before the preceding one has disappeared. When the last drop has been completely absorbed lay the paper flat on a clean tile and cover it with a piece of filter-paper which has been soaked in (*e*) and allowed to drain. Allow the covering paper to remain in position for a few seconds, then strip it off, return the other paper to the top of its beaker and leave for 15 min. Wash the paper about 6 times with 3 or 4 drops of (*e*) dropped into the centre and allowed to spread before adding the next wash. Finally dip it into (*f*), shake off the excess and allow to dry completely.

Aluminium is indicated by a scarlet ring, about 1½ to 2 in. from the centre, sharply defined on the inner and somewhat diffuse on the outer side; it is usually 1/6 to 1/8 in. broad. The ground within the ring should be white, that outside generally brownish, and outside this a broad purplish band of the dye itself. The record on the paper seems to be quite stable and, after drying, will keep indefinitely.

With 0·1% of Al a faint, with 1·0% a fairly strong, and with 3·8% a strong reaction is obtained.

Tried on: Samples Nos. 1, 2, 3, 4, 5, 6—Aluminium present; all gave positive results.
Nos. 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18—Aluminium absent; all results were negative.

(VII) Copper—*Reagents*—(*a*) Soln. of ammonium persulphate (10%), 1 vol.; dilute ammonia (10% of 0·880 ammonia), 1 vol. (*b*) Diluted sulphuric acid (1+3). (*c*) α-Benzoin monoxime (sat. soln. in alcohol), 10 vols.; diluted ammonia (1+1), 20 vols.; soln. of citric acid (50%), 5 vols.

Method—Place 1 drop of (*a*) on the surface of the steel and leave until the drop and the steel under it are covered with a brown ppt. Add 1 drop of (*b*) and leave for 2 or 3 min. Wash the drop off the steel with water, rinse with acetone and allow to dry. Place 1 drop of (*c*) on the spot resulting from the former treatment and allow to react for 2 or 3 min. Copper is indicated by a dirty green ppt.

With 0·08% a slight, with 0·5% a fairly strong, and with 0·9% a strong reaction is obtained; 0·04% can be detected by allowing the drop to stand for some hours.

Tried on: Samples Nos. 50, 51, 10, 52, 53, 54, 55—Copper present; all gave positive results.

Nos. 9, 8, 11, 7, 3, 12, 15, 16, 18, 17, 5, 13, 49 and electrolytic iron—Copper absent; all results negative.

Steels Nos. 17 and 18 had a preliminary attack with bromine in hydrochloric acid (sat. conc. soln.).

(VIII) LEAD[3]—*Reagents*—(*a*) Conc. acetic acid, 1 vol.; soln. of chromic acid (10%), 1 vol. (*b*) Dil. acetic acid (10%). (*c*) Soln. of dithizone (0·1%) in chloroform, 1 vol.; soln. of potassium cyanide (1·0%), 10 vols., freshly mixed and well shaken.

Method—The specimen requires further preparation after the initial rubbing down. Etch it with dil. nitric acid (sp.gr. 1·2) until the initial violent attack begins to slacken; rinse it with water, rubbing it with the finger in order to loosen and wash away carbon particles; finally rinse with acetone and allow to dry without touching further. Soak a piece of close-grained filter-paper of the required size and shape in (*a*), drain with its lower edge touching a piece of dry filter-paper and apply to the prepared surface of the steel. Smooth out gently with the fingers to remove air bubbles, taking care not to move the paper on the specimen; press down very firmly all over with a pad of dry filter-paper; leave for 5 min. Strip the paper off the steel and transfer to a beaker containing (*b*); leave until the iron has apparently all dissolved from the paper; transfer to another beaker and wash for 2 or 3 min. in running water. Transfer the paper again to a beaker containing (*c*) and leave, with occasional agitation, for 15 min. Again wash the paper in running water, drain, spread out on a glass plate and allow to dry.

Lead is indicated by red spots on a white background, the position of the spots showing the distribution of the lead; in absence of lead the paper is white. The prints appear to be reasonably stable; if desired, they can be attached to card with a strong gelatin soln. and then coated by further application.

Lead in alloy steels—Alloy steels may not disclose lead by the above treatment and the following modification must be used. After the usual preparation of the specimen, spread thinly but completely over the surface a 20% soln. of sodium hydroxide saturated with potassium persulphate and with sodium phosphate. Leave it for 20 min., rinse with cold water and then with acetone, allow to dry and proceed as usual.

Tried on: Samples Nos. 11, 27, 28, 66, 59, 69, 13—Lead present; all gave positive results.

Nos. 12, 49, 56, 10, 34, 9, 8, 29, 7, 14 (and two others of same type), 6, 70, 51, 57, 58—Lead absent; all results were negative.

(IX) TITANIUM[4,5]—*Reagents*—(*a*) Sat. soln. of bromine in 5% hydrochloric acid. (*b*) Soln. of stannous chloride (5%) in 10% hydrochloric acid. (*c*) Soln. of sodium salt of chromotropic acid (5%) in 5% hydrochloric acid.

Method—Place 1 drop of (*a*) on the surface of the steel and leave it to become decolorised. Add 2 drops of (*c*) and then 2 drops of (*b*); stir and allow to stand, if necessary until dry. A brownish-red colour, reaching full intensity in about 5 min., indicates titanium; the drop dries to a dark crimson ring crust surrounding a thin crimson film centre. Below, say, *ca.* 0·25% of Ti the centre ceases to be crimson and at *ca.* 0·1% the ring is only faintly coloured. In absence of titanium the drop is coloured pale brown (the colour of the reagent).

Tried on: Samples Nos. 19, 1, 20, 3, 21, 22, 7, 23, 24—Titanium present; all gave positive results.

Nos. 16, 15, 18, 17, 26, 12, 10, 13, 27, 4, 14, 25—Titanium absent; all results were negative.

Note—Samples No. 24 and 25, tungsten carbide powders, were first attacked with bromine and then moistened with dilute hydrochloric acid.

(X) COBALT—*Reagent*—Soln. of α-nitroso-β-naphthol (1·0%) in conc. acetic acid, 5 vols.; soln. of ammonium persulphate (10%), 5 vols.; "syrupy" phosphoric acid, 2 vols.

Method—Place 1 drop of reagent on the steel surface and allow it to stand. A fairly prompt appearance of a crimson ppt. indicates cobalt; a black or brownish ppt. on long standing (*e.g.*, 15 min.) is to be ignored. This test will reveal cobalt quite definitely down to *ca.* 1·0%; below this, brownish deposits (? carbon compounds derived from the steel) render the test uncertain. For lower amounts the following modification will show cobalt down to *ca.* 0·06%.

Place 1 drop of 10% ammonium persulphate soln. on the steel surface and leave for 10 min. Transfer the drop to filter-paper and allow it to spread; drop into the centre 2 drops of the composite reagent used for the first test and allow to stand. Cobalt is shown by an irregular reddish-brown (or rust-coloured) patch in the centre, denser at the edges; non-cobalt steels show a faint darkish ring in about the same position, but the characteristic colour shows up fairly even with 0·06%.

Tried on: Samples Nos. 78, 77, 68, 73, 72, 71, 55—Cobalt present; all results positive.
Nos. 14, 56, 11, 13, 10, 8, 9, 66, 7, 29, 12—Cobalt absent; all results were negative.

(XI) SELENIUM—Polishing of the specimen *must* be very thorough, preferably to a fine surface. *Reagent*—(*a*) Hydrochloric acid (5%) satd. with bromine.

Method—Place a drop of (*a*) on the steel surface, and leave for 5 to 10 min. Selenium is visible as a fine scarlet ppt. that gradually coagulates into red flocks which adhere to the steel. The only selenium steel available (58) contained 0·20% of Se; 32 different sections of this steel all gave the reaction.

Tried on: Samples Nos. 6, 8, 9, 56, 13, 7, 11, 10, 12, 29, 15, 26, 16, 17, 18, 14 and two others of same type—Selenium absent; all results were negative.

(XII) VANADIUM[6]—*Reagents*—(*a*) *Aqua regia* ($1HNO_3$:3HCl). (*b*) Sodium hydroxide soln. (20%). (*c*) Potassium cyanide soln. (sat.), 1 vol.; potassium cobalticyanide soln. (10%), 1 vol. (*d*) Potassium cyanide soln. (2%). (*e*) Ammonium chloride soln. (20%). (*f*) Diphenyl carbazone soln. (1·5% in alcohol), 1 vol.; pyridine buffer, 4 vols.* (*g*) Alcohol.

Method—Place 2 drops of (*a*) on the surface of the steel and leave until attack seems to be complete. Add 3 drops of (*b*) and thoroughly stir the ppt.; add 4 drops of (*c*), and again stir well (N.B.—if the specimen is small and it is necessary to transfer the drop at this stage, do so to a sheet of iron or mild steel, *not* to a watch glass, as the reducing effect of the iron saves the cyanide from being completely used up before completion of the reaction); the iron ppt. should be almost or completely converted into soluble ferrocyanide. Prepare a small filter by pressing filter-pulp into the end of one of the cut-off sections of tubing; place this upright on the centre of a piece of close-grained filter-paper standing on the open mouth of a beaker. Transfer the drop on the steel, a little at a time, to the filter and allow it to soak through into the filter-paper beneath; finally wash the filter in the same way with 3 drops of (*d*) and discard it. Run 6 single drops of (*e*) equispaced just inside the edge of the wet patch on the filter-paper, and leave for 10 min. Add 5 drops of (*f*) to the centre of the paper, followed, when spreading is complete, by a second 5 and leave for 2 or 3 min. Generally a purple or mauve ring develops; this may be due to several metals, notably nickel or to traces of iron in the paper. Add 6 drops of (*g*) to the centre, allow them to spread and follow with 2 more 6-drop additions. In presence of vanadium, when the alcohol reaches the inner edge of the mauve band a blackish-purple or maroon ring develops; the subsequent washings with alcohol move it out slightly but not much, but the nickel (?) band moves out fairly rapidly and detaches itself from the vanadium ring. When dry, there is generally a mauve band inside as well as outside the characteristically coloured vanadium ring. In presence of much vanadium the ring generally appears as a blackish purple band with a very jagged outer edge. The lower limit of detection seems to be about 0·05%.

Tried on: Samples Nos. 82, 76, 68, 75, 10, 43, 81, 79, 29, 44, 57, 38, 62, 19, 74, 55—Vanadium present; all gave positive results.
Nos. 50, 73, 12, 56, 66, 34, 9, 8, 13, 7, 11, 14—Vanadium absent; all results were negative.

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* The carbazone soln. is prepared by filling to 2/3 vol. a colourless glass bottle with a 1·5% soln. of diphenyl carbazide in alcohol and leaving it exposed to daylight, with daily shaking, for a fortnight. It should be dark orange in colour and keeps indefinitely. The pyridine buffer *must* be prepared from high grade pyridine; the water content of the pyridine is immaterial, but the impurities present in many of the so-called "pure" pyridines on the market destroy the effectiveness of reagent (*f*) and make it valueless. Suitable pyridine has been obtained from B.D.H. and from Hopkin and Williams. The buffer is prepared by diluting 300 ml of pyridine to 1500 ml with water, adding 20 ml of nitric acid (conc.), heating to boiling and cooling. It is desirable to test a reagent (*f*) if prepared from untried chemicals; with a soln. of lead nitrate it should give a cherry-red colour. Mixture (*f*) *must* be made up fresh daily.

Appendix: Specimens of Steels used in the Tests: Constituents Per Cent.

No.	Mark	Mn	Si	Ni	Cr	Mo	V	W	Co	Ti	Cu	Al	Pb	Se	Nb	Ta
1	S.414	0·15	0·05	—	—	—	—	—	—	0·25	—	0·10	—	—	—	—
2	S.416	0·15	0·05	—	—	—	—	—	—	0·32	—	0·20	—	—	—	—
3	S.411	0·18	0·18	—	—	—	—	—	—	0·77	—	0·35	—	—	—	—
4	NIT	—	—	—	—	—	—	—	—	—	—	1·0	—	—	—	—
5	RHU	0·30	0·20	—	—	—	—	—	—	—	—	1·01	—	—	—	—
6	RHX	0·34	0·19	—	—	—	—	—	—	—	—	3·75	—	—	—	—
7	QXL.17	—	—	—	—	—	—	—	—	3·12	—	—	—	—	—	—
8	R.42	0·54	0·10	1·4	17·2	—	—	—	—	—	—	—	—	—	—	—
9	91	4·9	0·92	14·6	—	—	—	—	—	—	—	—	—	—	—	—
10	CBT.2	1·48	0·50	0·20	0·58	0·59	0·34	—	—	—	0·83	—	—	—	—	—
11	2	0·81	0·12	—	—	—	—	—	—	—	—	—	0·25	—	—	—
12	BFF	0·46	1·25	—	1·06	0·52	—	1·65	—	—	—	—	—	—	—	—
13	WWD	0·40	0·14	3·1	1·2	0·74	—	—	—	—	—	—	0·10	—	—	—
14	Mild steel	0·29	0·05	—	—	—	—	—	—	—	—	0·02	—	—	—	—
15	CJL	0·41	0·24	4·84	1·51	0·18	0·02	—	—	—	—	—	—	—	—	—
16	BZL	0·41	0·22	0·36	3·48	0·49	0·13	—	—	—	—	—	—	—	—	—
17	BSR	1·01	0·50	9·0	18·1	3·45	—	—	—	—	—	—	—	—	—	—
18	BMY	4·05	0·37	9·3	18·9	—	0·03	—	—	0·03	0·03	—	—	—	—	—
19	L.567	—	0·01	—	—	—	0·11	0·06	0·12	0·10	0·10	—	—	—	—	—
20	S.417	0·18	0·05	—	—	—	—	—	—	0·54	—	0·25	—	—	—	—
21	S.412	0·25	0·30	—	—	—	—	—	—	1·16	—	0·35	—	—	—	—
22	S.413	0·25	0·30	—	—	—	—	—	—	1·73	—	0·50	—	—	—	—
23	QXL.29	—	0·96	—	—	—	—	—	—	5·50	—	—	—	—	—	—
24	WC (powdered)	—	—	tr.	—	—	—	76·0	6·0	10	—	—	—	—	—	—
25	„ „	—	—	tr.	—	—	—	87·9	6·0	—	—	—	—	—	—	—
26	BLY	0·40	0·19	2·94	1·80	0·43	0·18	—	—	—	—	—	—	—	—	—
27	FC	0·86	0·05	—	—	—	—	—	—	—	—	—	0·23	—	—	—
28	HS	0·96	0·07	—	—	—	—	—	—	—	—	—	0·17	—	—	—
29	CMQ	0·61	0·18	0·56	0·73	0·04	0·26	—	—	—	—	—	—	—	—	—
30	ROR	0·33	0·12	tr.	tr.	—	—	—	—	tr.	—	—	—	—	—	—
31	ROX	0·22	0·10	1·43	tr.	—	—	—	—	tr.	—	—	—	—	—	—
32	PTG	0·15	0·17	1·9	2·05	0·05	—	—	—	—	—	—	—	—	—	—
33	L.564	0·09	0·03	—	—	—	—	—	—	—	—	—	—	—	—	—
34	BCP	1·20	0·14	1·10	0·70	0·50	—	—	—	—	—	—	—	—	—	—
35	BCL	0·45	—	—	1·68	0·61	—	—	—	—	—	—	—	—	—	—
36	BCM	0·46	—	—	2·78	0·60	—	—	—	—	—	—	—	—	—	—
37	BCO	0·47	0·30	1·10	2·40	0·60	0·08	—	—	—	—	—	—	—	—	—
38	BCN	0·44	—	1·50	2·48	0·59	0·18	—	—	—	—	—	—	—	—	—
39	BCD	0·26	0·11	—	1·45	0·50	—	—	—	—	—	—	—	—	—	—
40	BCF	1·63	0·13	—	tr.	0·30	—	—	—	—	—	—	—	—	—	—
41	BCB	0·22	0·10	—	1·45	tr.	—	—	—	—	—	—	—	—	—	—
42	BCC	0·25	0·11	—	1·90	tr.	—	—	—	—	—	—	—	—	—	—
43	BCE	0·27	0·12	—	1·40	tr.	0·30	—	—	—	—	—	—	—	—	—
44	BCG	0·74	0·54	—	tr.	tr.	0·25	—	—	—	—	—	—	—	—	—
45	BCH	1·22	0·10	—	0·55	tr.	—	—	—	—	—	—	—	—	—	—
46	BCA	0·33	0·12	—	tr.	tr.	—	—	—	—	—	—	—	—	—	—
47	BCK	0·30	—	—	0·60	—	—	3·5	—	—	—	—	—	—	—	—
48	BC–O	0·48	—	—	0·64	—	—	3·5	—	—	—	—	—	—	—	—
49	BSB	0·18	0·26	⩾0·10	0·22	0·15	0·05	1·66	—	—	—	—	—	—	—	—
*50	S.439	1·0	1·0	1·0	1·0	—	—	—	—	—	1·0	1·0	—	—	1·0	
51	QUP.11	0·75	0·39	—	0·95	—	—	—	—	—	0·96	—	—	—	—	—
*52	S.435	0·5	0·5	0·5	0·5	—	—	—	—	—	0·5	0·5	—	—	0·5	—
*53	S.431	0·1	0·1	0·1	0·1	—	—	—	—	—	0·1	0·1	—	—	0·1	—
54	L.578	?	?	—	—	—	—	—	—	—	0·08	—	—	—	—	—
55	L.566	0·05	0·05	0·07	—	—	0·05	0·03	0·06	0·02	0·04	—	—	—	—	—
*56	S.387	—	—	—	—	—	—	1·0	—	—	—	—	—	—	—	—
57	G.4	0·39	0·13	2·42	0·84	0·71	0·24	—	—	—	—	—	—	—	—	—
58	47	0·56	0·23	—	—	—	—	—	—	—	—	—	—	0·20	—	—
59	3	0·59	0·09	—	—	—	—	—	—	—	—	—	0·20	—	—	—
60	CHNS	0·49	0·12	3·1	—	—	—	—	—	—	—	—	—	—	—	—
61	SMS	0·82	1·97	0·78	0·38	—	—	—	—	—	—	—	—	—	—	—
62	Cr–V steel	0·57	0·18	0·47	1·0	0·05	0·15	—	—	—	—	—	—	—	—	—
63	DLB	0·49	0·61	4·86	4·19	2·88	—	—	—	—	—	—	—	—	—	—
64	DLC	0·62	0·56	4·51	3·93	3·09	—	—	—	—	—	—	—	—	—	—
65	LBDO	0·45	0·51	1·79	17·6	<0·01	—	—	—	—	0·03	—	—	—	—	—
66	FCCH	1·21	0·10	—	—	—	—	—	—	—	—	—	0·21	—	—	—
67	BNO2	0·38	0·60	7·72	17·50	0·01	—	0·76	—	⩾0·01	—	—	—	—	—	—
68	"W" steel	0·10	0·19	0·44	3·01	0·05	0·79	16·21	4·76	—	0·06	—	—	—	—	—
69	LED	—	—	—	—	—	—	—	—	—	—	—	0·33	—	—	—

SPECIMENS OF STEELS USED IN THE TESTS: CONSTITUENTS PER CENT.—*continued*

No.	Mark	Mn	Si	Ni	Cr	Mo	V	W	Co	Ti	Cu	Al	Ph	Se	Nb	Ta
70	PKY	0·41	0·17	—	0·70	0·35	0·31	1·0	—	—	—	—	—	—	—	—
*71	S.433	0·1	0·1	—	—	0·1	—	—	0·1	—	—	0·1	—	—	—	0·1
*72	S.437	0·5	0·5	—	—	0·5	—	—	0·5	—	—	0·5	—	—	—	0·5
*73	S.441	1·0	1·0	—	—	1·0	—	—	1·0	—	—	1·0	—	—	—	1·0
*74	S.430	0·1	0·1	0·1	0·1	0·1	0·1	0·1	—	—	—	—	—	—	—	—
*75	S.434	0·5	0·5	0·5	0·5	0·5	0·5	0·5	—	—	—	—	—	—	—	—
*76	S.438	1·0	1·0	1·0	1·0	1·0	1·0	1·0	—	—	—	—	—	—	—	—
†77	Magnet	0·4	0·2	—	—	—	—	—	6·0	—	—	—	—	—	—	—
†78	Tool steel	0·30	0·26	—	3·8	—	1·9	14·2	6·4	—	—	—	—	—	—	—
79	S.359	0·72	0·27	3·02	1·47	0·67	0·27	—	—	—	—	—	—	—	—	—
80	L.565	0·02	0·09	0·02	—	—	0·02	0·02	0·02	<0·01	—	—	—	—	—	—
81	CLY	0·45	0·12	0·52	0·69	0·04	0·29	—	—	<0·01	—	—	—	—	—	—
82	DLD	0·30	0·44	—	4·40	9·85	1·30	4·22	—	—	—	—	—	—	—	—
83	LBAB	0·74	1·65	57·5	15·6	—	—	—	—	—	—	0·08	—	—	—	—
84	Stainless	0·30	0·60	7/9	17/19	tr.	tr.	—	—	0·2/0·3	—	—	—	—	—	—
85	CDX	0·49	1·63	tr.	0·92	0·25	tr.	—	—	—	—	—	—	—	—	—
86	DNW	0·51	0·75	8·10	18·00	0·05	0·04	0·20	—	<0·01	—	—	—	—	—	—
87	LBFE	0·30	0·57	8·40	18·10	0·12	—	—	—	0·40	0·10	—	—	—	—	—
88	LBDP	0·26	0·53	7·48	17·60	0·04	—	—	—	0·01	0·18	—	—	—	—	—
89	LBOG	1·49	0·17	0·92	0·59	0·16	—	—	—	—	—	—	—	—	—	—
‡90	SMT	0·75	2·00	0·62	0·49	—	—	—	—	—	—	—	—	—	—	—
91	DLA	0·60	0·07	—	—	—	—	—	—	—	—	0·054	—	—	—	—
92	WRU "Armoid"	1·54	2·37	—	0·10	—	—	—	—	—	—	—	—	—	—	—
93	Stainless	2·4	?	8·0	18·0	2·8	?	—	—	—	—	—	—	—	0·02	
94	MMA	0·21	0·03	—	5·55	—	—	1·60	—	—	—	—	—	—	—	—
95	MME	0·25	0·15	—	0·75	0·60	—	4·09	—	—	—	—	—	—	—	—
*96	S.440	1·0	1·0	—	1·0	1·0	—	1·0	—	1·0	—	—	—	—	—	—
97	S.436	0·5	0·5	—	0·5	0·5	—	0·5	—	0·5	—	—	—	—	—	—
98	S.432	0·1	0·1	—	0·1	0·1	—	0·1	—	0·1	—	—	—	—	—	—
99	B.T.E.	0·48	1·27	⩾0·1	1·09	0·61	⩾0·01	2·0	—	—	—	—	—	—	—	—
100	G.44	0·46	?	2·47	0·65	0·43	—	—	—	—	—	—	—	—	—	—
101	LBQ	1·40	?	0·85	0·60	0·21	—	—	—	—	—	—	—	—	—	—
102	ROL	0·41	?	3·20	0·77	0·53	—	—	—	—	—	—	—	—	—	—
103	PKB	0·38	?	2·97	1·07	0·39	tr.	—	—	—	—	—	—	—	—	—
104	DA	0·5	0·30	0·06	0·77	0·05	0·08	3·5	—	—	0·10	0·01	—	—	—	—

* Intended composition only; samples not analysed chemically.
† Probable composition only; Gregory and Stevenson, *"Chemical Analysis of Metals and Alloys,"* 2nd Ed., p. 361. ‡ Cast iron containing chromium.

TESTS ON UNKNOWN STEELS

The system of spot tests was finally tried out on a series of "unknown" steels, with the following results*.

	1	2	3	4	5	6	7
Nickel, % (by analysis)	1·2	0·9	3·5	1·1	0·4	trace	3·1
,, (spot test)	strong	strong	v. strong	strong	fair	trace	strong
Chromium, % (by analysis)	0·7	1·5	1·8	0·7	0·8	1·0	1·2
,, (spot test)	fair	medium	medium	fair	fair	fair	strong
Molybdenum, % (by analysis)	0·45	0·36	0·3	0·4	0·07	0·26	0·73
,, (spot test)	v. strong	strong	strong	v. strong	faint	strong	v. strong
Vanadium, % (by analysis)	—	—	—	—	0·21	—	—
,, (spot test)	—	—	—	—	low	—	—
Manganese, % (by analysis)	1·1	0·5	0·6	1·4	0·6	0·6	0·4
,, (spot test)	normal	normal	normal	normal	normal	normal	normal
Tungsten, % (by analysis)	—	—	—	—	—	1·25	—
,, (spot test)	—	—	—	—	—	strong	—
Titanium, % (by analysis)	—	—	—	—	<0·01	—	—
,, (spot test)	—	—	—	—	trace	—	—
Copper (by analysis)	not looked for						—
,, (spot test)	trace	trace	trace	trace	trace	trace	—
Lead, % (by analysis)	—	—	—	—	—	—	0·09
,, (spot test)	—	—	—	—	—	—	slight
Cobalt (by analysis)	—	—	—	—	—	—	—
,, (spot test)	—	—	—	—	—	—	—
Aluminium (by analysis)	—	—	—	—	—	—	—
,, (spot test)	—	—	—	—	—	—	—
Selenium (by analysis)	—	—	—	—	—	—	—
,, (spot test)	—	—	—	—	—	—	—

* Dashes indicate negative results.

NOTE ON THE TREATMENT OF 18 : 8 AUSTENITIC STEELS—Owing to their non-reactive character, modifications of the above tests are occasionally necessary in dealing with these steels

(I) *Nickel.* (II) *Chromium.* (III) *Manganese.* (IV) *Molybdenum*—The tests work well as given, but with molybdenum the indication obtained is not so strong.

(V) *Tungsten*—The necessary modifications are given with the ordinary test.

(VII) *Copper*—Treat first with a drop of 5% hydrochloric acid saturated with bromine, leave until decolorised, add 1 drop of 10% ammonium persulphate soln., allow to stand 5 min.; transfer the drop to a plate of clean mild steel, add 1 drop of diluted sulphuric acid (1+3), leave for 2 or 3 min., rinse off with water and finish as in the ordinary test. The results are rather weaker than in the ordinary test; 0·10% shows up slowly.

(IX) *Titanium*—The test as given for ordinary steels works, but is not so sensitive and the drop has to be allowed to dry completely; a brown crust (or edge below 0·4%) indicates titanium. Treatment of the dried spot with a drop or two of water gives the characteristic titanium colour. The test shows Ti down to approx. 0·2%.

(VI) *Aluminium*, (VIII) *Lead*, (X) *Cobalt*, (XI) *Selenium and* (XII) *Vanadium*—No specimens of 18 : 8 steels containing these elements could be obtained, and the tests therefore could not be verified for 18 : 8 steels.

In conclusion we wish to deprecate very strongly any attempt at quantitative interpretation of spot tests[7]; this *may* be feasible when dealing with steels of precisely similar type, and the temptation to use it is almost overwhelming, but attack by reagents varies so greatly from steel to steel that it is obviously impossible to rely on identical solution by drops of the same size. We have experienced this repeatedly.

Further, it is our experience that lead prints and selenium prints taken on a section transverse to rolling are apparently far heavier than those taken of the same steel longitudinal to rolling. We think, too, that many published spot tests for elements in steel have been over simplified and are not universally applicable.

SUMMARY—A system of spot tests is described for the detection of nickel, chromium, manganese, molybdenum, tungsten, aluminium, copper, lead, titanium, cobalt, selenium and vanadium in alloy steels.

Most of the tests are sensitive down to at least 0·1%. In the extensive trials made none of the tests was observed inexplicably to fail, and none was given or interfered with by any element likely to be present in steel.

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The Determination of Phosphorus in Steel Containing Titanium

BY J. L. WEST

IT is well known that titanium interferes with the determination of phosphorus, but some analysts consider the retention of phosphorus by any titanium in the siliceous residue as the only source of error. After removal of silica by evaporation with hydrofluoric acid it is customary to recover the phosphorus from the residue by fusion with sodium carbonate and filtering the boiled solution of the melt, thus retaining titanium in the insoluble portion and adding the alkaline filtrate containing phosphorus to the main solution. It can be shown,

however, that soluble titanium compounds inhibit the complete pptn. of ammonium phosphomolybdate by the customary nitro-molybdate reagent.

In the work here described three plain carbon steels, A, B and C, free from titanium, were used at first. On these the phosphorus values were established by the method recently published by the Standard Methods of Analysis Sub-Committee of the Iron and Steel Institute,[1] and designated I.S.I. Method in the following tables. For routine determination I use the well-known rapid method described by Ibbotson,[2] but wash the phospho-molybdate ppt. with 2% nitric acid until free from iron, and then with 1% potassium nitrate soln. until free from acid. The washed ppt. and paper are shaken with 100 ml of water, titrated with excess of sodium hydroxide soln., and back-titrated with sulphuric acid of equiv. strength (*N* 6·74, *i.e.*, 1 ml ≡ 0·01% of phosphorus on 2 g), phenolphthalein being used as indicator. The sulphuric acid is standardised against sodium carbonate, with methyl orange as indicator. Unless otherwise stated, the tests described below have been carried out by this method, designated Routine Method, modified as stated in the Tables.

The results in Table I show the effect of titanium up to 1%, added as a solution of purified titanium hydroxide (prepared by fusion with sodium carbonate, extraction with water, filtration, washing of the titanium residue and solution in nitric acid).

TABLE I

		Phosphorus, %. Routine method			
Steel	Phosphorus	Ti, nil	Ti 0·2%	Ti 0·5%	Ti 1%
A	0·061	0·062, 0·061 0·061, 0·061 0·061	0·059 0·061	0·047 0·051	0·018, 0·043 0·041, 0·029 0·033
B	0·051	0·051 0·051	0·049	0·044	0·026 0·017
C	0·015	0·016 0·015	0·015	0·010	0·0045

It will be seen that titanium up to 0·2% is without any appreciable effect on this particular method, but greater amounts cause low results. Similar results have been shown in more detail by Etheridge and Higgs,[3] who solve the problem by pptn. in stronger nitric acid soln. with vigorous stirring.

Fluorides bleach the yellow colour of a titanium soln. which has been peroxidised with hydrogen peroxide, so the effect of hydrofluoric acid (Table II) on the interference of titanium with the pptn. of the phosphomolybdate was tried. The hydrofluoric acid was added prior to the molybdate reagent.

TABLE II

		Routine method. 1% Ti added in each expt. Hydrofluoric acid (40% soln.) added as stated					
Steel	Phosphorus by the I.S.I. method, %	nil	0·5 ml	1 ml	1½ ml	2 ml	3 ml
A	0·061	0·018, 0·043 0·041, 0·029 0·033	0·057	0·060 0·059	0·059	0·056, 0·055 0·055, 0·041 0·053*	0·0065 0·007
B	0·051	0·026 0·017	0·050	0·051	0·051	0·043	nil†
C	0·015	0·0045 0·0035	0·009	0·013	0·012	0·001§	0·002‡

* 10 g additional ammonium nitrate, added to ascertain effect.
† 1 g of boric acid added to filtrate. P recovered 0·051%.
‡ 1 g of boric acid added to filtrate. P recovered 0·016%.
§ 2 g of boric acid added to filtrate at 60° C. P recovered 0·013%.

The results in Table II show that hydrofluoric acid overcomes the interference of up to 1% of titanium, provided that a certain optimum amount is added, but that beyond this amount the effect of hydrofluoric acid is to give seriously low results. Hydrofluoric acid in absence of titanium inhibits the pptn. of phosphorus; steel A, which contains 0·061% of P, yielded only 0·053% of phosphorus in presence of 2 ml of hydrofluoric acid. The possible solution of the problem appears to be addition of sufficient hydrofluoric acid, with no undue excess, to eliminate the effect of titanium, followed by addition of some reagent to eliminate

the effect of the excess of hydrofluoric acid, the excess of the reagent to have no harmful effects. Boric acid fulfilled these conditions, as is shown by results in Table III (see also footnotes to Table II).

TABLE III

EFFECT OF HYDROFLUORIC ACID FOLLOWED BY BORIC ACID

		No Ti added	1% of titanium added		
Steel	Phosphorus, %	2 ml of HF + 1 g of H_3BO_3	2 ml of HF + 1 g of H_3BO_3	2 ml of HF + 2 g of H_3BO_3	3 ml of HF + 2 g of H_3BO_3
A	0·061	0·061	0·062, 0·061	0·061	0·061*
B	0·051	0·0515	0·0505, 0·0495	—	—
C	0·015	—	0·0165	—	—

* Compare Table II, column 8, where only 0·007% of phosphorus was recovered.

As the elimination of the influence of excess of hydrofluoric acid in the expts. in Table III is evidently due to the formation of fluorboric acid, experiments were made in which 2 g of sodium borofluoride were added (see Table IV).

TABLE IV

Steel	Phosphorus, %	2 g of steel + 2 g of $NaBF_4$	2 g of steel + 1% of Ti + 2 g of $NaBF_4$
A	0·061	0·061	0·060, 0·061, 0·061 0·059, 0·060
B	0·051	0·051	0·051
C	0·015	0·016	0·015

It would appear that sufficient "fluoride" ions are present to eliminate the effect of titanium in this particular process, but it should be noted that here chloride ions are absent. The effect of chlorides is considered later.

Bearing in mind that in the Routine Method the silicon present is not separated, it was next of importance to test the effect of the proposed modifications upon a method in which silicon is deliberately separated. The following expts. (Table V) were therefore carried out by the I.S.I. method mentioned, except where otherwise stated. It will be noted that in some instances a volumetric finish was used.

TABLE V

			1% of titanium added before evaporation for removal of silica			
Steel	2 g of steel No addition	Ti nil 2 g. of $NaBF_4$	No $NaBF_4$ used	2 g $NaBF_4$ before nitro-molybd.	2 g $NaBF_4$ after nitro-molybd.	2 ml of HF before nitro-molyb. 1 g boric acid after nitro-molybd.
A	0·062 (vol.) 0·061 (grav.)	0·0625 (vol.)	0·037* (vol.)	0·062 (vol.)	0·062 (vol.)	0·0615 (vol.) 0·061 ,, 0·061 ,, 0·061 (grav.) 0·0605 ,,
B	0·050 (grav.) 0·0515 ,,	0·051	0·041 (grav.)	—	0·051 (vol.)	0·0505 (grav.) 0·0505 ,,
C	0·015 (grav.) 0·0165 ,,	0·016	0·0085 (vol.)	—	0·015 (vol.)	0·0165 (vol.) 0·015 (grav.)

* The missing phosphorus was fully recovered in the filtrate after addition of 2 ml of HF and 1 g of boric acid.

In the expts. in which a volumetric finish was used, the siliceous residues were treated with hydrofluoric acid, evaporated just to dryness, and then fused with 0·5 g of sodium carbonate. The melt was boiled with water and filtered, the alkaline filtrate being added to the main soln. In the expts. in which a gravimetric finish was used and where hydrofluoric acid was added, the siliceous residues were treated as before with hydrofluoric acid and evaporated just to dryness. The residue was then taken up with 2 ml of hydrofluoric acid and 1 ml of nitric acid and added to the main soln. after neutralisation followed by 3 ml

excess of nitric acid instead of 4 ml. In most instances, less than 2 mg of residue remained after addition of hydrofluoric acid, although the equivalent of 0·0333 g of titanium dioxide, as nitrate (= 1% of Ti on 2 g) was added prior to evaporation for removing silica. After removal of arsenic and addition of nitric acid a faint turbidity, due to hydrolysis of titanium, persisted up to and after neutralisation, followed by four ml excess of nitric acid. This turbidity may be kept to a minimum and even not produced at all if the nitric acid added to remove bromine is only gently warmed and *not boiled*, bromine fumes being blown out. In any event, the solution became clear in 30 sec. to 1 min. when hydrofluoric acid was added and more slowly (1 or 2 min.) when sodium borofluoride was used.

In the I.S.I. Method most of the chloride is removed during evaporation with ammonium bromide for the removal of arsenic. The following expts. were made to determine the influence of chlorides on the modifications (*i.e.*, HF and H_3BO_3) introduced for titanium steels. Conc. hydrochloric acid (30 ml) was added in addition to the 10 ml of conc. nitric acid after the evaporation. The determinations were then continued by the I.S.I. Method. The results are shown in Table VI.

TABLE VI

IN PRESENCE OF CHLORIDES

Steel	Phosphorus, %	2 g of steel + 1% of Ti	2 g of steel + 1% of Ti + 2 g of $NaBF_4$	2 g of steel + 1% of Ti + 2 ml of HF + 1 g of H_3BO_3
A	0·061	0·055	0·037	0·062
B	0·051	0·042	0·049*	0·051
			0·044†	0·050

* Recovered 0·0015 in filtrate with 1 g of H_3BO_3. † Recovered 0·006 in filtrate with 1 g of H_3BO_3.

Evidently sodium borofluoride is not as effective as hydrofluoric and boric acids in presence of chloride. The fact that addition of boric acid enabled the missing phosphorus to be recovered suggests that sodium borofluoride introduces more fluoride ions into the solution when chlorides are present than when nitrates only are present.

When 3 g of sodium borofluoride are added to the steel the recovery of phosphorus in presence of chloride ions is lower, showing definite evidence of the existence of free fluoride. Thus, on steel B only 0·032% was obtained. The filtrate on standing showed signs of becoming cloudy. On adding 1 g of boric acid to the filtrate which was at 50° C., and allowing it to stand 30 min., 0·018% was recovered, thus raising the total recovery to 0·050%.

Phosphorus in high chromium nickel steels containing titanium—Titanium is chiefly met with in austenitic chromium-nickel steels of the 18/8 type and the I.S.I. Method[1] for determination of phosphorus (with slight modification) is suitable for this type of material.

I.S.I. (MODIFIED) METHOD—*Procedure*—Heat to boiling a mixture of 20 ml of hydrochloric acid (sp.gr. 1·16), 20 ml of water, 5 ml of nitric acid (sp.gr. 1·42) and 5 ml of perchloric acid (sp.gr. 1·54) A.R. quality,* in a separate small beaker and immediately add it to 2 g of steel contained in a 400-ml squat beaker. Digest until dissolved, evaporate to dryness and bake at *ca.* 300° C.* for 20 min. with the cover on. Cool, take up with 40 ml of hydrochloric acid (sp.gr. 1·16) and boil until a clear soln. is obtained and any chromate is reduced. Add 20 ml of water and filter through a paper-pulp pad into a 400-ml conical beaker, washing with dil. hydrochloric acid and keeping the bulk as low as possible. Reserve the ppt. Add 5 g of ammonium bromide and, with the cover of the beaker removed, evaporate until the mixture is pasty and the vol. is reduced to *ca.* 4 ml.

Add 10 ml of nitric acid (sp.gr. 1·42) and warm gently until the bromine is eliminated. Avoid prolonged heating so as to minimise hydrolysis of titanium compounds. Dilute with 40 ml of cold water and add ammonium hydroxide (sp.gr. 0·880) in slight excess (about 8 ml). Just redissolve the pptd. hydroxides by cautious addition of 4 to 5 ml of nitric acid (sp.gr. 1·42) and add 3 ml in excess, neglecting any faint turbidity due to titanium. In the meantime gently ignite the reserved ppt. in a platinum capsule, add a few drops of hydrofluoric acid and evaporate just to dryness. Take up residue* (usually 2 or 3 mg) with 2 ml of hydrofluoric acid and 1 ml of nitric acid. Adjust the temp. of the main solution to 80° C. and add the contents of the platinum capsule, rinsing twice with washes of approx. 3 ml of water. Shake and allow 1 min. for any hydrolysed titanium ppt. to dissolve. Add 35 ml of filtered molybdate reagent, shake the solns., add 1 g of boric acid and continue shaking until the boric acid is dissolved. Leave for 20 min. or, with low phosphorus (0·010% approx.)

samples, until the supernatant liquid is clear. Then filter off the yellow ppt. and complete the determination gravimetrically as in the I.S.I. Method[1] or, alternatively, use a volumetric finish. Results are shown in Table VII.

TABLE VII

	No Ti added		Titanium added		
Steel	HF and H_3BO_3 not necessary		HF and H_3BO_3 omitted	2 ml of HF and 1 g of H_3BO_3	
D. (18 Cr; 8 Ni)	0·010	0·011	0·002	0·011	0·010
E. (18 Cr; 8 Ni)	0·042	0·043	0·006	0·043	0·044
B.C.S. No. 209			HF and H_3BO_3 omitted	2 ml of HF 1 g of H_3BO_3	
(18 Cr; 8 Ni; +0·58% Ti) (P 0·018%)	—		0·003	0·017	

* *Notes*—The addition of perchloric acid to the initial solvent decomposes refractory carbides and prevents the formation of difficultly soluble chromium oxides.

If the contents of the beaker are overheated the siliceous residue will be contaminated with chromium oxide; in that event, after removing silica with hydrofluoric acid, fuse the residue with 0·5 g of sodium carbonate, boil the melt with water and filter, adding the alkaline filtrate to the main soln. Add the 2 ml of hydrofluoric acid after 4 ml excess of nitric acid and prior to addition of molybdate reagent.

The phosphorus contaminating the silica ppt. is usually less than 0·001%.

Unless A.R. reagents are used the hydrofluoric and perchloric acids may contain considerable amounts of phosphorus.

SUMMARY—The results submitted show that the inhibiting effect of titanium in steel on the pptn. of phosphorus as phosphomolybdate may be prevented by adding hydrofluoric acid, followed by boric acid to counteract the effect of any excess of hydrofluoric acid.

I wish to thank Mr. W. J. Dawson, Assoc. Met., Metallurgical Director and Director of Research of Messrs. Hadfields, Ltd., Sheffield, for permission to publish this work. Thanks are also due to Mr. E. P. Underwood, B.Sc., A.R.I.C., for carrying out the various tests, and to Mr. G. B. Willey, A.R.S.M., F.R.I.C., for assistance with the presentation of the results.

REFERENCES

1. *J. Iron and Steel Inst.*, 1942, **1**, 290.
2. Ibbotson, F., "*The Chemical Analysis of Steel-Works Materials*," p. 58. Longmans, London, 1920.
3. Etheridge, A. T., and Higgs, D. G., ANALYST, 1940, **65**, 496.

CHEMICAL LABORATORY
HADFIELDS LTD., SHEFFIELD

September, 1944

Notes

THE RIBOFLAVIN CONTENT OF TEA

IN our paper on this subject (ANALYST, 1945, **70**, 2–5) the preparation of the yeast supplement from fresh yeast was described too briefly, so that some details were not particularised. The following description should supply the necessary information:

Grind 50 g of fresh pressed yeast to a paste with 25 g of sand and a few drops of distilled water. Transfer this paste with distilled water (total vol. used, 200 ml) to a 500-ml conical flask, steam for 2 hr., autoclave at 15 lb. for 45 min. and cool. Decant the liquor, and to 50 ml of it add 3·75 g of dry basic lead acetate, and then sufficient 10% aqueous ammonia to bring the *p*H to 10, and filter. Make the filtrate just acid with glacial acetic acid, and remove the lead in the solution with hydrogen sulphide and filter. Then make up the volume to 50 ml with distilled water (removal of excess of hydrogen sulphide is unnecessary). Use 20 ml of this de-riboflavinised extract in each 250 ml of medium. We have found it necessary to make the yeast extract fresh (starting from pressed yeast) for every batch of medium.

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February, 1945

THE NICOTINIC ACID CONTENT OF TEA

IN addition to the vitamins riboflavin and pantothenic acid, it has also been found that tea contains nicotinic acid, Barton-Wright[1] having reported finding by the microbiological method 61μg per g in a sample of tea. Since then we have made determinations of the total nicotinic acid content of seven samples of tea by the chemical method of Wang and Kodicek.[2] The tea was treated with sodium hydroxide to

hydrolyse any nicotinamide and the extract afterwards adjusted to *p*H 10 and boiled with active charcoal. Further decolorisation was effected by treatment with potassium permanganate after acidifying to *p*H 2 to 3 and extracting once (by shaking) with *iso*butanol, as described by Wang and Kodicek.

Tea No.	Source	Nicotinic acid (μg/g)
1	N. India	80
5	,,	94
10	Ceylon	61
11	,,	67
15	Nyasaland	71
17	China—Keemun	83
18	China—Lapsang	56

The numbers correspond to the identifying numbers of the tea samples of which the contents of riboflavin and pantothenic acid have recently been given (ANALYST, 1945, **70**, 2).

REFERENCES

1. Barton-Wright, E. C., *Biochem. J.*, 1944, **38**, 314. (Abst., ANALYST, 1945, **70**, 97.)
2. Wang, Y. L., and Kodicek, E., *Ibid.*, 1943, **37**, 530. (Abst., ANALYST, 1944, **69**, 132.)

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January, 1945

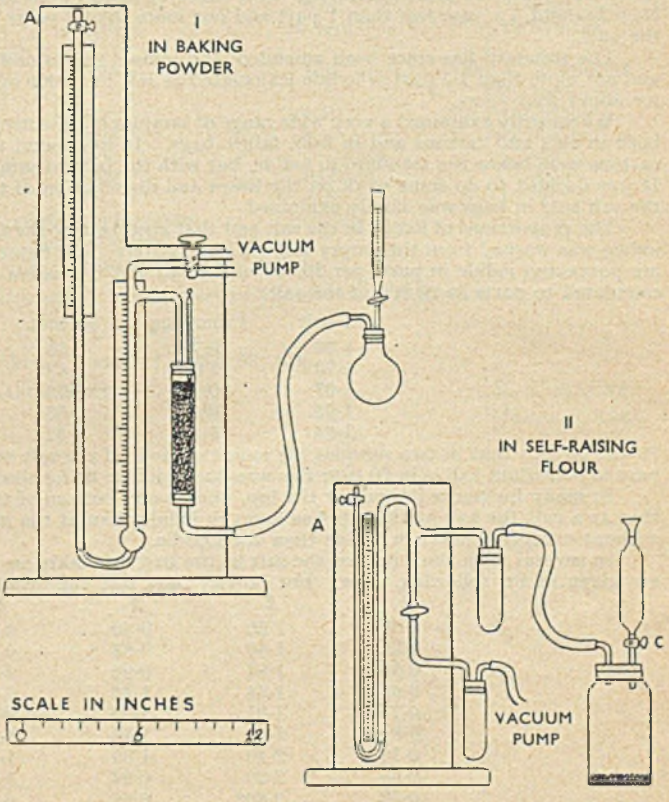
RAPID DETERMINATION OF CARBON DIOXIDE IN CARBONATE, BAKING POWDER, ETC.

THIS method was developed for the analytical control of the manufacture of baking powders and other prepared mixtures containing chemical aerating materials. The method was described at one of the early meetings of the Food Group and was mentioned in "*Modern Concepts of Analysis*" by E. B. Hughes, *Chem. and Ind.*, 1942, 103–110. In view of the numerous enquiries that have since been received for further details, it was thought that it would be helpful to describe the apparatus and method fully.

PRINCIPLE OF METHOD—The carbon dioxide is evolved in an evacuated space of fixed volume, and the resulting increase in pressure is measured, and from this, corrected to 0° C., the weight of carbon dioxide is given by direct reading from a graph prepared from data obtained by treating sodium bicarbonate of A.R. quality in a similar way.

APPARATUS—The type I apparatus is for use with baking powders. Pressure differences are measured on the millimetre scales attached to the closed-end manometer. The tap A is for ease in filling the manometer with mercury and remains closed thereafter. A capillary constriction at the base of the manometer is useful to prevent breakage when the mercury surges back on release of the vacuum in the apparatus. A 100-ml Pyrex bolt-head flask is used as the reaction vessel and a cut-down burette serves to measure the acid delivered to the reaction vessel. The trap contains glass-wool and a thermometer. It is essential that all taps be well ground and greased to withstand vacuum without leakage.

The type II apparatus is more suitable for self-raising flours, prepared cake mixtures, etc. The reaction vessel is a 500-ml wide-neck bottle, and the acid is contained in a 100-ml pipette provided with a delivery tap and a small funnel for filling. The traps contain glass-wool and are fitted on the back of the wooden stand holding the manometer.



METHOD FOR BAKING POWDER—The total carbon dioxide is determined as follows—Weigh 1 g of king powder into the bolt-head flask which is then connected to the apparatus and evacuated to a pressure of about 10 mm of mercury. Turn off tap B and, after waiting a few seconds to ensure that no leakage

is occurring, take the manometer reading. Add 5 ml of diluted hydrochloric acid (1 + 1) from the burette, taking care to avoid air being sucked into the apparatus. As soon as the reaction is complete, read the manometer again; the difference between the first and second readings, corrected to 0° C., gives the pressure due to the carbon dioxide evolved. Obtain the % of carbon dioxide in the sample from a calibration curve constructed from data obtained in a similar way by decomposing known weights of pure sodium bicarbonate in the apparatus. The relation between pressure difference in mm and the % of carbon dioxide evolved is linear.

Determine available carbon dioxide by first allowing the baking powder under test to react with water at 100° C. in the bolt-head flask before connecting it to the apparatus, and then determining the residual carbon dioxide. Subtract residual from total carbon dioxide to obtain available carbon dioxide.

Method for Self-raising Flour—Weigh the sample, 15 to 50 g depending on the CO_2 content, into the reaction vessel and add 20 to 30 glass beads. Evacuate the apparatus, turn off tap B, read the manometer, and run in slowly 100 ml of diluted hydrochloric acid (1 + 1). Then shake the reaction vessel vigorously, the glass beads aiding the breaking-up of any aggregates. When reaction is complete again read the manometer and convert the difference between the first and second readings to % of carbon dioxide from a calibration curve obtained by decomposing known weights of A.R. sodium bicarbonate, plus the appropriate amount of flour, in the apparatus.

If the sample contains sufficient fat to render wetting by the acid difficult, add 20 ml of a fat solvent of low vapour pressure (*e.g.*, benzyl benzoate).

Conclusions—The method is rapid, a determination of total CO_2 occupying 3 to 5 min., and it compares favourably in accuracy with gravimetric or volumetric methods. Evolution of the carbon dioxide under reduced pressure reduces the solubility of the carbon dioxide so appreciably that it is unnecessary to heat the reaction flask for the determination of total carbon dioxide.

It is probable that the principle could be applied to other reactions resulting in production of a gas.

I wish to thank J. Lyons & Co., Ltd., in whose laboratories this work was carried out, for permission to publish.

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C. H. F. Fuller

January, 1945

LOSSES OF IODIDE FROM IODISED SALT

A note with the above title, contributed by one of us (R. L. Andrew), was published in The Analyst (1938, 63, 179). It dealt specifically with losses of iodide from iodised salt of the standard then sold in New Zealand, *i.e.*, not less than 1 part and not more than 2 parts of potassium iodide in 250,000 parts of the salt.

The standard has since been amended, and iodised salt is now required to contain not less than 0·75 and not more than 1·5 part of iodide (calculated as KI) in 20,000 of the salt, and such salt has been on sale for about four years.

We recently examined a very wide range of samples representing all brands known to be on the market, both in tins and cartons and in 5-lb. fabric bags. It was found that many of those packed in tins and cartons were below the standard in iodide, but with the bagged samples there was much better compliance. It was decided to do some work on the losses and distribution of the iodide, and for various reasons only the salt sold in bags was closely examined.

The proportions of iodide in the salt and that absorbed by the fabric of the bag were determined. The iodide was washed from the empty bag with hot water. The figures given below from ten typical samples are potassium iodide in parts per 20,000 of the salt and the iodide washed from the fabric of the bag also calculated to parts in 20,000 of the salt.*

In salt	From bag	In salt	From bag
1·90	0·70	0·85	0·40
1·73	1·00	0·83	0·54
1·07	0·18	0·73	0·34
1·05	0·40	0·53	0·42
1·04	0·42	0·52	0·48

It will be seen that in two samples the iodide content of the salt was below the required minimum of 0·75 part of potassium iodide in 20,000; this was due to iodide being absorbed by the bag.

In many instances the salt at the top, middle and bottom of the bag was examined, and it was found that as a rule the salt at the top was lower in iodide than at the middle, and that the bottom was almost without exception lower in iodide than the middle.

In several tests the whole of the salt in the bag was taken in 100-g lots. The results of five of these are given in the following table. For brevity only half the results are tabulated.

1	2	3	4	5
0·60	1·50	0·30	0·30	1·05
0·53	1·60	0·63	0·45	1·15
0·64	1·87	0·96	0·42	1·20
0·69	1·68	1·46	0·66	1·09
0·78	1·91	1·73	0·84	1·21
0·81	2·10	1·40	1·24	1·25
0·70	2·40	1·09	1·40	1·19
0·65	2·20	0·94	1·03	1·18
0·56	2·80*	0·76	0·94	1·14
0·54	2·00	0·58	0·71	1·02

* All the determinations were made by the method of Andrew and Mandeno (Analyst, 1935, 60, 807).

With the exception of (5), which was plain salt, the above samples each contained added magnesium carbonate. We found from numerous results, that with the plain salt, the iodide was more evenly distributed. With one exception* the gradation in quantity of iodide was fairly uniform.

As the loss was greater at the top and bottom of the bags, it was assumed that the absorbed iodide, if not equally distributed throughout the fabric, would be higher at top and bottom. A number of emptied bags were cut transversely into four equal portions and the iodide, recoverable by washing with hot water was determined. The following are typical results (iodide calculated to 20,000 parts of salt).

Top	0·19	0·20	0·30	0·92
Middle ..	0·40	0·34	0·60	1·04
Middle ..	0·56	0·38	0·64	1·16
Bottom ..	0·44	0·26	0·34	0·90

It thus appears that there is a migration of the iodide to the middle portion of the fabric of the bag, probably due to that part having a higher moisture content than the ends.

The results obtained show that by loss of iodide to the bag, salt which complied with the standard at time of packing might fail to comply after storage under ordinary selling conditions, and also that the remaining iodide would be unequally distributed throughout the salt.

These two defects could be overcome by lining the bags with an impervious material. This would also avoid the staining of the bags through photochemical decomposition of the absorbed iodide when the bags are exposed to strong light.

Dominion Laboratory, Department of Scientific and Industrial Research, New Zealand
R. L. Andrew
G. W. Stace

THREE CASES OF STRYCHNINE POISONING

The following results, showing the distribution of the alkaloid in three recent cases of strychnine poisoning in which death occurred, may be of interest. In each case the strychnine was isolated and determined by the method of Daubney and Nickolls.[1]

	Case No. 1	Case No. 2	Case No. 3
Dose taken	4 grains strychnine hydrochloride	Unknown	One or two tablets Easton's Syrup, ½-drachm
Time elapsing before death ..	2 hr.	2 hr.	4 hr.
Age of person	49 years	50 years	19 months
Amounts found. *Strychnine alkaloid*, grain			
Stomach contents	0·25	1·08	0·2 gr. of quinine strychnine +
Liver	0·10	1·10	strychnine +
Kidneys	0·02	—	strychnine —
Spleen	0·005	—	do.
Brain	0·02	0·05	do.
Intestines	—	0·25	do.
Remarks	Overdose in medicine. Emetic given. Vomiting	Suicide	—

I wish to thank Dr. J. B. Firth, Director, for the interest he has shown in this work.

Reference

1. Daubney, C. G., and Nickolls, L. C., Analyst, 1938, **63**, 560.

Home Office Forensic Science Laboratory
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January, 1944

Department of Health for Scotland

THE FREEZING-POINT (HORTVET) TEST OF MILK

REPORT OF A SUB-COMMITTEE OF THE SCIENTIFIC ADVISORY COMMITTEE*

THE Sub-Committee was asked to give a scientific appraisement of the Hortvet test and of its limitations. The evidence considered by the Committee included about 250 original papers, Memoranda submitted by individuals including Professor H. D. Kay, Mr. J. B. McKean, Dr. G. W. Monier-Williams, Mr. H. E. Monk and Mr. J. R. Stubbs. In addition, the official views of the Society of Public Analysts and Other Analytical Chemists and of the Association of Public Analysts of Scotland were conveyed to the Sub-Committee.

The subject matter is discussed under the following sections: Need for a Confirmatory Test for Milk Adulteration. Physiological Bases of Freezing Point as a Criterion. Exceptionally Small Freezing Point Depressions. Minimum Freezing Point Depression of Genuine Milk. Estimation of Proportion of Added Water. Advantages of the Hortvet Method and Apparatus. Freezing Point Depression in relation to Solids-not-Fat. Hereditary or Environmental Influences. Effects of Acidity. Correction Factor for Acidity. Storage of Samples to Prevent Undue Acidity.

In formulating their recommendations† the Sub-Committee point out (i) the fact that the solids-not-fat of genuine milk may occasionally be less than 8·5%, and (ii) the judgment in *Lang* v. *Kerr* in the Judiciary Appeal Court in 1939 makes a confirmatory conclusive test of adulteration necessary if evidence that the milk has not been tampered with is to be disputed.

The f.pt. is the most constant of the physical properties of milk. In the opinion of the Sub-Committee it is justifiable to fix the min. f.pt. depression at 0·530° C. Since on rare occasions the f.pt. depression may be less than 0·530° C., the Sub-Committee consider that there should be a right to "appeal to the cow."

The Sub-Committee endorse the recommendation of the S.P.A., that the Hortvet apparatus and technique specified by the Association of Official Agricultural Chemists should be used. The modication of the apparatus devised by Temple (ANALYST, 1937, **62**, 709) gives exactly comparable results, and might therefore also be officially recognised. The acceptance of the Hortvet test would enable genuine milks with low solids-not-fat to be distinguished from watered milks.

The Sub-Committee are satisfied that no conditions of heredity or environment will cause the f.pt. depression of genuine milk to be less than 0·530° C.; also that the method is applicable to pasteurised and sterilised milks.

With an acidity not exceeding 0·18% (as lactic acid) the f.pt. depression requires no correction; when the acidity is substantially higher the original f.pt. depression may be found by means of a simple formula. In the Sub-Committee's opinion, however, it is preferable to prevent souring by storage at low temperature.

The Sub-Committee consider that the legal recognition of the Freezing Point (Hortvet) Test would go far towards providing a solution to the present legal difficulties. In their opinion a completely satisfactory solution could not be obtained without a fundamental change in the law relating to milk adulteration.

There are six Appendixes to the Report: I, Min. and Max. Values for Freezing Point Depressions given by Scientific Authorities (a chronological table). II, Freezing Point Depression of Samples of Genuine Milk naturally Low in Solids-not-fat Content (Golding). III, Relation of Freezing Point depression to Solids-not-fat Content in "Appeal to the Cow" Samples (Stubbs and Elsdon). IV, Relation of Freezing Point Depression to Solids-not-fat Content in Genuine and Adulterated Samples Respectively (Klamer). V, Correction of Freezing Point Depression (Hortvet) for Depression due to Souring. VI, List of References (80 items).

Ministry of Food

STATUTORY RULES AND ORDERS

1945 No. 109. Order, dated January 27, 1945, amending the Meat Products, Canned Soup and Canned Meat (Control and Maximum Prices) Order, 1944, and the Low Fat Soya Products (Control and Prices) Order, 1943.‡ Price 1d.

This Order provides for the prohibition (*after March* 31, 1945) of low fat soya in the manufacture *by way of trade* of pork sausages and pork sausage meat (including pork slicing sausage), *or after April* 7, 1945, *the sale or possession for sale of pork sausage or pork sausage meat containing any low fat soya product.* The compulsory inclusion of low fat soya in beef sausages and beef sausage meat (including beef slicing sausage) is unchanged.

In proceedings for infringement of the Article that beef sausages and sausage meat must have a low fat soya content of 7·5%, *the Court may disregard a variation between* 7 *and* 8%.

Legal Notes

CORDIALS: DEFINITION AND BREADTH OF WARRANTY

SOPERS OF HARROW, LTD., *v.* JOHNSTON & SON (LONDON), LTD.

ON November 16, 1944, an appeal from a judgment of Mr. Justice Tucker, on May 25, 1944, was heard in the Court of Appeal before Lords Justices Scott, Mackinnon and du Parcq. Mr. C. Gallop appeared for the

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* The Sub-Committee comprised Sir A. Macgregor, Medical Officer of Health, Glasgow (*Chairman*), T. Cockburn, A. Scott Dodd, A. M. Stewart, J. F. Tocher, Norman C. Wright and D. W. Swanston (*Secretary*)

The Report (pp. 19) is obtainable from H.M. Stationery Office. Price 4d.

† Dr. Tocher signed the Report on the understanding that the recommendations are a provisional measure.

‡ Obtainable from H.M. Stationery Office. Italics indicate changed wording.

appellants and Mr. J. W. Morris, K.C., and Mr. P. B. Morle for the respondents. The facts, as outlined by Lord Justice Scott, were as follows. In 1942 various drinks known as cordials were sold by Messrs. Collins, Arden & Co., Ltd., to Messrs. Henderson, who re-sold them to Messrs. Johnston & Son, who in turn re-sold them to Messrs. Sopers, and one question involved was that of the warranties on those sales. In the final transaction, that between the appellants and the respondents, the contract of sale was partly oral and partly in the terms of certain labels upon the bottles. In every one of the labels the drink was termed a "cordial" in large capital letters, and the substantial question raised was what was meant in the trade by the word "cordial." It was said that before the war "cordial" had come to mean, as defined in the Oxford Dictionary, a liquid that was invigorating or refreshing to the heart, and generally stimulating—owing to the presence of a substantial proportion of sugar (30 to 50%), and that this sweetening must be supplied by sugar, since alternative sweetening agents have not the effect of stimulating the heart.

There was, in fact, no sugar in any of the bottles, and the first question was whether the implied warranty of Sec. 13 of the Sale of Goods Act, that the goods complied with the description contained on the label, by reason of the word "cordial," was broken. The second question was whether the provisions of Sec. 3 of the Food and Drugs Act, 1938, had also been broken. The substitution of saccharin as a sweetening agent was irrelevant if the sweetening material had to be sugar to make a drink a cordial within the meaning of that word.

With regard to the meaning of the word "cordial" Lord Justice Scott said that at first he was inclined to doubt whether Mr. Justice Tucker had sufficiently applied the rule that a word must be treated as having the ordinary dictionary meaning unless a definite trade meaning was proved by witnesses with knowledge of the trade competent to give such evidence. But he was now satisfied that the question had been sufficiently before the learned Judge, particularly in view of the fact that no exception had been taken to the form of the evidence, by analysts and others called to say what was understood by "cordial," most of whom had said that it meant a drink containing a large proportion of sugar. Some evidence having been given that three named firms had before the war sold these soft drinks without any sugar in them under the name of "cordial," it was open to the learned Judge to hold that there was no such necessary meaning of the word in the trade. But after describing very fully in his judgment the evidence and the contentions on each side, and referring to the dictionary definition of "cordial," Mr. Justice Tucker had come to the conclusion that the plaintiffs were right; that by the outbreak of war the word "cordial" had acquired a commercial significance, and that it necessarily meant a drink, to be used in dilution, which contained a substantial percentage of sugar. That was a finding of fact, with which on the evidence it would be wrong for the Court of Appeal to interfere, and his Lordship accepted it.

On the other question raised, *i.e.*, whether the actual contents of the bottle as stated upon the label affected the existence of such a warranty as was alleged by the plaintiffs, Mr. Justice Tucker had said: "I do not think that that affects the real issue in this case, at any rate so far as the breach of warranty is concerned, that these goods complied with the provisions of the Food and Drugs Act, because the essence of that warranty was that this liquid was a cordial, and that warranty is in no way impaired by reciting certain ingredients which are to be found in this bottle. I think that that warranty has been broken, notwithstanding the fact that he was given notice of those terms of what the contents of the bottle were."

Again, his Lordship saw no reason for interfering with this conclusion of facts. In his view the warranty that the goods complied with the Act meant that they were goods which if sold on their description as a cordial, would not infringe Sec. 3 of the Act, so that these goods could still be sold without fear of any such infringement in fact, meaning that no successful prosecution could or would result. One reason for not interfering with the judgment was that the oral sale was carried out and an invoice was sent containing at the bottom these words: "The goods included in this invoice are guaranteed to be of the nature, substance and quality therein described, that is to say, by the Sale of Goods Act, and to comply with the Sale of Food and Drugs Act and other regulations relating to the sale of food." Consequently, in his Lordship's view, both warranties were broken because there was no sugar in these bottles.

For these reasons the learned Judge's decision must be affirmed and the appeal dismissed with costs.

Lords Justices Mackinnon and du Parcq concurred, and leave to appeal to the House of Lords was refused.

Seventh Addendum and the British Pharmacopoeia, 1932*

THIS Addendum was published on February 1, 1945, and became official from that date.

AMENDMENTS—The following monographs and addenda of the B.P. 1932 are amended: Acidum Acetylsalicylicum. Aneurinae Hydrochloridum. Belladonna Pulverata. Belladonnae Folium. Belladonnae Radix. Extractum Belladonnae Liquidum. Extractum Belladonnae Siccum. Extractum Pituitarii Liquidum. Insulinum. Menaphthonum. Oleum Limonis. Oleum Myristicae. Stilboestrol. Sulphanilamidum. Tabella Glycerylis Trinitratis. Terpineol. Tinctura Belladonnae. Unguentum Acidi Borici. Unguentum Acidi Salicylici. Unguentum Acidi Tannici. Unguentum Alcoholium Lanae. Unguentum Hamamelidis. Unguentum Hydrargyri Ammoniati. Unguentum Sulphuris. Unguentum Zinci Oxidi. Vaccinum Vacciniae.

The Addendum also includes Monographs and Addenda amended by Notice in the London, Edinburgh, Belfast and Dublin Gazettes.

With effect from November 30, 1943—Confectio Sulphuris, Extractum Colchici Liquidum. Mistura Sennae Composita. Paraffinum Liquidum. Tinctura Colchici. Trochisci.

With effect from February 18, 1944—Extractum Belladonnae Liquidum.

With effect from June 23, 1944—Oleum Hippoglossi.

With effect from July 25, 1944—Pancreatinum. Pepsinum. Pulvis Ipecacuanhae et Opii.

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* Published for the General Medical Council by Constable & Co., Ltd., London. 1945. Price 8s. 6d.

The following Appendixes are also amended.

I. Materials and Solutions Employed in Tests.
II.A Solutions Employed in Volumetric Determinations.
II.B Indicators Employed in Volumetric Determinations and in *p*H Determinations.
VI. Quantitative Test for Lead.
VII. Quantitative Test for Arsenic.
XV.H Biological Assay of Pituitary (Posterior Lobe) Extract.
XVI. Special Processes used in Preparing Solutions and Suspensions for Parenteral Injection.
XVII.A Tests for Purity of Vaccine Lymph.
XVII.B Deleted.

Changes in Official Names—The following changes are made.

Belladonnae Folium	becomes	Belladonnae Herba
Extractum Belladonnae Folii Liquidum	,,	Extractum Belladonnae Herbae Liquidum
Insulinum	,,	Injectio Insulini
Tabella Glycerylis Trinitratis	,,	Tabellae Glycerylis Trinitratis
Unguentum Zinci Oxidi	,,	Unguentum Zinci Oxidi Aquosum
Unguentum Zinci Oxidi Anhydrosum	,,	Unguentum Zinci Oxidi.

Additions to the B.P., 1932—Amethocainae Hydrochloridum. Amphetamina. Amphetaminae Sulphas. Cyclopropanum. Dextrosum Hydratum. Injectio Insulini Protaminati cum Zinco. Liquor Sodii Citratis Anticoagulans. Liquor Sodii Citratis cum Dextroso. Oestradiolis Monobenzoas. Oestronum. Pentobarbitonum Solubile. Potassii Sulphas. Progesteronum. Strophanthinum-G. Sulphacetamidum. Sulphacetamidum Solubile. Sulphadiazina. Sulphadiazina Solubilis. Sulphaguanidina. Sulphapyridina. Sulphapyridina Solubilis. Sulphathiazolum. Sulphathiazolum Solubile. Tabellae. Tabellae Acidi Acetylsalicylici. Tabellae Acidi Ascorbici. Tabellae Acidi Nicotinici. Tabellae Atropinae Sulphatis. Tabellae Barbitoni. Tabellae Barbitoni Solubilis. Tabellae Calcii Lactatis. Tabellae Carbromali. Tabellae Codeinae Phosphatis. Tabellae Ephedrinae Hydrochloridi. Tabellae Erythritylis Tetranitratis. Tabellae Hexaminae. Tabellae Hydrargyri cum Creta. Tabellae Hydrargyri Subchloridi. Tabellae Mepacrinae Hydrochloridi. Tabellae Nicotinamidi. Tabellae Phenacetini. Tabellae Phenazoni. Tabellae Phenobarbitoni. Tabellae Phenobarbitoni Solubilis. Tabellae Phenolphthaleini. Tabellae Potassii Bromidi. Tabellae Potassii Chloratis. Tabellae Quininae Bisulphatis. Tebellae Quininae Hydrochloridi. Tabellae Sodii Bicarbonatis Compositae. Tabellae Sodii Citratis. Tabellae Sodii Salicylatic. Tabellae Stilboestrolis. Tabellae Sulphadiazinae. Tabellae Sulphaguanidinae. Tabella Sulphanilamidi. Tabellae Sulphapyridinae. Tabellae Sulphathiazoli. Theophyllina cum Aethylenediamina. Thiopentonum Solubile. Unguentum Hydrargyri Ammoniati Aquosum. Unguentum Zinci Oxidi Aquosum.

Appendix XV.w—Biological Assay of Protamine Zinc Insulin.
Appendix XXII—Types of Stomata.
Appendix XXIII—Fluorimetric Assay of Aneurine Hydrochloride.

Monographs added to the B.P. 1932 by Notice in the London, Edinburgh, Belfast and Dublin Gazettes.
With effect from November 30, 1943—Extractum Colchici Cormi Liquidum.
With effect from February 18, 1944—Extractum Belladonnae Folii Liquidum.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Precipitation of Dextrin in Honey. G. P. Walton (*J. Assoc. Off. Agr. Chem.*, 1944, **27**, 585–586)—Expts. were made with honeydew honey (14·9% moisture) and buckwheat honey (20·7% of moisture), representing the extremities of the moisture range of honey, to determine the wt. relationships between abs. alcohol, water and amount of sample existing in the mixture in which dextrin is pptd. in the A.O.A.C. method for its determination in honey. The honey was weighed in a glass-stoppered 100-ml flask, 4 ml of water were added, and the honey was dissolved by warming slightly. Abs. alcohol was added, a little at a time, with vigorous mixing after each addition, until the flask was filled nearly to the mark. The flask was left overnight at 20° C., the vol. was then adjusted to 100 ml with abs. alcohol, and the flask was weighed. The following results (those for buckwheat honey being in brackets) were obtained, vol. and density being measured at 20° C. Wt. of honey, 4·0165 g (7·7293 g); water added, 3·9830 g (3·9788 g); total water present, 4·5815 g (5·5788 g); abs. alcohol added, 74·3246 g (72·3711 g); vol. of alcohol, 94·183 ml (91·686 ml); wt. of total water and alcohol, 78·9241 g (77·9499 g); alcohol by wt. in this mixture, 94·195% (92·84%); density of this mixture, 0·8065 (0·8103); vol. of this mixture, 97·86 ml (96·20 ml); alcohol by vol., 96·24 ml (95·30 ml); wt. of honey dry-matter, 3·4180 g (6·1293 g); vol. occupied by the dry-matter, 2·14 ml (3·80 ml) or 0·626 ml/g (0·619 ml/g); wt. of added water and alcohol, 78·3256 g (76·3499 g); alcohol by wt. excluding total honey, 94·915% (94·79%); density of this alcoholic soln., 0·8045 (0·8048); vol. of this soln., 97·362 ml (94·865 ml); apparent vol. occupied by the sample of liquid honey, 2·638 ml (5·135 ml) or 0·657 ml/g (0·664 ml/g). The results show that in the current A.O.A.C. method for determining dextrin in honey the concn. of alcohol attained in the soln. in which the dextrin is pptd. may vary from 95·30 to 96·24% by vol. according to the wt. of sample taken and its moisture content, and approx. the same proportionate variation occurs in the figures for the apparent vol. occupied by the sample of honey. The actual variation is, however, only 0·007 ml per g, and the aver. value of 0·660 ml per g for the apparent vol. occupied by the honey in the complete alcoholic mixture may be applied generally in the A.O.A.C. method. This suggests a means of calculating the quantity of abs. alcohol that must be added to bring the vol. of the mixture to 100 ml, as required by the method, without actually making the determination in a volumetric flask, thus permitting the weighing of the honey in a convenient type of flask and either weighing or measuring

(at 20° C.) the amount of alcohol to be added—an improvement in ease of manipulation and in precision. Since the figure for "% of alcohol by wt. excluding total honey" varies only slightly in the two determinations, the aver. value of 94·85% of alcohol by wt. may be used for the general calculation without significant error. The amount of water added as solvent must always be 4 ml, as specified in the method. Alcohol of 94·85% by wt. has a density of 0·80466 g/ml at 20° C. and is equiv. to 96·691% alcohol by vol. If H is the wt. of honey taken, the apparent vol. occupied by it is 0·66 H and the vol. of added water and alcohol is (100 − 0·66 H) ml. As shown (*supra*), this added water and alcohol yields a liquid containing approx. 96·691% of alcohol by vol. at 20° C. Hence the vol. of abs. alcohol to be added is 0·96691 (100 − 0·66 H) ml at 20° C.; or the wt. of abs. alcohol to be added is 0·78934 (96·691 − 0·63816 H) g.

A. O. J.

Determination of Residual Ethylene Dichloride in Fumigated Wheat Products. F. P. W. Winteringham (*J. Soc. Chem. Ind.*, 1944, 359–363)—Residual ethylene dichloride in wheat products cannot be recovered completely by dry hot aeration. Expts. described suggest that this retention is physical and that there is no chemical decomposition of the ethylene dichloride in the product. To determine the total residual ethylene dichloride in granular products, aerate 50 g at 100° C. for 3 hr. in a 350-ml aeration flask and determine the recovered ethylene dichloride by the method of thermal decomposition (*J. Soc. Chem. Ind.*, 1942, **61**, 190), modified so that less than 10 mg can be more accurately determined (*Id.*, 1944, **63**, 144). This aeration removes most of the moisture; if the moisture content is not above 10%, the time may be reduced. Grind the aerated grain in a mill, which must be air-tight to prevent loss of the dichloride. A Christy and Norris 5-in. laboratory mill, slightly modified, is described and illustrated. Introduce the product into the hopper of the running and heated mill, replacing the bung immediately. Mill for 3 or 4 min., remove the driving belt and stretch the rubber cap over the bearing to seal it. Continue hot aeration for 3 hr. at the rate of 10 ml per sec., and determine the recovered ethylene dichloride as before. Dismantle the mill and remove the sample. Determine the dichloride by the ashing method, applying a correction for changes in moisture content during milling. Determine moisture and total chlorine on the unfumigated samples also. Finely divided products, *e.g.*, flour, do not require milling. Aerate these for 3 hr. at 100° C. in a 350-ml aeration flask at 10 ml per sec., and determine the recovered ethylene dichloride and that in the sample as described for the ground product.

Ashing method—Heat 2·5 g of the sample with 5 ml of a 5% soln. of sodium in ethyl alcohol, in a Monax sealed test-tube. Break the tube, rinse the contents into a silica dish and evaporate to dryness with 5 ml of 10% sodium carbonate soln. at 100° C. Determine chloride as in A.O.A.C. method for plant products (*J. Soc. Chem. Ind.*, 1942, **61**, 187).

E. B. D.

Determination of Aminoazoxylene in D & C Red No. 18. O. L. Evenson (*J. Assoc. Off. Agr. Chem.*, 1944, **27**, 572–573)—The use of D & C Red No. 18 (Oil Red OS), 1-xylylazoxylylazo-2-naphthol, in drugs and cosmetics is permitted in U.S.A. In the preparation of this colour another azo dye, aminoazoxylene, is used as an intermediate. To determine the residual intermediate in the dye it is separated from a light petroleum soln. of the dye by extraction with an acidic water and alcohol mixture and removed from the extract by steam distillation in a 500-ml flask with a distilling head furnished with a steam inlet tube reaching nearly to the bottom of the flask. Numerous fine holes at the tip of the tube allow the steam to spread at the bottom of the flask. The still head is connected with a vertical, 20-in. straight-tube condenser by ground-glass joints. To 250 ml of light petroleum in a 500-ml separator add 5 ml of a 1% soln. of D & C Red No. 18 in chloroform and extract the aminoazoxylene by shaking vigorously with several 20-ml portions of an acidic mixture made by adding 200 ml of 95% alcohol to a cooled mixture of 600 ml of water and 200 ml of sulphuric acid. Dilute the combined extracts with water to 250 ml (or to 100 ml if less than 0·1% of intermediate is present in the dye). To an aliquot containing *ca.* 0·1 mg of aminoazoxylene in the distillation flask cooled in an ice-bath add sodium carbonate in successive small amounts until the liquid is just alkaline to litmus, dilute the mixture to *ca.* 50 ml, add *ca.* 20 g of sodium chloride and steam distil slowly at first, avoiding bumping and boiling of the liquid. When *ca.* 85 ml of distillate have collected, disconnect the distillation flask and rinse the condenser into the receiver with *ca.* 15 ml of 95% alcohol. Extract the intermediate from the distillate with 3 portions (30, 25 and 25 ml) of ether, drain the extracts into a wide Nessler glass or suitable test-tube, and remove the solvent at room temp. by means of a gentle stream of air dried by passage through sulphuric acid. Dissolve the residue in 20 ml of 95% alcohol and compare the colour with that of standards containing 0·05 to 0·15 mg of aminoazoxylene in the same vol. of solvent. Aminoazoxylene distils readily, all but a small proportion coming over in the first few min. The distillate may sometimes be nearly colourless owing to lowering of the *p*H by carbon dioxide coming over with the steam. Aqueous solns. of low concn. are nearly colourless at *p*H 3·5, yellow at *p*H 5 and red at *p*H 2·5. Xylidenes, if present, come over with the steam but do not interfere with the colorimetric test. Expts. with samples of the dye containing known amounts of aminoazoxylene showed that the recovery of the intermediate by the method described is *ca.* 90%.

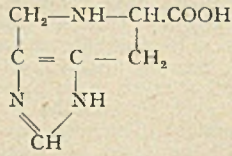
A. O. J.

Spectrophotometric Analysis of Coal-tar Colours. I. Ext D & C Yellow No. 5. G. R. Clark and S. H. Newburger (*J. Assoc. Off. Agr. Chem.*, 1944, **27**, 576–581)—To prepare the standard sample, 3-nitro-4-aminotoluene (m.p., 117° C.) was diazotised and coupled with acetoacetanilide (m.p., 83° C.) in alkaline soln. The product, twice re-crystallised from 1,4-dioxan, showed no change of m.p. (258° C.) when a portion was re-crystallised from nitropropane. The dye (20·04 mg) was dissolved by warming in 80 ml of chloroform and diluted at room temp. to 100 ml with the same solvent. Aliquots of this soln. were further diluted and examined spectrophotometrically with a recording spectrophotometer (G.E., U.S.A.) with slit adjustments for an 8-$m\mu$ wave-length band. The curve showed max. absorption at 413 ± 2 $m\mu$, and the ratio of the extinction values at 410 and 430 $m\mu$ was $1{\cdot}23 \pm 0{\cdot}02$. This ratio serves to identify the colour. The ratios of extinction to concn. indicate that at 413 $m\mu$ deviations from Beer's law are less than 1% for solns. of the dye in

chloroform containing 2·5 to 20 mg per litre, and with four solns. containing 20, 10, 5 and 2·5 mg of dye per litre respectively the average ratio of extinction to concn. at this wavelength was 0·063. Two commercial samples of certified Ext D & C Yellow No. 5 (Hansa Yellow) were examined spectrophotometrically by the method described and by determination of the nitrogen content. The values obtained by the two methods were in satisfactory agreement. The method may be applied to determine the pure dye content of lakes by extracting the dye under reflux with chloroform, removing the insoluble matter by filtration and diluting the filtrate to a suitable concn. A. O. J.

Biochemical

Reaction between Histidine and Formaldehyde. A. Neuberger (*Biochem. J.*, 1944, **38**, 309–314)—The reaction between formaldehyde and amino acids occurs in two stages, the first being a reversible reaction leading to an aldimine or N-methylol structure which dissociates readily into the original components, and the second consisting of irreversible reactions which vary with different amino acids. It has now been shown that histidine reacts with 1 mol. of formaldehyde to give a tetrahydro-pyrido iminazole carboxylic acid,



whilst in presence of excess of formaldehyde the very insoluble N-methylol derivative of this substance is obtained. It is concluded that, since acylated histidines do not condense with formaldehyde, this compound is not formed during the reaction of formaldehyde with proteins in the Sørensen titration method unless some of the α-amino groups present in proteins are those of histidine. It is possible, however, that methylene bridges may be formed by formaldehyde between the iminazole groups of proteins and neighbouring amino acids. On the other hand, the rapid reaction of histidine with formaldehyde may lead to errors in the estimation of β-hydroxy-α-amino acids by the periodate method, especially in the estimation of serine, which is based on the measurement of the formaldehyde evolved. F. A. R.

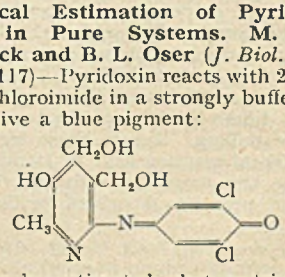
Microbiological Assay of Tryptophan in Proteins and Foods. R. D. Greene and A. Black (*J. Biol. Chem.*, 1944, **155**, 1–8)—The organism used was *Lactobacillus arabinosus* 17–5 cultured by the method of Snell and Wright, using an inoculum from the basal medium plus 0·5 mg of *l*-tryptophan per 10 ml. The basal medium had the following composition: charcoal-treated hydrolysed casein, 0·5 g; cystine, 0·01 g; glucose, 1·0 g; sodium acetate, 0·6 g; adenine sulphate, 1·0 mg; guanine hydrochloride, 1·0 mg; uracil, 1·0 mg; aneurine hydrochloride, 0·02 mg; nicotinic acid, 0·02 mg; pyridoxin hydrochloride, 0·02 mg; *p*-aminobenzoic acid, 0·02 mg; calcium pantothenate, 0·02 mg; riboflavin, 0·02 mg; biotin, 0·00004 mg, per 100 g. Inorganic salt solutions, A and B*, 0·05 ml each per 10 ml of medium.

* Solution A: KH_2PO_4, 25 g; K_2HPO_4, 25 g; water to make 250 ml.

Solution B: $MgSO_4.7H_2O$, 10 g; NaCl, 0·5 g; $FeSO_4.7H_2O$, 0·5 g; $MnSO_4.4H_2O$, 0·5 g; water to make 250 ml.

To prepare the casein hydrolysate, boil 200 g of vitamin-free casein under reflux with 1 litre of 20% hydrochloric acid for 8 hr., concentrate to a thick syrup, add 750 ml of water and repeat the concentration. Dissolve the residue in water, adjust to *p*H 3 with sodium hydroxide soln. and dilute to 2 litres. Stir with 40 g of Norit A at 50–60° C. for 1 hr. and filter. Adjust the filtrate to *p*H 6·8, dilute to 2 litres and preserve under toluene. Two methods of digesting the samples can be used: (*a*) *Pancreatic digestion*—To a 0·1% soln. or suspension (*p*H 8·2) of 0·1 g of protein add 5 mg of pancreatin and incubate at 37° C. for 24 hr. In some instances pre-digestion with 1% pepsin or autoclaving with water for 30 min. improves the pancreatic digestion. Adjust the digest to *p*H 4·0 and extract with two 100-ml portions of ether and then with 30 ml of toluene. Finally, adjust to *p*H 6·8. (*b*) *Barium hydroxide digestion*—Mix 0·5 g of the sample with 4·2 g of anhydrous barium hydroxide and 8 ml of water and autoclave for 7 hr. at 15 lb. pressure. Transfer the hydrolysate to centrifuge bottles and adjust to *p*H 4 with 10 *N* sulphuric acid. Dilute to 101·5 ml (the barium sulphate occupies a vol. of 1·5 ml) and centrifuge. Extract the soln. with two 100-ml portions of ether and then with 30 ml of toluene, and adjust to *p*H 6·8. This second method is to be preferred as, when pancreatic digestion is employed, a correction must be applied for the amount of tryptophan (up to 1·5%) in the enzyme preparation. Where barium hydroxide is used the observed values must be multiplied by 2 to correct for racemisation. Prepare the basal medium at twice the concn. shown given above and add 5 ml to each tube; to the standards add 0, 2, 4, 6, 8, 10 and 12 μg of *l*-tryptophan, and, to another series of tubes, add up to 0·6 ml of the extract to be tested, autoclave, inoculate, incubate at 37° C. for 72 hr. and titrate in the usual way. Recoveries of 94 to 104% of *l*-tryptophan added to various foodstuffs were obtained. There was excellent agreement when different amounts of the same samples were taken for analysis, whilst replicates on the same sample were also satisfactory. The method was used to estimate the tryptophan in various proteins and foodstuffs. F. A. R.

Chemical Estimation of Pyridoxin. Reactions in Pure Systems. M. Hochberg, D. Melnick and B. L. Oser (*J. Biol. Chem.*, 1944, **155**, 109–117)—Pyridoxin reacts with 2 : 6-dichloroquinone chloroimide in a strongly buffered alcoholic soln. to give a blue pigment:



which can be estimated photometrically. Errors due to the reaction of other compounds with the reagent can be eliminated by carrying out a second reaction in presence of excess borate. The borate renders the pyridoxin unreactive without affecting the reaction with other coupling compounds. To a tube containing 1 ml of pyridoxin soln. (100 mg in 1 litre of 0·1 *N* hydrochloric acid), 5 ml of *iso*propanol, 2 ml of ammonia-ammonium chloride soln. (160 g of ammonium chloride in 700 ml of water, mixed with 160 ml of conc. ammonia and diluted to 1 litre) and 1 ml of 5% boric acid soln., add 1 ml of chloroimide reagent. (Purify the solid reagent

by dissolving 1 g in 50 ml of acetone and precipitating by addition of small amounts of water with stirring. Dissolve 100 mg of the dried, recrystallised substance in 250 ml of *iso*propanol. Store the soln. in a glass-stoppered bottle in the refrigerator for not more than one month, discarding it before this time if a pink colour develops.) Adjust the photometer at 100% transmission 60 sec. after addition of the reagent, and measure the absorption of the soln. and that of a similar mixture containing water in place of the boric acid soln., using a 620 $m\mu$ filter. When the readings are taken 60 sec. after mixing, the relation between pyridoxin concn. and photometric density is linear. Replicates gave results agreeing on the average within ±1·1%. Of various other phenolic compounds tested, only 2-methyl-3-hydroxy-4 : 5-bis(acetoxymethyl)-pyridine, which is said to be biologically equivalent to pyridoxin, showed any appreciable difference between the reactions in presence and absence of boric acid. In the presence of relatively high concns. of some interfering coupling compounds, the reaction between pyridoxin and the chloroimide may be partly or completely inhibited within the period of measurement. Thus, for example, in presence of sufficient resorcinol or naphthylamine hydrochloride, the photometric density due to a given amount of pyridoxin is much less than when the reaction is carried out in pure solution, so that if a reference curve prepared from pure pyridoxin is used, erroneous values are obtained. This is undoubtedly due to the removal of much of the reagent by the resorcinol or naphthylamine, but in spite of this, the addition of small amounts of pyridoxin is insufficient to affect the residual chloroimide appreciably, and this source of interference can therefore be overcome by the addition of a known amount of pyridoxin to an aliquot of the test soln. containing the inhibitory substance. This procedure, being a difference method, is less accurate, but otherwise gives satisfactory results. F. A. R.

Chemical Estimation of Pyridoxin in Biological Materials and Pharmaceutical Products. The Multiple Nature of Vitamin B_6. M. Hochberg, D. Melnick and B. L. Oser (*J. Biol. Chem.*, 1944, **155**, 119–128)—Comparison of the vitamin B_6 content of biological materials by biological and microbiological procedures fails to show good agreement, because of the variable vitamin B_6 activity of compounds other than pyridoxin for the test organisms employed. Reaction with 2 : 6-dichloroquinone chloroimide (*cf.* preceding abstract) has now been used for the estimation of pyridoxin in biological materials and pharmaceutical preparations. The results confirm the presence of compounds, other than pyridoxin, with vitamin B_6 activity. Weigh a quantity of the sample, containing approx. 100 μg of pyridoxin, into a test-tube calibrated at the 20-ml mark and add 10 ml of 4 *N* hydrochloric acid. Introduce a stirring rod and immerse the tube in a boiling water-bath for 1 hr. with occasional stirring. Cool, neutralise to *p*H 3 with an external indicator, add 3 ml of buffer soln. of *p*H 3 (73 g of $Na_2HPO_4.2H_2O$ and 167 g of citric acid in 1 litre) and add 2·5 g of Lloyd's reagent. Stopper the tube and shake occasionally during the next 5 min. Centrifuge and discard the supernatant liquid. Wash the residue once with 15 ml of 0·001 *N* hydrochloric acid, again centrifuge and discard the supernatant liquid. Add 5 ml of 2 *N* sodium hydroxide, dilute to the 20-ml mark and shake the suspension gently for 3 min. Centrifuge, mix 10 ml of the eluate with 50 ml of *iso*propanol, and again centrifuge. Decant the supernatant liquid and adjust to *p*H 5–7 with a few drops of 12 *N* hydrochloric acid, using an external indicator. For development of the colour set up the following tubes, adding the solns. in the order given, to prevent pptn. of salts: Tube 1: 6 ml of extract, 2 ml of ammonia-ammonium chloride soln., 1 ml of boric acid soln. (for preparation of reagents, see preceding abstract); Tube 2: 6 ml of extract, 2 ml of ammonia-ammonium chloride soln., 1 ml of water; Tube 3: 6 ml of extract, 2 ml of ammonia-ammonium chloride soln., 1 ml of pyridoxin standard (10 μg). Set the photometer at 100% transmission 60 sec. after adding 1 ml of the chloroimide reagent to tube 1, using a 620 $m\mu$ filter. Measure the blue colour of each of the other tubes 60 sec. after addition of 1 ml of chloroimide reagent. The amount of pyridoxin (μg per g) is calculated from the expression: $\frac{L_2}{L_3 - L_2} \times \frac{10}{6} \times \frac{60}{10} \times \frac{18{\cdot}5}{W}$ where L_2 is the photometric density $(2 - \log G)$ due to the pyridoxin in the 6 ml of extract in tube 2, $L_3 - L_2$ is the increment in photometric density due to the added 10 μg of pyridoxin, and W is the weight of the sample in g. The expression includes a correction for the vol. (1·5 ml) occupied by the Lloyd's reagent. Recoveries of 95 to 104% were obtained when known amounts of pyridoxin were added to various pharmaceutical preparations, but results were less satisfactory with substances containing relatively large amounts of other coupling compounds. The amount of pyridoxin liberated from various biological materials by hydrolysis was examined by the chemical method and by the biological and microbiological methods. It was found that, whereas 90% of the pyridoxin was in the bound form in a rice bran concentrate according to the chemical method, all the vitamin in a dried liver powder and a dried yeast appeared to be present in the free form. Only in the assay of the rice bran concentrate were the results by the chemical method in agreement with those obtained by the other two methods. The discrepancies with the liver and yeast preparations were shown to be due to other substances with vitamin B_6 activity. Ascorbic acid interferes with the reaction of pyridoxin and 2 : 6-dichloroquinone chloroimide. In pharmaceutical preparations, interference from this source can be eliminated by oxidising with manganese dioxide. Suspend the sample, containing 80–200 μg of pyridoxin, in 15 ml of 0·5 *N* sodium hydroxide in a tube calibrated at 20 ml, immerse in a boiling water-bath for 15 min. with constant shaking, cool and add 200 mg of manganese dioxide. Dilute to 20 ml, shake for 5 min., add a 5-ml portion to 25 ml of *iso*propanol and centrifuge. Use 6 ml aliquots of the supernatant liquid for colour development, as described above. The method gives results with an error of only ±2%. F. A. R.

Microbiological Assay of Nicotinic Acid in Cereals and other Products. E. C. Barton-Wright (*Biochem. J.*, 1944, **38**, 314–319)—The method of Snell and Wright (*J. Biol. Chem.*, 1941, **139**, 675) has the disadvantage that the standard curve is non-linear with concns. of nicotinic acid greater than 0·15–0·2 μg/ml. Krehl, Strong and Elvehjem (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 471) overcame this difficulty by increasing the concn. of glucose and sodium acetate to 2%, by doubling the concn. of cystine and halving the concentration of biotin (*i.e.*, 0·2 instead of 0·4 μg

per litre). Further improvements have now been made by doubling the concn. of casein hydrolysate (1% instead of 0·5%), maintaining the concn. of biotin at 0·4 μg per litre and adding xanthine (1 mg per 100 ml) and xylose (0·1%). The high blanks previously obtained were due to nicotinic acid in the casein hydrolysate, the *l*-tryptophan and the biotin concentrate. This difficulty was overcome by modifying the method used for hydrolysing casein, by the use of synthetic *dl*-tryptophan and of crystalline biotin. The organism employed was *Lactobacillus arabinosus* 17–5, stock cultures of which were carried on a yeast-water-glucose agar to which had been added 0·6% of sodium acetate. The cultures were stored in a refrigerator at 4° C. and renewed at fortnightly intervals. The composition per ml of the basal medium was as follows: Acid-hydrolysed casein, 10 mg; *dl*-tryptophan, 0·1 mg; *l*-cystine, 0·2 mg; glucose, 20 mg; sodium acetate, 20 mg; xylose, 1 mg; *dl*-calcium pantothenate, 0·1 μg; pyridoxin, 0·1 μg; riboflavin, 0·2 μg; *p*-amino-benzoic acid, 0·1 μg; biotin, 0·0004 μg; adenine, 0·01 mg; guanine, 0·01 mg; uracil, 0·01 mg; xanthine, 0·01 mg; sodium chloride, 5 mg. Inorganic salts: Solution A (K_2HPO_4, 25 g and KH_2PO_4, 25 g in 250 ml of water), 5 ml per litre. Inorganic salts: Solution B ($MgSO_4.7H_2O$, 10 g; $MnSO_4 4H_2O$, 0·5 g; $FeCl_3$, 0·03 g in 250 ml of water acidified with 5 drops of conc. hydrochloric acid), 5 ml per litre. All the stock cultures were stored in a refrigerator with a thin layer of toluene on the top of each. Glass-distilled water was used, and possible contamination of the constituents of the medium with nicotinic acid was always tested for by using *Proteus vulgaris* in the medium recommended by Stephenson (*Bacterial Metabolism*; 1938). The casein hydrolysate was prepared as follows. Shake 100 g of "vitamin-free casein" with two 300-ml portions of 85% ethanol for 20 min. and filter. Add the casein gradually to 1 litre of distilled water at 50° C. with constant stirring, stir for a further 30 min., and then slowly add 30% NaOH soln. with constant stirring until the casein is dissolved. Stir the viscous mass for a further 20 min., adjust to *p*H 4·6 with 10% HCl and filter. Repeat this operation three or four times and then wash the alkali-extracted casein with water at 50° C. Hydrolyse with 500 ml of 25% w/v sulphuric acid for 10 hr. at 15 lb. pressure in an autoclave, or reflux for 16 to 20 hr. on a sand-bath. Add 200 g of litharge and filter off the lead sulphate, add barium hydroxide to neutralise the remaining sulphuric acid and filter off the barium sulphate. Adjust the hydrolysate to *p*H 3, make up the volume to 700 ml, shake for 30 min. with active carbon (Norit A) and filter. Adjust the *p*H to 6·8 with barium hydroxide and dilute or concentrate so that the soln. contains 100 mg of dry matter per ml. Preserve under toluene in a refrigerator. Any pptd. tyrosine may be disregarded. Transfer the organism from the agar stab culture to a tube of the Snell and Strong riboflavin medium, incubate for 18–20 hr. at 37° C., centrifuge and re-suspend in twice the vol. of 0·9% saline soln. This gives the heavy growth required for the assay. Grind the sample to be tested, suspend 5-g quantities in 50 ml of *N* hydrochloric acid, and autoclave for 15 min. at 15-lb. pressure. (De-fat materials containing a high proportion of fat by a preliminary Soxhlet extraction with light petroleum for 10 hr.) Cool, adjust the extract to *p*H 6·8 with 30% sodium hydroxide soln. and dilute to 100 ml. The final solution should contain approx. 0·05 μg per ml of nicotinic acid. Transfer 5 ml of the basal medium of double the strength given above to each tube, add 0, 0·5, 1·0, 1·5, 2·0, 2·5, 3·0 and 3·5 ml of a standard nicotinic acid soln. (0·1 μg per ml) to a series of tubes in duplicate, and dilute each with distilled water to 10 ml. To another series of tubes, also in duplicate, add 1, 2, 3 and 4 ml of each extract. Plug the tubes with cotton wool, autoclave for 10 min. at 10 lb. pressure, cool and inoculate with 1 drop of inoculum per tube from a sterile pipette. Incubate for 72 hr. at 37° C. and titrate with 0·1 *N* sodium hydroxide, using bromothymol blue as indicator. Plot a standard curve in the usual way, and from it calculate the nicotinic acid content of the extract. The replicate determinations should differ by not more than ±10%. The following results were obtained: Wheat (English), 48; wheat (Manitoba), 55–66; wheat germ 55–77; wheat bran, 267–325; National flour (85% extraction), 12–18·7; barley (various strains), 85–147; commercial malt, 91–108; maize (starchy), 11·5–20·0; maize (sweet), 26–37; oats, 4·9–7·0; rye, 7·7–10·0; beer, 7·8–17·0; vinegar, 9; dehydrated meat, 100–110; coffee, 132; cocoa, 16; tea, 61; milk powder, 9·2 μg per g; and milk, 0·8–1·0 μg per ml. F. A. R.

Macro-fermentation Method for Aneurine Assay. N. S. Scrimshaw and W. B. Stewart (*J. Biol. Chem.*, 1944, **155**, 79–86)—When the method of Schultz, Atkin and Frey (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 35) was used for the assay of meat and eggs, three sources of error were observed: (*a*) the range over which the response of the yeast to increasing amounts of aneurine was linear varied with the substance assayed and with the sample of yeast used; (*b*) the activity of crystalline aneurine was greater in presence of other constituents of the food samples than in the basal medium alone; (*c*) the sulphite cleavage procedure did not completely destroy the activity of aneurine. These sources of error were eliminated by the following modifications of the original procedure: Make a preliminary run for each type of substance assayed, adding graded amounts of aneurine to the blank; this will indicate the range over which the response to aneurine is linear. Secondly, in each complete assay, include, in addition to the blank and the sample, a tube containing the reagents together with a known amount of aneurine. The difference in gas production between this tube and the blank is a measure of the effect of the known amount of aneurine, whilst the difference between the blank and the sample indicates the effect due to the aneurine in the sample, whence the actual amount of aneurine can be calculated. In this way any inhibitors present in the sample act equally on the aneurine of the sample and on that of the standard. Values of 28·8 and 29·8 μg per g were obtained for egg yolk by this procedure, whereas the original method gave 44·5 and 36·4 μg per g. in simultaneous runs. Finally, determine the effectiveness of the sulphite cleavage for each type of substance assayed on a blank containing a known amount of added aneurine and, if necessary, apply a correction for the activity of the cleavage product. F. A. R.

Effect of Vitamin C on the Estimation of Sulphanilamide. L. Karel and C. W. Chapman (*J. Biol. Chem.*, 1944, **155**, 27–32)—When sulphanilamide and reduced vitamin C were estimated by the methods of Bratton and Marshall (*J. Biol. Chem.*, 1939, **128**, 537) and Farmer and Abt (*Proc. Soc. Exp. Biol. Med.*, 1935, **32**, 1625; 1926, **34**, 146), respectively, in the blood of guinea-pigs to which both had been administered, only small amounts

of vitamin C could be detected in the blood, and it was thought that sulphanilamide might interfere with the estimation of the vitamin. This was disproved, however, and the low vitamin C content was probably due to the fact that after administration of sulphanilamide the animals ceased to take nourishment. The expts. also showed that ascorbic acid did not interfere with the estimation of sulphanilamide in amounts up to 10 mg per 100 g when up to 3 mg of the reduced form of ascorbic acid per 100 g was present. Ascorbic acid in excess of this amount caused interference, and this was greater the larger the quantity of vitamin present. Interference with colour production was found to be proportional, not to the quantity of vitamin C, but to the ratio of ascorbic acid to sulphanilamide. A reaction appears to take place between the reduced form of vitamin C and sulphanilamide when the soln. is heated for 1 hr. under reflux.

F. A. R.

Reported Growth Stimulation for *Lactobacillus casei*. E. J. Chu and R. J. Williams (*J. Biol. Chem.*, 1944, **155**, 9–11)—It has been reported by previous workers that some samples of peptone contain an unknown factor which stimulates the growth of *Lactobacillus casei* and which therefore may introduce an error into assays in which this organism is employed. When the basal medium was modified by addition of 1·2 mg of pyridoxin, 0·4 mg of *p*-amino-benzoic acid and 0·2 g of asparagine per litre, the effect of peptone was eliminated. It is believed that the effect of peptone is not due to a single factor, but to its content of *p*-aminobenzoic acid, a sustance with pyridoxin activity, and various amino acids and peptides.

F. A. R.

Variations in the Vitamin C Content in Guavas. D. P. van der Merwe (*Clin. Proc., Cape Town*, 1944, **3**, 441–444)—The vitamin C content of guavas ranges from 100 to over 700 mg per 100 g according to the variety and the season. The species producing the bulk of the Florida and Californian guavas is *Psidium guajava*, but owing to cross pollination all varieties are very much mixed. Most of the S. African varieties of guava are grown from seed, but because of cross pollination seed sown from one guava may yield several varieties. The so-called Madeira, an early flowering type, is not badly mixed, but later varieties are worse, and selected varieties with high vitamin C content for canning are therefore propagated by the vegetative method so as to be true to type. Allowance being made for natural factors such as humidity, temperature and pests, the following results (mg per 100 g of fruit) were recorded for the Madeira type during its ripening season: *Transvaal*, May, 148·3; May, 158·7; June, 258·0. *Cape Province*, July 2nd, 171·4; July 9th, 228·3; July 16th, 223·1. The Retief type grown in the Transvaal yielded 710 mg per 100 g, and 600 mg per 100 g when grown in Cape Province. The Madeira type gives low yields wherever grown. A variety with a particular colour may have a high vitamin content, but the colour is not correlated with the vitamin C content. Thus 6 different types of white guavas gave results ranging from 104·5 (Madeira type) to 640 mg (Simonsvlei type) of vitamin C per 100 g of fruit. The selected and vegetatively propagated varieties Rosseau-Malherbe-Retief and the white varieties, Midseason and Simonsvlei, contain the most vitamin C.

Bacteriological

Presence in Raw Cow's Milk of a Bactericidal Substance Specific for certain Strains of Coliform Organisms. C. S. Morris (*Nature*, 1945, **155**, 22)—It has been found that when certain strains of coliform organisms are inoculated into raw "sterile" milk, resazurin and methylene blue are not reduced and the organisms are actually destroyed by holding the milk at 37° C. for 6 hr. (Morris, *J. Dairy Res.*, 1943, **13**, 115). All tests for the presence of a bacteriophage were negative and, as the destruction of the organisms appeared to be closely correlated with the temp. at which the milk was held, it was considered that the effect might be due to a specific thermolabile bactericide. The effect of heat on the substance was investigated by inoculating raw "sterile" milk after heating to various temps. between 52 and 53° C. for 30 min. with young broth cultures of susceptible organisms so as to give an inoculation count on MacConkey's agar of *ca.* 500,000 to 2,000,000 organisms per ml. Plate counts on MacConkey's agar were carried out at inoculation and after incubation for 4 hr. at 37° C. with the following results:

	Temp. to which milk was heated for 30 min. before inoculation	Count per ml at inoculation	Count per ml after 4 hr. at 37° C.
Culture I	52° C.	1,328,000	1,000
	53° C.	848,000	40,000,000
Culture II	52 °C.	316,000	31,000
	53° C.	640,000	28,000,000

These results indicate that the bactericide is destroyed by heating to 53° C. for 30 min. and that the destruction is critical to within 1° C. The cultures of susceptible organisms were obtained from raw milk which the presumptive coliform test showed to contain coliform organisms in 0·001 ml, but which did not reduce resazurin or methylene blue in 6 hr. at 37° C. Differential tests on the organisms indicated that the majority were of intermediate types.

J. A.

Effect of Temperature, Humidity and Glycol Vapours on the Viability of Air-borne Bacteria. K. B. De Ome (*Amer. J. Hyg.*, 1944, **40**, 239–249)—Apparatus is described with which rapid estimations can be made of the death rate of airborne bacteria in presence of glycol vapour under rigidly controlled conditions, and results of expts. are recorded. The test organism employed was *Salmonella pullorum*, which is known to be airborne in egg incubators. This organism, dispersed into air by water spray, was exposed to varying conditions of temp., relative humidity and concn. of triethylene and propylene glycol for 2·5, 15·5 and 27·5 sec., after which samples of air were withdrawn and the viable bacteria were determined by culture. The index of death rate was taken as the seconds required for a 50% reduction of the number of viable bacteria, the number recovered from the 2·5 sec. exposure being taken as base. Semi-logarithmic curves were plotted and values were worked out from these. With glycol-free and dust-free air the death rate of *S. pullorum* is quite considerable and increases as the temp. rises from 28° to 37° C. and as the R.H. increases from 15 to 80%. In presence of glycol vapour the death rate decreases as the temp. rises fron 28° to 37° C. and as the R.H. deviates from 45% . (It was previously demonstrated by Robertson *et al.* that glycol vapour was most effective at R.H. between 40 and

60%.) When the R.H. falls to 15% or rises to 80%, triethylene glycol has no appreciable bactericidal effect. This glycol is much more effective than propylene glycol, which requires about 100 times the concn. of the former to produce the same death rate. The following recording may be cited as practical examples:

	Triethylene glycol	Propylene glycol
Concentration by vol. ..	1 ml in 300 million ml	1 ml in 3 million ml
Temperature	28° C.	27° C.
Relative humidity ..	45%	51%
Bacteria per litre after exposure of 2·5 sec.	19,173	3,531
,, ,, 15·5 ,,	883	1,024
,, ,, 27·5 ,,	494	6
Index of death rate (calculated)	3·0	3·5

D. R. W.

Agricultural

Dilute Hydrochloric Acid as Solvent for Phosphates, with Special Reference to Defluorinated Phosphates and other Phosphorus Supplements for Livestock. D. S. Reynolds, W. L. Hill and K. D. Jacob (*J. Assoc. Off. Agr. Chem.*, 1944, **27**, 559–571)—Among the substitutes for bone products, thermally defluorinated superphosphates and phosphate rock are of special interest, but there is no standard method for determining the assimilable phosphorus in these substances, although extraction with hydrochloric acid of the range of concn. found in animal stomachs has been used by some workers without formulation of a standarised procedure. Superphosphate of American manufacture is essentially a mixture of anhydrous calcium sulphate (anhydrite) and monocalcium phosphate, and may contain 1·2 to 2·0% of fluorine, which must be removed before the material can serve as a mineral ingredient of cattle food. To remove fluorine the superphosphate is heated in a rotary kiln at 600°–800° C. or higher, and in the process monocalcium phosphate is replaced by crystalline metaphosphate, pyrophosphate or tricalcium phosphate or a mixture of the three according to the temp. and uniformity of heating. Calcium orthophosphates, the acid salts, tricalcium phosphate and apatites are assimilated by animals. Data concerning the assimilation of crystalline meta- and pyro-phosphates are not yet available, but expts. showed that the three classes of phosphate differ markedly in the readiness with which the crystalline forms are attacked by dil. acid, so that the amount of phosphorus dissolved when the material is digested with hydrochloric acid should indicate the classes of phosphate present. Commercial phosphate rock of American origin is essentially a mixture of fluorapatite and silica. It is defluorinated by heating in a current of steam at or above 1400° C., the product being fused or calcined phosphate rock according as the temp. is maintained above or below the m.p. of the rock. The principal phosphate in both products is the high temp. α-modification of tricalcium phosphate, and the high feeding value of fused phosphate rock was to be expected. The following standard procedure was adopted. Shake 1 g of the sample in a stoppered 250-ml flask for 30 sec. with 100 ml of exactly 0·4% (0·1097 *N*) hydrochloric acid and digest for 1 hr. at 25° C., with vigorous shaking at intervals of 5 min. Filter and wash the residue with water until the filtrate measures 200 ml. If a ppt. forms in the extract add enough hydrochloric acid to dissolve it, and finally dilute the extract to 250 ml. Boil aliquots for 2 hr. or longer to convert meta- and pyro-phosphates into orthophosphate and determine the phosphorus content by the volumetric molybdate method of the A.O.A.C. (*Methods of Analysis*, 1940). Although most of the samples investigated were ground to pass 100-mesh sieves, 80-mesh material is probably fine enough for routine testing. Variation of the acid concn. (up to 1%) and alteration of the temp. of digestion had little effect upon the amount of phosphorus extracted from defluorinated superphosphate, but products prepared below 700° C. proved markedly sensitive to alteration of digestion temp. Except with vitreous calcium metaphosphate little advantage was gained by prolonging the digestion. Although the type of agitation was not studied systematically, continuous agitation by inversion on a rotating machine of 3 laboratory preparations of defluorinated superphosphate showed increases of 7·2, 17·9 and 1·6% of the total phosphorus for materials prepared at 600°, 760° and 1010° C., respectively. Since the method is empirical, the amount of extracted phosphorus is likely to be affected by the ratio of sample to extractant. The increase in extracted phosphorus when the wt. of sample was reduced to 0·5 g ranged from zero for natural aluminium phosphate to nearly 30% of the total phosphorus in bone char and a defluorinated superphosphate prepared at 760° C. On the basis of the results for extracted phosphorus the materials investigated differed widely. For the pure crystalline constituents, the "solubility" of the metaphosphates is only *ca.* 1% and that of the tricalcium phosphate and hydroxy apatite 77–78%, pyrophosphates occupying an intermediate position (21·51%). Similarly the results for commercially prepared materials range from 100% for a bone meal to 29·2% for "Accofos" (a defluorinated phosphate rock), whilst those for commercial defluorinated superphosphates range from 33·4 to 76·4%. A phosphate that is only slightly attacked by 0·4% hydrochloric acid (*e.g.*, crystalline calcium metaphosphate) cannot be expected to show favourable results in feeding tests, but "solubility" is apparently not an infallible criterion of availability, for Shelling and Asher (*J. Biol. Chem.*, 1932, **96**, 195) found no evidence of assimilation of water-sol. sodium metaphosphate. Results of rat feeding expts. with certain defluorinated superphosphates (N. R. Ellis, private communication) place these materials in the same order as do the "solubility" data, and similar expts. Fraser *et al.* (*Ind. Eng. Chem.*, 1943, **35**, 1087) showed that the availabilities of defluorinated phosphate rock (fused), crude vitreous calcium metaphosphate and pure calcium metaphosphate are 96, 73 and 49 respectively (sodium orthophosphate ≡ 100) in comparison with the sequence 80, 55 and 25 obtained from solubility data with steamed bone meal as standard of reference. A. O. J.

Preparation of Hydrochloric Acid Extracts of Soils for Quantitative Spectrochemical Analysis. A. C. Oertel (*J. Soc. Chem. Ind.*, 1944, 379–380)—The apparatus and method used in a standard acid extraction of 50 g of soil (*cf.* Piper, "*Soil and Plant Analysis*,") are modified for 10 to 20-g samples, in order to obtain reproducibility. The digestion unit is a Pyrex glass Erlenmeyer flask and Pyrex glass air condenser fitted with interchangeable standard ground joints,

the upper end of the condenser being of almost capillary dimensions and turned through a semi-circle, to prevent entry of condensed water into the flask. To prepare the extract, digest the sample with 35–70 ml of hydrochloric acid of constant b.p., which has been distilled in a Pyrex still and kept in a Pyrex bottle for 48 hr. After the digestion, wash the joint of the apparatus with acidified double-distilled water before removal of the condenser. Filter and transfer aliquots of the extract to Pyrex glass dropping bottles. From these, transfer the extract dropwise to heated graphite electrodes, which are supported by holes drilled in a free hot-plate provided with handles. This hot-plate, made of steel, rests on an electrically heated hot-plate, both plates being protected by heat- and acid-resisting enamel. Keep the temp. of the upper ends of the electrodes just below the b.p. of the added soln. and raise gradually as the soln. in the electrodes becomes more concentrated. If necessary, store the plate with loaded electrodes in an oven at *ca.* 120° C. Keep the samples dry immediately before arcing or sparking in spectrographic analysis, by using a hot-plate to keep electrodes at *ca.* 110° C. This method minimises the risk of contamination of the sample; the purity of the graphite electrodes is probably the limiting factor. If internal standard elements are required, add them in a minimum of solvent to samples in the flask and dry at *ca.* 98° C. E. B. D.

Relationship of the Diameter of Derris Roots to the Rotenone Content. G. T. Bray (*J. Soc. Chem. Ind.*, 1944, 384)—In normal times the roots most favoured commercially have diameters of $\frac{3}{8}$ to $\frac{1}{2}$ in. Previous investigations have indicated that the thinner roots are usually, but not invariably, richer in rotenone than the thicker ones. In thick, older roots, starch-bearing tissue predominates, whilst resin cells, which alone contain rotenone, are more frequent in smaller roots (*Rep. Puerto Rico Exp. Sta.*, 1939, p. 71). Chemical examination, at the Imperial Institute, of *Derris elliptica* roots from various parts of the British Empire has confirmed this conclusion, but in samples from St. Lucia and the Seychelles the very fine rootlets contained less rotenone than the somewhat thicker, but fine, ones. Maximum yields were: (*a*) St. Lucia, root diam. $\frac{1}{8}$ to $\frac{3}{8}$ in., 9·7%; (*b*) Uganda, up to $\frac{3}{8}$ in., 6·6%; (*c*) Seychelles, medium, 6·9%; (*d*) Tanganyika (i) up to $\frac{1}{2}$ in., 4·7%; (ii) up to 1/20 in., 9·3%; (*e*) Fiji, 1/20 to $\frac{1}{4}$ in., most $\frac{1}{8}$ in., 1·8%; (*f*) New Guinea, 1/5 to $\frac{1}{2}$ in., mostly *ca.* $\frac{1}{2}$ in., 3·2%. E. B. D.

Detection and Determination of Traces of Methyl Bromide. O. F. Lubatti (*Nature*, 1945, **155**, 109)—The use of methyl bromide as a fumigant suffers from the disadvantage that it is toxic in the concns. likely to be employed for this purpose. A method of detection and determination has been devised wherein a stream of air is drawn through a vertical glass tube near the bottom of which is mounted a platinum spiral. This is caused to glow by the passage of a current from a small 4-volt cell, and the bromine liberated by the catalytic combustion of the methyl bromide is determined by the intensity of the colour produced on a paper, perforated in the middle and moistened with a pale yellow soln. of fluorescein, fastened to the top of the tube. The eosin, which appears as a red ring surrounded by a white border can readily be matched against standard discs. By varying the duration of the test and by using different colour standards, determinations of methyl bromide can be made over a wide range of concns. covering those of toxicological importance. J. A.

Organic

Identification of Thioglycollic Acid. J. H. Jones (*J. Assoc. Off. Agr. Chem.*, 1944, **27**, 574–576)—Several colour and precipitation reactions for thioglycollic acid in cold permanent waving preparations have been described (Hoshall, *J. Assoc. Off. Agr. Chem.*, 1940, **23**, 727; Analyst, 1940, **65**, 667) most of which are not specific for thioglycollic acid, but are given by other thiols and are sometimes obscured by sulphites, thiosulphates and sulphides occurring in the preparations. More specific identification may be obtained by conversion of the thioglycollic acid into dithiodiglycollic acid, which may be extracted from acid soln. with ether and identified by its m.p. and its equiv. wt. Slightly acidify an aliquot containing 0·2–1·0 g of thioglycollic acid in a separating funnel with hydrochloric acid and, using starch soln. as indicator, oxidise the sulphur compounds with *N* iodine. Decolorise the mixture with 5% sodium bisulphite soln., filter if necessary and adjust to the starch-iodine end point with 0·1 *N* iodine. Add *ca.* half the vol. of the soln. of conc. hydrochloric acid, shake with 20 ml of chloroform and discard the chloroform layer. If a large amount of oil is present repeat the chloroform extraction several times. Extract the aq. layer with 3 portions of ether (50, 25 and 25 ml) and wash the combined extracts with two 10-ml portions of water, disregarding the small amount of iodine that may remain in the extract. Filter the extract through a cottonwool plug in a long-stemmed funnel and evaporate the filtrate to dryness on the steam bath. Dissolve the residue in the minimum amount of a boiling mixture of 9 vols. of benzene and 1 vol. of ethyl acetate, filter, cool and induce crystallisation by scratching the sides of the vessel. Collect the crystals by filtration, wash with cold benzene, dry and determine their m.p. To determine the equiv. wt. of the acid, titrate a weighed amount dissolved in a small quantity of water with standard sodium hydroxide, using phenolphthalein indicator. Dithiodiglycollic acid is a white, non-hygroscopic, odourless solid, very soluble in water, alcohol, ethyl acetate and ether, but only slightly sol. in benzene, chloroform and light petroleum. Its m.p. is given in the literature as 100° C. and 107–108° C. The mixture of benzene and ethyl acetate appears to be a suitable medium for the re-crystallisation of small amounts, and material prepared from commercial permanent wave solns. melted above 100° C. after a single re-crystallisation. When sufficient material for several re-crystallisations was available, the m.p. of the final product agreed with the higher values given. The theoretical equiv. wt. is 91·2. The method of extraction described is not quantitative, but sufficient material for identification can be obtained from 0·2 g of thioglycollic acid. With suitable modifications the method can probably be applied to the identification of thioglycollic acid in depilatories. A. O. J.

Conductometric Analysis as a Method of Control in the Alkaline Pulping Process. S. D. Wells, G. E. Martin and D. R. Moltzau (*Paper Trade J.*, 1944, **119**, 9th Nov., *T.A.P.P.I. Sect.*, 188–194)—An apparatus suitable for recording continuously the conductivity of alkaline black

liquor flowing through a pipe-line, is described; also its application to the alkaline cellulose pulping process. J. G.

Conditioning Paper and Paperboard for Testing. Anon. (*Paper Trade J.*, 1944, **119**, 5th Oct., *T.A.P.P.I. Sect.*, 145)—A revision of T.A.P.P.I. Official Standard T 402 m-41. The specified conditions are 50 ± 2% R.H. and 23° ± 2° C. The specimen is suspended in the conditioned air, which must have free access to all parts of it, until there is no significant change in wt. (*e.g.*, less than 0·1% in 2, 12 or 24 hr. according to the type, thickness and degree of water vapour resistance of the paper); 4 hr. of exposure usually suffices. It is advisable to approach equilibrium from the drier state, to eliminate hysteresis effects, and the sample should therefore first be dried in a desiccator at 60° C. or lower, until its moisture content is *ca.* 50% of the final value after conditioning. Conditioned specimens should be handled and breathed upon as little as possible. Directions are given for checking the R.H. and temp. of the atmosphere used. J. G.

Inorganic

Detection of Nickel in Aluminium Alloys. L. J. Hibbert (*Metal Progress*, 1944, **46**, 486–487)—Apparatus for a simple electrographic sorting test consists of a 6-volt dry battery, a graphite or carbon rod, 3 in. long and ¼ in. diam., and two battery clips and flex for connections. *Method*—Connect the specimen to the positive terminal of the battery and the carbon rod to the negative terminal. Place a drop of nitric acid (1 + 1) on a strip of lintless absorbent paper (2 in. × ½ in.), lay the paper on the specimen and press the end of the carbon electrode on to the wet spot with a force of 10 to 20 lb. weight for 5 sec. Remove the paper and apply 1 or 2 drops of conc. ammonia soln. and 1 or 2 drops of 1% alcoholic soln. of dimethylglyoxime. A pink fleck develops if the specimen contains 0·75% or more of nickel. The normal amounts of iron and up to 4·5% of copper cause no apparent interference. L. A. D.

Detection of Nickel. Spot Test for High Conductivity Copper Alloys. W. T. Edwards (*Metal Industry*, 1944, **65**, 329)—A spot test for nickel is described which may be used by unskilled operators and is useful when sorting high conductivity copper alloys. An acid soln. of the alloy is treated with a reagent soln. containing ammonia, dimethylglyoxime and thioglycollic acid. The thioglycollic acid prevents the formation of the blue copper-ammonia complex, which would mask the nickel reaction, appparently by forming a colourless complex ion and thus removing free copper ions from the soln. Unlike cyanide, the thioglycollic acid does not appear to form a similar complex with nickel. *Reagents*—Acid mixture: 3 parts of nitric acid, 3 parts of sulphuric acid and 10 parts of water. Developing soln., 8 ml of ammonia soln., sp.gr. 0·880, 2 ml of water, 1 g of ammonium acetate, 4 ml of 1% alcoholic dimethylglyoxime soln., 2 ml of 0·1 *N* iodine, 2 ml of 20 vol. hydrogen peroxide and 2 ml of thioglycollic acid. *Method*—Clean a small area of the surface of the sample and, with a fine glass tube, place on it a small drop (*ca.* 0·001 ml) of acid mixture. After about 10 sec. take up the drop in the centre of a piece of absorbent paper, *e.g.*, white blotting paper. Add a drop of developing soln. and if, after 5 sec., the spot contains a black deposit of copper compounds add enough developing soln. to dissolve it. A red or pink spot then indicates nickel. Iron gives a red colour which spreads and fades in about 1 min.; the colour due to nickel is confined to the area of the acid spot and does not fade. L. A. D.

Chromometric Determination of Reducible Metals, including Tungsten and Molybdenum. R. Flatt and F. Sommer (*Helv. Chim. Acta*, 1944, **27**, 1518–1522; 1522–1532)—The technique and apparatus for potentiometric titrations with chromous salts have been described (*Id.*, 1942, **25**, 684). The procedure is applicable to the following metals. *Tungsten*—Treat the ammonium tungstate soln. (0·05–0·2 g W in 10 ml) with 40 to 50 ml of strong hydrochloric acid added all at once. The white ppt. of tungstic acid readily dissolves. Transfer the soln. to the titration flask, expel the air by carbon dioxide free from oxygen, heat to 70°–90° C. and titrate with 0·1 *N* chromous chloride. The end-point $W^{VI} \rightarrow W^{V}$ is marked by a small but sudden break, after which every drop of chromous soln. produces an oscillation of the galvanometer needle characteristic for tungsten and ascribed to a slight evolution of hydrogen at the electrode. Titration in sulphuric acid soln. is impracticable, the soln. being unstable; if phosphoric acid is added, the soln. becomes deep blue. *Uranium* is reduced to the quadrivalent stage in chloride as well as sulphate soln. Titrate hot, adding a trace of ferrous salt; acidity, *N* to 6 *N* sulphuric or 2 *N* to 6 *N* hydrochloric acid. *Iron and titanium*—The redox potentials are $Fe^{II}/Fe^{III} + 0{\cdot}77$ volt, and $Ti^{III}/Ti^{IV} - 0{\cdot}04$ volt, the second break at the titanium end-point being smaller but quite sharp. Titrate the soln. (10% sulphuric or 8% hydrochloric acid) at 90° C. with chromous sulphate or chloride respectively. The titration may be checked by permanganate titration of the reduced soln. *Iron and vanadium*—In sulphuric acid soln. 3 reduction stages are observed: (1) $V^{V} \rightarrow V^{IV}$; (2) $Fe^{III} \rightarrow Fe^{II}$; (3) $V^{IV} \rightarrow V^{III}$. The authors titrate in 10–15% sulphuric acid soln., which gives a sharp break at the first end-point (*a* ml). The second end-point not being easily observed at the acidity chosen, they continue the titration to the third end-point (*b* = total number of ml of chromous sulphate soln. used; *b*–2*a* = ml equivalent to iron). *Iron and molybdenum*—Titration at 90° C. in 5 to 30% sulphuric acid gives 2 well-defined stages: (1) $Fe^{III} \rightarrow Fe^{II}$; (2) $Mo^{VI} \rightarrow Mo^{V}$. *Copper and molybdenum*—Use a chloride soln. containing 15 to 20% of hydrochloric acid. At 90° C. 2 breaks are observed: (1) $Cu^{II} \rightarrow Cu^{I} + Mo^{VI} \rightarrow Mo^{V}$; (2) $Mo^{V} \rightarrow Mo^{III}$. *Molybdenum and titanium*—Serviceable results are obtained in 15% hydrochloric acid soln. at 90° C. First break: $Mo^{VI} \rightarrow Mo^{V}$; second break: $Mo^{V} \rightarrow Mo^{III} + Ti^{IV} \rightarrow Ti^{III}$. *Molybdenum and vanadium*—Sulphate soln. (90° C.) containing 15% sulphuric acid. First break: $V^{V} \rightarrow V^{IV}$. Second break $V^{IV} \rightarrow V^{III} + Mo^{VI} \rightarrow Mo^{V}$. *Iron and Tungsten*—The difference between the redox potentials is *ca.* 0·8 volt. Treat the soln. with sufficient strong hydrochloric acid to effect rapid solution of the pptd. tungstic acid, replace air with carbon dioxide, and titrate at 75° C. with chromous chloride. First sharp break: $Fe^{III} \rightarrow Fe^{II}$. Second (smaller) break, followed by the oscillations (*cf. supra*): $W^{VI} \rightarrow W^{V}$. *Copper and tungsten*—In hot strong hydrochloric acid soln. in absence of air, as preceding. Two breaks: (1) $Cu^{II} \rightarrow Cu^{I}$; (2) $W^{VI} \rightarrow W^{V}$. *Chromate and tungsten*—Two titrations are required: (1) the soln.

is acidified with sulphuric and phosphoric acids and titrated with chromous sulphate ($Cr^{VI} \rightarrow Cr^{III}$). (2) The soln. is treated with a large excess of hydrochloric acid as before, some chromate being reduced. Titrate as in the preceding instance. Neglect the volume of chromous soln. consumed in reaching the first break; the second break gives $W^{VI} \rightarrow W^{V}$. *Molybdenum and tungsten*—Proceed exactly as for tungsten. The first sharp break indicates $Mo^{VI} \rightarrow Mo^{V}$. The second break is smaller but definite, and is followed by the oscillations; it gives $Mo^{V} \rightarrow Mo^{III} + W^{VI} \rightarrow W^{V}$, the molybdenum consuming twice as many ml of chromous soln. as in the first stage. *Iron, molybdenum and tungsten*—Two titrations are required. (1) In slightly acid sulphate soln. with 0·1 *N* chromous sulphate. First break (*a* ml): $Fe^{III} \rightarrow Fe^{II}$. Second break (*b* ml): $Mo^{VI} \rightarrow Mo^{V}$. (2) In strongly acid chloride soln. as for tungsten, with 0·1 *N* chromous chloride. First break (*c* ml): $Fe^{III} \rightarrow Fe^{II} + Mo^{VI} \rightarrow Mo^{V}$. Second break (*d* ml): $W^{VI} \rightarrow W^{V} + Mo^{V} \rightarrow Mo^{III}$. *b* should equal *c*. (*b*–*a*) ml: $Mo^{VI} \rightarrow Mo^{V}$. (*d*–*c*)–2 (*b*–*a*) ml: $W^{VI} \rightarrow W^{V}$. W. R. S.

New Reaction for Cerium. P. Wenger, Y. Rusconi and R. Duckert (*Helv. Chim. Acta*, 1944, **27**, 1479)—A saturated aq. soln. of *p*-phenetidine gives with ceric salts a violet colour, due to oxidation. Other oxidising ions (Sb^{V}, Au^{III}, Ir^{IV}, V^{V}, Cr^{VI}) interfere, but ferric iron can be masked by addition of phosphate. Fluoride prevents the cerium reaction. Treat a drop of slightly acid ceric soln. on a spot plate with a drop of reagent. The reaction detects 1 μg of cerium in 0·03 ml ($1 : 3 \times 10^{4}$). W. R. S.

New Method for the Polarographic Determination of Nitrate. I. M. Kolthoff, W. E. Harris and G. Matsuyama (*J. Amer. Chem. Soc.*, 1944, **66**, 1782–6)—The method, based on the polarographic reduction of nitrate in presence of uranyl ions, permits quantitative determination of very dilute nitrate solns. It is preferable to the use of a large excess of lanthanum chloride (Tokuoka and Ruzicka, *Coll. Czech. Chem. Commun.*, 1934, **6**, 339), since the diffusion current is then proportional to the nitrate concn. over a limited range only. Prepare a stock soln. 10^{-3} *M* in uranyl chloride, 0·5 *M* in potassium chloride and 0·05 *M* in hydrochloric acid. Measure a suitable vol. of the unknown nitrate soln., rendered, if necessary, just acid to 1 drop of methyl red, add 5·00 ml of the stock soln. and dilute to 25·00 ml with conductivity water, so that the final nitrate concn. is between 5×10^{-5} and 4×10^{-4} *M*. Transfer to a polarographic cell, remove dissolved air by bubbling with hydrogen or nitrogen, and measure the apparent diffusion current at a potential of −1·2 volt vs. saturated calomel electrode (manual apparatus was used). Subtract the "residual" current obtained by diluting 5·00 ml of stock soln. to 25·00 ml and proceeding as above. The corrected diffusion current is proportional to the concn. of nitrate. The latter value is obtained from a standard current-concentration curve (linear) constructed by using a nitrate soln. of known concn. Where the nitrate concn. is less than 5×10^{-5} *M* after dilution, reducing the uranyl chloride concn. in accordance with a table given permits more accurate determination. Chlorate does not interfere, nor does sulphate unless present in large excess. Oxalate, phosphate, and substances in large amounts which give reduction waves before the nitrate wave interfere, and must be removed. J. T. S.

Microchemical

Use of the Schneider Distillation in the Determination of Small Amounts of Arsenic. E. Schaaf and J. Maurer (*Z. anal. Chem.*, 1943, **126**, 298–300)—In the separation of arsenic by distillation as arsenious chloride various distilling-times ranging from 10 min. to 20 sec. after boiling begins have been recommended. It was emphasised by Bang (*Biochem. Z.*, 1925, **161**, 196) that, if the distillation is taken too far, sulphur dioxide may be produced from the ferrous sulphate used to reduce the arsenic. The sulphur dioxide distils with the arsenious chloride and a high result is obtained on titration with potassium bromate soln. The effect of the time of distillation upon the bromate titre of the distillate was studied. The reaction-mixture consisted of 3 ml of conc. sulphuric acid, 5 ml of water, 5 ml of conc. hydrochloric acid, 0·1 ml of 20% potassium bromide soln. and 25 mg of ferrous sulphate. To this were added 23·4 μg of arsenic. Sulphuric acid was incorporated, since it would be present if biological material had been destroyed. The distillate was titrated with 0·0005 *N* potassium bromate, using methyl orange as indicator. The titre remained almost constant in the range 0·5 to 2·5 min. and then increased rapidly. A blank showed a similar increase in titre. The expts were repeated, with first twice and then five times the amount of reaction-mixture, addition of arsenic remaining at 23·4 μg. The ranges of almost constant titre were approx. 1·5 to 3·5 min. and 2·5 to 5 min. respectively. Although not proportional to the volume of reaction-mixture, the optimum distilling-time increases with this volume, thus explaining the divergences in procedure recommended by previous workers. The distilling-time should be controlled to fall within the range of constant titre. Similar results were obtained when 2 mg of arsenic were added and 0·01 *N* potassium bromate was used in the titration. J. T. S.

Physical Methods, Apparatus, etc.

Adsorption Colorimetry as an Analytical Technique. J. Yudkin (*Nature*, 1945, **155**, 50)—In devising a simple method for the determination of mepacrine (atebrin) in urine, a technique, termed "adsorption colorimetry," has been adopted. The intensity of the colour produced on a measured quantity of a suitable white adsorbent is proportional to the concn. of mepacrine in the urine or extract of urine. The adsorbent may be conveniently measured with a small scoop made by drilling a hole in a piece of wood and calibrating with a powder of known specific gravity. For mepacrine, the best adsorbent is silica gel which may be used by adding a measured quantity to a known vol. of urine for a given time or to an ethereal or chloroform extract of alkalised urine. Concns. of 1 mg per litre or less may be determined and the error at a concn. of 5 mg per litre is less than 20%. Using silica gel, it is possible to detect bile salts in urine in concns. less than those detected by the iodine or Gmelin tests, and the sensitivity is about equal to that of the Fouchet or similar adsorption methods. Ribflavin is adsorbed by a white preparation of fuller's earth and preliminary tests indicate that this technique should prove capable of assaying with reasonable accuracy and sensitivity the riboflavin content of substances of biological interest. With fluorescent substances, the sensitivity may be increased 100-fold by viewing the adsorbent in ultra-violet light; by application of this principle

it may prove possible to determine mepacrine in blood. Details of the technique, as applied to the determination of mepacrine in urine and to the detection of bile pigments in urine, will be published elsewhere. J. A.

Simplified Conductometric Titration Apparatus. E. M. Buras, Jnr., and J. D. Reid (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 591)—The 8-volt output of a constant voltage transformer operated from the A.C. mains is applied to the electrodes of the titration cell, an A.C. milliammeter being placed in series. By this means conductometric titration is simplified, since it is only necessary to read one meter. By connecting the low impedance winding of an audio-output transformer (impedance ratio about 500 to 1, turn ratio of 22 to1, low impedance winding 4–8 ohms) in place of the milliammeter, a 2·5-volt range 1000 ohm per volt rectifier type A.C. voltmeter may be used to read the current in relative units. The voltmeter is connected to the high impedance windings of the transformer. A simple beaker form of titration cell is used, closed by a stopper carrying the glass tubes into which the electrodes are sealed. With simple precautions an accuracy of 0·5 to 1% can be obtained. J. T. S.

New Method of Gas Analysis. W. J. Gooderham (*J. Soc. Chem. Ind.*, 1940, **59**, 1–8)—A stream of gas is passed at constant pressure through scrubbers and furnaces which successively remove or decompose the constituents of the gas. The vol. change at each stage is indicated by the change in the rate of (vol.) flow of the gas. This rate is measured by timing the travel of soap films between graduation marks in calibrated tubes ("calibrators"). An analysis is conducted by taking a series of stop-watch readings. The apparatus* is in a cabinet which keeps all calibrators at the same temp. Gas enters through a dust filter and a calcium chloride tube. Two vessels containing butyl phthalate give a constant head at the inlet of the capillary which governs the gas flow. After being satd. with water-vapour, the gas flow is measured by passing through the first calibrator. Carbon dioxide is then removed by caustic potash solution in the first scrubber and the vol. decrease found by measuring the rate of flow in the second calibrator. Subsequent scrubbers and calibrators allow vol. changes due to the removal of other constituents to be detd. One form of apparatus has 4 calibrators; carbon dioxide, oxygen and small amounts of carbon monoxide in waste gas may be detd. to within 0·1%. The other has calibrators and additionally unsatd. hydrocarbons, hydrogen, methane, ethane and nitrogen may be detd. Passage over copper oxide at 280° converts hydrogen into water and carbon monoxide into carbon dioxide, and a copper oxide-iron oxide catalyst at 580° C. permits the combustion of satd. hydrocarbons. Scrubbers and calibrators are incorporated at appropriate points. Each calibrator is fitted with a film-forming device consisting of a vertical glass spiral dipping into "soap" solution (0·75% "Acrosol" or 2·5% "Igepon"—both proprietary wetting agents). An external handle rotates all spirals together, whereby a soap film is formed at the top of each calibrator and is broken on reaching the bottom by a second glass spiral. A diaphragm holder for storing gas under pressure without contamination is also described. J. T. S.

* Apparatus made by Messrs. Griffin & Tatlock under B.P. 489,117.

Soap Film Calibrators. W. J. Gooderham (*J. Soc. Chem. Ind.*, 1944, **63**, 351–2)—The apparatus, a modification of that of Barr (*J. Sci. Instr.*, 1934, **11**, 324), consists of a vertical calibrated tube similar to a burette, to the lower end of which is sealed a U-shaped reservoir containing soap solution. Gas enters just above the surface of the solution, passes up the tube and thence on to the flow meter to be calibrated. Alternatively, the meter may precede the calibrator. By pinching quickly a rubber cap on the free end of the reservoir, the soln. momentarily blocks the gas inlet, so that a soap film is formed and is carried up the tube to give a visual measurement of the rate of travel of gas. At the top of the tube a tightly-pressed spill of blotting paper breaks the film. The back-pressure caused by the film is negligible. Solns. made from the newer soap-like materials are preferable to those made from true soaps. A soln. made by dissolving 0·75% by weight of "Aerosol OT" (Cyanamid Products, Ltd.) in hot distilled water can be used with most gases, including sulphur dioxide, although it deteriorates slowly. Three sizes of apparatus for measuring up to 40 litres per hour are described, as well as a meter prover of similar principle, which can be used at higher rates. In the latter apparatus the soln. is contained in a cup which acts as a two-way valve, so that the gas flow is not stopped while a film is being made. A "blow-off" device containing butyl phthalate maintains the supply of gas at constant pressure. J. T. S.

Device for Projecting an Image of a Reading Scale. C. Tuttle and F. M. Brown (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 645)—In routine analysis observation of the deflection of the pointer of a Kuhlmann microbalance by means of a monocular magnifier causes considerable eyestrain, whilst a projected scale image is easily observed. By replacing the light-scattering white ivory scale by one of optically polished stainless steel, sufficient light is reflected to permit projection without using a source of wattage high enough to cause danger of convection currents within the balance case. The optical system consists of an overhead 21 C.P. 6-volt lamp, the light from which passes through heat-resisting glass (Corning Aklo) and then through the top of the outer glass cabinet surrounding the balance case. A spectacle lens focusses the filament image slightly above the scale. By means of a 1 in. objective the images of the scale and of the shadow of the pointer are projected forward and slightly upward and are then reflected downward by a small plane mirror, to fall upon a white screen on the bench in front of the balance. A magnification of 8× is obtained and the image is clearly visible in a well-lighted room. J. T. S.

Water Vapour Permeability of Moisture-sensitive Materials. G. J. Brabender (*Paper Trade J.*, 1944, **119**, 19th Oct., *T.A.P.P.I. Sect.*, 160–163)—Determinations of the water-vapour permeabilities of certain new-type wrappings by the T.A.P.P.I. Official Method (ANALYST, 1944, **69**, 166) present certain difficulties. Thus moisture-proof, triple-ply glassine (which consists of 3 sheets of glassine laminated together with 2 films of microcryst. wax) tends to absorb moisture on the glassine surface, although this cannot penetrate owing to the wax. Troubles arise as a result of sheet distortion in the testing dish, the prolonged period elapsing before the sheet reaches equilibrium with the testing conditions, and the low rate of

change in wt. due to true water transfer. Precise control over the prevailing humidity conditions are also important. Modifications designed to minimise the above effects are described. J. G.

Application of a Thermal Conductivity Method to the Determination of Moisture Vapour Transmission of Packaging Materials. L. Boor and J. K. Dixon (*Paper Trade J.*, 1944, 119, 2nd Nov., *T.A.P.P.I. Sect.*, 176–184)—The thermal conductivity of a gas may be measured by determining the temp. of an electrically-heated wire, surrounded by the gas, in a container whose walls are maintained at a given const. temp.; as the conductivity increases the wire temp. decreases. The determination of the temp. of the wire in terms of its electrical resistance is the principle of the Shakespeare "Permeameter," and, if the instrument is suitably calibrated against air of known moisture contents, the method may be used to measure moisture vapour transmission. Details of the apparatus and method are given. J. G.

Adaptation of the Conway Micro-burette for the Delivery of Larger Volumes of Fluid. G. A. Levvy (*Chem. and Ind.*, 1945, 4)—The Conway horizontal burette, normally used to deliver not more than 0·25 ml (*cf.* Conway, "*Micro-Diffusion Analysis and Volumetric Error*"), can be adapted to deliver 2 to 4 ml without loss of accuracy or of other advantages. The burette, for 0·25 ml, has the same accuracy as a Bang 2-ml burette. The meniscus of a horizontal column of water remains vertical in clean glass tubing of 2·5 mm diam., but is at an angle of about 45° when the diam. is *ca.* 3·5 mm; for a vertical meniscus, the internal diameter must not exceed 3 mm. Within this limit, a 4-ml graduated tube is not inconveniently long for use in the burette. The error involved in moving a column of water along a tube of 3·5 mm internal diam. was examined by comparison at 20° C. of the weight of water delivered from this tube when used as a pipette and when incorporated in the horizontal burette; for titrations of *ca.* 2 ml differences were similar to those obtained with the tube of 2·5 mm internal diam. E. B. D.

Review

ORGANIC SYNTHESES: ANNUAL PUBLICATION OF SATISFACTORY METHODS FOR THE PREPARATION OF ORGANIC CHEMICALS. Editor-in-Chief, N. L. DRAKE. Vol. 24, pp. vi+119. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. Price $2 (10s. 6d.).

The war years seem to have had very little effect on the quality of the work recorded in Vol. 24, but the binding and paper, conforming to the "recommendations of the War Production Board," are definitely below the previous standard. The usual satisfactory arrangement of subject matter has been followed. The thirty-seven preparations dealt with are, on the whole, varied and interesting, as may be judged from the following selection—4-amino-2.6-dimethylpyrimidine, 4-amino-1.2.4-triazole, *nor*-desoxycholic acid, glyoxal bisulphite, *o*-nitrobenzaldehyde, selenophenol and vinyl acetic acid.

In the course of the descriptions sundry matters of general interest arise. Thus a timely warning on the use of metallic potassium is given and hydrogenated cottonseed oil is recommended for oil-baths up to 310° C. A full description of the (Clarke-Rahrs) methyl ester fractionating column suggests other possible applications of this device.

Some of the methods offer examples of general reactions and others appear to be of general application. In the first category may be placed the conversion of desoxycholic acid to *nor*-desoxycholic acid (Barbier-Wieland degradation of carboxylic acids) and to the second the preparation of γ-di-*n*-butylaminopropylamine, which appears to be an extension of Gabriel's phthalimide reaction.

It seems therefore that the research worker and those engaged in the manufacture of fine organic chemicals, even if not interested in the actual substances listed, may find inspiration in the methods described. Like its predecessors, Vol. 24 is well worthy of perusal.

HAROLD TOMS

ADVICE TO AUTHORS

THE Council has approved the following notice by the Publication Committee, which is here given in condensed form.

The Society publishes papers concerned with all aspects of analytical chemistry, inorganic and organic, as, for example, food and drugs analysis, analysis of water (including its bacteriological examination), gas analysis, metallurgical assays, biological standardisation and micro-analysis. Papers on these and allied subjects may be submitted for presentation and publication; they may:

(1) Record the results of original investigations into known methods or improvements therein;
(2) Record proposals for new methods and the investigations on which the proposals are based;
(3) Record analytical results obtained by known methods where these results, by virtue of special circumstances, such as their range or the novelty of the materials examined, make a useful addition to analytical information;
(4) Record the application of new apparatus and new devices in analytical technique and the interpretation of results.

Communications.—Papers (which should be sent to the Editor) will normally be submitted to at least one referee, on whose advice the Publication Committee will be guided as to the acceptance or rejection of any communication. Papers or Notes accepted by the Publication Committee may not be published elsewhere except by permission of the Committee.

Abstracts.—The MS. should be accompanied by a brief abstract of about 100 to 150 words indicating the scope and results of the investigation.

Notes on the writing of papers for THE ANALYST

Manuscript.—Papers and Notes should preferably be typewritten.

The title should be descriptive and should set out clearly the scope of the paper.

Conciseness of expression should be aimed at; clarity is facilitated by the adoption of a logical order of presentation, with the insertion of suitable paragraph or sectional headings.

Generally, the best order of presentation is as indicated below:

(*a*) General, including historical, introduction.
(*b*) Statement of object of investigation.
(*c*) Description of methods used. Working details of methods are usually most concisely and clearly given in the imperative mood, and should be given in this form, at least while economy of paper is pressing, *e.g.*, "Dissolve 1 g in 10 ml of water and add . . .". Well-known procedures must not be described in detail.
(*d*) Presentation of results.
(*e*) Discussion of results.
(*f*) Conclusions.

To be followed by a short summary (100 to 250 words) of the whole paper: items (*e*) and (*f*) can often be combined.

Illustrations, diagrams, etc.—The cost of setting up tabular matter is high and columns should therefore be as few as possible. Column headings should be brief or replaced by a number or letter to be used in combination with an explanatory footnote to the table.

Sketches or diagrams should be on white Bristol board, not larger than foolscap size, in Indian ink. Lettering should be in light pencil.

Tables or graphs may be used, but normally not both for the same set of results. Graphs should have the co-ordinate lines clearly drawn in black ink.

References.—References should be numbered serially in the text and collected in that order under "REFERENCES" at the end of the paper. They should be given in the following form:

1. Dunn, J. T., and Bloxam, H. C. L., *J. Soc. Chem. Ind.*, 1933, **52**, 189T.
2. Allen, A. H., "*Commercial Organic Analysis*," Churchill, London, 1882.

Notes on the Presentation of Papers before Meetings of the Society are appended to the "ADVICE," copies of which may be obtained on application to the Secretary, 7/8, Idol Lane, London. E.C.3.

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