MAY, 1936 Vol. 61, No. 722

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held on April 1st in the Chemical Society's Rooms, Burlington House, the President, Dr. G. Roche Lynch, being in the chair.

Certificates were read in favour of Ir. Willem Jan Pieter Pelle, George Hugh Walker, Ph.D., B.Sc., F.I.C., Herbert Wood Watson, M.Sc., Harold Frank Philip Webber, B.Sc., A.I.C.

The following were elected members of the Society:—Lewis Goudin Spire Hebbs, A.I.C., William Charles Johnson, and James Young, A.I.C.

The following papers were read and discussed:—"The Sulphuric Acid Test for Liquid Paraffin," by C. E. Sage, F.I.C., A.M.I.Chem.E., and S. G. E. Stevens, B.Sc., A.I.C.; "The Determination of Moisture-content by Distillation with Liquids Immiscible with Water," by L. A. Warren, Ph.D., B.Sc., A.I.C.; "An Apparatus for the Determination of Small Percentages of Water and Oil," by I. C. P. Smith, B.Sc.; and "The Mydriatic Effect of Cocaine and its Differentiation from the Atropine Group of Alkaloids," by K. R. Ganguly, M.Sc.

NORTH OF ENGLAND SECTION

A MEETING of the Section was held in Leeds on April 4th, 1936. The Chairman (Mr. Arnold R. Tankard) presided over an attendance of forty; the President (Dr. Roche Lynch) was present.

A discussion on "The Ash of Vegetable Drugs: its Importance and Determination," was introduced by A. D. Powell, A.I.C. The following paper was read: "The Estimation of the Original Freezing-point of Sour Milk," by H. J. Evans, B.Sc., F.I.C. A discussion, in which the President took part, was introduced by S. E. Melling, F.I.C., on the question of changing the name of the Society.

Tea and Coffee, with Special Reference to their Alkaloids and Tannins

THE following papers were read at the Joint Meeting of the Society with the Food Group of the Society of Chemical Industry on February 5th, 1936:

THE CONSTITUTION OF TANNINS INCLUDING THOSE OF TEA AND COFFEE

BY PETER MAITLAND, B.Sc., PH.D.

The tannins are a class of amorphous, rarely crystalline substances, which occur widely in nature and possess the property of changing hide into leather. They are remarkable for their astringent taste and for their many precipitation reactions with lime, lead acetate, alkaloids, gelatin, albumin and other proteins, and also for their colour reactions with iron salts.

There have been many attempts to classify tannins, and the best and simplest of these is that of Freudenberg, who divided them into (i) hydrolysable tannins; (ii) condensed tannins; (iii) unclassified tannins. In spite of the enormous amount of work done upon tannins, most of them unfortunately belong to class (iii), and this is due to their amorphous and colloidal nature, which makes exact investigation difficult.

The tannins which have been selected for this brief survey are shown in the following scheme:

(1) Hydrolysable
- (*a*) Turkish gallotannin
- (*b*) Chinese gallotannin
- (*c*) Coffee tannin
- (*d*) Ellagic acid tannins

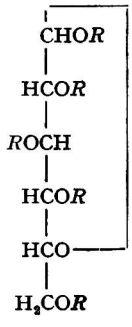
(2) Condensed
- (*e*) Catechin tannin
- (*f*) Quebracho tannin

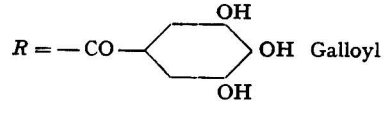
(*d*) + (*e*) → (*g*) Tea tannin

GROUP I. HYDROLYSABLE TANNINS

(*a*) *Turkish Gallotannin*[1]

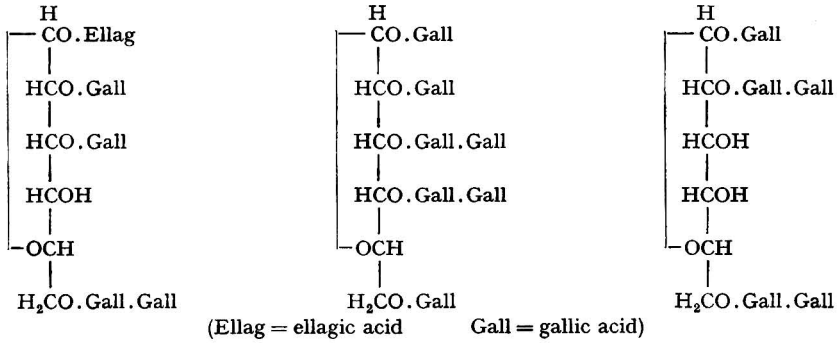
Turkish gallotannin is obtained from Aleppo galls. Emil Fischer suggested that this tannin was probably a pentagalloyl-glucose, as in formula I (*R* = galloyl),





I

but recognised that this was an ideal formula. As a result of recent work, Karrer has put forward the view that this tannin is a mixture of several glucose derivatives, of which the three formulae (II) below are types.

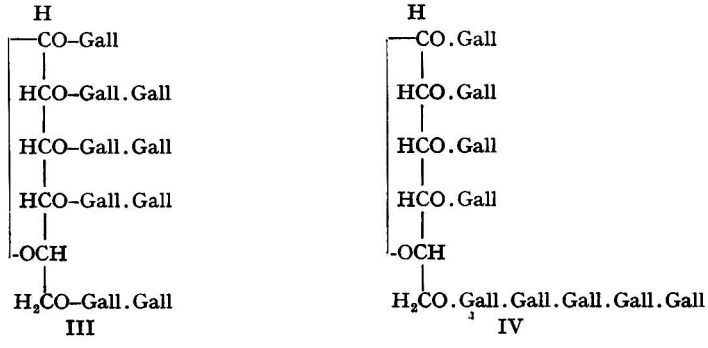


(Ellag = ellagic acid Gall = gallic acid)

II

(*b*) *Chinese Gallotannin*[2]

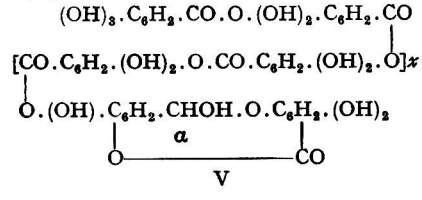
This tannin is obtained from Chinese galls. Fischer suggested that it was a penta-digalloyl glucose, but realised that this also was an ideal formula. Freudenberg has suggested that the experimental evidence shows the tannin to be a complex mixture of a great variety of (probably) nona-galloylated α- and β-glucoses, the limits of the possibilities of the arrangement of the gallic acid residues lying between formulae III and IV.



III IV

A penta-digalloyl glucose (III + one more Gall.) was actually synthesised by Fischer and Bergmann, and this synthetic product and its methyl and acetyl derivatives were shown to be very similar to the natural product and its derivatives.

Quite a different type of formula has been brought forward by Nierenstein[3] for Chinese gallotannin (V).

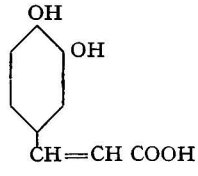


V

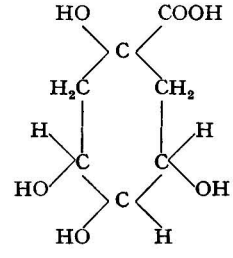
He suggests that the galloyl residues are all linked, and that the above substance sometimes occurs as a glucoside, the glucose being attached to the position marked α. In support of this, Nierenstein has shown that the methylated tannin on hydrolysis gives a methylated glucose, whereas a compound of Fischer and Freudenberg's formula, if methylated and hydrolysed, should give free glucose.

(c) *Coffee Tannin*[4]

The tannin in coffee yields on hydrolysis caffeic acid (VI) and quinic acid (VII) and a residue the constitution of which is not known. The two acids from the hydrolysis have been shown to arise from the presence of chlorogenic acid (VIII) in the coffee.

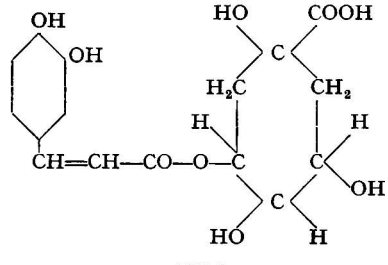


VI



VII

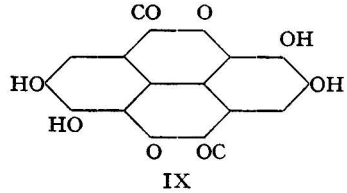
The actual tannin may be a derivative of chlorogenic acid or it may be a mixture of several substances, amongst them chlorogenic acid.



VIII

(d) *Ellagic Acid Tannins*

Many tannins on hydrolysis yield ellagic acid (IX), which is derived from two molecules of gallic acid by oxidation and condensation. The ellagic acid

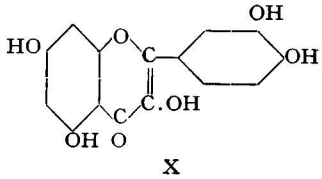


IX

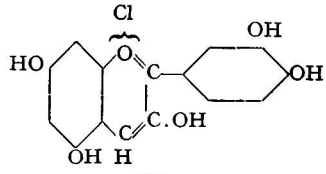
tannins are therefore probably variously substituted ellagic acids, the substituent groups being linked to the ring by means of the phenolic oxygen atoms.

Group II. Condensed Tannins

The condensed tannins are either unaffected by acids or they are merely polymerised further. According to Freudenberg, many of them are derived from simple crystalline substances called catechins, some of which have been found in nature. These catechins are related to the yellow flavanols and the highly coloured anthocyanidin salts which also occur in nature, either free or in the form

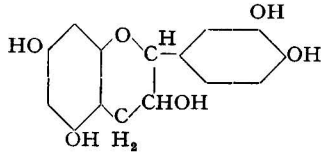


X



XI

of derivatives. Thus ordinary catechin (XII) is related to quercetin (X) and cyanidin chloride (XI).



XII

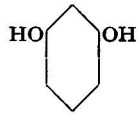
(*e*) *Catechin Tannin*

Catechin itself, a crystalline compound, is not a tannin, but by heating it with dilute acid or alkali, in the presence or absence of air, or by the action of enzymes it is easily polymerised to a substance which will tan hides. In many of the trees in which catechin occurs there is found also a tanning material. This has probably resulted from the polymerisation of catechin, but the exact connection between this naturally occurring tannin and the synthetic polymerised catechin has not yet been established.

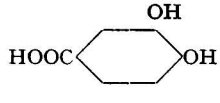
(*f*) *Quebracho Tannin*

Quebracho tannin is obtained from the wood of *Quebracho Colorado* trees, which are found in the northern part of the Argentine Republic and also in the Gran Chaco. It is one of the most abundant and widely used tanning materials known.

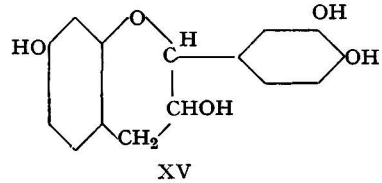
In 1925 Freudenberg surveyed all the evidence as to its constitution then available, and suggested that it might be derived from a catechin-like substance. Nierenstein had shown, in 1906, that the products of potash fusion were mainly resorcinol (XIII) and protocatechuic acid (XIV), and therefore Freudenberg put forward the formula (XV) for the hypothetical quebracho catechin, the



XIII



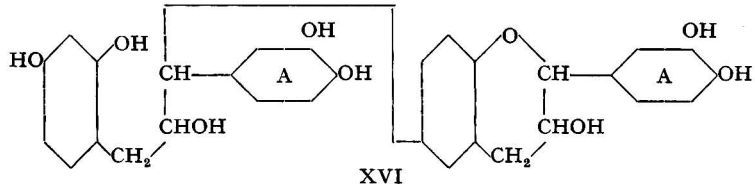
XIV



XV

supposed stem-substance of the quebracho tannin. Freudenberg and Maitland,[5] in 1934, therefore synthesised this catechin and polymerised it with dilute acid. They were able to establish a connection between the synthetic and natural quebracho tannin on three grounds: (1) Analytical results of the same order; (2) the same degradation products; (3) the same type of condensation to "phlobaphenes" without elimination of the elements of water.

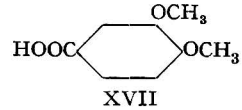
A tentative suggestion was put forward for the mode of linking of the catechin units in the molecule of the synthetic tannin. This was based on analyses and a degradation reaction. A simple two-unit molecule of the type (XVI) would have the same C and H values as the crystalline quebracho catechin



XVI

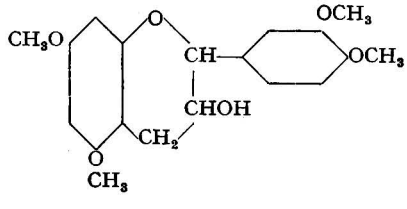
from which it was derived, but a higher acetyl value, and this was actually observed. The second oxygen ring can open and the condensation can then proceed further, and it is very probable that the synthetic tannin is a high molecular compound with the units joined as in formula (XVI).

The proof that the link between the molecules is not in the catechol ring, A, was found in the observation that oxidation of all the methylated compounds, both synthetic and natural, gave only veratric acid (XVII).

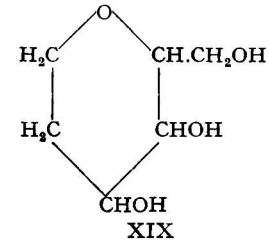


XVII

The discovery of this completely unexpected type of condensation without the elimination of the elements of water led to a further study of the necessary conditions for a polymerisation of this type. Bergmann and Pojarlieff[6] had already made some investigations on this "phlobaphene reaction." They first showed that tetramethyl catechin (XVIII) could also undergo the reaction, which proved that the phenolic hydroxyl groups were not necessary for the polymerisation. Examination of the reaction of acids with hydroglucal (XIX)

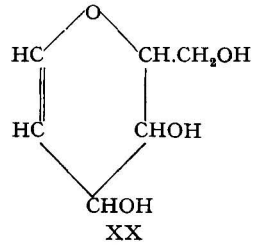


XVIII



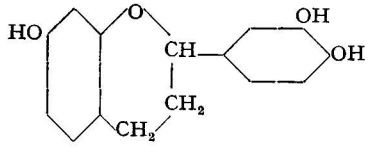
XIX

and glucal (XX) showed that the first was stable and the second easily polymerised. They therefore concluded that three essentials were necessary for polymerisation:— (1) Pyran ring; (2) double bond in the pyran ring; (3) hydroxyl in the pyran ring.

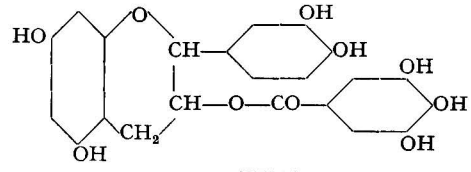


XX

Freudenberg and Maitland, however, prepared (XXI) synthetically, and showed that it also was very sensitive to acids. The presence of a hydroxyl in the pyran ring, therefore, does not seem to be necessary.



XXI



XXII

(*g*) *Tea Tannin*

The evidence for the constitution of this tannin is conflicting, some investigators having reported it as a "hydrolysable" tannin, and others as a "condensed" tannin. An interesting explanation of these divergent views has been brought forward by Tsujimura,[7] who has suggested that the tannin is a galloyl catechin, in which the galloyl residue replaces a hydrogen atom of the alcoholic hydroxyl (XXII).

It will be seen from the foregoing brief survey of a few of the well-known tannins that the chemistry of these complex substances is still in its infancy, in spite of the many advances made within the last fifteen years.

References

1. E. Fischer and K. Freudenberg, *Ber.*, 1914, **47**, 2485; P. Karrer, R. Widmer and M. Staub *Annalen*, 1923, **433**, 288.
2. K. Freudenberg, *Tannin, Cellulose, Lignin*, p. 38–44.
3. M. Nierenstein, *The Natural Organic Tannins*, p. 163; criticised by O. Schmidt, *Annalen*, 1930, **479**, 1.
4. K. Freudenberg, *Ber.*, 1920, **53**, 232; H. O. L. Fischer and G. Dangschat, *Ber.*, 1932, **65**, 1037.
5. K. Freudenberg and P. Maitland, *Annalen*, 1934, **510**, 193.
6. M. Bergmann and G. Pojarlieff, *Collegium*, 1931, p. 244.
7. M. Tsujimura, *Sc. Papers Inst. Phys. and Chem. Research (Tokyo)*, 1931, **15**, 155.

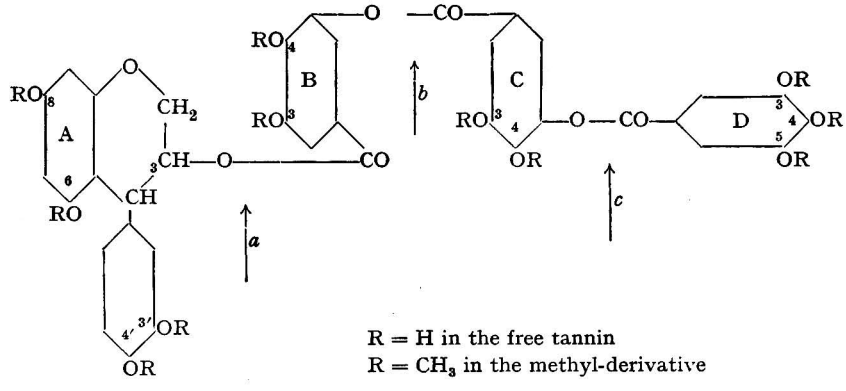
THE UNIVERSITY
CAMBRIDGE

EXPERIMENTAL WORK ON TEA TANNIN

By M. Nierenstein, D.Sc., Ph.D.

Green Assam tea contains a well-crystallising tannin, which is best prepared by the caseinogen method,[1] in which the amorphous tannin is removed by fractional adsorption.

The following formula is provisionally assigned to tea tannin:



(i) On methylation with diazomethane a well-crystallising methyl-derivative is obtained, which yields, on hydrolysis: 1 molecule of 6, 8, 3′, 4′-tetramethyl-*l*-acacatechin (A), 2 molecules of 3, 4-dimethyl-gallic acid (B, C), and 1 molecule of trimethyl-gallic acid (D), when hydrolysis takes place at *a*, *b*, and *c*.

(ii) Tea tannase, obtained by growing *Aspergillus niger* in a medium containing tea tannin, hydrolyses tea tannin at *a*, *b*, and *c*, and yields 1 molecule of *l*-acacatechin (A) and 3 molecules of gallic acid (B, C, D).

(iii) Gallotannase, obtained from the same mould in a medium of gallotannin,[2] hydrolyses tea tannin, however, only at *b* and *c*, and yields 3-galloyl-*l*-acacatechin (A + B) and gallic acid (C, D).

(iv) Tannase, obtained by growing *Aspergillus niger* in a medium containing 3-galloyl-*l*-acacatechin (A + B), added to gallotannase hydrolyses tea tannin at *a*, *b*, and *c*; it thus behaves like tea tannase, and produces *l*-acacatechin (A) and gallic acid (B, C and D).

Tea tannase thus consists of *two* tannases, namely, 3-galloyl-*l*-acacatechin-tannase and gallotannase.

References

1. M. Nierenstein, *J. Chem. Soc.*, 1922, **121**, 23.
2. —— *Biochem. J.*, 1922, **16**, 514.

Biochemical Department
The University, Bristol

A SURVEY OF THE METHODS OF ANALYSING TANNINS

By C. Ainsworth Mitchell, D.Sc., F.I.C.

From its earliest days our Society has interested itself in the methods of determining tannin, especially in tea, and various gravimetric, volumetric and colorimetric methods have first been published in The Analyst.

Precipitation with Metallic Compounds.—*Lead Acetate.*—During the first session of the Society, Wigner[1] gave an account of his application of the lead acetate method to tea. It is not surprising that his results were high, ranging from 27 to 45·5 per cent. of tannin. Although it was known that gallic acid and other non-tannins are adsorbed by lead tannate, the method found its later supporters. Thus Trillich and Göckel[2] used it to determine tannin in coffee, a sample of which they found to contain 11·37 per cent. A modification of the method was suggested by Manea,[3] the reagent consisting of a mixture of acetic acid and lead acetate solution.

Precipitation with Iron Salts.—Handtke[4] was the first to suggest the use of ferric acetate as a precipitant for tannin after conversion into sodium tannate. The reagent was also used by Beckmann[5] as a substitute for gelatin in the separation of tannin in Löwenthal's permanganate method. This method has the same drawback as the lead acetate method—that of co-precipitating a large proportion of any gallic acid present. To prevent this, Ruoss[6] precipitated the tannin as a basic tannate in the presence of sodium tartrate, and dried the precipitate (to which he attributed the composition $C_{14}H_9O_9(FeO)$) at 120° C. In my experience slight variations in the conditions of precipitation (which with unknown substances cannot be controlled) results in the formation of basic ferric tannate of varying composition. Even complete oxidation with hydrogen peroxide does not always yield concordant results.

Other Metallic Precipitants.—Among the other metallic compounds recommended for the precipitation of tannins are potassium antimonate (Gerland[7]), copper oxide (Flick[8]), mercuric oxide (Krug[9]), and aluminium hydroxide.[10]

Precipitation with Gelatin.—The use of gelatin as a reagent dates back to 1797, when it was shown by Seguin[11] that tannins form a precipitate with gelatin. Whilst gelatin certainly precipitates tannin, it also precipitates very many other substances, including gallic acid; in fact, Jones[12] published a list of 88 non-tannins which were precipitated. Trunkel,[13] who studied the nature of the reaction, obtained precipitates containing 3 parts of tannin to 1 of gelatin, but concluded that, since alcohol extracted up to 97 per cent. of the tannin from the precipitates, the process is one of adsorption rather than of chemical combination. Whether chemical or physical, however, the process has been widely used in combination with the permanganate and other processes.

The Hide-powder Method.—The method of estimating tanning capacity by adsorption of tannins with hide powder was first suggested by Bell-Stephens in 1826, and was re-introduced in 1887 by Weiss. Every detail relating to the purification and preparation of the hide powder, and to the conditions necessary for obtaining comparable results, has been minutely studied, and an Official

Method has been standardised by the Society of Leather Trades Chemists.[14] Other standard methods are the "International" Method, official for Germany, Holland, Sweden, and Norway,[15] and the Official Method of the American Leather Chemists' Association.[16]

Whilst the process is of great practical value for leather chemists, it has the drawback that it does not always afford a quantitative determination of tannin, since it has been shown that hide powder may adsorb non-tannins (including gallic acid) in addition to tannin.[17] A striking illustration of this fact is afforded by the recent work of Woodard and Cowland on maté.[18] The application of every recognised test, including the gold-beater's skin test, had established the absence of tannin, and yet in the hide-powder process 12 per cent. of water-soluble constituents were adsorbed.

It is also interesting to consider the results obtained by this method on a specimen of Chinese gallotannin. This specimen contains 11·5 per cent. of water, 10·7 per cent. of gallic acid, about 0·5 per cent. of glucose, and (by the colorimetric method) 77·8 per cent. of tannin. Hooper,[19] in several determinations by the hide-powder method, found 76·8 per cent. of tannin, by the cinchonine precipitation method 76·8 per cent., and by the colorimetric method 77·8 per cent.

Dr. D. Jordan Lloyd has kindly had the same specimen examined in her laboratory, with the following results:—water, 11·2; total soluble matter 88·8; non-tans, 9·5; substances adsorbed, 79·3 per cent.

As this tannin has been found independently by Mitchell, by Nicholson, and by Hooper to contain from 10·7 to 10·9 per cent. of gallic acid, it would seem that about 1·4 per cent. of gallic acid was adsorbed by the hide powder in the official method.

Adsorption with Casein.—Nierenstein[20] found that casein could be used as a substitute for hide powder, and that it did not adsorb gallic acid or glucose. His results, however, were from 1 to 1·5 per cent. higher than those given by the hide-powder method, and he does not appear to have ascertained the nature of the additional adsorbed substances.

Spiers[21] also used casein as a precipitant in conjunction with the permanganate method, the tannin being taken to correspond with the difference between the titration results before and after the precipitation. In this way he obtained concordant results in determining the tannin-content of cider.

The Gold-beater's Skin Test.—This test is essentially a tanning operation in miniature, for it depends upon the fixation of tannin by animal fibre. It was devised by Atkinson and Hazleton,[22] and elaborated by Price,[23] who showed that it was capable of detecting 0·005 mg. of gallotannin in 1 ml. of water. The value of the method has also been confirmed by several other chemists.[24] In applying the test, the gold-beater's skin is first prepared by treatment with very dilute hydrochloric acid, then washed, tanned for 30 minutes with a dilute solution of the substance under examination, washed free from non-tannins, and finally stained with a dilute solution of ferrous sulphate.

In my experience the method affords the best means yet devised of detecting minute traces of true tannin in the presence of gallic acid and other tannin derivatives.

THE DICHROMATE TEST.—The use of potassium dichromate as a reagent for tannins originated with Henry[25]; it afterwards became known as the Sanio test,[26] and was commonly accepted as specific for tannin. It was shown by Drabble and Nierenstein,[27] however, that gallic acid is also precipitated by potassium dichromate, and by Fear,[28] that numerous other non-tannin substances react similarly.

PRECIPITATION WITH ALKALOIDS.—Although it has long been known that an infusion of cinchona bark would give a precipitate with gallnut tannin, it was not until 1834 that Pelouze[29] suggested the use of quinine as a qualitative test for tannins, and in the same year Henry[30] asserted that alkaloids as a class were precipitants of tannin. Fear,[31] investigating this commonly accepted belief, found that gallotannin formed precipitates with only six alkaloids (*viz.* quinine, strychnine, brucine, cinchonine, cinchonidine and caffeine); that certain others (*e.g.* atropine, emetine, cocaine) gave only a slight turbidity; and that others, again, (*e.g.* pilocarpine, aconitine, berberine, betaine) gave no indications of any reaction. Ware and Smith,[32] however, have shown that precipitation depends upon the correct adjustment of the *p*H value, and that if the solution is brought to *p*H 7 to 7·5 by the addition of sodium bicarbonate, tannin is precipitated by pilocarpine, emetine, cocaine, morphine, and ephedrine.

Wagner,[33] having studied the behaviour of strychnine, quinine and cinchonine, found that, for quantitative work, the best results were obtained with cinchonine. In his gravimetric method he precipitated the tannin with cinchonine sulphate, dried the cinchonine tannate at 120° C., extracted the cinchonine and determined it gravimetrically as sulphate (dried at 120° C.).

He also devised a volumetric method, in which the tannin was precipitated with a standard solution of cinchonine sulphate in presence of an indicator (rosaniline acetate). His alkaloid solution was standardised by the results of his gravimetric determinations.

In 1905 Trotman and Hackford[34] recommended the use of strychnine, 1 mol. of which they found to combine with 1 mol. of tannin; the strychnine tannate was dried first in the air and then *in vacuo* at about 60° C. Spiers[21] found that the method was accurate for cider tannin, but not for gallotannin. (Possibly the explanation is that his "pure" gallotannin contained gallic acid.) Chapman[35] introduced a refinement into Wagner's method of precipitation with cinchonine sulphate. After drying the cinchonine tannate to constant weight at 100° C., he determined the nitrogen therein by Kjeldahl's method, and from the result calculated the amount of cinchonine in the precipitate, thus obtaining a factor by means of which he could calculate the amount of tannin in similar precipitates from infusion of hops. His preliminary experiments were made on a sample of "pure" gallotannin which he assumed to have the formula, $C_{14}H_{10}O_9.2H_2O$.

Next Tatlock and Thomson[36] applied the alkaloid method to tea, precipitating the tannin with a solution of basic quinine sulphate, and drying the precipitate at 100° C. On the average, their precipitates contained 25 per cent. of quinine to 75 per cent. of tannin. Using this method, they found Indian teas to contain from 13·3 to 15 per cent., Ceylon teas from 10·1 to 13·9 per cent., and China teas from 7·3 to 10·9 per cent. of tannin.

Smith,[37] working under the Society's Analytical Investigation Scheme,

studied the application of Chapman's technique to the determination of tannin in tea.[37] After precipitating the cinchonine tea-tannate he extracted the dried precipitate with chloroform to separate caffeine adsorbed by the cinchonine tannate, weighed the purified tannate after drying it at 100° C., and multiplied the weight by the factor to obtain the tannin present. In this way he obtained results varying from 15·1 to 16·9 for Indian, and from 11·6 to 13·5 for China tea. The results were about 1 to 3 per cent. higher than those obtained by the permanganate method, the difference being greater for China than for Indian teas.

THE PERMANGANATE METHOD.—For many years the method, first devised by Löwenthal,[38] of determining tannin by measuring its oxidisability by potassium permanganate was regarded as the standard method, and various modifications and simplifications of it were put forward. Thus Monier[39] introduced the use of an indigo indicator, and Procter[40] standardised the permanganate on gallic acid instead of on Neubauer's[41] "pure" tannin, and used gelatin with salt to precipitate the tannin. The difference between the oxidation values before and after the precipitation was taken to be a measure of the tannins present.

The permanganate method gives results for a particular tannin that are comparable among themselves, but the oxidation values of the various tannins differ, as was shown by Gantter,[42] and the permanganate solution therefore requires standardising for each kind of tannin of which the constitution is not known. Moreover, as has already been mentioned, precipitation with gelatin does not always effect a complete separation of gallic acid from tannin.

Hill,[43] using Procter's modification of the permanganate method, found China teas to contain from 6·8 to 7·5 per cent.; black teas from 7·8 to 15·0 per cent., and green teas from 9·1 to 24·9 per cent. of tannin. As the tannin was precipitated with gelatin, it is probable that some of these figures were too high.

IODINE METHODS.—Both gallic acid and tannin absorb iodine, and according to Gardner and Hodgson[44] each OH-group requires 1 mol. of iodine.

In Jean's method the reagent is a potassium iodide solution of iodine, standardised on 0·1 per cent. solutions of "pure" tannin and gallic acid, and the absorption is determined in alkaline (potassium bicarbonate) solution. In the first titration the whole of the iodine-consuming substances are determined. The tannin is then separated by precipitation with egg albumin, and the iodine absorption of the filtrate is determined, the difference corresponding with the tannin.

Boudet,[45] adding an excess of iodine and back-titrating, found that 1 g. of iodine was equivalent to 0·469 g. of gallic acid. For mixtures, he used hide powder to precipitate the tannin.

Cormimboeuf,[46] however, found that variable results were obtained either by Jean's direct or Boudet's indirect method, and that there was no finality in the absorption. To this Jean[47] replied that the results are accurate provided that the solution is saturated in the cold with sodium bicarbonate.

Colorimetric Method.—The colorimetric method which I devised several years ago[46] is based upon the fact that ferrous tartrate reacts with pyrogallol or the pyrogallic nucleus in gallic acid or tannin to form a violet ink, the intensity of the colour of which is proportional to the amount of that nucleus present. It is then

possible, if the constitution of the substance containing the nucleus is known, to calculate its amount. This method afforded, for the first time, an accurate means of determining gallic acid in tannins. The total tinctogenic substances in the tannin are first estimated colorimetrically by comparison with a standard solution of gallic acid (or pyrogallol), the tannin is then precipitated with quinine hydrochloride, and the gallic acid in the filtrate is estimated colorimetrically as before, the difference between the two results corresponding with the tannin in terms of gallic acid or pyrogallol.

The accuracy of the method has been repeatedly established (*e.g.* by Nicholson and Rhind,[47] by Hooper,[48] and by others), and Glasstone[49] has established the limits for *p*H for obtaining the maximum colour not only with pyrogallol tannins, but also with catechol tannins.

The analytical evidence appears to indicate that "pure" commercial tannins are mixtures containing large amounts of gallic acid, and this probably accounts for the conflicting and erratic results obtained by various methods standardised on "pure" gallotannin. The specimen of Chinese gallotannin which I used in most of my experiments is probably a mixture of various galloyl glucoses with digallic anhydride, for it can be fractionated until it gives a compound which gives a colour closely approximating that which would correspond with a substance of the constitution of Fischer's penta-digalloyl glucoside.

In my original experiments I made a few determinations of the gallic acid and tannin in teas. Not knowing the constitution of tea tannins, I had to be content with expressing my results in terms of gallic acid, but one advantage of the method is that results previously obtained can be calculated into the pyrogallol equivalent of any formula subsequently established.

I found the usual difference between China and Indian teas by this method, a sample of the former containing 3·3 per cent. of tannin (in terms of gallic acid) and one of the latter 7·9 per cent. The respective amounts of gallic acid were 0·84 and 0·80 per cent.

The method is not applicable to coffee, but I was able to get comparable results by another colorimetric method, with osmium tetroxide as the reagent.[50] The drawback of this method is that it is difficult to determine when the maximum intensity of colour is reached, and that to get concordant results it is necessary to standardise the conditions exactly.

References

1. G. Wigner, *Proc. Soc. Public Analysts*, 1876, **1**, 235.
2. H. Trillich and H. Göckel, *Z. Unters. Nahr. Genussm.*, 1898, 101; Abst., Analyst, 1898, **23**, 179.
3. A. Manea, *Chem.-Ztg. Rep.*, 1905, **29**, 381; Abst., Analyst, 1906, **31**, 80.
4. R. Handtke, *J. Prakt. Chem.*, 1860, **82**, 345.
5. E. Beckmann, *Z. anal. Chem.*, 1886, **25**, 527; Abst., Analyst, 1886, **11**, 236.
6. H. Ruoss, *Z. anal. Chem.*, 1902, **42**, 717; Abst., Analyst, 1903, **28**, 116.
7. B. W. Gerland, *Chem. News*, 1863, **8**, 54.
8. H. Flick, *Wagner's Jahresber.*, 1860, 531.
9. W. H. Krug, *J. Amer. Chem. Soc.*, 1895, **17**, 811; Abst., Analyst, 1895, **20**, 283.
10. H. Wislicenus, *Z. angew. Chem.*, 1904, **25**, 801.
11. A. Seguin, *Annales de Chim.*, 1797, **20**, 15.
12. A. E. Jones, Analyst, 1927, **52**, 275.
13. H. Trunkel, *Biochem. Z.*, Abst., Analyst, 1910, **35**, 444.

14. Cf. *Allen's Commercial Organic Analysis*, 5th Ed., Vol. V, p. 137 *et seq.*
15. *Id.*, p. 153 *et seq.*
16. *Id.*, p. 157 *et seq.*
17. F. Jean, *Ann. chim. anal.*, 1898, **3**, 145; Abst., ANALYST, 1898, **23**, 245.
18. W. A. Woodard and A. N. Cowland, ANALYST, 1935, **60**, 135.
19. D. Hooper, *Id.*, 1925, **50**, 162.
20. M. Nierenstein, *Chem.-Ztg.*, 1911, **35**, 31; Abst., ANALYST, 1911, **36**, 123.
21. C. W. Spiers, *J. Agric. Sci.*, 1914, **6**, 77; Abst., ANALYST, 1914, **39**, 127.
22. E. Atkinson and E. O. Hazleton, *Biochem. J.*, 1922, **16**, 516.
23. P. H. Price, ANALYST, 1924, **49**, 25.
24. F. Hardy and F. H. S. Warneford, *Ind. Eng. Chem.*, 1925, **17**, 49.
25. O. Henry, *J. de Pharm.*, 1834, **20**, 429.
26. C. Sanio, *Bot. Ztg.*, 1863, **21**, 17.
27. E. Drabble and M. Nierenstein, *Biochem. J.*, 1907, **2**, 96.
28. C. Fear, ANALYST, 1929, **54**, 227.
29. J. Pelouze, *Ann. Chim. Phys.*, 1834, **57**, 423.
30. O. Henry, *J. de Pharm.*, 1834, **20**, 429.
31. C. Fear, ANALYST, 1929, **54**, 316.
32. A. H. Ware and V. Smith, *Pharm. J.*, 1933, **131**, 148; Abst., ANALYST, 1933, **58**, 703.
33. R. Wagner, *Z. anal. Chem.*, 1866, **5**, 1.
34. S. Trotman and J. E. Hackford, *J. Soc. Chem. Ind.*, 1905, **24**, 1096; Abst., ANALYST, 1906, **31**, 53.
35. A. C. Chapman, *J. Inst. Brew.*, 1907, **13**, 646; 1909, **15**, 360; Abst., ANALYST, 1908, **33**, 95; 1909, **34**, 372.
36. R. R. Tatlock and R. T. Thomson, ANALYST, 1910, **35**, 104.
37. H. L. Smith, *Id.*, 1913, **38**, 312.
38. J. Löwenthal, *Z. anal. Chem.*, 1877, **16**, 33.
39. E. Monier, *Compt. rend.*, 1858, **46**, 577.
40. H. R. Procter, *Chem. News*, 1877, **36**, 58; 1878, **37**, 256.
41. C. Neubauer, *Z. anal. Chem.*, 1871, **10**, 1.
42. F. Gantter, *Z. angew. Chem.*, 1889, 577.
43. A. Hill, ANALYST, 1881, **6**, 95, 233.
44. W. H. Gardner and H. H. Hodgson, *Id.*, 1909, **34**, 371.
45. M. Boudet, *Bull. Soc. Chim.*, 1906, **35**, 760; ANALYST, 1906, **31**, 370.
46. C. A. Mitchell, ANALYST, 1923, **48**, 2.
47. W. N. Nicholson and D. Rhind, *Id.*, 1924, **49**, 505.
48. D. Hooper, *Id.*, 1925, **50**, 162.
49. S. Glasstone, *Id.*, 1925, **50**, 49.
50. C. A. Mitchell, *Id.*, 1924, **49**, 162.

85 ECCLESTON SQUARE
LONDON, S.W.1

THE PHARMACOLOGY OF CAFFEINE AND OF TEA AND COFFEE

BY G. ROCHE LYNCH, O.B.E., M.B., B.S., F.I.C.

I will deal briefly with the pharmacology of caffeine and then suggest one or two lines of thought. I understand that it is agreed that tea contains somewhere between 2·5 and 4·5 per cent. of caffeine, and coffee 0·5 to 1·5 per cent.

THREEFOLD ACTION OF CAFFEINE.—The effects of caffeine on the body can be divided into three groups:—(i) its effect on the central nervous system; (ii) its action on muscular tissue (including heart muscle and that controlling the intestines); (iii) its diuretic action or promotion of the flow of urine.

The action of caffeine on the central nervous system is almost entirely a psychical function, that is to say, it acts on the higher centres of the brain. If it is taken in toxic doses it may exert an influence similar to that of strychnine, namely, in producing convulsions. In the course of its action on the central nervous system caffeine facilitates the perception of sensory stimuli and the

association of ideas, so that consciousness becomes, under its influence, more acute. One of the results of that is a condition of wakefulness or increased alertness, and so any tendency to drowsiness or fatigue is made to disappear or is less pronounced. A corollary to this is that interpretations of sensory stimuli received by the brain from various external sources become more perfect and accurate. Even more important is the fact that these stimuli are correctly placed in relation to each other. In this respect there is a profound difference between the effect of caffeine and that of cocaine, for with the latter, in addition to the increased perception of the higher centres, enhanced perceptions from the lower centres are also received, and the impressions are not so perfect as in the case of caffeine. Thus with cocaine the tendency is for the judgment to be impaired; with caffeine the accuracy of the judgment is enhanced. Caffeine also causes a constriction of the musculature of the blood-vessels, leading to a rise in blood-pressure, and respiration is stimulated. The centres controlling these functions are situated in the lower part of the brain, and that is an additional fact in the pharmacology of caffeine. If a person takes a very large dose of caffeine, the process just described is intensified, and the result is a confusion of thought and disorders of sensation which are associated with flashes of light in the eyes and noises in the ears—so-called tinnitus. If extreme doses are given, this excitation proceeds to restlessness, and the receiver becomes tremulous and may develop convulsions, such as follow strychnine poisoning.

With regard to the action of caffeine on muscle tissue I might remind you that, from the medical point of view, muscle is divided into three kinds: voluntary muscle, the working of which is controlled by the will; cardiac muscle, a specialised form; and the involuntary muscle such as that in the intestines and the blood-vessels, not under the immediate control of the will. Although not definitely known, it is believed that caffeine acts directly on the muscle-cells, not on the nerve-cells; and the muscular work performed by the person taking caffeine can be increased without the person feeling fatigued in corresponding degree. Here a difficulty arises, as it is impossible to say whether or not the abolition of the feeling of fatigue is due to an effect of the drug on the muscles or on the central nervous system. As might be expected from what I have said, caffeine is a factor in producing contraction of blood-vessels and intestines, and their more vigorous action. There occurs also in those who have taken caffeine a general acceleration of the heart-beat, with a diminution of the diastolic period; hence, if the dose were large over a period of time, the effect on the heart might be definitely unfavourable. In ordinary medicinal doses, however, the taking of caffeine seems to have no deleterious effect. The cardiac state, after large doses of the drug, may take the form of auricular fibrillation. Conceivably this might lead to death, though actually death from caffeine is rare.

With regard to the diuretic action of caffeine, the increased flow of urine promoted by it is due to a greater output of water, so that the urine itself becomes more dilute than normal; but, tested over an appreciable period, there is found to be an increase not only in the total urinary output, but also in the total solids passed. This elimination of water is among the valuable results of the medicinal use of caffeine, as seen in patients who are suffering from dropsy; hence the special

value of the drug in heart failure or in kidney disease. This increased elimination of water has been found to be due partly to the raised blood-pressure, and partly to the specific action of caffeine on the cells of the kidney, enabling them to excrete water and, to some extent, solids too, in greater amount. Some of the caffeine is decomposed in the body, some is excreted in the urine in an unchanged condition, and some in a partly de-methylated form, *i.e.* as mono- or di-methyl xanthine (caffeine is trimethylxanthine).

OVERDOSE.—I have not yet encountered a case in which death was definitely caused by an overdose of caffeine. As much as 60 grains of the drug have been taken at a time, and there was recovery from the serious illness. After taking very large doses of caffeine the person manifested the form of excitation which may be seen in people drunk from alcohol: dizziness, a ringing and buzzing in the ears, trembling, confusion of ideas, palpitation of the heart, and even strychnine-like convulsions.

CAFFEINE ADDICTION.—Caffeine, of course, cannot be classed with the drugs which come under the heading of addiction. Those who take caffeine in the form of tea or coffee become accustomed to it, and find difficulty in doing without it. Still, unlike cocaine and morphine, it can be given up without much mental effort or feeling of loss, and its indulgence does not cause the serious train of symptoms which follows the habitual taking of cocaine or morphine. In post-mortem examinations I do not believe that any changes occur in those who have drunk largely of the beverages tea and coffee which can be associated with such drinking. I know of no cases warranting the suggestion that either the caffeine or the tannin can produce such effects.

CAFFEINE AND SLEEPLESSNESS.—In conclusion, I want just to mention the question of sleeplessness. I am in difficulty over this, and it is here that I invite suggestions. It appears to me very extraordinary that we all know people who will not take coffee, as they say they cannot sleep all night after it. Also, strong coffee administered per rectum is a common remedy given to patients suffering from any form of narcotic poisoning. *But*, if a patient who says he cannot take coffee because it keeps him awake all night is given caffeine citrate in a medicine, unknown to him, there is often no interference with his sleep. This suggests that the association of tea and coffee with sleeplessness may be largely psychical. Although I have pointed out various attributes of caffeine, such as increased stimulation, I feel that there must be some further factor in these beverages which has definite effects as regards sleep, but the nature of which can at present only be conjectured.

ST. MARY'S HOSPITAL
PADDINGTON, W.1

THE TANNIN-CONTENT OF TEA

By P. J. Norman, B.Sc., A.R.C.S., A.I.C., and E. B. Hughes, D.Sc., F.I.C.

The available methods for the determination of the amount of tannin bodies in tea fail to some extent because of the lack of knowledge of the exact nature of tea tannin and of its oxidation and condensation products. Before describing some work carried out with the object of comparing the results obtained by various methods, it may be of interest to remark that tea-tannin, a natural constituent of all tea-leaf, undergoes some change in the course of the fermentation for the production of black teas—some of it becoming insoluble and some remaining soluble and producing the characteristic colour of the infusion. Green tea, little drunk in this country, has not undergone this fermentation, and the tannin remains soluble and unchanged in colour. Oolong teas are lightly fermented. Tannin is an important constituent of tea, in that it contributes to a considerable extent to those properties which characterise the quality of a tea. There is more tannin in good leaf than in poor leaf and less in stalk than in leaf.

A considerable amount of work has been carried out, chiefly by workers in the Tea Research and Experimental Stations, on the tannin-content of tea-leaf at different stages of growth, under different cultural conditions, etc., and during the stages of manufacture.

Methods.—The methods that have been used in these comparisons are:

(*a*) Alkaloid precipitation method: Smith's[1] application of Chapman's method for tannin estimation, by precipitation from extract or infusion by saturated cinchonine sulphate solution, has been used. We use an extract of 1 per cent. w/v diluted, after filtration, to 2½ volumes (*i.e.* equivalent to 0·4 per cent. w/v), as this does not become cloudy on standing or cooling and, moreover, it is not necessary to remove caffeine from the liquid before adding the cinchonine sulphate, *e.g.*

Tannin extracted (as per cent. of dry tea)	
(*a*) direct from tea extract	(*b*) after chloroform extraction of the tea extract
15·8	16·0
14·8	15·0
10·2	9·9
11·0	11·0

Note that a difference of 0·3 per cent. represents only one mg. of cinchonine tannate. The agreement is within the limits of experimental error.

(*b*) The Löwenthal method,[2] by which tannin is determined as the constituent(s) of tea (from infusion or extraction) precipitable by saline gelatin and oxidisable by potassium permanganate, with indigo carmine as an indicator of the oxidation. Results are expressed as the gallotannic acid equivalent of the permanganate: 1 ml. of 0·1 *N* oxalic acid = 0·0042 g. of gallotannic acid.

(*c*) The hide-powder method[3]: the official method of the International Association of Leather Trades' Chemists, which estimates tannin as the total solids removed by freshly-chromed hide-powder from an extract or infusion.

RESULTS.—All results given in the paper are as percentage of dry tea. Table I gives amounts of tea-tannin, as obtained by the different methods, in typical samples of unblended teas.

TABLE I

	Extractable tea-tannin (per cent. of dry tea)		
	Method (*a*)	Method (*b*)	Method (*c*)
A. *Black Teas*			
Keemun (China) tea	10·1	6·2	10·1
Lapsang Souchong (China) tea	10·4	5·3	—
Darjeeling Orange Pekoe ..	14·7	12·0	14·4
Ceylon Orange Pekoe	12·8	11·1	11·6
Java Orange Pekoe	14·0	9·6	13·3
Nyasaland Broken Pekoe ..	12·9	9·2	11·1
Annam Orange Pekoe	14·7	13·5	—
Annam Souchong	13·4	7·4	—
Japan black tea..	10·8	6·7	9·6
B. *Green and Oolong Teas*			
Moyune Young Hyson (green tea)	12·7	13·5	14·2
Moyune Gunpowder (green tea)	9·5	10·1	11·9
Formosa (Oolong) tea	15·1	15·4	17·9

These results are represented on Graph I.

It will be seen that, in Group A, the results by method (*b*), the Löwenthal method, are always lower, sometimes considerably so, than those obtained by either the cinchonine method (*a*) or the hide-powder method (*c*), and that the results by these last two do not differ greatly. These teas are all black teas—*i.e.* teas which have undergone full fermentation in manufacture.

The teas of Group B do not show this lower Löwenthal result. These are two green teas, which have not been fermented, and an Oolong tea (lightly fermented).

These results suggest that the fermentation has affected the tea-tannin in such a way that the permanganate required for its oxidation has decreased; this decrease is greatest (as a proportion of the cinchonine-precipitated tannin) in the China tea, which is more fully withered and fermented than the usual Indian or Ceylon black teas. The amount of cinchonine tannate precipitate is apparently not so affected. It may be significant that we have found that the tannins of cacao can be subjected to severe oxidation treatment without appreciably altering the amount of cinchonine precipitate given.

In Table II and Graph II we give similar results for commercial blends of tea. All, with the exception of Nos. 1 and 2 (blends sold simply as "tea"), are teas for which some specific claim, such as "Digestive," "Invalid," etc., is made.

No. 5 is a China tea obviously similar to No. 2. With regard to the others, which are black teas of the Indian or Ceylon (mainly Ceylon) type or blends, they are seen to be very similar in tea-tannin content, by whichever method it is estimated.

Teas Nos. 1, 2, 4, 5, 6 are black teas similar to those of Group A, Table I,

GRAPH I

RELATIVE TANNIN CONTENTS OF UNBLENDED TEAS.

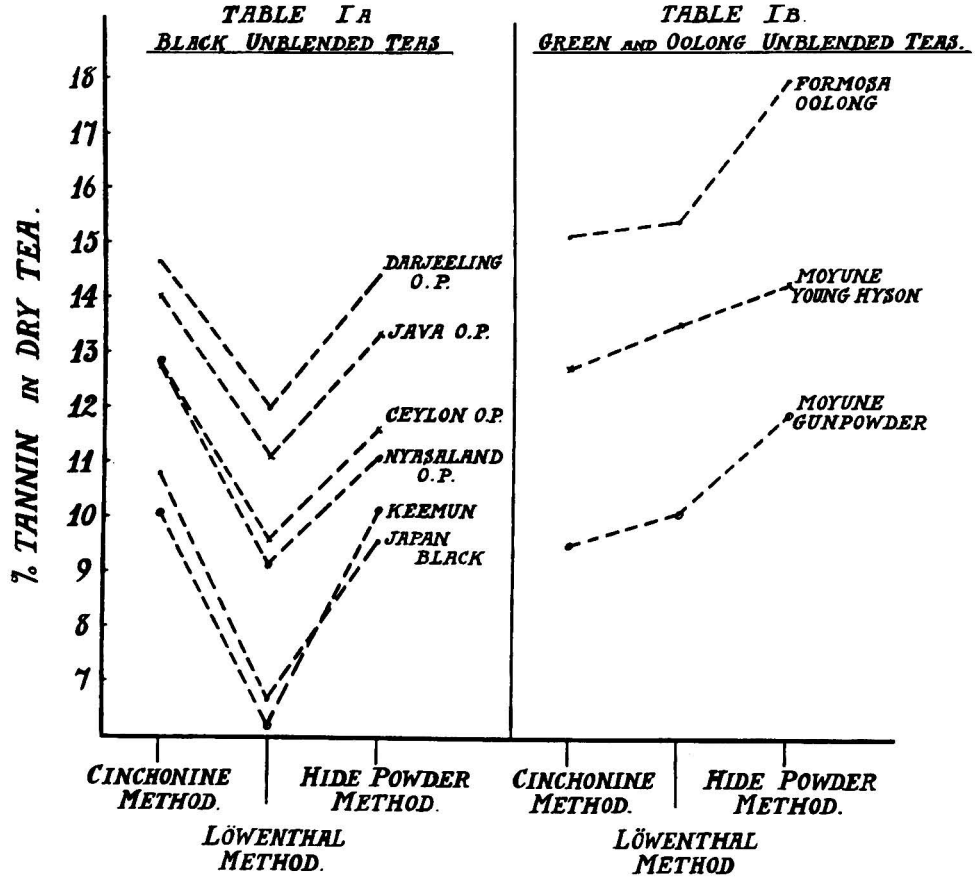


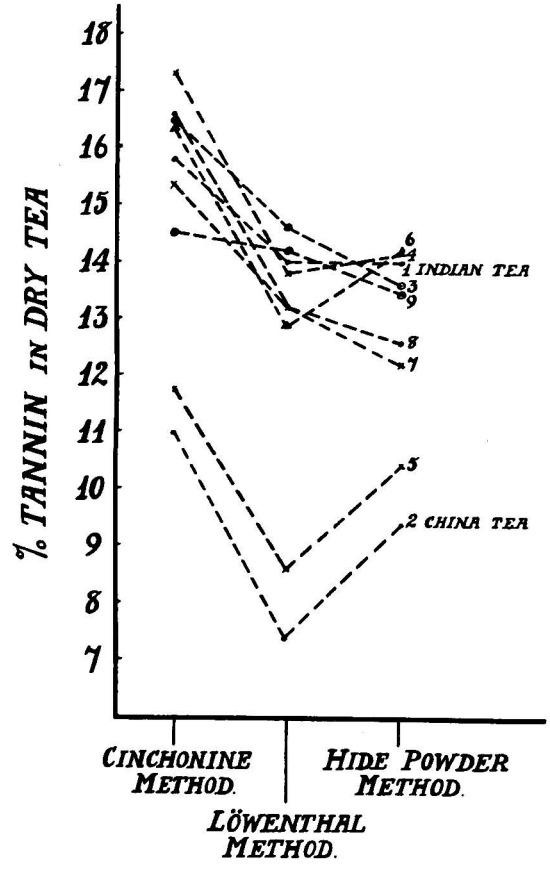
TABLE II

Tea.		Extractable tannin (as per cent. of dry tea) Method (*a*)	Method (*b*)	Method (*c*)
1.	(Blend of Indian and Ceylon teas) ..	15·8	14·0	14·0
2.	(Blend of China teas)	11·0	7·4	9·4
3.	"Special" teas	16·5	14·6	13·6
4.		17·3	13·8	14·1
5.		11·8	8·6	10·4
6.		16·4	12·9	14·2
7.		15·4	13·2	12·2
8.		16·6	13·2	12·6
9.		14·5	14·2	13·5

having lower results for the Löwenthal method than for the cinchonine or hide-powder method. The other samples, although they are black teas, and accordingly have lower Löwenthal than cinchonine values, show still lower results for the hide-powder method. This may possibly be due to the grading of the tea; we have some evidence suggesting that "fannings,"* of which these teas mainly consist, behave in this way.

GRAPH II

RELATIVE TANNIN CONTENTS OF BLENDED TEAS.



We have, in general, used only the cinchonine method for the determination of tea-tannin, and some further results by this method for such teas as those in Table II are given in Table III.

* The broken tips, etc., of the rolled leaf broken off during manufacture and separated by sieving.

TABLE III

		Extractable tannin (per cent. of dry tea) Method (*a*)
1.	Indian and Ceylon blends	14·9
2.		17·3
3.		15·8
4.		14·6
5.	"Special" teas	14·1
6.		14·9
7.		16·8
8.		16·2

Nos. 1 to 4 are ordinary commercial blends of Indian and Ceylon black teas, and Nos. 5 to 8 are teas sold as "Digestive," etc., teas.

TABLE IV

TANNIN-CONTENT OF UNBLENDED TEAS

		Extractable tannin (per cent. of dry tea) Method (*a*)
China green teas:	Moyune Gunpowder ..	9·5
	Moyune Young Hyson ..	12·7
China black teas:	Lapsang Souchong ..	10·4
	Keemun	10·1
N. India:	Patrakola broken Pekoe	14·1
	Chalouni broken Orange Pekoe ..	16·8
	Darjeeling Orange Pekoe	14·7
	Darjeeling Pekoe	13·4
	Assam broken Pekoe	14·3
	Assam Orange Pekoe	15·1
S. India:	Letchmi broken Pekoe	15·6
	Travancore	17·2
Ceylon:	Broken Pekoe	13·4
	Orange Pekoe	12·8
	Broken Orange Pekoe	15·5
Nyasaland broken Pekoe		12·9
Java Orange Pekoe		14·0
Java broken Pekoe		13·6
Indo-China:	Annam Souchong	13·4
	Annam Pekoe	14·6
	Annam Orange Pekoe	14·7
Formosa Oolong tea		15·2
Japan black tea		10·8
Korea broken Pekoe		16·6

In this table are given the tannin-contents (by the cinchonine method) of a more extended range of unblended teas than are recorded in Table I.

It is, however, not actually the whole amount of tannin that can be extracted by prolonged boiling from the tea which concerns the user, but the amount dissolved

out in the ordinary way of making tea. For such tests we make a standard infusion by adding 29 parts by weight of boiling water to one part of tea, and decanting (and filtering) after 3½ minutes.

The factors which obviously would be expected to influence the amount of tannin obtained in an infusion of tea are:—(i) the length of time of the infusion; (ii) the ratio of the amount of tea to water; (iii) the temperature of the water.

(i) *Time of Infusion.*—A sample of a commercial blend of Ceylon and Indian tea of medium price gave the following results for infusions made during various periods of time:

TABLE V

STANDARD INFUSION, VARYING TIME

Time of infusion in minutes	Present in infusion (per cent. of dry tea)	
	Tea-tannin (Method (*a*))	Non-tannin solids
2	11·5	19·4
3	12·5	20·6
4	12·5	22·5
5	13·3	21·4
6	14·2	21·2
7	14·1	21·7
8	13·7	22·7
9	14·2	21·8
10	13·8	21·9

From these figures it is seen that there is an increase in the amount of tannin up to 6 minutes, but that the non-tannin soluble solids go more quickly into solution.

(ii) *Ratio of Tea to Water.*—A similar type of commercial black tea gave the following results for increasing ratio of tea to water. Conditions as for Table V and time of infusion 3½ minutes.

TABLE VA

Tea:Water (w/v)	Amount in infusion (per cent. of dry tea)	
	Tannin	Non-tannin solids
0·2 : 29·8	11·0	21·0
0·4 : 29·6	11·0	21·8
0·6 : 29·4	11·0	20·9
0·8 : 29·2	10·9	21·5
1 : 29·0	10·9	23·2
2 : 28	8·8	19·9
3 : 27	9·0	20·6

These figures indicate that the amount of tea does not cause appreciable decrease of the degree of extraction of tannin until the proportion of tea to water is greater than 1 to 29.

(iii) *Temperature of the Water.*—Table VB gives results for infusions prepared with water at various temperatures, otherwise with "standard" proportions and time.

TABLE Vb

$3\frac{1}{2}$ mins., 1 in 30

Temp. of infusion °C.	Amount in infusion (per cent. of dry tea)	
	Tannin	Non-tannin solids
60	5·2	14·4
70	6·9	18·0
80	9·7	19·0
90	11·5	20·5
100	12·5	21·1

Clearly the temperature of the water is a matter of considerable importance. Under the standard conditions which we employ the temperature of the liquid during the infusion of $3\frac{1}{2}$ minutes does not fall below 90° C. (about 92° C. at the end of the infusion).

Table VI shows the amount of tannin removed by infusion, under "standard" conditions, from the same teas as those for which total extractable tannin-contents were given in Table II.

TABLE VI

STANDARD INFUSIONS

Tea	Tannin extracted (per cent. of dry tea) Method (*a*)
1.	9·6
2.	4·8
3.	10·4
4.	10·1
5.	5·2
6.	10·5
7.	9·2
8.	10·4
9.	9·9

It will be noticed that, as for the total tea-tannin, the figures are much the same for all the non-China black teas and likewise for the two China teas, and that they are, in general, in the same relative order as for the total tannin of the same teas, though the actual amounts removed are less (about 50 per cent. for China teas, Nos. 2 and 5, and about 70 per cent. for the other black teas).

The results we have given in the paper indicate the importance of specifying exactly the method used (and also the procedure) for estimation of tea-tannin, though for comparisons of teas of the same type (China, non-China black teas, green teas) the relative results are not seriously affected by the choice of method.

We desire to thank J. Lyons & Co., Ltd., in whose laboratory this work was carried out, for permission to publish.

REFERENCES

1. H. L. Smith, ANALYST, 1913, **38**, 312.
2. J. Löwenthal, *Z. anal. Chem.*, 1877, **16**, 33.
3. *Allen's Commercial Organic Analysis*, 5th Ed., Vol. V, p. 137 *et seq.*

"TANNINLESS" TEA

By H. H. Bagnall, B.Sc., F.I.C.

During the past six years I have received, at intervals, a number of samples of packet teas bearing on the labels statements concerning the tannin-content. In nearly every instance this statement indicated either that no tannin at all was present (which is an obvious mis-statement), or that the amount of tannin was less than was usual in teas of other types.

As a rule, the inference was drawn that the tea would be "more digestible," would "promote digestion" or, as one bold statement asserted, would actually "cure indigestion." These statements appear to be simply assertions made without any particular basis of scientific fact.

The tannin was determined in all these samples, and in a few others for comparison, by Thomson and Tatlock's quinine method,[1] the directions given being followed exactly. Smith's cinchonine method[2] was tried in a few cases, but the process was longer, and troublesome emulsions were sometimes obtained during the extraction of caffeine by chloroform. However, the figures obtained on the same tea by the two processes did not differ significantly, being usually a little lower by Smith's method.

As the figures obtained were intended to be comparative only between one tea and another, and in view also of the fact that all methods are only approximate, the exact nature of the tannin being unknown, the simpler quinine method was followed throughout the series of determinations. The amount of tannin varied, for Indian and Ceylon teas, from 9·9 to 16·4 per cent., the average being 12·8 per cent.

Twenty-two samples of 29 fell within the range 11·0 to 14·1 per cent. Two China teas which were examined each contained 8·6 per cent. of tannin. Of the 31 samples in which the tannin was determined, 16 were made the subject of enquiry, and although no case was taken to Court, the packers in every instance recognised the weakness of their position, and agreed to omit references to tannin which were regarded as contravening the provisions of Section 30 of the Food and Drugs (Adulteration) Act.

In the following table is given a list of the fifteen samples regarding which action was taken, the offending portion of the label being quoted:

Date	Tannin Per Cent.	Extracts from labels
Aug., 1929	12·5	"Free from crude tannin found in all ordinary tea, therefore good for indigestion, gastritis etc. . . . Cures indigestion."
Feb., 1930	14·9 (caffeine 3·36)	"Contains the maximum of theine with the minimum of tannin," and other statements implying that its value was greater than that of other teas.
Apr., 1930	13·9	"Remarkably free from objectionable tannic acid, the chief cause of indigestion to users of ordinary full leaf teas. Contains only the delicate, harmless portions of the leaf, avoiding the coarser parts which contain injurious 'tannics'."

Date	Tannin Per Cent.	Extracts from labels
May, 1930	14·0	"Free from crude tannin. Practically tanninless."
May, 1930	12·7	"Fine tea contains very little tannin and consequently . . . this tea can be used freely . . . by persons who suffer from indigestion, etc."
June, 1932	14·7	"No crude tannin present."
Jan., 1933	12·7	"Free from tannin."
Jan., 1933	14·9	"Tannin minimised."
Mar., 1933	11·2	"Practically free from tannin."
May, 1933	13·6	"All stalks wherein lies the tannin eliminated."
July, 1933	14·1	"Composed only of the tips of leaves and, therefore, tanninless."
Jan., 1934	13·9	"Contains all the essential goodness without any injurious tannin."
Jan., 1934	8·6 (China)	"Practically free from tannin."
June, 1934	11·7	"Contains the minimum of tannin."
June, 1935	16·4	"Contains the maximum of caffeine, and the minimum of tannin. Digestive because non-tannic. Free from stalks, etc., which contain crude tannin."

All the teas mentioned in the table were so-called "Digestive" teas, and were finely ground to give the appearance of the popular "Leaf tips." In addition to the samples contained in the table, one or two others were labelled in a dubious manner.

The label of one (June, 1934) stated that one spoonful would more than equal two spoonfuls of ordinary leaf. The implication here, of course, was that the tea would go twice as far, but the actual fact was that, owing to the tea being finely ground, the spoon would hold a greater weight than it would of a coarser variety. The water extract, determined on a 0·25 per cent. solution, was 39·9 per cent.—an average figure.

The label of another sample (June, 1934) contained the statement that a half-pound would go as far as one pound of ordinary tea, and the tea was described on another part of the packet as "double strength." The water extract in this case was 42 per cent., and the claim made was obviously preposterous.

A sample (January, 1934) was also stated to go twice as far as ordinary tea, and was further described as a great nerve tonic, being composed of "tea tips of immense strength."

Another interesting sample (November, 1933) was labelled "Rich in vitamins," and was described as "a blend of Empire leaf combined with the tiny leaves of a wonderful tropical plant which has remarkable curative properties in cases of indigestion, rheumatism, neuritis, etc." Black tea contains no vitamins, except a possible trace of vitamin *E*. The tropical plant referred to was maté, which was present to the extent of about 7 per cent.

A sample (May, 1933) contained 14·0 per cent. of tannin, and an analysis made by "a celebrated London analyst," appeared on the label, giving a figure of 11·2 per cent. It was not stated, however, by what method or at what date

this analysis had been carried out. It was described as "Real edge and leaf tip tea," and claimed that it could be "enjoyed by persons of weak digestion owing to its low tannin-content as compared with that of common coarse leaf tea."

Representations to the firms concerned in the packing of the above samples have resulted, in most cases, in a modification of the statements to which objection was taken.

It is believed that, by reason of the administrative action taken, there are now very few teas on the market to the labels of which serious objection can be taken, and, incidentally, there is good reason for thinking that the persuasive methods employed to induce the packers to revise their labels were far more successful than the more forcible (and expensive) method of taking legal proceedings.

References

1. R. R. Tatlock and R. T. Thomson, Analyst, 1910, **35**, 104.
2. H. L. Smith, *id.*, 1913, **38**, 312.

City Analyst's Department
Birmingham

Discussion

Mr. D. M. Freeland said that he had heard that tea-blenders made different blends of tea for different parts of the country because of the variations in water. Did it really make any difference whether distilled or tap water were used for the infusion?

Dr. H. H. Mann replied that the character of the water undoubtedly had an influence, and that this was taken into account in preparing blends for use in different places.

Dr. H. E. Cox observed that according to recent papers in the *Zeitschrift Untersuchungs Lebensmittel*, there was still much doubt as to the presence of chlorogenic acid in coffee. Some said there was none; others showed about 7 per cent. Discrepancies were also apparent in relation to caffeine. It was known that chlorogenic acid was easily hydrolysed, but he would like to know what was the relationship between caffetannin and chlorogenic acid, and whether there was any probable explanation for the manifest discrepancies in the published papers.

Dr. Lampitt remarked that the papers had demonstrated the very indefinite state of our knowledge, and it seemed to him that, as Dr. Nierenstein had isolated some beautiful crystalline products, it would be very valuable if they could be submitted to various standard methods of analysis in order to see if some correlation could be obtained. Thus, if a definite tannin were obtainable from tea, it should be possible to get some factor to which they would be able to refer their results for tea-tannins.

Dr. Nierenstein referred Dr. Cox to a chapter in his book. He really did not know. The whole chemistry of caffetannin was most unsatisfactory. There were three possibilities—either that the acid was the caffetannin, or that the acid was the parent of the caffetannin, or that it was derived from the caffetannin. He agreed that, if practicable, the suggestion of Dr. Lampitt was a valuable one, but until the crystalline derivative could be obtained in quantity it would not be possible to co-ordinate results. He had not yet determined the colorimetric ratio of the tannin.

Mr. R. F. Innes said that he regarded these papers as valuable contributions to the subject, especially the survey of the methods of analysis. Apparently Dr. Mitchell did not rate the hide-powder method very highly, but it was accepted in the leather trade as an empirical method which gave results approximating closely to those obtained in actual tanning practice. The colorimetric method

devised by Dr. Mitchell gave an accurate measure of the tannin in solution from one point of view, but tannin was a variable substance, and it did not seem likely that the method would distinguish between pyrogallol and catechol tannins. Presumably, the method gave the results for both in terms of one.

Mr. A. W. KNAPP asked whether the colorimetric method was very sensitive to *p*H. Some years ago there were two papers (one by Adams and one by Jensen) on the determination of tannins in cocoa. In each the tannin was determined by the cinchonine method. Apparently the only difference was that Adams took the bean as it was, whereas Jensen did what he called "neutralising the natural acid of the bean" before determining the tannin. Would a slight difference in *p*H make a difference?

Dr. MITCHELL, replying to Mr. Innes, said that it was not possible to distinguish colorimetrically between pyrogallol and catechol tannins in admixture, unless, possibly, by rigid control of the *p*H conditions. The *p*H also had a pronounced effect upon the precipitation of tannin by cinchonine.

Mr. H. S. REDGROVE pointed out that a great deal of the coffee made in England did not taste like coffee. Thus, it would seem that the English public was more interested in the caffeine than in the flavour. He thought this question of flavour was important. It played a large part in the price which could be got for tea in this country. From the point of view of flavour it did not matter what tannins one had there, beyond the fact that tannin gave a certain astringent taste; the flavour was due to an essential oil. Efforts had been made in certain perfume factories in France to extract the flavour from tea. He wanted to stress the point that taste and flavour were different phenomena, because it had struck him that they might go away from this meeting without anything having been said to the effect that the flavour could not possibly be due to a non-volatile substance such as tannin, but must be due to essential oil.

Dr. H. H. MANN said that his long connection with the tea industry had led him to think that the present meeting would interest him, and it had certainly done so. In the first place, as a representative of the producers, the question of the relation of the various constituents to the value of the tea was to him the most important matter before the meeting. All investigation up to the present seemed to show that the proportion of caffeine in the tea did not affect its market value at all. One could get low-priced tea with high caffeine-content and high-priced tea with a small proportion of caffeine. Regarding the relationship of the amount of tannin to the value of tea, it might be said that, generally speaking, the higher the amount of tannin, the higher the price of the tea. Most people thought that the opposite was the case, and indeed such a relationship was not by any means universal, but the statement represented the general position when comparing teas of a similar class. The exceptions were sufficiently numerous, however, to make it important for further study. His own idea was that the reason for the absence of a constant connection between the amount of tannin and the value was that the tannin contained in a commercial sample of tea was not a single body, and was not the tannin originally contained in the leaf, but was a mixture of tannin and tannin derivatives in an infinity of stages and conditions of oxidation. In all the analyses that were normally made all these were taken together, and while this was done it was quite impossible for the analyses to show any connection with the market value. By varying the conditions of manufacture the proportion of these oxidation products could be varied very greatly, and so the value of the tea produced could be very greatly modified. Until the analyses employed could differentiate between the various forms in which the tannin and tannin products occurred in commercial tea, it was probable that determinations of tannin would be absolutely useless in connection with the valuation of the tea. At one time he thought he had got a method which would serve for this purpose, but while it applied in some cases, it gave results in others

which were contrary to the opinion of the market and the price of the tea. At present he doubted whether the determination of the tannin by any known method was of any use to the consumer, and they were compelled to go back to the taster for the value of tea. Until analysts could go further than they could at present, the determination was not worth the time spent on it.

It must be remembered that the tannin of tea was of a different type from most of the tannins that were usually discussed. The tannin of tea was not a residual product. It was present in largest quantity in the earliest leaf growth, and it seemed probable that, in tea, tannin took the place of starch in connection with the metabolism of the plants. He was extremely interested by the formulae presented by Dr. Nierenstein as representing the composition of the tannin of tea-leaf, but there seemed a good deal of probability, as a result of the work of Shaw and Jones in South India, that there were differences in the structure of tannin in different types of tea, and even between that in tea-leaf at different times of the year, and that such slight differences were very important in connection with the quality of tea. This matter was, however, in such an early stage of investigation that he would not pursue the subject at the moment.

At present he was very anxious to emphasise the point that he did not think that analyses of tea, merely giving a total figure for tannin, were of any value whatever. What was needed now was not the determination of tannin as a whole, but some method of fractionation of the tannin, if such analyses were ever to be of use in determination of the value of teas.

Dr. LAMPITT entirely agreed with Dr. Mann. It seemed to him a waste of time and money to determine the tannin when it bore no certain relationship to the quality and flavour of the tea. It was for the flavour that people took it. He could illustrate the importance of the tannin in tea. In Germany to-day there was a process (which he had fully investigated) whereby tannin could be taken from tea; and having taken it out, what had one left? Nothing, for it did not taste remotely like tea.

With regard to tannin in tea, he was perfectly certain that legitimate traders in tea did not want to be concerned in any way with the alleged tannin question. Mr. Bagnall's paper showed quite definitely that there was a number of firms who were stimulating sales of tea by pandering to the few. He was glad to hear Dr. Roche Lynch say that in no case of a post-mortem examination of tea-drinkers had he found anything abnormal attributable to the drinking of tea. That was one of the most important statements that had been made.

Dr. HUGHES stated that they had carried out a few tests on the application of Mitchell's colorimetric method to the determination of tannin in tea infusions. In order to obtain a result for the tannin equal to that given by the cinchonine precipitate method it was found that the pyrogallol equivalent, as determined colorimetrically, should be multiplied, not by the factor 2, but by a factor of about 1·5 for green tea, 2·1 to 2·2 for non-China tea, and 2·4 to 2·5 for China tea. This indicated that the fermentation of tea-tannin affected the colour equivalent in this method in the same way as the permanganate absorption in the Löwenthal method, the cinchonine precipitate remaining much the same. The gallic acid figures obtained were 1·25 per cent. for green tea, 1·3 per cent. for non-China black tea, and 0·9 per cent. for China tea. In estimating the gallic acid in the filtrate from the cinchonine precipitate it was found necessary to precipitate the cinchonine with the requisite amount of sodium carbonate (without excess).

Dr. Hughes also drew attention to the question of the ratio of caffeine to tannin in tea. Harler has pointed out that there was no constant ratio, and that it might vary from 1:3 to 1:12 according to the strength of the infusion, and they had found this to be so, the ratios varying, even for unblended teas, from 1:1·7 to 1:4·5, and also varying with the time of the infusion.

Further Experiments with Phenosafranine, Tartrazine and Rose Bengal as Adsorption Indicators

By A. J. BERRY, M.A.

It is interesting to review the modifications that have been introduced into the original volumetric process for the reciprocal determination of halogens and silver devised by Gay Lussac just over one hundred years ago. Various refinements, chiefly due to Stas, have resulted in the method becoming one of the most accurate known to chemists. Rapidity of working, at the expense of a certain degree of accuracy, was realised by Mohr by employing potassium chromate as an indicator for titrating chlorides in neutral solution. Mohr's method was followed by Volhard's well-known thiocyanate method for determining silver in acid solution. In more recent years argentometric methods have been further improved by the use of adsorption indicators due to Fajans. It is no exaggeration to claim that the introduction of adsorption indicators is the most important advance which has been made in this branch of analysis since the time of Mohr and of Volhard, and the value of these indicators may be judged by their rapidly increasing use. Recently Fajans has published a most interesting monograph on this subject, entitled "Adsorptionsindikatoren für Fallungstitrationen," in which the theory and practical applications of the subject are discussed in detail, together with a useful index of the literature.[1] In the present paper some new experiments are described which amplify results already published,[2,3] and also illustrate the use of these indicators in various types of volumetric determinations which are commonly effected by other methods.

Two of the indicators, namely, phenosafranine and tartrazine, give satisfactory results for the titration in nitric acid solution up to an acid concentration of about normal. It is therefore possible to employ either indicator in conjunction with potassium bromide as the titrant for any determination which would otherwise be effected by Volhard's method. The analysis of arsenates in approximately $N/10$ concentration and of silver in Levol's alloy in solutions of $N/100$ concentration may be quoted by way of illustration. The third indicator, Rose Bengal, was found by Fajans and Wolff[4] to be useful in the determination of iodide in presence of chloride by titration with silver nitrate, but its use is restricted to neutral or very feebly acid solutions. The use of these indicators in the analysis of mixtures of cyanides, chlorides, and iodides is illustrated. Finally, a method for determining halogens in electrolytes of limited ionisation involving the use of tartrazine is described.

In carrying out titrations in which adsorption indicators are used for determining the end-point, it is always desirable to adjust conditions to facilitate flocculation of the silver halide from the colloidal condition. As has been noted previously,[3] flocculation may be effected by adding a bivalent electrolyte, such as strontium nitrate. In the absence of substances which give rise to complications

this should always be done. When, however, such a proceeding would involve the production of a sparingly soluble precipitate, it should be avoided. No precipitate, other than the silver halide, should be present when an adsorption indicator is used. For this reason, in one of the methods described below for the analysis of mixtures of cyanide, chloride and iodide, as potassium bitartrate is used for eliminating the cyanide from solution, strontium nitrate must not be added, since it would involve the separation of strontium tartrate. In these and in other similar cases, flocculation must be effected by patient and sometimes prolonged shaking.

1. MIXTURES OF CYANIDE, CHLORIDE AND IODIDE.—In the titration of potassium cyanide in such mixtures with silver nitrate, the end-point of the reaction corresponding with the complete production of potassium argenticyanide can be seen perfectly well at the slightest appearance of permanent opalescence, particularly if a black surface is placed under the titration vessel; and, so far as my experiments are concerned, there is no advantage in having an adsorption indicator present. Even at so low a concentration as $N/50$, accurate end-points are obtained without difficulty. If, however, the further titration is attempted in presence of such an indicator, the silver cyanide adsorbs the dyestuff with gradual change of colour before the end-point is reached. It was found to be absolutely essential to eliminate the cyanide before proceeding to the determination of the halide with the aid of an adsorption indicator in the analysis of mixtures. Special experiments with mixtures of potassium cyanide and potassium bromide (approximately $N/10$) showed that the two constituents could be determined with accuracy by first titrating the cyanide with silver nitrate directly, then taking a measured volume of the original solution, eliminating the cyanide by boiling with a small quantity of nitric acid, and titrating the bromide with silver nitrate, with phenosafranine as indicator. Alternatively, after determination of the cyanide, a known excess of silver nitrate and a little nitric acid are added, the silver cyanide and bromide are removed, and the silver remaining in solution is titrated with a solution of potassium bromide, either phenosafranine or tartrazine being used as indicator. Complete agreement was realised between the two methods, and satisfactory results were obtained at a concentration of $N/50$.

Fajans and Wolff[4] have shown that it is possible to determine a chloride and an iodide together in the same solution by titration with silver nitrate, with the use of two different adsorption indicators, the success of the method depending partly upon differences in adsorbing capacity of the two anions and partly upon the relative degrees of insolubility of the two silver halides. In the presence of various halogenated fluoresceins, such as Rose Bengal (dichloro-tetraiodofluorescein), a marked colour change takes place when silver iodide is precipitated completely, and the chloride remaining in solution can be determined by titration with silver nitrate, with fluorescein as indicator.

Numerous experiments on various mixtures of chloride and iodide have verified the findings of Fajans and Wolff, so far as the accurate determination of the iodide with the aid of Rose Bengal is concerned. However, the titration of the chloride remaining in solution, with silver nitrate and fluorescein as indicator, was found to be altogether unreliable. Very satisfactory results were nevertheless

obtained by decanting the liquid through a filter, washing the precipitate with very dilute nitric acid, and titrating the filtrate with silver nitrate, with phenosafranine as indicator. Numerous experiments also showed that the colour-change with Rose Bengal coincides strictly with the quantitative precipitation of silver iodide, and without any co-precipitation of silver chloride. Moreover, it was found that, whilst Rose Bengal cannot be used in the presence of strong acids, this indicator gives excellent results in presence of very weak acids. In the analysis of cyanide-chloride-iodide mixtures, it was found convenient to effect elimination of the cyanide by boiling the solutions with a small quantity of potassium bitartrate for about a quarter of an hour. Iodide and chloride could then be determined in the resulting (cooled) liquid in the manner indicated.

Three separate titrations are thus required to determine the constituents of a cyanide-chloride-iodide mixture. First, a portion of the solution is titrated directly with silver nitrate, without an indicator, to the opalescent stage for determination of the cyanide. Secondly, a fresh quantity of the solution is boiled with a slight excess of potassium bitartrate to eliminate the cyanide, and the iodide and chloride are determined as described above. In the earlier experiments, the chloride was determined by difference as follows:—Excess of silver nitrate, followed by a little dilute nitric acid, was added to a fresh quantity of the solution, the mixed precipitate of silver halides and cyanide were removed by filtration, and the silver remaining in solution was titrated with a solution of potassium bromide, tartrazine being used as indicator.

The accuracy of these methods was verified by experiments on a large number of solutions containing the constituents in varying proportions. In the first place, some titrations of a mixture of potassium cyanide and bromide (approximately $N/10$) may be quoted to illustrate the agreement between the titration values for the potassium bromide (i) after removing the cyanide by boiling with a little normal nitric acid, and (ii) by adding excess of silver nitrate, removing the silver cyanide and bromide, and titrating back with potassium bromide.

	Volume of silver nitrate required for visible opalescence	Volume of silver nitrate required after boiling out the hydrocyanic acid
(i)	14·7 ml.	31·8 ml. (indicator phenosafranine)
	Volume of silver nitrate required for visible opalescence	**Volume of silver nitrate calculated from the potassium bromide back-titration**
(ii)	14·7 ml.	31·8 ml. (indicator tartrazine)

When these solutions were diluted to one-fifth of their original concentrations the same titration values were obtained. Experiments on the same lines on various cyanide-chloride-iodide mixtures showed satisfactory agreement in the titration values both for the cyanide and for the iodide and chloride. One example may be quoted, in which the chloride was determined by the "difference" method, after determination of the cyanide and iodide, by back-titration with potassium bromide and tartrazine.

	For cyanide	For iodide	For chloride
Observed silver nitrate titrations ..	12·2 ml.	10·6 ml.	10·5 ml.*
Calculated ,, ,, ,, ..	12·2 ,,	10·6 ,,	10·45 ,,

* From back-titration with potassium bromide.

Two more examples may be quoted. In these the iodide was titrated in the usual way in presence of Rose Bengal, and the chloride was determined in the filtrate from the silver iodide in very dilute nitric acid solution, phenosafranine being used as indicator.

		For iodide	For chloride
(*a*)	Observed silver nitrate titrations	40·8 ml.	16·3 ml.
	Calculated ,, ,, ,, ...	40·7 ,,	16·45 ,,
(*b*)	Observed ,, ,, ,, ...	10·2 ,,	40·65 ,,
	Calculated ,, ,, ,, ...	10·2 ,,	40·5 ,,

2. Comparison of Results obtained in Determinations of Silver in Acid Solution by Volhard's Method and by Titration with Potassium Bromide with Phenosafranine or Tartrazine as Indicator.—The results showed most satisfactory agreement. For work at concentrations of about $N/10$ either adsorption indicator is equally useful, but at much greater dilution phenosafranine is preferable. By way of illustration, the following analyses of Levol's alloy* in $N/100$ concentration may be quoted:

Pure silver (0·4424 g.) was dissolved in nitric acid, and the solution was diluted to 500 ml. Of the alloy, 0·4736 g. was dissolved and the solution was diluted to 500 ml. Quantities of 50 ml. were taken for each titration.

	Volumes of potassium thiocyanate required	Volumes of potassium bromide, using phenosafranine as indicator, required
For the pure silver solution ..	39·7 ml.	40·95 ml.
For the alloy solution	30·35 ,,	31·2 ,,

The calculated percentages of silver in the alloy are 71·4 by Volhard's method and 71·2 by the adsorption indicator titration method.

The two methods were also compared in the well-known silver method for the determination of arsenates. Solutions of approximately $N/10$ concentration were used in these experiments. The silver arsenate was precipitated by adding an excess of silver nitrate, in presence of a little nitric acid and a large excess of sodium acetate, to measured volumes of a solution of sodium arsenate. The washed precipitates were dissolved in N nitric acid, and the solutions were titrated with potassium bromide with tartrazine as indicator, and by Volhard's method. The weights of silver found per 20 ml. of the solution of sodium arsenate were 0·330 g. by Volhard's method and 0·331 g. by the adsorption indicator method.

3. Titration of Halogens in Thallous-thallic Salts.—It has been shown that chlorine in thallic chloride cannot be determined by Volhard's method

* Levol's alloy, discovered in 1854 by Levol, is an alloy of silver (71·9 per cent.) and copper. The concentration $N/100$ refers, of course, to the concentration of silver in the solutions of alloy in nitric acid which were being titrated.

on account of the oxidising action of thallic ions on thiocyanate (Cushman,[5] Berry[6]). Further, as the thallic halides are weak electrolytes, their behaviour on titration with silver nitrate with the use of adsorption indicators is irregular (Berry[3]). It was found, however, that the method of reduction with zinc amalgam in presence of a little dilute sulphuric acid, applied to the determination of the total chlorine in chloropentammine cobaltic chloride, could be used for the determination of halogens in these compounds. A 2 per cent. zinc amalgam was used for the reductions, and the reduced solutions were run from the burette into a known quantity of a silver nitrate solution, tartrazine being used as indicator. Thus, 3·074 g. of thallous thallic chloride (thallium sesquichloride) was reduced and the solution was diluted to 200 ml. A solution of 0·3557 g. of silver in nitric acid required 36·8 ml. of the reduced solution, corresponding with a total weight of thallium sesquichloride of 3·073 g. Again, 1·768 g. of thallous thallic bromide (thallium dibromide) was reduced, and the solution diluted to 200 ml. Twenty ml. of silver nitrate (16·7 g. per l.) required 40·2 ml. of the reduced solution, corresponding with a total weight of thallium dibromide of 1·760 g.

SUMMARY.—1. A method for determining the constituents of mixtures of cyanides, iodides, and chlorides is described. Since silver bromide is intermediate between silver chloride and iodide in solubility and adsorptive capacity for dyestuffs, the method is not applicable to the determination of bromides in presence of the other halides.

2. The titration of silver in acid solution with potassium bromide with the use of adsorption indicators yields results which compare satisfactorily with those obtained by Volhard's method.

3. A method for using adsorption indicators in the titration of halides of limited or reversible ionisation, such as the thallous-thallic halides, is described.

Rose Bengal gives very satisfactory results in the titration of iodides in neutral or very weakly acid solution. Tartrazine and phenosafranine are well suited for the titration of silver in nitric acid solution up to an acid concentration of about normal. Phenosafranine is somewhat more restricted in its applicability than tartrazine, but is preferable for work at extreme (N/100) dilution.

REFERENCES

1. K. Fajans, *Die Chemische Analyse*, Bd. **33**, pp. 161–207.
2. A. J. Berry and P. J. Durrant, ANALYST, 1930, **55**, 613.
3. —— *Id.*, 1932, **57**, 511.
4. K. Fajans and H. Wolff, *Z. anorg. Chem.*, 1924, **137**, 233.
5. A. S. Cushman, *Amer. Chem. J.*, 1901, **26**, 508.
6. A. J. Berry, *Proc. Camb. Phil. Soc.*, **22**, 367.

CHEMICAL LABORATORY
UNIVERSITY OF CAMBRIDGE

Some Properties of Sodium Hexametaphosphate

By R. T. THOMSON, F.I.C.

(*Read at the Meeting of the Scottish Section, November* 13, 1935)

Sodium hexametaphosphate is prepared by heating sodium metaphosphate ($NaPO_3$) or acid sodium pyrophosphate ($H_2Na_2P_2O_7$) to 700° C., but at lower temperatures intermediate compounds, such as the trimetaphosphate, are produced. It is known that sodium hexametaphosphate has a definite solvent action on certain calcium and magnesium compounds, such, for example, as those in boiler incrustations. Thus:

$$Na_6P_6O_{18} + CaSO_4 = CaNa_4P_6O_{18} + Na_2SO_4.$$

This means that 100 g. of sodium hexametaphosphate will dissolve 22·2 g. of calcium sulphate, and that represents the limit of solvent action. Similarly, one atom of the metal in calcium or magnesium carbonate will replace 2 atoms of sodium in $Na_6P_6O_{18}$, and 100 g. of that substance will dissolve 16·3 g. of calcium carbonate, or 13·7 g. of magnesium carbonate.*

The total phosphoric anhydride in sodium hexametaphosphate was determined by boiling 1 g., in aqueous solution, with hydrochloric acid in order to covert the meta- into ortho-phosphate, and then precipitating with magnesia mixture in the usual way. It was also determined volumetrically in quantities of 1 to 3 g., hydrochloric acid being added, the solution evaporated to dryness to expel excess of acid, and the residue dissolved in water and made exactly neutral to methyl orange by addition of a suitable solution of sodium hydroxide. The acidity was determined with $N/2$ sodium hydroxide solution (1 ml. = 0·0355 g. P_2O_5), with phenolphthalein as indicator, after addition of the requisite quantity of sodium chloride. The results were 99·98 per cent. of $Na_6P_6O_{18}$ by the volumetric, and 99·47 per cent. by the gravimetric method. The latter figure is undoubtedly nearer the truth, as although no impurities, such as sulphates or chlorides were present, the material lost 0·8 per cent. on ignition.

A number of tests were then made on the effect of sodium hexametaphosphate on various metallic compounds, and the results are recorded below.

Calcium Compounds.—Solutions of sodium pyrophosphate have no solvent action on calcium carbonate or calcium sulphate. If calcium chloride is precipitated with ammonium oxalate, the calcium oxalate is immediately dissolved on addition of the requisite quantity of hexametaphosphate solution. If trisodium phosphate is added to calcium chloride solution, the usual calcium phosphate precipitate produced is immediately dissolved on addition of hexametaphosphate.

* Messrs. Albright & Wilson manufacture, under the name of "Calgon," a patented product consisting of 90 per cent. of sodium hexametaphosphate and 10 per cent. of neutral sodium pyrophosphate, the object of the latter being to raise the pH value to about 7 in a 0·25 per cent. solution. The claims for Calgon include its capacity for dissolving boiler scale, dissolving calcium and magnesium soaps, softening hard waters without forming a precipitate, and holding calcium oxalate in solution. Analysis of a sample gave: $Na_6P_6O_{18}$, 88·2; $Na_4P_2O_7$, 11·0; loss on ignition, 0·6 per cent. There was no sulphate, chloride or carbonate present.

Strontium Compounds.—Strontium phosphate, sulphate, carbonate and oxalate behave similarly to the analogous calcium compounds.

Barium Compounds.—Barium chloride and sodium sulphate solutions, in proportions to form 376 mg. of barium sulphate, were added separately and gradually in the order stated, to a solution containing 1 g. of sodium hexametaphosphate. No opalescence or precipitate was formed after one hour; the solution was then acidified with hydrochloric acid and, after standing for 3 hours, it was still quite clear. After standing for 20 hours, the solution was distinctly opalescent, but no precipitate had deposited. When heated, the opalescence increased, and boiling for a few seconds produced a dense precipitate.

If the barium chloride and sodium sulphate are first mixed, the precipitate of barium sulphate does not dissolve on addition of sodium hexametaphosphate. Also, a barium sulphate precipitate, dried at 100° C., was quite insoluble in hexametaphosphate solution, no trace having dissolved after 48 hours' digestion.

The dry sulphates, when treated with hexametaphosphate solution, behave as would be expected from the known properties of the three metals, *i.e.* calcium sulphate is easily soluble, strontium sulphate difficultly soluble, and barium sulphate quite insoluble when treated under the same conditions. Barium phosphate and oxalate behave similarly to the analogous calcium compounds.

Barium chloride and potassium chromate solutions, in proportions to form 340 mg. of barium chromate, were added separately to a solution containing 1 g. of hexametaphosphate, but no precipitate was formed. If the barium chloride and potassium chromate are mixed, the barium chromate precipitate does not dissolve on addition of sodium hexametaphosphate.

Magnesium Compounds.—A quantity (130 mg.) of $Mg_3(PO_4)_2$, prepared by adding an equivalent quantity of trisodium phosphate to a solution containing the requisite quantity of magnesium chloride, gave a precipitate which dissolved on addition of hexametaphosphate. Addition of excess of sodium phosphate did not produce a precipitate, but when ammonia was added, the magnesia was nearly all precipitated, about 3 mg. remaining in solution.

Magnesium carbonate behaved in the same way as calcium carbonate.

Ferrous Carbonate and Ferrous Hydroxide.—These compounds were held in solution when ferrous sulphate was used with sodium carbonate and sodium hydroxide, respectively, as precipitants. With each the solution became of a dark green colour, increasing gradually in intensity as the alkali was slowly added.

Reference has been made to the theory that one atom of a dibasic metal, such as barium, replaces 2 atoms of sodium in $Na_6P_6O_{18}$, at which stage the otherwise insoluble compound may, for practical purposes, though perhaps not with strict accuracy, be said to be held in solution. Experiment showed that no more of the compounds so far dealt with could be held in solution, and the results practically agree with the theory.

Ferric Oxide.—Iron alum and sodium hydroxide were used in this test, the ferric oxide being held in solution to the extent of 253 mg. The solution had a dark brown colour, and from it ferric hydroxide was precipitated on addition of ammonia. In another test the $Fe_2(OH)_6$ was previously precipitated, and then only 7 mg. of ferric oxide were dissolved by digestion with 1 g. of $Na_6P_6O_{18}$.

Somewhat contrary to expectation, two atoms of ferric iron were absorbed by $Na_6P_6O_{18}$, and it is rather difficult to explain this by any hypothesis that would seem reasonable.

Alumina.—A test, similar to that with ferric oxide, was made with potassium alum and sodium hydroxide, and here, also, 2 atoms of the tribasic metal were taken up by the $Na_6P_6O_{18}$. If aluminium hydroxide is previously precipitated and digested with 1 g. of $Na_6P_6O_{18}$, only 10 mg. of aluminia go into solution.

Zinc Carbonate.—Zinc chloride and sodium carbonate were used in this test, and only one half, approximately, of the compound was held in solution, so that this dibasic metal does not conform to the theory just mentioned.

Lead Carbonate and Chromate.—Lead acetate and sodium carbonate were the reagents used; only 139 mg. of lead carbonate was held in solution, whereas theory for dibasic lead requires 436 mg. Of white lead digested with a solution containing 1 g. of $Na_6P_6O_{18}$, only 134 mg. of lead carbonate were dissolved.

In experiments with lead chromate, in which lead acetate and potassium chromate were used as reagents, only half, approximately, of the theoretical quantity remained in solution. In these cases also there is divergence from the theory.

Portland Cement.—English Portland cement was digested with an aqueous solution containing 1½ times as much sodium hexametaphosphate as would theoretically dissolve all the lime and magnesia in the cement. During frequent shaking for 30 to 40 minutes the cement became gradually disintegrated, and then, suddenly, what appeared to be silicic acid was thrown out of solution, and settled quickly on standing. The mixture was allowed to digest for about 20 hours, and then filtered, the insoluble residue was washed with cold water, and certain constituents were determined in the filtrate and in the insoluble matter. The results were as follows:

	Soluble Per Cent.	Insoluble Per Cent.	Total Per Cent.
CaO	58·41	6·36	64·77
MgO	0·20	0·74	0·94
SiO_2	10·85	11·60	22·45
Al_2O_3	None	4·15	4·15
Fe_2O_3	None	1·60	1·60

Iron Portland cement, treated exactly as described above, behaved in the same way as the English article, except that on dissolving the insoluble matter, hydrogen sulphide was given off, which was due to part at least of the sulphur (1·14 per cent.) existing as sulphide. The results were as follows:

	Soluble Per Cent.	Insoluble Per Cent.	Total Per Cent.
CaO	36·96	21·17	58·13
MgO	0·71	1·40	2·11
SiO_2	4·35	19·25	23·60
Al_2O_3	None	9·14	9·14
Fe_2O_3	None	2·60	2·60

There is a striking difference in the solubility of lime, magnesia and silica shown by the two types of cement, and it might be possible to deduce some information as to the cause.

In the following table are collected the results of the more important tests described in the text. The figures given represent the number of grams of each substance held in solution by 100 g. of the $Na_6P_6O_{18}$ used, and side by side are stated the quantities that might be expected, theoretically, to be dissolved by the absolutely pure salt. Substances marked with an asterisk were tested by direct action of a solution of sodium hexametaphosphate on the dry compound in powder form.

	Theoretical	Found
Barium sulphate	38·13	37·6
Barium carbonate ..	32·24	31·8
Barium oxalate	36·82	36·5
Barium chromate ..	41·39	40·8
Barium phosphate ..	32·73	32·4
Strontium sulphate ..	30·01	29·6
*Calcium sulphate	22·24	22·1
*Calcium carbonate ..	16·35	16·2
*Magnesium carbonate ..	13·77	13·5
Iron carbonate	18·92	18·4
Zinc carbonate	20·48	10·1
Lead carbonate	43·65	13·9
Lead chromate	52·80	26·0
Ferric oxide	—	25·3
Alumina	—	16·4

156 BATH STREET
GLASGOW, C.2

The Sulphuric Acid Test for Liquid Paraffin

BY C. EDWARD SAGE, F.I.C., A.M.I.CHEM.E., AND
SIDNEY G. E. STEVENS, B.Sc., A.I.C.

(*Read at the Meeting, April* 1, 1936)

THE preparation of medicinal liquid paraffin from certain selected distillates necessitates the treatment of the suitable fractions with "oleum," and subsequently with sulphuric acid, and finally washing the oil and filtering.

Not every crude paraffin will yield a suitable finished product, but by careful selection of raw material paraffin can be supplied to many specifications, and the requirements enumerated in the British Pharmacopoeia under "Tests for Purity" are not difficult of attainment.

Medical opinion has decreed that paraffin with a minimum Redwood viscosity of 260 seconds at 100° F. may be used, but most of the higher priced paraffins are more viscous, and about 300 seconds is the more usual figure met with; the facts recorded below relate to such oils.

As a measure of a suitable state of refinement, a test given in the Pharmacopoeia reads as follows:

"Place 3 millilitres with 3 millilitres of nitrogen-free sulphuric acid in a test-tube previously rinsed with the acid, and heat with frequent shaking in a

boiling water-bath for ten minutes: no colour deeper than pale brown is produced."

In the past most analysts would have assumed their ordinary supplies of pure sulphuric acid to be the suitable reagent, but the Appendix to the Pharmacopoeia specifies that such acid is to be of Reagent purity containing 96 per cent. w/w of H_2SO_4, and the question then arises what colour exactly is "pale brown," and it appears that neither buyer, seller, nor analyst can agree about this definition. Thus we are left with the personal factor to settle what is, or should be, the amount of refinement necessary to ensure that a given sample will satisfy the requirements of the B.P. tests.

In the discussion between the works and the laboratory it was soon made plain that only precise strength of acid would afford reasonable agreement, since sulphuric acid of sp.gr. 1·841 at 15·5° C. may be of either 99·5 or 94·5 per cent. strength, and variations in the results obtained have been already pointed out by Evers.[1]

The test in the B.P. 1914, in which acid of 98/99 per cent. strength is used, ensured a more refined product than that obtained with 96 per cent. acid, and one's conception of the meaning of "pale brown" has become altogether different from what it was years ago.

Hampshire and Page[2] have suggested a standard for the pale brown colour by comparing the coloured acid separated from a test with the standard glasses of a Lovibond tintometer, and the values they suggest for a B.P. oil are not more than 2·5 red and 6·5 yellow in a 1 cm. cell; it is with a view to criticising these figures that we communicate the following results of an investigation made recently.

To arrive at some better understanding of the significance of the acid test we have prepared acids of various strengths, and have carried out series of tests with the results recorded later.

It was felt that some standard technique should be adopted, and the method used was as follows:

"To 4 ml. of sulphuric acid were added 4 ml. of sample in a stoppered cylinder, and the tube shaken and placed in a boiling water-bath. At intervals of 30 seconds the tube was removed and shaken vigorously during 5 seconds. At the end of 10 minutes the tube was removed from the water-bath and the contents transferred to a small, dry, clean, separating funnel, and allowed to stand for 10 minutes. At the end of this period separation had taken place, and the acid layer was then run into a 1 cm. cell of the Lovibond instrument, and the colour matched in the usual manner."

INFLUENCE OF STRENGTH OF ACID AND TIME OF REACTION

Lovibond units	Strength of acid Per Cent.	Time of reaction in minutes									
		2	2½	4	5	7½	10	12½	15	20	25	30
Yellow ..	96	—	1·2	—	3·1	4·3	6·2	—	6·2	6·3	6·3	6·8
	97	—	2·3	—	4·1	6·4	9·6	11·0	16·2	20·1	24·1	28·0
	98	6·3	—	10·2	12·2	17·0	19·5	26·4	29·1	too dark		—
Red ..	96	—	0·5	—	1·1	1·4	2·0	—	2·1	2·7	3·0	4·1
	97	—	1·0	—	1·4	2·1	3·2	4·1	4·4	5·6	6·6	8·6
	98	2·2	—	3·5	3·8	5·4	7·3	9·9	9·9	too dark		—

The figures were then plotted on the following graphs:

Fig. 1. The increase in the yellow units against time of reaction.

Fig. 2. The increase in the red units against time of reaction.

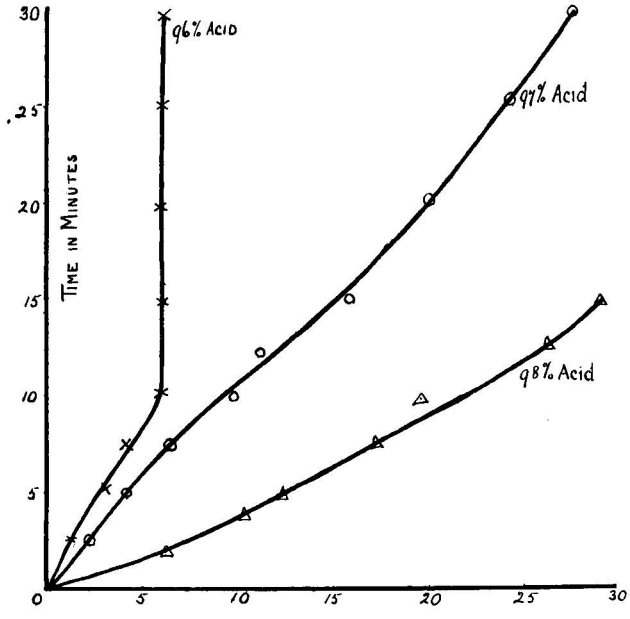


Fig. 1. Yellow Units (Lovibond)

From a study of the graphs we concluded that even after 10 minutes' reaction the 96 per cent. acid was not capable of indicating the amount of impurities present, since a slightly stronger acid yielded an increase in depth of colour with further increase in time, whereas the 96 per cent. acid showed scarcely any increase in tint.

Experience has convinced us that many of the samples which would have been rejected under the test of the old B.P., with the use of 98/99 per cent. acid, would have to be passed under the conditions of the present test, and thus an inferior product could be supplied to the public. This state of affairs is to be deprecated, since an increase in the amount of impurities sometimes results in an objectionable odour and taste developing after the paraffin has been stored for a short while.

The following results are those of a few typical samples submitted to us as conforming to the B.P. 1932:

Mark	Strength of acid	Yellow	Red
A	96 per cent.	4·7	1·8
B		4·1	1·8
C		3·1	1·4
D		1·7	1·1
E		6·2	2·0
A	97 per cent.	6·2	2·2
B		10·1	4·1
C		5·3	2·1
D		4·6	3·0
E		9·6	3·2

From the foregoing results we are of the opinion that a sulphuric acid of 97 per cent. w/w strength gives a more satisfactory indication of the completeness of refining than one of 96 per cent. strength. The reaction with the weaker acid seems to be delayed after ten minutes, whereas the 97 per cent. acid is progressive in reaction. For this reason we would prefer to stipulate a time limit for the test of ten minutes in a boiling water-bath, and a tintometer reading of not more than 10 yellow and 4 red when the 97 per cent. acid is employed.

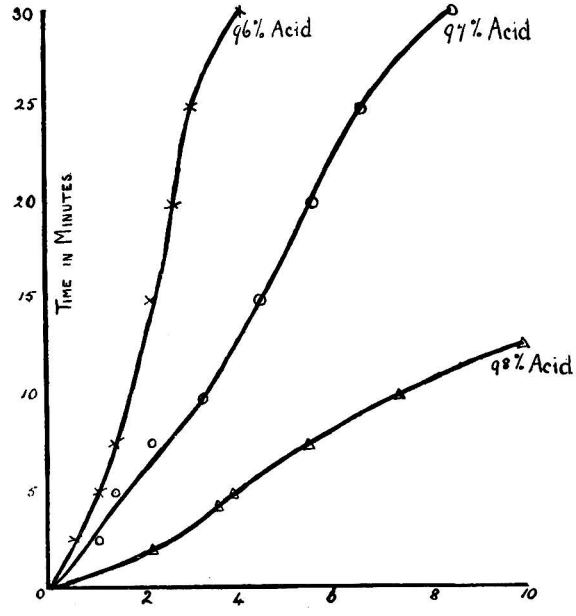


Fig. 2. Red Units (Lovibond)

ADDENDUM.—Since these notes were first submitted to the Society, early in December, 1935, the British Pharmacopoeia Commission has issued a report embodying the recommendations of several revision Committees, and for liquid paraffin it is suggested that the colour of the acid layer from the test be compared by means of the Lovibond tintometer, adopting a maximum standard of 6·5 yellow and 2·5 red, but using nitrogen-free sulphuric acid of only 96 per cent. strength. We hoped to have published our results before this recommendation was made, for the reasons already stated.

Further, the United States Pharmacopoeia, eleventh edition, has been printed, and will become official on June 1st next, and that requires a similar acid test, but with the use of sulphuric acid of 94·5 to 95·5 per cent. strength, which will not be so stringent as the one recommended by the B.P. Commission.

The U.S.P., however, have adopted a method of matching the colour, and employ mixed solutions of ferric chloride, cobaltous chloride, and cupric sulphate to make a standard by which to judge the sulphuric acid test results, but owing

to the use of a weaker acid the degree of refinement is considerably lower than the British one.

References

1. N. Evers, *Pharm. J.*, 1933, **133**, 195.
2. C. H. Hampshire and G. R. Page, *Quart. J. Pharm.*, 1934, **7**, 354; Abst., Analyst, 1934, **59**, 635.

10 London Street, E.C.3

Discussion

The President said that this emphasised, once again, the necessity, when dealing with empirical tests, for standardising every detail of the procedure. So far as colorimetric estimations were concerned, he could, personally, endorse what Mr. Sage had said. He remembered that when his late colleague was alive, the reading of the colorimeter by his colleague was always a fraction higher than his own. This showed the difference introduced by the personal factor.

Mr. N. Evers remarked that the only satisfactory test for liquid paraffin was "taste," but as that could not be put in the Pharmacopoeia one had to use the sulphuric acid test. He agreed with Mr. Sage as to the effect of the strength of the acid, but when liquid paraffin which was absolutely satisfactory for medical purposes was tested with too strong an acid, too much colour was obtained. He thought that 96 per cent. sulphuric acid was the most satisfactory strength to use. He had tried a number of experiments on the use of the colour standard instead of the tintometer, but had found that different paraffins gave different shades of colour, so that it was difficult to match the colours; he had had to come back to the tintometer. The great difficulty was that the shade of colour largely depended on the violence of the shaking; there was a very great difference in results, according to whether the shaking was very violent or merely vigorous.

Dr. H. E. Cox remarked on the value of Mr. Sage's observations of the colours produced by sulphuric acid, but thought that the most important point really was to discover, if possible, what was the chemical nature of the impurities present, and possibly determine the quantity. Could Mr. Sage give any indication of the nature of the unsaturated hydrocarbons or other bodies which produced the colours?

Mr. A. L. Bacharach called attention to the difficulty that had been experienced in persuading the Pharmacopoeia Commission to refer in the 1932 British Pharmacopoeia to a "tintometer" colour-standard. He drew attention to the analogous position that had arisen over the cod-liver oil blue test and to the procedure that had been adopted to meet the case.

Mr. A. E. Parkes asked for definite information about the method of shaking the sample; was there not considerable risk in shaking a mixture of paraffin and concentrated sulphuric acid which had been heated for ten minutes in a water-bath? The other point was the strength of sulphuric acid used. Different strengths would considerably modify the results. Every analyst who had done Gerber tests on milk would understand this; by altering the strength one could get a fat layer which was almost colourless, or one which was almost too dark to distinguish.

Mr. I. C. P. Smith said that, for removing unsaturated substances from hexane, pure sulphuric acid (96 per cent.) gave the best results when it was stirred very vigorously (much better than by shaking vigorously). The time of stirring was a very important factor; the colour would develop as long as unsaturated substances were there, even if one stirred for a week. A stronger acid often had the effect of oxidising saturated hydrocarbons, and producing colour when unsaturated bodies had been removed.

Mr. S. G. E. Stevens, replying, said that, by the method suggested, quite comparable results could be obtained, since the heat-penetration in the water-bath

was quite rapid, and that, after two minutes, the temperature had risen sufficiently high for the reaction with the unsaturated products to take place. With regard to the shaking, "vigorous" was the best description to apply to it (*i.e.* sufficient to effect thorough admixture). A slight personal factor would always have an influence in tintometer work. The use of standard colour solutions for the limit-test was unsatisfactory, since no two paraffins would give the same tint, although, for an empirical method, such a standard might perhaps be adopted. In an endeavour to determine the relative amounts of the unsaturated bodies present, experiments had been made with iodine and bromine in inert organic solvents, but without satisfactory results. To avoid further complications in the investigation, only nitrogen-free sulphuric acid had been used.

The Determination of Tin in Alloys with Antimony and Lead. (Antimony less than 2 per cent.)

By H. F. HOURIGAN, B.Sc., A.I.C.

It was found necessary some four or five years ago in this Laboratory to find a rapid volumetric method for the determination of tin in the presence of antimony and lead. The method of Brearley and Ibottson (reduction of a solution of tin, antimony and lead with a spiral of iron wire, and the titration of the solution with iodine without removal of suspended antimony) was found to be erratic in its results. Further investigation showed that the assumption on which the method (in presence of antimony) is based is incorrect. It might be true to say that, if antimony powder from a bottle be added to a cold acid stannic chloride solution no action will take place, but this is not true of a suspension of freshly-precipitated antimony, since the addition of stannic chloride to such a suspension in the cold has been observed in this laboratory to cause the disappearance of the antimony in less than one minute with shaking at normal temperature. Further experimental evidence confirming this statement will be given later.

The potassium iodate method of Andrews is erratic for the same reason. In both methods one must titrate rapidly to an end-point which does not persist. When the proportion of antimony present is small, compared with the amount of tin, and the titration is carried out with rapidity by an experienced operator the result is, of course, only slightly high, but with a less experienced and more leisurely operator and a high proportion of antimony, serious errors may creep in. It was also considered that the methods represented a compromise towards simplicity on the part of their originators. Indeed, for iodate titration, which has much to recommend it, the published method makes no reference whatsoever to antimony, and it is to be presumed that it was originally assumed that the suspended metal played no part in the reaction. It is, of course, the fact that, since stannic chloride is the end-product of both iodine and iodate titrations, both methods are equally at fault in that respect.

It is the modern practice to add antimony chloride at the time of solution of the alloy. This is reputed to help solution, but there seems little doubt that the main object is that the presence of much suspended antimony guarantees that all

the tin will be in the stannous form at the time of titration. This exchange of oxidation between stannic salt and metallic antimony is probably represented by

$$3SnCl_4 + 2Sb \rightarrow 3SnCl_2 + 2SbCl_3,$$

and it is evident that if any tin is reduced twice, the error would be greater in terms of tin than might, at first sight, be expected.

It will, however, be seen later that in the method to be described it is not only not permissible or necessary to have suspended antimony present, but that any dissolved antimony vitiates the result. (See note on Interference of Antimonious Salt.)

As regards the solution of the sample, it is generally accepted practice to oxidise the solution, thereby dissolving the antimony, lead, and tin, and then to reduce the solution with iron, aluminium, or zinc, in an atmosphere of carbon dioxide, thereby again precipitating the antimony. This procedure is not necessary if use is made of the self-reducing property of the alloy in passing into solution in concentrated hot hydrochloric acid in an inert atmosphere.

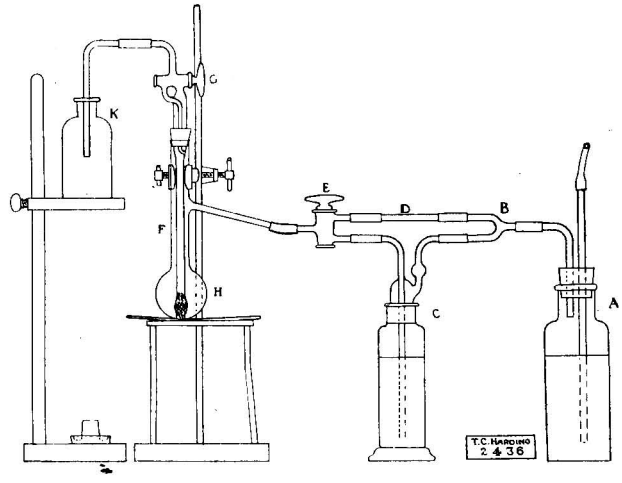


Fig. 1. Arrangement of Apparatus

It is improbable that any subsequent reduction will be as exact or perfect or less prone to complications than the first solution of the alloy, provided that all possibility of oxidation is rigorously excluded from the system.

It has been found, as the result of experience over several years, that under such conditions the tin is in solution completely in the stannous form, and that it is easy to detect when only suspended antimony remains undissolved. Even pure tin will dissolve in a reasonable time if the sample is fairly finely divided, while the time for solder of the 2 of lead to 1 of tin type is four minutes for a sample finer than 40-mesh. The use of this self-reduction method simplified the problem of dealing with the suspended antimony. Also, by the use of specially designed, but inexpensive, apparatus, it is possible to obtain the reduced tin solution free from suspended antimony in a matter of minutes.

The apparatus is shown in Fig. 1. Carbon dioxide is passed through a pyrogallol solution, A, and then through a three-way tube, B, which is connected with

a Drechsel bottle, C, and also with a short piece of glass tube, D. The other end of the tube and the other side of the Drechsel bottle are connected with a three-way glass tap, E, the single end of which is connected with the side-arm of a dry 100-ml. distillation flask, F. Passing through a bung in the neck of the latter is a specially designed (by-pass) filter-tube which was made for me. This special piece of apparatus is shown in more detail in Fig. 2. By means of the tap, G, just above the bung, the liquid in the flask can be forced up the tube through the filter-pad, H, of glass wool, asbestos and glass wool, and over into the 6-oz. stoppered bottle, K.

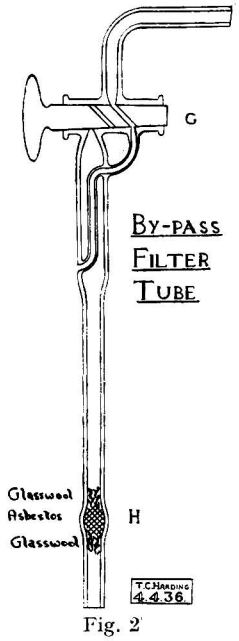


Fig. 2

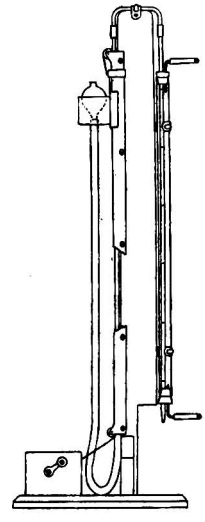


Fig. 3. Macro Burette (5 ml.)

A sample (0·1 g. of solder) is introduced into the distillation flask, and the Drechsel bottle is filled with conc. hydrochloric acid. With the three-way tap arranged to "by-pass" the Drechsel bottle, the whole apparatus is now swept out with carbon dioxide. After two minutes the control tap of the by-pass filter-tube and the one following the Drechsel bottle are turned over, and about 20 ml. of the acid are blown into the flask, the tap being again turned to restore the carbon dioxide through the by-pass tube of the Drechsel bottle. Gentle heat is applied, and the alloy is dissolved. The solution, with its suspended antimony, is boiled vigorously for three minutes, and then the tap at the top of the flask is turned, the solution being forced up the tube through the filter-pad, into the ground-glass stoppered bottle. Both taps are then turned, and about 10 ml. of acid are admitted to wash out the flask and then, in turn, blown over into the bottle. The washing is repeated, four times more, the bottle is then removed, and its stopper inserted, and the solution is ready for titration.

The solution is titrated with standard potassium iodate from a 5-ml. burette of a special type, reading accurately to 0·005 ml. (Fig. 3). The iodate is run in rapidly until a brown colour just persists in the solution, after which 1 ml. of

carbon tetrachloride is added, the stopper is inserted, and the bottle is shaken until the tetrachloride becomes purple. The titration is now continued to the point of complete disappearance of the purple tint in the carbon tetrachloride layer, vigorous shaking following the addition of each fresh portion of potassium iodate solution.

$$2SnCl_2 + KIO_3 + 6HCl \rightarrow 2SnCl_4 + KCl + ICl + 3H_2O.$$

It will be noticed that conc. hydrochloric acid only is used. This prevents the precipitation of lead chloride and also keeps the end-point sharp. The standard solution of potassium iodate (9·02 g. per l.) is made strong for the same reason, and a special burette was designed for the use of such a strong solution. The burette proper (Fig. 3) is a thick-walled glass tube with a bore of 0·01 cm., calibrated, in 0·01 ml., to 5·0 ml. The level of the solution is controlled by means of a mercury column adjusted in its turn by means of a reservoir and flexible connection (pressure tubing).

The apparatus described earlier has also been used for the determination of tin in the alloy (99 per cent. of Pb; 0·5 per cent. of Sn; 0·5 per cent. of Sb). A 0·2-g. sample was used, and the solution was titrated from a pneumatic burette of 0·2-ml. capacity calibrated to 0·001 ml. The end-point was sharp, but the time taken for the solution of the sample was much longer (30 minutes).

HIGH-ANTIMONY ALLOYS.—It is recognised that when the antimony-content is high (over 2 per cent.), it is necessary to oxidise into solution, and it is our practice under such conditions to reduce the oxidised solution with aluminium in the distilling flask and blow over and titrate in the normal manner. The aluminium must be completely dissolved and the solution boiled for one minute. The quantity of aluminium must also be such as to secure the complete precipitation of all the antimony present.

EXPERIMENTAL.—In order to test the reaction between a cold acid solution of stannic chloride and a freshly precipitated suspension of metallic antimony, the following experiments were made:

(1) A cold acid solution of stannic chloride was titrated with potassium iodate and gave no reaction.

(2) Metallic antimony (0·5 g.) was dissolved in conc. hydrochloric acid by means of potassium chlorate (bromine would upset the subsequent iodate titration) and made up to 250 ml. with 20 per cent. hydrochloric acid.

Twenty-five ml. of this solution were reduced with metallic aluminium (iron cannot be used with potassium iodate titration at the end), the aluminium being made to dissolve completely in the apparatus described earlier. The solution (after cooling) and subsequent washings were blown over into the bottle and titrated. No reaction was observed.

(3) In a further series 25-ml. portions of antimony were reduced with aluminium as in (2). Five ml. of a stannic chloride solution (fuming diluted 1 to 10) were added to the cold suspension and shaken with it for the time indicated. The results, although rough, show very little difference in the amount of stannous tin formed in five minutes and in three-quarters of a minute.

	Potassium iodate ml.
5 minutes	2·7
4 ,,	2·86
3 ,,	2·00
2 ,,	1·52
1 minute	2·63
0·75 ,,	2·37

To test the effect of temperature the solutions were cooled to 5° C. before mixing, left in contact for one minute, and then blown over. The results were:— One minute at 5° C.; 1·53 ml. of potassium iodate.

It is considered, therefore, that not only does cold stannic chloride react with a fresh suspension of antimony, but also that the velocity of the reaction is rapid—at all events too rapid to permit of accurate titration of stannous tin in presence of suspended antimony.

In view of the fact that antimonious salt is oxidised by iodate, it might be suggested that the results described depended, in the main, on some antimonious chloride being in solution. There is no doubt that some of the iodate was used up by antimony, since antimonious chloride is one of the products of the reaction between stannic chloride and metallic antimony.

Some experiments were carried through, the final titration being made with *N*/10 iodine solution, and the following results were obtained :—

1 minute at 9° C.	5·41 ml.
,, ,, ,, 1·5° C.	2·91 ,,

The experiments described offer a partial explanation of the apparent impossibility in the older methods of expressing the equivalence of the solution in terms of tin and in terms of other standardising reagents. It is an understood thing that the iodine or iodate solutions should be standardised against pure tin. It is, moreover, regarded as essential that the conditions with regard to additions of antimony solution, oxidising agent and reducing metal should also be standardised. And thus it seems impossible to give a formula for the reaction.

While it is desirable in most cases that a standard solution should be standardised against the substance to be determined, any such inability to establish even an approximate theoretical relationship must leave the method under suspicion, and this probably explains why some of the more responsible analytical authorities ignore methods, one of which at least has been in existence since the end of the last century. On the other hand, the method now put forward gives results closely approximating to the theoretical, as the following results show.

Weight of tin g.	Volume of potassium iodates ml.
0·05	5·03
0·05	5·03
0·05	4·995
0·05	5·035
0·05	5·02
0·05	5·00

The persistence of the theoretical relation for varying amounts of tin is shown by the following results:

Weight of tin g.	Volume of potassium iodate solution ml.
0·02	1·985, 2·005
0·04	3·985, 4·03
0·06	6·000, 5·995
0·08	7·985, 8·06
0·10	10·02, 10·08

INTERFERENCE OF ANTIMONY CHLORIDE.—The following table shows the erratic results due to the presence of antimonious salt in solution.

Samples of tin were dissolved in the apparatus, and a solution containing 0·01 g. of antimony in the antimonious state was added to each solution in the titration bottle. The results obtained were:

Weight of tin g.		Potassium iodate ml.
0·05	=	5·95
0·05	=	5·55
0·05	=	5·65
0·05	=	5·97
0·05	=	5·96
0·05	=	5·66

It is suggested that the variation is due to the tin being preferentially oxidised, followed by the oxidation of the free iodine and antimony indiscriminately in the final stage of the reaction.

It is of interest to record that the statement that stannic acid has no action on suspended antimony in the cold has appeared without challenge in all editions of Sutton's *Volumetric Analysis* since 1904.

My thanks are due to Dr. J. C. Duff, of Birmingham Technical College, for advice in the preparation of this paper, and to the Engineer-in-Chief, G.P.O., for permission to publish it.

POST OFFICE ENGINEERING DEPARTMENT
TEST SECTION
FORDROUGH LANE, BIRMINGHAM, 9

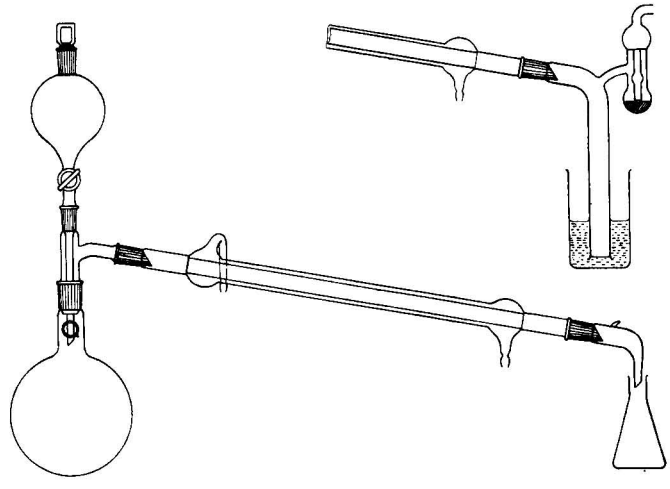
Notes

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

AN ASSEMBLY OF APPARATUS WITH GROUND-GLASS JOINTS

I HAVE found that assemblies of apparatus with standard ground-glass joints throughout are of inestimable value for many operations in the analysis of foods and drugs.

The assembly shown in the sketch has been used for the distillation of ammonia in water analysis with the plain receiver adapter. With the mercury-seal adapter the same apparatus has been used successfully for the destruction of quantities up to 100 g. of foodstuffs in the determination of metals.



With the end of the mercury-seal adapter immersed in 20 per cent. caustic soda solution, I have been able to oxidise with sulphuric and nitric acids very rapidly in the open laboratory without any discomfort from fumes.

The mercury-seal adapter was originally designed and used in the laboratories of The British Drug Houses, Limited, who have kindly permitted Quickfit & Quartz, Limited, to supply me with it. It overcomes the tendency, in the oxidation with nitric acid, for the absorption liquor to be sucked back through the condenser. This trap, on the liquor rising in the adapter to a small limit, allows air to flow into the apparatus, but holds a pressure up to an inch of mercury against the flow of gases which are being absorbed. The trap may be connected by its top tube with a reservoir of inert gas.

HERMAN LEE

81 WHITCHURCH GARDENS
EDGWARE

THE GRAVIMETRIC DETERMINATION OF SULPHUR IN SOME PHARMACEUTICAL PREPARATIONS

(*Read at the Meeting of the North of England Section, February* 1, 1936)

ALTHOUGH volumetric methods[1,2] have been described for the determination of sulphur in certain B.P. articles, it is advisable, for purposes of official testing, to check results by a reliable gravimetric method.

It was shown by Henville[3] that the method of determining sulphur in ointment, by weighing the residue insoluble in petroleum spirit, is unsound.

Fleck and Ward[4] pointed out that the gravimetric method of Evers and Elsdon,[5] as described, gives high results. I have found that this method gives correct results if the well-known precaution is taken of removing nitric acid by evaporation before precipitation of barium sulphate. Incidentally, I found that the amount of bromine may safely be reduced from 3 ml. to 1 ml., since the basis has now a much smaller bromine-absorption than the lard basis of the 1914 B.P.

A NEW GRAVIMETRIC METHOD, AS APPLIED TO SULPHUR OINTMENT.—The following somewhat quicker method has been tested and found to be satisfactory. The principle is the same as that of Petersen.[6]

About 0·5 g. of the sample is weighed accurately in a 50-ml. conical flask of "resistant" glass. Two ml. of 20 per cent. w/v caustic soda solution are added, and the flask is heated on a small hole of the water-bath. (The contents of the flask should not be boiled over a flame, as this causes some of the sulphur to coalesce into small aggregates which do not readily dissolve.) From time to time the flask is gently rotated so as to bring down any particles of sulphur from the sides, which, if necessary, may be finally rinsed by a small quantity of hot water from a fine jet. After 30 minutes to an hour the sulphur dissolves entirely, and both oily and aqueous layers are quite clear (the latter being yellow in colour). Five ml. of "20 vol." hydrogen peroxide are added, and the flask is heated, as before, for a further 15 minutes (a small funnel being placed in the neck of the flask to prevent loss by effervescence). About 20 ml. of hot water are added, and the contents of the flask are cautiously acidified with dilute (1:3) hydrochloric acid, care being taken to avoid a large excess (about 4 to 5 ml. required). The contents of the flask are filtered hot through a wet filter-paper into a beaker, the flask being thoroughly washed with several quantities of hot water (poured through the same filter). To the filtrate and washings (having a total bulk of about 60 to 70 ml.) barium chloride is added, and sulphate is determined in the usual way. A blank test is made on the reagents (the chief contributor to the results obtained is the hydrogen peroxide, which is commonly preserved with a little sulphuric acid).

Tested on a specimen of Sulphur Ointment B.P. 1932 (carefully prepared in this laboratory, in such a way as to prevent losses and to insure very complete mixing, from tested and dried B.P. materials) this method gave the following results:

Ointment taken g.	Barium sulphate g.	Equivalent to sulphur (after correction) for the blank) g.	Sulphur found (present 10·0 per cent.) Per Cent.
0·5022	0·3630 (blanks=0·0024, 0·0024)	0·0495	9·85
0·5304	0·3872	0·0528	9·96
0·5184	0·3786	0·0516	9·96
0·5068	0·3684	0·0502	9·91

APPLICATION TO OTHER PREPARATIONS OF SULPHUR.—The same method is applicable without modification to compound liquorice powder. It is advisable

to moisten the powder (after being weighed into the small flask) with 1 ml. of water, which is allowed to soak in so that no dry lumps are left. The vegetable constituents produce a very dark liquid with caustic soda, so that the yellow particles of sulphur can be seen clearly. When sulphur can no longer be seen the flask is warmed for a further 30 minutes on the water-bath, and the process is completed exactly as described above.

A specimen of compound liquorice powder made up in the laboratory (the same batch of sublimed sulphur as before being used) gave the following results:

The constituents other than sulphur were found to yield very little sulphate by this process.

Amount taken g.	Barium sulphate g.	Equivalent to sulphur (after correction for the blank) g.	Sulphur found (present 8·0 per cent.) Per Cent.
0·5210	0·3028 (blank=0·0024)	0·0412	7·92
0·5120	0·3002	0·0408	7·97
0·5068	0·2976	0·0405	7·99
0·5106	0·2998	0·0408	7·98
Constituents other than sulphur, corresponding to 0·5 g. of sample:			
	0·0046 (blank=0·0024)	0·00030	0·06
	0·0044	0·00027	0·05

These amounts were not deducted from the four preceding results.

The method is directly applicable to confection of sulphur (of which about 0·1 g. is taken) and to sulphur lozenge (B.P. 1914) (about 0·15 g. previously reduced to powder being used).

A. N. LEATHER

REFERENCES

1. N. L. Allport, *Quart. J. Pharm.*, 1933, **6**, 431; Abst., ANALYST, 1933, **58**, 705.
2. H. R. Fleck and A. M. Ward, *Quart. J. Pharm.*, 1934, **7**, 179; Abst., ANALYST, **1934, 59**, 636.
3. D. Henville, ANALYST, 1930, **55**, 385.
4. H. R. Fleck and A. M. Ward, *id.*, 1936, **61**, 28.
5. N. Evers and G. D. Elsdon, *id.*, 1922, **47**, 199.
6. J. Petersen, *Chem.-Ztg. Rep.*, 1902, 355; Abst., ANALYST, 1903, **28**, 86.

CITY ANALYST'S DEPARTMENT
PUBLIC HEALTH LABORATORY
MANCHESTER

TEST FOR BANANA SAP IN MILK

IT was suspected that milk supplied to a hospital was being adulterated with banana sap (ANALYST, 1936, 117), and the following test was found to be the most satisfactory method of detecting the addition.

One ml. of concentrated hydrochloric acid is added to 4 to 5 ml. of the sample to be tested, and the tube is placed in boiling water for about five minutes. If banana sap is present, the white curd, which normally separates, is coloured pink, the depth of the colour depending on the proportion of banana sap in the sample, but the colour is quite distinct with as little as 0·1 per cent. of sap, and is unaffected by the presence of such other adulterants as formaldehyde, borax or sucrose. So far only one case of such adulteration has been detected.

J. A. R. STOYLE

GOVERNMENT LABORATORY
LE REDUIT, MAURITIUS

THE MACKEY CLOTH OIL TESTER—SUGGESTED TECHNIQUE

THE Mackey apparatus for the testing of cloth oils has received criticism in many quarters on the ground that different laboratories obtain widely different results upon the same oil. As an example, an olive oil which we found to reach a temperature of 500° F. in 125 minutes, was found in other hands to reach 252° F. in 300 minutes. The following modification of Mackey's technique has proved to give consistent results and to differentiate between olive oils of different oxidisability in a satisfactory manner:

Fourteen g. of the oil to be tested, and 7 g. of medicinal cotton-wool are separately weighed. The cotton is teaseled, a little at a time, between two hand "cards." These cards are made from wire filleting of the kind known to the textile industry as "card clothing," and the wire surface measures $2\frac{5}{8}$ in. by 7 in. New cards should be cleaned with a good olive oil before they are used for the first time. As the cotton is added to the cards oil is poured on in small quantities, a little being added after each addition of cotton, until the required amounts of oil and cotton have been used.

The saturated cotton is transferred entirely to one of the cards, and is then stripped on to a glass plate, where it is thoroughly mixed by the tips of finger and thumb.

During the impregnation of the cotton-wool, the Mackey apparatus has been prepared by keeping the water-jacket boiling, the lid of the apparatus, containing the thermometer as a permanent fixture (set in the thermometer opening with a little rubber solution) being in position. The thermometer supplied with the instrument, which reads only to 400° F., is replaced by one reading to 600° F. This is set in the lid with the bottom of the bulb $2\frac{3}{16}$ in. below the inside of the lid, the 200° F. mark being then just visible outside the lid.

The saturated cotton is pressed lightly into one of the wire cages, a glass rod being held down the centre during the packing process, to prepare a place for the thermometer. A small wad of cotton-wool is placed at the bottom of the cage as a base, before the glass rod is put into position. The glass rod is withdrawn, the cage is placed in position in the apparatus, and the lid is fitted, care being taken that the thermometer-stem slides exactly into the hole left by the rod.

The water in the jacket is boiled vigorously; it is advisable to stand the apparatus at the edge of the sink and to allow the water to boil over into the sink. Boiling water is added at short intervals, thus ensuring that the jacket is kept full to the top, and the water therein kept vigorously boiling. The thermometer is read at intervals of 15 minutes, until about 240° F. has been reached, and at intervals of 5 minutes afterwards.

After use, the cards and cage and the inside of the lid are well washed in methylated spirit and dried in a warm, but not hot, stove before being used again. No attempt is made to remove carbon from the wire cage after each test, but periodically the cage is cleaned in a Bunsen flame. The methylated spirit removes traces of vegetable oils and has no action upon the rubber bedding of the wires forming the "cards." The amount of iron present in the cotton-wool plays a very important part in the results obtained; we have recently compared two cotton-wools containing, respectively, 0·0003 and 0·0007 per cent. of iron, and found a difference of an hour between the times taken by the same oil to reach 400° F. It is therefore necessary to standardise each fresh batch of cotton-wool upon a sample of olive oil.

The essential points are: first and most important, the thorough and even distribution of the oil over the cotton-wool. In our experience this is impossible, using the fingers, as suggested by Mackey, and some form of "card" is essential. Astonishingly divergent results can be obtained unless attention is given to this point. Secondly, the water-jacket must be kept full, and boiling.

It was not found necessary to have an artificially induced air-supply of constant volume per minute, as suggested by Archbutt (*J. Soc. Chem. Ind.*, 1899, 347), and, provided the air-tubes of the apparatus are kept clean, no difficulty should be experienced. Water vapour entering with the air has no disturbing effect, nor has the presence of traces of water in the olive oil.

W. GARNER
W. LEACH

LISTER & CO. LTD.
MANNINGHAM MILLS
BRADFORD

Trinidad and Tobago

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1935

IN his Annual Report the Government Analyst (Mr. H. S. Shrewsbury, F.I.C.) states that 4458 samples and exhibits were examined, being an increase of 227 over the previous year's work. The total number of food and drug samples was 1374, of which 75 were adulterated.

SPIRIT ADULTERATION.—Samples are no longer taken under the Food and Drugs Ordinance, but under a Customs and Excise Ordinance (Sec. 30, Sub-sec. 8 of Ordinance 31 of 1933). This is a decided check on spirit adulteration. It is no longer possible for counsel to raise the quibble that the spirit was not sold to the disadvantage of the purchaser because the said purchaser had already made a rough preliminary test with his hydrometer, and suspected the liquor to be adulterated, and was therefore not prejudiced. Moreover, the penalties are reasonably severe under the Ordinance, whereas the usual penalty inflicted for food adulteration is inadequate to protect the public.

COFFEE ADULTERATION.—There was much less coffee adulteration in 1935 than in 1934, so far as can be inferred from the samples found to be adulterated. In 1934, of 157 samples, 24, or 15·2 per cent., were adulterated and, moreover, the adulteration took the gross form of large percentages of roasted peas. Whilst gross in one sense, it is refined in another, since not easily detected except by special methods of chemical and microscopical analysis. It is to be hoped that this form of sophistication will not now recur. Of 103 coffee samples examined in 1935, 2, or 1·9 per cent., were found to be adulterated. The adulterant was burnt sugar.

LARD SUBSTITUTES.—Friola lard substitute, friolene oil and "buttercup" oil are analysed to determine whether they have the correct composition under the Food and Drugs Ordinance, or whether they satisfy the standards of quality laid down by the Copra Products (Control) Ordinance, No. 1 of 1932. Of 98 samples analysed, 3 (two of friolene and one of "buttercup" oil) did not comply with the Food and Drugs Ordinance. The two friolenes, *i.e.* coconut oils, were adulterated with olive oil, which is more expensive and would by many people be considered of greater dietetic value. The "buttercup" oil, also coconut oil, was adulterated with cottonseed oil. No sample failed to comply with the Copra Products (Control) Ordinance, No. 1 of 1932.

SACCHARIN IN MINERAL WATERS.—Of the 618 samples (soda water, lemonade, kola, etc.) examined, only five were adulterated, four being contaminated with lead and one containing saccharin. Adulteration with saccharin is practically a thing of the past, but it is still necessary to take many samples in order to hold it in check.

Union of South Africa

ANNUAL REPORT OF THE DIVISION OF CHEMICAL SERVICES FOR THE YEAR 1935

THE Division of Chemical Services, whilst constituting a Division of the Department of Agriculture and Forestry, is also required to render any chemical services demanded by any other State Department. In order to indicate more clearly the wide extent of the duties of the Division, the name was changed, as from February, 1935, from that of the "Division of Chemistry" to its present title.

In this Report, the Chief of the Division (Dr. St. C. O. Sinclair, F.I.C.) gives an outline of the research and investigational work of the Division, including soil survey, the study of erosion, work on the preparation of a soil map of the Union, problems connected with irrigation water, pasture problems and fertiliser experiments.

LOCUST POISON RESEARCH.—Among the questions studied was that of a suitable substitute for arsenical poisons. After experiments with a large number of poisons, it still remains a problem to find a substitute for arsenic which can be relied upon under field conditions and the use of which at the same time is economically possible. In such connection the study of emulsifying agents (of local origin) which promote the dispersion of insecticidal oils in water is being continued, and the oxidation products of certain mineral oils are being investigated with the object of ascertaining their toxic properties. Certain fractions of tar oils in the form of a dilute emulsion have proved to be excellent insecticides.

The chemists of the Division have also been very largely concerned in experiments to evolve a suitable "poison bait."

Working together with the Division of Veterinary Services at Onderstepoort and the Director of locust research, the Division is carrying out experiments with a view to ascertaining the change in the degree of toxicity of grass and soil from areas sprayed with locust poison after certain intervals of time. Experiments, to determine the extent to which soil retains arsenical compounds, are also in progress.

FREEZING-POINT OF MILK.—For some time past, the freezing-point test has been regularly applied in the Capetown laboratories in all cases in which adulteration by the addition of water was suspected, and investigations are now in progress in the Johannesburg laboratories to ascertain how far the routine use of the test is of assistance under local conditions. The determination of the freezing-point is carried out by means of a Hortvet cryoscope.

PEANUT BUTTER (BORON IN PEANUTS).—Investigations have been put in hand to ascertain how far boron compounds occur normally in peanuts grown in various localities, and whether the element can be present as a natural constituent in peanut butter as marketed. Results so far available indicate that boron may be a normal constituent of the peanut plant grown in certain localities.

VITAMIN CONTENT OF FRUIT.—The effect of cold storage upon the vitamin *C* content of oranges is being investigated. The results of the work thus far carried out reveal no evidence that the vitamin *C* content of the fruit per ml. of juice is decreased, even after lengthy periods of storage. The work will be continued for some years, and comparative studies will be undertaken on different varieties of oranges grown on different soils and under varying conditions of climate and fertiliser treatment.

PUBLIC HEALTH.—In connection with the operation of the Food, Drugs and Disinfectants Act, administered by the Department of Public Health, 3803 samples of food, drugs, etc., were analysed in the laboratories at Johannesburg and Capetown. Samples of foodstuffs, submitted by various municipalities under the provisions of the Act, were also dealt with in the Johannesburg laboratories.

FRUIT FOR EXPORT.—Under the provisions of the Fruit Export Act, at the instance of the chief fruit inspector, the arsenic content of 2121 samples of fresh fruit intended for export was determined in the Capetown laboratories.

The export of dried fruit is governed by regulations issued under the provisions of the Agricultural Produce Export Act, and, to ensure compliance with these regulations, 170 samples of dried fruit were dealt with in the Capetown laboratories. The samples were tested as to the presence of arsenic or sulphurous oxide in excess of the permissible amounts.

Queensland

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDED JUNE, 1935

THE Government Analyst (Mr. J. B. Henderson, F.I.C.) reports that 12,550 samples were examined during the year, 6002 of which were for the Health Department. Among the points of interest to which attention is directed are the following:

ARSENIC ON VEGETABLE PRODUCE.—Trouble was experienced through growers sending out cabbages with poisonous insecticide adhering to them. Of 21 cabbages brought in by inspectors as showing insecticide, 9 proved to be contaminated with lead arsenate, the remaining 12 having been sprayed with lime only. In the same category come the 1848 samples of tobacco which were examined for arsenical preparations. Since the previous year the position has still further improved, as only 67 samples contained more than traces of arsenic, the proportion of samples showing more than the tolerated amount, being only 3·6 per cent., as against 8·8 per cent. in 1934.

Apples from the Southern States also suffer from the same trouble, and of 242 samples which were sent as showing insecticide, 219 were stopped as yielding more than one-hundredth of a grain of arsenic trioxide per pound.

INVESTIGATION OF LEAD POISONING AMONG CHILDREN.—Crayons, faeces and urine, paint scrapings, toys, and a few other miscellaneous samples were examined in connection with the investigations into lead poisoning among children. Of 63 samples of crayons, 25 contained lead varying in proportion from 0·3 per cent. to 18·3 per cent., and also arsenic to the amount of three-sixteenths to thirty-three grains per pound. The paint scrapings from verandah rails showed 68 of 94 samples to contain more than the 5 per cent. of soluble lead permitted by the Health Acts, most of the condemned samples being ordinary lead paints. Of the 9 toys sent in as possibly being contaminated with lead, 7 were found to yield lead and 2 were passed.

FORMALDEHYDE IN SMOKED FISH.—Twelve samples of canned fish all reached the standard, and of the other fish, samples from 5 shipments of cod-fish blocks were passed, but one shipment was condemned on account of the presence of formaldehyde. The fish from this shipment was almost white in colour. It had a soft moist surface, and gave off a marked odour of formaldehyde. Samples varied in yield of formaldehyde from 100 to 650 p.p.m. It was unsmoked fish preserved with formalin. Smoked fish, produced locally, yielded from 10 to 40 parts of formaldehyde per million. Little information seems to be published as to the proportion of formaldehyde which can be expected from genuine smoked fish. It is known that formalin is sometimes added to the sawdust used in producing the smoke in the treatment of both fish and bacon, so that results of analyses of commercial smoked fish do not necessarily give a reliable indication as to the proportion of formaldehyde which should be expected in smoked fish. A short investigation was therefore made in the laboratory by conducting a series of experiments, in which the details of methods in use locally for smoking fish were followed. Fresh fish were cleaned, salted, partly dried, and smoked, portions being withdrawn from time to time to determine the rate of absorption of formaldehyde. It was

found that the maximum proportion of formaldehyde was attained in about 4 hours, the proportion after that time falling off slightly. Mullet fish of an average cleaned weight of seventeen ounces, and an exposed surface of about 84 square inches, gave, after 4 hours' smoking, a maximum recoverable proportion of 18 parts per million. Tailer fish, of an average cleaned weight of 9 ounces and a surface of about 66 square inches, smoked at the same time, gave a maximum recoverable proportion of 45 p.p.m. The results indicate that for genuinely smoked small fish not more than about 45 p.p.m. of recoverable formaldehyde are likely to be present, with a smaller proportion from larger fish. The method used for the determination of the formaldehyde was the usual distillation with phosphoric acid and colour reaction with phenylhydrazine. The usual controls by this method showed the presence of formaldehyde in the smoke, and its absence from the fresh fish. The proportion in the outer flesh was higher than in the inner flesh, and the proportion of recoverable formaldehyde in the smoked fish decreased fairly rapidly for a few days, the decrease becoming slower as time went on.

General Medical Council

BRITISH PHARMACOPOEIA COMMISSION
REPORTS OF COMMITTEES
No. 9*

THIS Report contains the collected Reports of Committees on material prepared for an Addendum to the British Pharmacopoeia, 1932.

It is pointed out in the introductory section that these reports are published in order that the principal recommendations relating to the Addendum may be available for discussion before they are finally adopted, and that these recommendations have not yet any official authority, the British Pharmacopoeia, 1932, remaining without alteration or addition until the Addendum has been published.

British Standards Specifications

THE following Standard Specifications have been issued by the British Standards Institution:

No. 391—1936.	TUNG OIL, TYPE F (forming one of a series of standard specifications for paints, varnishes and paint ingredients)
No. 615—1936.	KOHLRAUSCH FLASKS
No. 650—1936.	CASTOR OIL ("FIRSTS" QUALITY)
No. 651—1936.	CRUDE MAIZE OIL
No. 652—1936.	CRUDE PALM KERNEL OIL
No. 653—1936.	CRUDE SOYA BEAN OIL
No. 654—1936.	PERILLA OIL
No. 655—1936.	REFINED COTTON SEED OIL
No. 656—1936.	SESAME OIL
No. 658—1936.	DISTILLATION APPARATUS
No. 662—1936.	CARBON DISULPHIDE
No. 663—1936.	ETHYL LACTATE.

These can be obtained from British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2s. net, post free 2s. 2d.

The Institution has also published a Handbook of Information, including Indexed Lists of B.S.I. Specifications and Methods of Test. Price 1s.

* Published by the authority of the General Medical Council, 44, Hallam Street, London, W.1. February, 1936. Price 2s. 6d.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Talc-Content of Faced Rice and Two Methods for its Rapid Determination. V. Moucka. (*Z. Unters. Lebensm.*, 1936, **71**, 175–180.)—Two rapid methods are described. Some 20 to 30 grains of rice are covered in a small glass capsule with an iodine-potassium iodide solution (1 g. iodine and 2 g. potassium iodide made up with water to 100 g.). Floating grains are immersed with the aid of a glass rod, but shaking or tilting of the vessel must be avoided. After the lapse of about four minutes the solution is poured off. The rice grains are now stained black and, still without any shaking of the capsule, they are washed by decantation, first with two portions of water to remove potassium iodide (which, if allowed to remain, would crystallise at a subsequent stage of the process), and then successively with alcohol and ether to remove excess of iodine and fat. The capsule is placed on the water-bath and the grains are dried, but only sufficiently to detach them from the walls of the vessel. If the rice is unfaced, the surface presents a matt, charred appearance. Talc-faced rice, on the other hand, has a metallic lustre or a polished-graphite appearance. Remains of the pericarp (silver skin) are distinguished from talc by their brown, matt appearance. By examining single grains under a magnification of ten to twenty diameters the distribution of talc on the surface can be observed, facing of under 0·1 per cent. on the dry sample is detectable, and with practice the talc-content can be roughly estimated. In the second method the procedure is as follows:—A test-tube is filled to a quarter or a third of its volume with rice, ether is added until the meniscus stands about 2 cm. above the rice, after which the tube is shaken vigorously for a minute. The turbid liquid is immediately decanted into a glass capsule, the ether is removed on the water-bath, and the residue is transferred with the aid of a spatula to a clean previously ignited piece of platinum foil, upon which it is ignited until no particles of unburnt carbon are visible. If the rice is unfaced, only a few specks immediately soluble in acid remain. Faced rice yields a white or grey mass. This is mounted in a drop of dilute hydrochloric acid and boiled, after being covered with a cover glass. The isolated talc can be recognised under the microscope as transparent colourless scales or thin leafy particles. By this method talc can be recognised when the staining method gives uncertain results. In the rare instances when rice contains sand or other siliceous matter there is no difficulty in distinguishing these from talc particles. The moisture-content, oil extractable by petroleum spirit and the talc-content (*i.e.* acid insoluble ash) of forty kinds of rice are given. The moisture varies from 11·1 to 13·4, the oil from 0·03 to 0·35 per cent. on the dry sample, and the talc from 0·08 to 0·77 per cent. on the dry sample. It is suggested that the highest permissible limit for the talc-content should be 1 per cent., that as rice, and especially rice meal containing siliceous matter other than talc, has a sandy taste, especially when cooked, this sensory test should be applied, and that if rice gives a petroleum spirit extract greater than 0·4 per cent. oiling may be suspected. A. O. J.

Monobromoacetic Acid and Bromine normally present in Wines. L. Chelle and G. Vitte. (*Ann. Falsif.*, 1936, **29**, 98–103.)—Two wines were tested for the presence of brominated derivatives as preservatives, which is illegal. The wines were ashed by Genuil's magnesia method (*Précis de Chimie*, Denigès and Chelle-Labat, 1904, **1**, 378), and the bromide was isolated by Damiens' method (*Bull. des Sciences pharmacol.*, 1921, 42) and detected and determined by the Denigès–Chelle method; these methods are described. The results indicated the presence of 0·2 to 0·3 mg. of bromine per l., which is improbable, as this amount would not prevent fermentation. On addition of 1 and 2 mg. of bromine (as potassium bromide and as monobromoacetic acid) to these wines and subsequent determination, the results corresponded with the amounts added. Subsequent investigation showed 0·2 mg. of bromine per l. to be present in a blank test, and it was then found that the magnesia, bought as pure, contained 0·0003 per cent. of bromine. The method was therefore modified as follows:—Fifty or 100 ml. of wine in a porcelain dish are evaporated to dryness on a water-bath or sand-bath, further dried in an oven, carbonised on a small flame of a spirit-lamp, pulverised, and transferred to a small platinum dish. This is placed at the mouth of a red-hot muffle furnace, where the residue burns white without reddening of the dish, and the ash is washed with 5 ml. of twice-distilled water, filtered into a test-tube, and washed until 10 ml. of filtrate are obtained. No appreciable loss of bromine occurs through ignition.

The Damiens method of isolation was omitted and the 10 ml. of filtrate examined directly by the Denigès and Chelle method. Eight drops of pure hydrochloric acid are added, followed by 8 drops of 10 per cent. potassium chromate solution and 2 ml. of sulphuric acid. The tube is shaken and cooled in water for 5 minutes, 2 ml. of sulpho-fuchsine reagent are added, then 2 ml. of chloroform which has been well washed. The tube is shaken vigorously for 1 minute and allowed to stand, and a violet colour of the chloroform indicates the presence of bromine. The bromine is determined colorimetrically by comparison with standards containing known amounts of potassium bromide (0·25, 0·50, 1, 2, 4, 6, 8, and 10 mg. of bromine per l.), which have been treated similarly to the 10 ml. of the sample. Wines known to be free from added bromine derivatives and examined by this method contained from 0·1 to 0·7 mg. of bromine per l. It was therefore concluded that the 0·2 to 0·3 mg. per l. present in the samples questioned existed normally in those wines. E. B. D.

Investigation of Bromine Preservatives in Foods, especially in Wines, Grape-juice and Fruit Juices. Florentin and Munsch. (*Ann. Falsif.*, 1936, **29**, 104–105.)—The bromine occurring naturally in wines and grape juice (*cf.* preceding abstract) is considered to be present originally as inorganic bromide, not as an organic derivative which can be extracted by means of ether. The following method for the determination of bromine present in organic form (*e.g.* as bromoacetic acid) is recommended:—From 20 to 200 ml. of wine, etc., are extracted 3 or 4 times with ether in a separating funnel, 50 to 250 ml. of ether being used. The ether is separated, filtered through a dry filter-paper, and evaporated slowly on the water-bath with 1 to 2 ml. of distilled water. After

evaporation of the ether, a small quantity of pure, bromine-free magnesia, or magnesia of known bromine-content, is added to the residue, which is dried on the water-bath and ignited carefully on a small gas flame or at the mouth of a muffle furnace. The ash is taken up 2 or 3 times with a few ml. of boiling water, and the solution, concentrated, if necessary, is tested for bromine by the sulpho-fuchsin reagent or by Hahn's reaction. The former test is sensitive to 0·5 mg. of organic bromine per l. of wine when 100 ml. of wine are taken; this sensitiveness can be increased, but is usually sufficient. By Hahn's method (bromination of fluorescein; cf. *Compt. rend.*, 1933, **197**, 245; Abst., ANALYST, 1933, **58**, 567) quantities less than 0·1 mg. per l. can be detected. A blank test on the reagents is made. A preliminary test for total bromine may be made by evaporating 25 or 50 ml. of wine, igniting the organic matter with a little magnesia, and treating the residue as above. Unless the total bromine thus found approaches 1 mg., added bromine may be considered absent, and the ethereal extraction method is unnecessary.

E. B. D.

Detection of Thujone in Absinthe-type Liqueurs. J. B. Wilson. (*J. Assoc. Off. Agric. Chem.*, 1936, **19**, 120–124.)—With (*a*) solutions of known quantities of thujone in 10 ml. of 65 per cent. alcohol, the modified Legal test (*cf.* Rocques, *Ann. chim. anal.*, 1908, **13**, 227) gives strongly positive results if 5 mg. or more are present, but may be doubtful for 1 or 2 mg. If (*b*) known quantities of thujone in 25 ml. of water are steam-distilled, and 20 ml. collected, the above test is positive for 2 mg. or more. The distillate is extracted with ether, and the test is made on the ethereal solution. With (*c*) known amounts of thujone, separated from 80 per cent. alcohol by the Enz method (*Schweiz. Wochschr.*, 1911, **49**, 337 and 507; Abst., ANALYST, 1911, **36**, 495), give positive results for the Legal test if 2 mg. are originally present, but for a modified Enz method (*d*) at least 3 mg. are required to give a positive result on the proper fraction.

The Enz method, as here used for (*c*), is as follows:—Five ml. of semi-carbazide reagent (10 g. of semi-carbazide hydrochloride and 12 g. of sodium acetate dissolved in water and diluted to 100 ml.) are added to each of several 100-ml. solutions of thujone in 80 per cent. alcohol. After standing overnight, the alcohol is distilled off at about 60 mm. pressure on a water-bath in a Widmer distilling apparatus (*Helv. Chim. Acta*, 1924, **7**, 59), until only about 15 ml. of liquid remain; the temperature is about 35° C. After disconnection of the Widmer column and addition of about 10 ml. of water, the residual liquid is steam-distilled, and about 15 ml. of distillate are collected. The condenser is washed out twice with alcohol and twice with water; the undistilled liquid is then steam-distilled after acidification with about 1 ml. of sulphuric acid (1 : 1), and 20 ml. are collected and extracted with ether, 10 ml. of 65 per cent. alcohol are added, and the ether is allowed to evaporate spontaneously. For (*d*) known amounts of thujone were added to 500-ml. portions of 50 per cent. alcohol, and distilled slowly, and two 100-ml. fractions were collected and each treated as in (*c*). The Legal test is made on 10 ml. of alcoholic (65 per cent.) solution. One ml. of zinc sulphate solution (10 per cent.) and 0·25 ml. of freshly-prepared sodium nitroprusside solution (0·1 g. per ml. of water) are added. Slowly, with constant stirring, 2 ml. of 5 per

cent. sodium hydroxide solution are then added, and, after 1 or 2 minutes, 1·5 ml. of glacial acetic acid are mixed with the solution. A raspberry-red precipitate, resembling the alcohol precipitate of a red fruit juice, indicates the presence of thujone; its absence is shown by a precipitate like that from light-coloured fruit.

In method (*c*), the distillate from the acidified portion is examined; the first distillate is usually rejected. The odour of thujone may be detected in the 65 per cent. alcoholic solutions for the following minimum amounts:—(*a*) 2 mg., (*b*) 2 mg., (*c*) 2 mg., (*d*) 3 mg. of the proper fraction, and also, for the first distillate of (*c*), in similar solutions from 10 mg. of thujone. In absinthe from wormwood oil, thujone may vary from 1·8 mg. to 45 mg. per litre; it varies from 2 to 34 mg. per l. in absinthe from *Artemisia absinthium*. Hence, negative tests do not necessarily indicate absence of appreciable amounts of oil or herb extract. In the examination of absinthe liqueurs, 500 ml. are heated under reflux with 1 ml. of freshly-distilled aniline and 1 ml. of syrupy phosphoric acid for 30 minutes on a water-bath. Two 100-ml. portions are distilled, and the second is examined by (*c*).

E. B. D.

Determination of the Preservative Value of English Hops. H. F. E. Hulton. (*J. Inst. Brewing*, 1936, **42**, 130–131.)—In making this determination by the method of Ford and Tait (*id.*, 1932, **38**, 351; *cf.* Walker and Hastings, ANALYST, 1933, **58**, 702; and Comrie, *id.*, 1935, **60**, 48), the preservative value (*P.V.*) is obtained from the expression $10\ [\alpha + (T.S.R. - \alpha)/3]$, where *T.S.R.* is the percentage of total soft resins and α is the percentage of α-resin. Since the determination of the former is a lengthy process, whilst the latter is rapidly carried out, the possibility of using a constant factor for β ($= T.S.R. - \alpha$), which is applicable to all (or to most) hops is considered. The suggested factors calculated from the expression (average per cent. β-resin $\times$ 10/3) and based on the β-values for 60 English hops of all kinds and ages obtained during the past 3 years, are 26 for samples having an α-resin content of 1 per cent. or over, and 28 for samples with abnormally low α-resin contents, and these are added to the α-value $\times$ 10 in the above expression for *P.V.*; a factor obtained independently (by Ford) and representing analyses of 200 English hops (normal yearlings from the past 2 seasons, and containing 1 per cent. or more of α-resin) is 27. The corresponding extreme errors in the *P.V.*, caused by the use of these factors, are +5 or −4, +6 or −5, and +7 or −14, respectively. The relatively small errors involved by the use of this method are due to the facts that the β-value is divided by 3, and that some 90 per cent. of the β-resin is destroyed during the copper boil; in view of the approximate nature of the *P.V.* these are considered of little significance compared with the saving in time involved.

J. G.

Identification of Small Quantities of Apomorphine in the Presence of Morphine. M. Jardillier. (*Bull. Biol. Pharm.*, 1936, **32**, 72–75.)—The method of the French Codex for the identification of small quantities of apomorphine in the presence of morphine is criticised, and the method of von Fritz Wischo is preferred. This test is based on the red colour formed when sulpho-vanadic acid reacts with phenolic substances having the hydroxyl group in the ortho position. It was found that apomorphine could be detected in a dilution of 1 in 400,000 in the

presence of 1 per cent. of morphine hydrochloride. It is emphasised, however, that the colour is fugitive and cannot be made the basis of a quantitative test.
S. G. S.

Note on *Strophanthus Emini*. T. C. Denston. (*Pharm. J.*, 1935, **136**, 341.)—The fruits of *S. Emini* resemble those of other species of *Strophanthus*, and consist of two follicles which diverge at the base as ripening occurs. The specimens examined had the following dimensions: length 24·5 cm. to 29·5 cm.; greatest width, 3·0 to 9·0 cm.; width at the base, 2·3 to 4·0 cm.; the bulbous apex, 5 to 12 mm. in diameter. A single follicle contained 175 seeds which resembled in general structure those of *S. kombé*. The awns were from 9 to 13 cm. long, and the seeds from 13 to 20 mm. long, with an average of 17 mm. The width was from 3 to 4·5 mm., and the thickness from 1·5 to 2 mm. at the widest part. The shape was bluntly lanceolate to lanceolate, with a few seeds elongated rhomboidal. The seeds contained a very narrow endosperm surrounding large white and oily cotyledons. These figures are in general agreement with those of the Pharmacopoeia Commission, except that the length was rather greater. Glycosides were absent in the awns, pericarps and stems, but the seeds gave strong positive reactions for the tests described by Smelt (*Quart. J. Pharm.*, 1933, **6**, 467.) S. G. S.

***Psyllium* and the Seeds of certain other Species of *Plantago*. E. W. Skyrme.** (*Quart. J. Pharm.*, 1935, **8**, 609–621.)—Commercial samples of psyllium seeds consist not only of the seeds of *Plantago psyllium*, but also, partly or even entirely, of the seeds of *P. arenaria* or *P. lanceolata*. The seeds of *P. cynops* are said to be used for similar purposes in Italy, Spain and South France, and those of *P. amplexicaulis* are named by a number of authors as yielding a drug "brown ispaghul" or "ejag pipli." An examination of the seeds of all these species has therefore been made to provide data for identification. The average weights per 100 seeds shows the *P. amplexicaulis* seeds to be the largest (0·37 g.), *P. cynops* next (0·2 to 0·19 g.), *P. arenaria* (0·14 g.), and *P. psyllium* (0·09 to 0·10 g.). Detailed drawings of typical shapes of the seeds are given, and it is noted that the characteristic colours of the species differ somewhat. It is, however, in the anatomy that the distinct points of difference are found. Drawings of the transverse sections of the testa and endosperm and of surface sections of the five species are given. The outermost epidermis consists of flattened polygonal prismatic cells with a thin smooth cuticle covering the outer periclinal walls. In *P. amplexicaulis* the radial dimensions of the cells are only about one-eighth those of *P. ovata*. In *P. psyllium, arenaria* and *lanceolata* the thin cell-walls are pectosic, and give a light purple colour with haematoxylin and a darker purple with methylene blue. The cells are almost filled with a colourless mucilage which swells in water, is stained pink by corallin soda, and is of a hemicellulosic nature. In *P. cynops* the remains of the cell-lumen form an irregularly shaped "tube" running from the outer to the inner periclinal wall in the centre of the cell. The middle or "collapsed" layer of the seed-coat consists, in all species except *P. ovata*, of a tissue only 1 cell in thickness. The walls of the polygonal prismatic cells of the inner epidermis of the seed-coat are thin, colourless and suberised, and the characteristic variations may be in the dimensions, the shape of the walls, or form

of the contents; as this layer is easily found in the powder of the seeds, it affords the most certain means of identification. The maximum radial and tangential measurements of these cells of the pigment layer, and the thickness of the outer walls (against the endosperm) are, respectively:—*P. psyllium*, 2·0μ, 65·0μ and about 0·3μ; *P. arenaria*, 10·0μ, 65·0μ, 1·0μ; *P. amplexicaulis*, 10·0μ, 22·0μ, 1·0μ; *P. lanceolata*, 15·0μ, 30·0μ, 5·0μ; *P. cynops*, 22·0μ, 45·0μ, 3·0μ; *P. ovata*, 5·0μ, 50·0μ, and about 0·3μ. For other details of difference reference should be made to the original. D. G. H.

Biochemical

Deuterium as an Indicator in the Study of Intermediary Metabolism. Desaturation of Fatty Acids in the Organism. R. Schoenheimer and D. Rittenberg. (*J. Biol. Chem.*, 1936, **112**, 505–510.)—Mice were fed with saturated fatty acids containing deuterium. The fatty acids obtained from the fat of the entire animals were fractionated and all the deuterium-containing saturated acids were removed by a modification of Twitchell's method. The mixture of crude unsaturated acids was precipitated with lead acetate in alcoholic solution. After 24 hours the crystalline precipitate (*a*) was filtered off, and a mixture of stearic and palmitic acids in alcohol was added to the mother liquor. After separation of the precipitate (*b*) the procedure was repeated (precipitate *c*). The precipitates and the final mother liquor (fraction *d*), which contained the lead salts of the unsaturated acids, were decomposed with hydrochloric acid and ether in the usual way. The high deuterium-content of the unsaturated fatty acids so obtained proved that fatty acids were readily desaturated in the organism. S. G. S.

Paths of Excretion and Mineral Balance in Animals Drinking Saline and Alkaline Waters. V. G. Heller and M. Haddad. (*J. Biol. Chem.*, 1936, **112**, 439–447.)—When the mineral-content of the drinking water supplied to rats was increased to the maximum amount which did not seriously injure these animals, it was found that the urine and faeces had an abnormal mineral-content, and that the normal paths of excretion were altered. About 90 per cent. of the chlorides were excreted through the urine, although more was found in the faeces than reported previously, and this was especially noticeable when the intake was increased or when acid-producing ions accompanied the chlorides in the drinking water. It is suggested that the increase of chlorides in the faeces was due to the change of osmotic pressure caused by the increased salt-content of the alimentary tract and the resulting cathartic action. Chloride retention was greatest when calcium chloride was administered. Sulphur was excreted equally in the urine and the faeces, the path depending on the quantity and form ingested. If an ion which formed insoluble sulphates was present, the phosphorus-content of the faeces was increased. An increase in the sulphur-intake caused an increase in the sulphur retention, as well as an increase in the content of the urine. The amount of calcium retained by the body corresponded approximately with the amount consumed. Calcium chloride was most favourably absorbed and produced a more positive balance, as well as an increase in the percentage found in the urine.

It was found that, if the intake was abnormal, the excess was excreted in the faeces. Magnesium was excreted in the urine to a relatively greater extent than calcium, and large amounts of calcium displaced magnesium from the body. An increase in the phosphorus-intake also increased the amount retained and the amount excreted in the urine. More phosphorus was found in the faeces than previously reported, and this increase was very marked if large amounts of calcium or magnesium salts were also present in the drinking water. S. G. S.

***Ricinus* Lipase, its Nature and Specificity. H. E. Longenbecker and D. E. Haley.** (*J. Amer. Chem. Soc.*, 1935, **57**, 2019–2021.)—*Ricinus* lipase was prepared from large hulled and macerated castor beans (*Ricinus communis*) by removing the fat with petroleum spirit (b.p. 20 to 40° C.), the dry residue being then pulverised and passed through a 60-mesh sieve (*cf.* Haley and Lyman, ANALYST, 1922, **47**, 173). The lipolytic activity was measured by adding to 1·00 g. of oil in a hard-glass bottle with a paraffined cork, 2 drops of toluene (as a preservative), a weighed quantity (*e.g.* 0·1 g.) of the sample, and sufficient 0·1 *N* acetic acid to produce a *p*H value of 4·8. This mixture was shaken for 3 minutes, and digestion was allowed to proceed at 37° C. After a definite period the mixture was added to 50 ml. of hot 95 per cent. alcohol, and the free fatty acids were titrated with 0·1 *N* alkali (to phenolphthalein), the reaction-time being calculated from the time of adding the acetic acid, as no hydrolysis occurs before this or after adding the mixture to the alcohol. Since the difference between the titration-volumes given by the sample and a blank is a measure of the fatty acids resulting from direct cleavage of glycerides by lipase, and the ester value is a measure of the total fatty acids in glyceride combination, the percentage hydrolysis is obtained by the following formula

$$\frac{\text{ml. of 0·1 } N \text{ alkali (sample)} - \text{ml. of } N \text{ alkali (blank)}}{\text{Saponification value*} - \text{acid value*}}$$

(*cf.* Wilson and Merrill, *J. Amer. Leather Chem. Assoc.*, 1926, 1). This method has been used to show that a sample of enzyme prepared in 1924 by the above method still had a considerable activity, and this is attributed principally to the fact that it had been produced and stored as a dry preparation. Tests with Sudan III and conductivity measurements indicated that (with olive oil) the formation of a water-in-oil emulsion favours *Ricinus* lipase action, which may therefore be assisted by shaking the digestion mixture, and by maintaining it at a lower temperature (*e.g.* 27° to 28° C.); it was found that the shaking period and temperature used in the method described did not give the maximum rate of hydrolysis, although they enabled reproducible results to be obtained. Oils may be graded as follows in decreasing order of rate of lipolytic hydrolysis by *Ricinus* lipase:—arachis, castor, cottonseed, soya bean, rape, olive, linseed, neat's foot, peach-kernel, coconut, whale and fish oils. These results appear, with few exceptions, to support the argument that *Ricinus* lipase has a relative specificity for glycerides of high molecular weight (*cf.* Falk, *J. Amer. Chem. Soc.*, 1913, **35**, 616), although, if the number of moles of glycerides hydrolysed after a given time is considered, the results are all of the same order of magnitude. J. G.

* Expressed in ml. of 0·1 *N* alkali.

Determination of Glutamine in the Presence of Asparagine. H. B. Vickery, G. W. Pucher, H. E. Clark, A. C. Chibnall, and R. G. Westall. (*Biochem. J.*, 1935, **29**, 2710–2720.)—The method of Chibnall and Westall (*Biochem. J.*, 1932, **26**, 122) for the determination of glutamine in plant extracts has been modified to give greater accuracy and extended to include an independent determination of asparagine, which often occurs with glutamine. In order to calculate the glutamine and asparagine content of a mixture of these two substances, it is only necessary to determine the total amide-nitrogen after hydrolysis with *N* acid and the glutamine amide-nitrogen after hydrolysis at *p*H 6·5. Four methods may be used for the preparation of the plant tissues: (i) extraction with cold water after cytolysis of the fresh tissue with ether; (ii) grinding with sand in a mortar, diluting the pulp with water, heating to 80° C. to coagulate the protein, cooling and filtering; (iii) freezing with carbon dioxide snow, thawing and expressing the juice; (iv) drying the tissue in a suitable air-oven and subsequently extracting with water. For the determination of glutamine, an aliquot portion of the solution, diluted with water to make 5 ml., is placed in a test-tube (20 × 200 mm.), together with 10 ml. of a phosphate-borate buffer of such reaction and molar strength as to give a final reaction, after a 2-hour hydrolysis, of about *p*H 6·5. Frequently a 0·1 *M* buffer of *p*H 7·0 is satisfactory, but sometimes buffers of two to four times this concentration are required. The tube is closed with a rubber stopper carrying 20 cm. of 1-mm. bore heavy-wall glass tubing, the lower surface of the stopper and the orifice of the tube having previously been moistened with a few drops of water. The tube is then placed in a constant-level boiling water-bath for exactly 2 hours, and then removed and cooled in cold water, a few drops of water being allowed to be drawn down the capillary tube in order to wash back any ammonia which has volatilised. The contents of the tube are transferred to a distillation apparatus (Pucher *et al.*, *Ind. Eng. Chem. Anal. Ed.*, 1935, **7**, 152) with 20 ml. of water, and the ammonia is distilled *in vacuo* at 40° C. after the addition of 3 ml. of a reagent prepared by dissolving 5 g. of borax in 100 ml. of 0·5 *N* caustic soda solution. The distillate is diluted, treated with 5 ml. of Nessler's solution, and made up to 50 ml., and the extinction coefficient is determined by means of a Zeiss-Pulfrich spectrophotometer. The amount of ammonia in the distillate is obtained from the calibration curve of the instrument and corrected for the apparatus blank. The total amount of amide-nitrogen is determined by adding to an aliquot portion of the solution sufficient water to give a volume of 5 ml., and mixing this with 1 ml. of 6 *N* sulphuric acid. This is heated for three hours at 100° C. in a test-tube similar to that used for the glutamine. The solution is then washed into the ammonia distillation apparatus with 20 ml. of water, and 5 ml. of *N* caustic soda solution are added, followed by 5 ml. of the alkaline borate mixture. The ammonia is distilled and determined as before. This determination includes any free ammonia-nitrogen (which should also be determined), and the sum of this and the glutamine nitrogen, subtracted from the total nitrogen, gives the asparagine nitrogen. Substances such as urea and allantoin would be calculated as asparagine and work on the elimination of these is in progress. S. G. S.

Separation of Guanidine and Methyl Guanidine by means of β-Naphthalene Sulphonyl Chloride. W. C. Hess and M. X. Sullivan. (*J. Amer. Chem. Soc.*, 1936, **57**, 2231–2232.)—A solution of 4·5 g. of β-naphthalene sulphonyl chloride in 10 ml. of ether was shaken thoroughly in a separating funnel with a mixture of 1 ml. of 5 *N* sodium hydroxide solution and a solution of 1·5 g. of guanidine carbonate in 10 ml. of water. The mixture was allowed to stand for 5 minutes, and the heavy white precipitate was separated by filtration, and washed with alcohol and ether (yield 93 per cent.); after re-crystallisation from hot water containing a little hydrochloric acid it was obtained as long sabre-shaped crystals, m.p. 204 to 206° C. (uncorr.). Hydrolysis with 20 per cent. hydrochloric acid yielded β-naphthalene sulphonic acid and free guanidine, and analysis indicated the formula $C_{21}H_{17}N_3O_4S_2$; 2 mols. of water of crystallisation (volatile at 105° C.) were present in specimens which had been dried in a desiccator, and at 24° C. the solubility was 9·0 mg. in 10 ml. of water. Methyl guanidine gave no precipitate, and from mixtures of 50 mg. each of this compound and guanidine it was possible to recover 90 per cent. of the latter; creatine, creatinine, glycocyamine and glycocyamidine also gave negative results. If, however, the reaction was carried out in the presence of 2·5 ml. of alkali, methyl guanidine yielded a mono-acylated derivative after prolonged shaking and standing (yield 65 per cent.), which could be recrystallised in long, slightly-curved, branching needles, $C_{12}H_{13}N_3O_2S$, m.p. 101 to 102° C. (uncorr.), solubility 21 mg.; the hydrolysis reaction was analogous to that obtained with guanidine, but it is considered that the guanidine derivative is diacylated. This method is preferable to that of Ackermann (*Z. physiol. Chem.*, 1906, **47**, 366; **48**, 382), which is based on the formation of the benzene sulphonyl derivatives. J. G.

Vitamin *A*, *B*, *C*, *D*, and *G* (B_2) Content of the Outer Green Leaves and the Inner Bleached Leaves of Iceberg Lettuce. H. E. Munsell and M. H. Kennedy. (*J. Agric. Res.*, 1935, **51**, 1041–1046.)—The outer green leaves and the inner bleached leaves of the Iceberg lettuce (*Lactuca sativa*) have been assayed for vitamins *A*, B_1, B_2, *C*, and *D*. Vitamin *A* was assayed by the Sherman–Munsell technique, 34·5 Sherman units per g. being found in the green, and 1 unit per g. in the bleached leaves. The test for vitamin B_1 was carried out by the method of Chase and Sherman, the results being 0·24 and 0·27 Sherman unit per g. for the green leaves, and 0·30 and 0·39 unit per g. in the bleached leaves. The method used for vitamin B_2 (*G*) was essentially that of Bourquin and Sherman. The values found were 0·46 Sherman unit per g. and 0·24 unit per g. for the green and bleached leaves, respectively. Another test gave 1·18 unit and 0·67 unit for the two kinds of leaf. The vitamin *C* test indicated that the minimum protective level for the green leaves was slightly more than 21 g. The bleached leaves gave almost complete protection with 21 g. No vitamin *D* was detected in either variety of leaf, although 5 g. per day were fed to the test animals (rats). S. G. S.

Vitamin *D* Activity of Cacao Shell. I. Effect of the Fermenting and Drying of Cacao on the Vitamin *D* Potency of Cacao Shell. II. The Origin of Vitamin *D* in Cacao Shell. A. W. Knapp and K. H. Coward. (*Biochem. J.*, 1935, **29**, 2728–2735.)—Cacao beans taken from one plot on the plantation were

submitted to four different methods of preparation, and the vitamin *D* contents of their shells (testa) were determined biologically. The results obtained were:—(*a*) Dried in the dark for six days, 0; (*b*) dried in the sun for more than 21 days, washed, 0·6; (*c*) fermented and dried in the dark for 4 days, 0; (*d*) fermented and dried in the sun for 22 days, 21·0 I.U. per g. It is suggested that neither vitamin *D* nor ergosterol was present in the fresh shell of the bean, but that during fermentation, yeast containing ergosterol developed in the pulp on the shell, and that during the drying in the tropical sun this ergosterol was converted into vitamin *D*.

S. G. S.

Observations on the Excretion of Ascorbic Acid. H. E. Archer and G. Graham. (*Lancet*, 1936, **230**, 710–713.)—The ascorbic acid excreted in the urine of a patient suffering from scurvy was determined before and during the administration of this substance. For six days before treatment, the excretion varied from 6 to 18 mg. per day. When 187 mg. of ascorbic acid were ingested per day for 10 days the excretion varied from 10 to 19 mg. per day. When the amount taken in was increased to 281 mg. per day the excretion rose to between 115 mg. and 190 mg. This was followed by an intake of 210 mg. per day and an average excretion of 110 mg. was found. Thus when 4950 mg. had been ingested the excretion amounted to 53 per cent. of the intake. In the case of a second patient who had been living on a diet deficient in vitamin *C*, an intake of 400 mg. of ascorbic acid per day caused no increased excretion until 1200 mg. had been ingested. The excretion rose to an average of 48 per cent. of the intake after 1600 mg. had been ingested and to 75 per cent. after 3200 mg. had been ingested. When 400 mg. of ascorbic acid per day was fed to a healthy man who had been living on a diet containing sufficient of this substance, the excretion exceeded the intake within two days. It is suggested that the percentage output is much more valuable evidence that a patient has scurvy than the amount of ascorbic acid taken before the excretion increases or the amount excreted after a test dose.

S. G. S.

Toxicological and Forensic

Comparison of the Physiological and Toxic Actions of Synthetic and Fermentation Alcohol. J. Křiženecký and F. Diakov. (*Z. Unters. Lebensm.*, 1936, **71**, 149–159.)—The synthetic alcohol used was a commercial product manufactured from coke-oven gas converted by the action of catalysts, under pressure, into ethylene which is absorbed in sulphuric acid, the alcohol being subsequently liberated by neutralisation with ammonia. The sample contained 0·30 per cent. of acetone, 0·05 per cent. of acetaldehyde, 3·70 per cent. of isopropyl alcohol, with small amounts of other impurities such as nitrogenous bases and sulphur compounds. For these experiments alcohol certified free from methanol and containing only about 0·1 per cent. of higher alcohols giving the isopropyl reaction was available. The experiments were carried out upon four female and three male subjects. Measurements of metabolic changes were made by means of Benedict's Portable Respiration Apparatus, which measures the oxygen intake but not the carbon dioxide expired. The respiratory coefficient was therefore not determined.

The oxygen consumption was expressed per kg. of body weight and per sq.m. of body surface, the surface being calculated by the formula of Du Bois,

$$S = 71{\cdot}84 \times H^{0{\cdot}725} \times W^{0{\cdot}425},$$

where H is the height in cm. and W the weight in kg. To eliminate disturbances in the nervous system the subjects were inured to the experimental conditions for about fourteen days, after which the basal metabolic rate was determined under controlled conditions of diet and rest. Alcohol was then administered in quantities of 0·5 ml. of absolute alcohol per kg. of body weight diluted to 35 to 38 per cent. with distilled water. Corresponding with their weights the individual subjects took 28 to 41 ml. of absolute alcohol in each experiment. Twenty-five to 30 day intervals were allowed for the elimination of the effects of each experiment. The results are given as c.c. of oxygen consumption per sq.m. of body surface and per kg. of body weight, and in addition the calories produced per sq.m. per minute were calculated. The metabolic rate in the female subjects showed practically no difference in the effects of synthetic and fermentation alcohol. Two, who were accustomed to the moderate use of alcoholic beverages, exhibited a rise in the metabolic rate, followed by a fall, this being true for both kinds of alcohol. The other two, who were practically abstainers, showed no change in metabolic rate. Although it is not claimed that these results are connected with the use or disuse of alcohol, it is not excluded as a possible explanation. The metabolic rate of the three male subjects with fermentation alcohol was strongly increased, sooner or later, and then rapidly diminished either to its basal value or slightly below it. With synthetic alcohol each of the three subjects gave a different reaction, *viz.* no change, moderate diminution, and a slight temporary rise followed by a diminution, the rise being of the same order of magnitude as that of the female subjects. The conclusion is reached that sex is a basic factor in the influence of alcohol on the metabolic rate, males being more sensitive to the stimulating effect, and that synthetic alcohol does not cause so strong a rise as fermentation alcohol, having only the same effect on males as both kinds of alcohol on females. From a consideration of the results of all the experiments it appears that synthetic alcohol contains some substance which inhibits the stimulating effect of alcohol on metabolism and therefore exerts a certain narcotic effect on the metabolic functions. The effects of both kinds of alcohol on the respiration of the subjects was observed. After administration of synthetic alcohol the breathing was more regular than after fermentation alcohol. The action of each kind of alcohol upon the pulse frequency and the body temperature is very similar, as also is their diuretic effect. The narcotic effect of synthetic alcohol is much stronger than that of fermentation alcohol; the subjects experienced a great tendency to sleep during and after the experiments with synthetic alcohol. The toxicity of the two kinds of alcohol was investigated by experiments upon rats and upon the crustacean *Daphnia pulex.* With rats, 2 to 4 ml. administered daily in a 40 per cent. concentration produced no symptoms, but when the dose was increased to 6 ml., toxic symptoms, *viz.* weakness and irregular breathing appeared. Complete anaesthesia was not attained. Differences between the toxic action of synthetic and fermentation alcohol were not observed. With *Daphnia pulex,* alcohol

concentrations of 0·5, 1·0, 2·0, 4·0, and 6·0 per cent. were used. A concentration of 4 per cent. proved fatal in 20 to 50 minutes. At lower concentrations the animalcules lived from four to six hours. The interesting observation was made that the direction of motion of the animalcule with respect to light (phototaxy) was reversed by alcohol. No difference in the toxic effects of alcohol from the two sources was observed. A. O. J.

Sources of some Poisons and their effects on Animals. G. W. Clough. (*Vet. Record*, 1936, **16**, 53–67.)—Industrial poisons recorded to have caused cases of poisoning among cattle and poultry include arsenic and sulphuric acid deposited on vegetation as the result of roasting of mineral ores, hydrogen sulphide from the effluents from artificial silk factories and fruit-canning works, and hydrofluoric acid from a phosphate factory (*Deutsch. tierärztl. Woch.*, 1931, **39**, 203), and from a factory where cryolite was worked (*Norsk. Vet. Tidskr.*, 1934, **46**, 61). Animals fed on pastures adjoining such works have shown symptoms of anaemia, emaciation, stiffness of joints and a tendency to fracture of the bones. The increasing use of cyanides in metallurgical operations and for fumigating purposes has led to some cases of poisoning in domestic animals (*Vet. Record*, **1933**, **13**, 538). Deaths of cattle on pastures adjoining coke ovens were attributed by Dunn and Bloxam (*J. Soc. Chem. Ind.*, 1932, **51**, 100T; Abst., ANALYST, 1932, **57**, 330) to the presence of lead compounds, but the author (*J. Soc. Chem. Ind.*, 1932, **51**, 526) considered the evidence of poisoning inadequate. Metallic lead has caused the death of birds picking up lead shot (*U.S. Dept. Agric.*, 1919, *Bull.* 793), and lead poisoning has resulted from cattle licking lead-containing paint from their boxes; lead arsenate from fruit sprays is another common cause of poisoning among domestic cattle (*Vet. Med.*, **1934**, **29**, 512). Arsenical poisoning among animals has frequently resulted from the use of weed-killers. Potassium and sodium chlorate have a low toxicity for animals, but have the drawback of increasing the risk of fire. The following approximate lethal doses of arsenious oxide (as sodium arsenite), sodium chlorate and potassium chlorate are given by Steyn (*Onderstepoort J.*, 1933, **1**, 157):

	Arsenious oxide Grains	Sodium chlorate Oz.	Potassium chlorate Oz.
Horse ..	30 to 45	5	9
Cow ..	30—60	10	18
Sheep ..	6—10	2	4
Dog	5	—	2

Cases of suspected poisoning from arsenical sheep dip are estimated to reach several thousand yearly (Van Zyl, *Union of S. Africa, Dept. of Agric. Ann. Rep.*, 1929, 1189); fatal accidents sometimes follow the use of carbolic dips, and de Kock and Steyn made an experimental investigation of the effects of such dips upon sheep (*id.*, 643). Shawcross (*Vet. Record*, 1933, **13**, 92) records that a mare recovered in 10 days after receiving a pint of undiluted lysol. Dippel's oil (hydrocarbon oils) used as a dressing for warble fly, is stated to have caused the death of cattle (cf. *Vet. Record*, 1925, **5**, 720). Mowrah seed (*Bassia longifolia*), used for the destruction of worms in lawns, contains a toxic principle (*cf.* Moore,

Biochem. J., 1911, **5**, 94); cows grazing on a golf course dressed with the seed became very ill, the prominent symptoms being diarrhoea and paralysis. Of the poisons used for the destruction of rats and other vermin, strychnine has caused the greatest mortality in dogs, and cases of poisoning in dogs and poultry by barium carbonate have been recorded. Thallium sulphate, extensively used in Germany and America as a rat poison, is highly toxic (*cf.* Roche Lynch and Scovell, *Lancet*, 1930, **219**, 1340; Abst., ANALYST, 1931, **56**, 268). Experimental investigations by Newsom, Loftus and Ward have shown that the lethal dose is about 11 mg. of thallium per lb. of body weight. In feeding experiments on cattle with sodium fluoride and fluosilicate it was found that 50 to 100 grains of these salts cause acute poisoning, whilst 30 to 45 grains given daily produce gradual emaciation.

Drugs.—Numerous cases of poisoning of sheep and cattle by carbon tetrachloride have been recorded. According to Daubney (*Vet. J.*, 1930, **86**, 5) very large doses may be given if magnesium sulphate solution is also administered. Tetrachloroethylene is less toxic than carbon tetrachloride or chenopodium oil (Lamson, Robbins and Ward, *Amer. J. Hyg.*, 1929, **9**, 430). Tetrachloroethane is very poisonous to sheep, whilst the vapour of trichloroethylene, also used as a vermicide, is much less toxic than that of tetrachloroethylene. Numerous cases of poisoning of pigs by chenopodium oil are cited by Vajda (*Wien. tierärztl, Monats.*, 1935, **22**, 142).

Foods.—An outline is given of investigations of the poisonous action of *Lathyrus sativus*, cyanogenetic glucosides, and of acorns. Södermark has encountered 20 cases of acorn poisoning of cattle (15 fatal) in Sweden (*Svensk. Veter. Tids.*, 1934, **39**, No. 15); the symptoms, which are similar to those of oak-leaf poisoning, are attributed to the action of tannin.

Agricultural

Occurrence of Selenium in Natural Phosphates, Superphosphates and Phosphoric Acid. L. F. Rader and W. L. Hill. (*J. Agric. Res.*, 1936, **51**, 1071–1083).—Selenium has been determined in 96 samples of phosphate rock and 3 samples of apatite from different parts of the world, 8 samples of commercial superphosphates manufactured from American rock, and 4 samples of crude phosphoric acid produced by the sulphuric acid process. The amount of selenium ranged from <0·1 p.p.m. in a Tennessee brown rock to 55 p.p.m. in Wyoming and Algerian phosphates; a few samples from Europe contained up to 1 to 2 p.p.m. The selenium comes from organic matter representing the remains of plant life that grew on seleniferous soil, and from inorganic sulphides contained in the rock. Deposits belonging to the Permian and Cretaceous ages contained the most selenium. The quantity of selenium in superphosphate ranged from < 0·8 to 4 p.p.m., and in phosphoric acid from 0·5 p.p.m. downwards; it was concluded that only a small fraction of the selenium in the raw materials finds its way into these products. The method of determination used was substantially that of Robinson, Dudley, Williams and Byers (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 274).

S. G. C.

Improvement in the Gross and Smith Colorimetric Method for the Determination of Rotenone and Deguelin. L. D. Goodhue. (*J. Assoc. Off. Agric. Chem.*, 1936, **19**, 118–120.)—In the original method (*J. Assoc. Off. Agric. Chem.*, 1934, **17**, 336–339; Abst., ANALYST, 1934, **59**, 567–568), an intense yellow colour is produced by the reagents, while instability and variation of colour occur during analysis of derris root extracts, owing to the difficulty of controlling the amount of nitrite present. The colour due to the sample can be controlled, and examination with Lovibond colour slides in a colorimeter shows no red, and a trace only of yellow colour in a blank determination, when the reagents and procedure used are as follows:—*Reagents.*—(*a*) Sulphuric acid solution; 1 volume of conc. sulphuric acid, free from nitrous acid, to 3 volumes of water. (*b*) Alcoholic solution of sodium nitrite; 10 ml. of 10 per cent. sodium nitrite solution, made up to 1 litre with 95 per cent. alcohol. (*c*) Potassium hydroxide solution; 40 g. of potassium hydroxide dissolved in 100 ml. of water. (*d*) Alcoholic potassium hydroxide and sodium nitrite; 1 volume of (*c*) mixed with 7 volumes of (*b*), prepared fresh daily.

Method.—Two ml. of (*d*) are added to 2 ml. of an acetone extract of the sample, corresponding with from 0·005 to 0·25 mg. of rotenone per ml., in a dry test-tube, and the tube is immersed in a water-bath at 25 ± 5° C. for 5 minutes. Five ml. of (*a*) are added, and the tube is stoppered, shaken, and replaced in the water-bath. The red colour obtained reaches a maximum in about 15 minutes and remains unchanged for 2 hours. It is matched, after a minimum time of 4 minutes, against standards prepared at the same time and temperature from rotenone. As in the original test, tephrosin and toxicarol do not interfere, but deguelin gives the same amount of colour as rotenone, and is probably the cause of results for derris root which are about double those obtained by the Jones method (*Ind. Eng. Chem.*, Anal. Ed., 1933, **5**, 23).

Organic

Identification of Acids and Esters. D. V. N. Hardy. (*J. Chem. Soc.*, 1936, 398.)—The method depends on the conversion of esters into the corresponding anilides by treatment with anilino magnesium bromide (*cf.* Bodroux, *Compt. rend.*, 1904, **138**, 1427; *Bull. Soc. Chim.*, 1905, **33**, 832), which is easily obtainable from any simple Grignard reagent and aniline. Thus, $2R.NH.MgX + R''.COOR''' \rightarrow R''C(OMgX)(NHR)_2$, which is hydrolysed to $R''CO.NHR + RNH_2 + OH.MgX$. Aniline (4 g.) is added slowly to a cold solution of ethyl magnesium bromide (prepared from 1 g. of magnesium, 5 g. of ethyl bromide and 30 ml. of pure dry ether). When evolution of ethane has ceased, the ester (0·02 mol.) is added, and the mixture is warmed on the water-bath for 10 minutes and cooled, dilute hydrochloric acid being then added to dissolve the magnesium compounds and the excess of aniline. The ether is removed, and the anilide is obtained as a solid crust on the surface of the solution. The method is speedy and economical, the yields being almost theoretical, and it may be used in conjunction with the separation of acid mixtures by fractional distillation of the corresponding methyl or other ester (*cf.* Hardy, *id.*, 1936, 362, 364); if the aniline is replaced by other aromatic amines, substituted anilides may be obtained. J. G.

Simultaneous Volumetric Determination of Oxalate and Hydrogen Peroxide. A. Simon and T. Reetz. (*Z. anal. Chem.*, 1936, **104**, 249–255.)—A rapid method for use in bleaching practice consists in acidifying the liquor with sulphuric acid and titrating it with 0·1 *N* permanganate, first cold, then hot: this gives the sum of the peroxide and oxalate. A second portion of liquor is treated with 4 to 5 times the required amount of calcium nitrate in *M* solution containing 10 per cent. of ammonia, and about 1 ml. of a 0·1 *N* solution of ferric chloride (as a catalyst), and boiled for 3 to 5 minutes in a covered conical flask for the destruction of the peroxide. The hot liquid is then acidified with sulphuric acid and titrated with permanganate. The two determinations may be made in 20 minutes. W. R. S.

Analytical Uses of Nessler's Reagent. Detection of Aldehydes. Quantitative Determination of Glucose. Part I. M. Goswami, H. N. Das-Gupta and K. L. Ray. (*J. Indian Chem. Soc.*, 1935, **12**, 714–718.)—It has been suggested by Gros and Bougault (*J. Pharm. Chim.*, 1922, **25**, 5, 170; Abst., ANALYST, 1922, **47**, 405) that Nessler's reagent can be used for the determination of some ketones and aldehydes. The method recommended by Gros and Bougault for the determination of ketones was applied to carefully purified glucose, and under standardised conditions was found to be successful. In order to see whether Gros and Bougault's observations could be extended to other aldehydes and ketones, their work was repeated, but it was found that their conclusions could not be corroborated. In general, ketones do not reduce alkaline Nessler's solution, but aldehydes do. Some exceptions were found, *viz.*:—(*a*) hydroxyaldehydes do not reduce, but when the —OH group is protected, usually reduction occurs; (*b*) hydroxyketones (benzoin and fructose) reduce. It has been found that potassium mercuric iodide is easily and rapidly reduced in a strongly alkaline medium. The strength of alkali is important in the reduction of the reagent with glucose or fructose. The extent of reduction depends upon the strength and nature of the alkali (NaOH, KOH or Na_2CO_3) and the temperature of the reaction. Thus, if 10 per cent. sodium hydroxide solution be used and the reactants heated, the oxidation of glucose and fructose proceeds to an extent equivalent to the absorption of 5 atoms of oxygen per mol. of the sugar. If a 10 per cent. sodium carbonate solution be used, the oxidation of glucose corresponds with the absorption of 2 atoms of oxygen, but that of fructose proceeds still further. The Nessler's reagent used had the composition: $HgCl_2$ 2·5 g., KI 8 g., water 100 ml., NaOH 50 ml. of a 30 per cent. solution. To investigate its action with aldehydes and ketones 1 ml. was added to a few drops of the liquid under investigation. The results were as follows:—Reduction in the cold: formaldehyde, acetaldehyde, propylaldehyde, glyoxal, chloral hydrate, heliotropin, furfuraldehyde, cinnamic aldehyde, benzaldehyde, *o*-, *m*- and *p*-nitrobenzaldehyde, paraldehyde; reduction facilitated by gentle heating: aldehyde C_8, C_9, C_{10}, C_{11} and C_{12}; no reduction in hot or cold solution: acetone, methylethyl ketone, acetophenone, benzophenone, cyclo-hexanone. The following are the results in exceptional cases:—in the cold: anisaldehyde, veratric aldehyde, fructose, benzoin; no reduction either in hot or cold: salicyaldehyde and vanillin.

The method adopted for the determination of glucose was as follows:—The standard glucose solution used contained 1·6356 g. of glucose dissolved in 250 ml. of water. Ten ml. of this solution were mixed with 35 ml. of potassium mercuric iodide solution and 50 ml. of 10 per cent. sodium carbonate solution were added. The mixture was slowly heated until reduction began, after which heating was continued to boiling, until the liquid became clear and a black precipitate separated. The solution was cooled and acidified with 15 ml. of glacial acetic acid, 25 ml. of *N*/10 iodine solution were added, and the mixture was shaken until the finely-divided black precipitate completely dissolved. The excess of iodine was then titrated with *N*/10 sodium thiosulphate solution. The percentage error in a series of determinations varied from 0·1 to 0·8. The factor used to convert ml. of *N*/10 iodine into glucose was 0·0045, corresponding with the absorption of 2 atoms of oxygen per mol. of glucose. The method was successfully applied to the determination of a known amount of glucose in urine. A. O. J.

Telfairic Acid. G. D. Goodall and R. D. Haworth. (*J. Chem. Soc.*, 1936, 399.)—The so-called telfairic acid isolated by Thoms (*Arch. Pharm.*, 1900, **238**, 48) from the seeds of *Telfairia pedata* (Koeme seeds) and considered by him to be an isomer of linolic acid, has now been shown to be identical with that acid. The method used was saponification of the oil extracted from the seed by petroleum spirit (yield, 60 per cent.; iodine value, 89·0; saponification value, 192·5), liberation and isolation of the acids, and separation of the unsaturated portion by the lead salt and ether method. This was then brominated by Rollett's method (*Z. physiol. Chem.*, 1909, **62**, 410), and the formation of tetrabromostearic acid was confirmed by the method of mixed melting-point; methyl tetrabromostearate (m.p. 58° C.) and tetrahydroxystearic acid (m.p. 174° C.) were also prepared and identified by comparison with authentic specimens from poppy-seed oil. J. G.

Oxidation Products of the Unsaturated Acids of Linseed Oil. L. C. A. Nunn and I. Smedley-Maclean. (*Biochem. J.*, 1935, **29**, 2742–2745.)—The unsaturated acids of linseed oil were oxidised with a dilute solution of potassium permanganate. From the products of the reaction, a dibasic acid, $C_{12}H_{22}O_6$, whose constitution was determined as 11-carboxy-9:10-dihydroxyundecanoic acid, was isolated as the zinc salt. The corresponding lactonic acid was also present. Labile forms of the hexa- and tetra-hydroxystearic acids were apparently formed during the oxidation, but these readily suffered further degradation. The determination of the hydroxyl groups of sativic and dihydroxystearic acids and of the acid $C_{12}H_{22}O_6$ was carried out by the method described by Criegee (*Ber.*, 1931, **64**, 260). S. G. S.

Qualitative Test for Linolenic Acid; its Value and Limitations. (*J. Amer. Chem. Soc.*, 1936, **58**, 364–365.)—One ml. of the oil to be tested is layered over 5 ml. of the arsenophosphotungstic acid (prepared as for the determination of uric acid by Benedict's method, *J. Biol. Chem.*, 1931, **92**, 161), and the tube heated for 1 hr. in a boiling water-bath. The production of a blue colour in the reagent layer indicates the presence of linolenic acid. Since more highly unsaturated acids (which would probably give positive reactions) are not present in

vegetable oils, the test is in such cases specific for linolenic acid or its esters. With animal fats and oils, arachidonic acid and perhaps other highly unsaturated acids would invalidate the test. Such oils as linseed, perilla, chia seed and hemp-seed oils give intense blue colours, whilst oils of the soya, lumbang, mustard and rape oil group, the members of which contain about 2 per cent. of linolenic acid, give weak colours. The test could be used to indicate rancidity or adulteration in oils of the group. Arsenic and phosphoric acids, sodium tungstate and phosphomolybdic acid do not give a blue colour with linolenic acid. The reaction, at present, is only to be regarded as roughly quantitative, owing, in part at least, to the difficulty of obtaining adequate miscibility of oil and reagent. Although tung oil gave no reaction, oiticica oil reacted positively, but the significance of this fact cannot be interpreted, owing to lack of knowledge of the structural formulae of the oils. D. G. H.

Liver Oil of Man-Eating Shark. M. Tsujimoto. (*J. Soc. Chem. Ind., Japan*, 1936, **39**, 82–83B.)—The oil was obtained from the liver of a man-eating shark, *Carcharodon carcharias* (Linné), or "Hôjirozamé," kept in an aquarium, and measuring over 3·64 m. in length. The liver, which weighed 38 kg., yielded some 40 per cent. of yellow oil, which deposited a large amount of solid material in winter and had: sp.gr. at 15°/4° C., 0·9199; $n_D^{20°}$, 1·4733; saponification value, 178·1; iodine value (Wijs), 105·9; acid value, 1·31; and unsaponifiable matter, 6·97 per cent. With sulphuric acid a deep violet-red colour was produced, and with antimony chloride a blue colour. The fatty acids consisted of a pale yellow, crystalline mass of m.p. 33–34° C.; neutralisation value, 199·4; iodine value, 107·5; and ether-insoluble bromide, 18·7 per cent., containing 69·69 per cent. of bromine. The orange-yellow crystalline unsaponifiable matter contained 50·5 per cent. of cholesterol, and the sterol-free substance consisted chiefly of selachyl and batyl alcohols. D. G. H.

***Cryptocarya latifolia* Nuts from South Africa.** (*Bull. Imp. Inst.*, 1936, **33**, 451–453.)—*Cryptocarya latifolia* nuts from Natal and East Griqualand, were obtained from a 60-ft. tree known to the Zulus as "umtungwane"; they were about 1 in. in diameter with a fairly thick woody shell and contained oily kernels covered with a thin brown papery skin with greyish veins. The average weight of a nut was 4·5 g., consisting of 55·4 per cent. of shell and 44·6 per cent. of kernel. The kernels contained 4·8 per cent. of moisture and 61·1 per cent. of oil. A brown resinous saponifiable material was extracted with petroleum spirit, in addition to the light brown semi-solid fat which had the following constants: sp.gr. 100/15° C., 0·8647; m.p., 26·0° C.; $n_D^{40°}$, 1·4585; saponification value, 213·0; iodine value (Wijs), 75·2; acid value, 56·5; unsaponifiable matter, 1·4 per cent.; soluble volatile fatty acids, 11·1 per cent.; insoluble volatile fatty acids, 0·3 per cent.; solidifying-point of fatty acids, 39·5° C. The buff coloured residual meal had the following percentage composition: moisture, 12·8; crude proteins, 23·1; ethereal extract (not fatty and probably resinous material), 14·7; carbohydrates, 36·1; crude fibre, 6·7; ash, 6·6. The meal was intensely bitter and contained a substance (or substances) giving positive reactions for alkaloids. The oil can only be regarded as a low-grade soap-making oil, and the meal would not be suitable as a feeding stuff. D. G. H.

Sensitive Colour Reaction of Urea. J. A. Sanchez. (*Ann. Chim. anal.*, 1936, **18**, 65–66.)—The reaction, which is sensitive to about 1/100 mg., depends upon the conversion of urea into phenyl semi-carbazide or phenyl carbazide, both of which give a fine red colour with vanillin hydrochloride. The reagents required are an aqueous 1·5 per cent. solution of phenyl hydrazine hydrochloride, an aqueous 0·1 per cent. solution of urea and the vanillin reagent prepared by dissolving 0·5 g. of vanillin in 100 ml. of hydrochloric acid. Five drops of the phenyl hydrazine solution and 3 drops of the urea solution are heated in a test-tube in a glycerin-bath, the temperature of which is not allowed to exceed 120° C. until all the liquid has evaporated. The temperature of the bath is now raised to 160° C. and when it reaches this value the time is noted and heating is continued for exactly 5 minutes between 160° and 170° C., after which the tube is removed from the bath, cooled and 10 drops of the vanillin reagent are added. The tube is then placed in a boiling water-bath for 1 minute. A fine red colour is produced in the presence of urea. By the reaction between urea and phenyl hydrazine at 160° C., phenyl semi-carbazide or phenyl carbazide is formed, and either of these gives the red colour with vanillin. The reaction has been obtained, though with less intensity, with methyl and ethyl urethanes and with barbituric acid and some of its derivatives by heating them with phenyl hydrazine hydrochloride to 160° C. An intense colour is produced when cryogenine (*m*-benzamide semi-carbazide) and maretine (*m*-tolyl semi-carbazide), which contain the group $NH_2.CO.NH.NHR$, are gently heated with the vanillin reagent. A. O. J.

Inorganic

Detection and Determination of Mercury. C. Mahr. (*Z. anal. Chim.*, 1936, **104**, 241–245.)—Ammonium tetrathiocyanato-diammine-chromiate ("Reinecke's salt") gives a pale-red voluminous precipitate, $Hg[(CNS)_4Cr(NH_3)_2]_2$ with mercuric salts in 0·1 *N* hydrochloric acid solution. The reaction is extremely sensitive, as 2·5γ of mercury can be detected in 5 ml. after 2 minutes' standing. The only other metals precipitated by the reagent from acid solution are gold, silver and thallium; other metals do not interfere. For quantitative work the solution, which may contain moderate amounts of nitric, sulphuric, acetic, or tartaric acid, is treated with hydrochloric acid to 0·5 *N* concentration, and heated almost to boiling on a steam-bath in a covered beaker. The mercury concentration should not exceed 0·02 g. per 100 ml.; with more than 0·05 g. of metal the precipitate is inconveniently bulky. The solution is treated, drop by drop, with a fresh, filtered, slightly acid solution of the reagent (0·05 g. per 0·01 g. of metal). After a few minutes the beaker is removed from the heat, allowed to stand for 5 minutes, and the precipitate collected in a sintered-glass crucible and thoroughly washed with hot water.

Volumetric determination.—The precipitate is dissolved in the crucible by addition of 0·2 to 0·3 g. of potassium cyanide and hot water, the filtrate being received in a 400-ml. conical flask. Any chromic hydroxide that separates is dissolved in a little *N* hydrochloric acid, and the crucible is well rinsed and discarded. The filtrate is diluted to 100 to 250 ml. according to the amount of mercury,

treated with 3 to 7 ml. of strong sulphuric acid and 2 to 3 g. of potassium bromate, and boiled for 15 minutes. The oxidation to chromic acid is promoted by addition of a drop of nickel nitrate solution. The bromate is then destroyed by 20 minutes' boiling with addition of 5 to 7 g. of ammonium sulphate and 5 to 6 ml. of *N* hydrochloric acid. A current of carbon dioxide may be used to expedite the removal of the bromine. The original volume is maintained during boiling by addition of water. The cooled solution is treated with 2 to 3 g. of potassium iodide, and titrated with thiosulphate. One ml. of 0·1 *N* solution = 0·0033435 g. Hg.

Gravimetric determination.—The precipitate is washed as above with water, then with alcohol, and dried for 1½ hours at 105° to 110° C.; it contains 23·96 per cent. of mercury. With large amounts, the results may show a positive error of 0·5 to 1 per cent. Ignition of the precipitate to chromic oxide, however, gives correct results. This mode of working is recommended for quantities exceeding 0·05 g., the precipitate being collected in a porous porcelain crucible or on a filter paper. The conversion factor for Cr_2O_3 to Hg is rather high, *viz.* 1·3196.

W. R. S.

Application of Copaux's Method to the Determination of Arsenic Acid. J. Courtois. (*J. Pharm. Chim.*, 1936, **23**, 269–283.)—Copaux's method for the determination of phosphoric acid consists in precipitating this acid in the form of an insoluble yellow oily complex molybdenum compound, which can be separated by centrifuging in a graduated ampoule and measured. It was found with arsenic acid that the composition and amount of the precipitate formed are variable, depending on the temperature and the nature and concentration of the mineral acid present. The method is therefore limited to comparing the amount of arsenic present with that in a standard under strictly similar, but empirically chosen, conditions.

S. G. C.

Detection of Tin and Antimony. J. A. Gautier. (*J. Pharm. Chim.*, 1936, **23**, 283–290.)—To the solution of the sulpho-salts of tin and antimony obtained in the usual course of qualitative analysis by treating the Group II sulphides with ammonium sulphide, acetic acid is added to precipitate the sulphides. The precipitate is filtered off, introduced into a capsule, and dilute hydrochloric acid (1 : 3) is added. The liquid is heated for 2 minutes somewhat below the boiling-point (80° C.). Practically all of the antimony sulphide dissolves, together with most of any copper sulphide which may be present, but much of the tin sulphide remains undissolved. A part of the supernatant liquid is filtered off, and to the filtrate antipyrine and iodide reagent (1 g. of antipyrine and 2 g. of potassium iodide dissolved in 30 ml. of water) is added: antimony gives an orange precipitate; a whitish precipitate indicates the presence of tin. To the remaining material in the capsule more hydrochloric acid is added, and the liquid is boiled for 5 minutes in order to dissolve the tin sulphide; it is diluted with water, and any residue is filtered off and rejected. The presence of tin in the filtrate is shown by the usual process of reducing with iron powder, filtering, and adding mercuric chloride to the cooled liquid, when a white precipitate of mercurous chloride is formed.

S. G. C.

Determination of Gold without Cupellation. J. Donau. (*Z. anal. Chem.*, 1936, **104**, 257–270.)—The author practises inquartation of the unknown alloy with a cadmium-zinc alloy (87 per cent. cadmium) in a small Jena-glass tube in a current of hydrogen, with subsequent parting by nitric acid in the usual manner. The amount of cadmium alloy required can be varied within fairly wide limits, 4 to 9 times that of the gold present in the assay. If substantial amounts of palladium are present, inquartation and parting should be repeated. Alloys containing tin require special treatment. If the tin-content is less than about 30 per cent., the metal is fused with a quantity of cadmium alloy not less than the weight of gold present and not more than twice that amount. If the tin-content exceeds 30 per cent., the alloying operation is dispensed with. In either case, the metal is parted with nitric acid, and the carefully washed gold and stannic acid are heated with ammonium chloride in the glass tube. The tin is volatilised as chloride; the treatment with ammonium chloride is repeated. Full directions are given in the paper. W. R. S.

Determination of Tungsten and Silicon in Steels by means of Perchloric Acid. A. Clauberg and P. Behmenburg. (*Z. anal. Chem.*, 1936, **104**, 245–249.)—The determination is claimed to be accurate, and capable of being carried out within 3½ hours. Two g. of drillings (1 g. if tungsten exceeds 5 per cent.) are treated in a porcelain dish with 35 (25) ml. of perchloric acid (sp.gr. 1·67) by heating in an air-bath for 5 minutes, then by gentle boiling until dissolved (10 minutes). The solution is cooled, and boiled for some minutes after addition of 1:1 hydrochloric acid (50 ml.). The acid is then diluted with an equal volume of hot water, and left to stand for an hour at 80° C. The yellow precipitate is collected on a double filter, and washed with dilute hydrochloric acid and finally with water. The ignited and weighed precipitate, consisting of tungstic oxide and silica, is treated with hydrofluoric acid, etc., in the usual manner. W. R. S.

Microchemical

Organic Micro-analysis. K. Lindenfeld. (*Mikrochem.*, 1934–35, **16**, 153–170.)—*Carbon-hydrogen determination.*—The Pregl method is somewhat modified; Flaschenträger's absorption tubes with taps are substituted for the Pregl type, and are weighed full of oxygen, so that the use of air is dispensed with. Ascarite, mixed with soda-lime, is the filling in the carbon dioxide absorption tube, as this prevents the increase in resistance with use that results with ascarite alone.* Calcium chloride, previously dried in a desiccator and heated at 200° C., is used for the absorption of water. The Pregl filling in the combustion tube is retained, except that cerium dioxide on pumice replaces the oxidising filling. During the combustion a slightly higher velocity of gas is used—5 to 6 ml. per minute instead of 4 ml. A platinum contact is placed in the combustion tube about 4 cm. behind the boat containing the substance; this is heated with a Bunsen burner during the combustion and prevents any back diffusion of unburnt gases which may occur in the Pregl method when combustion is too rapid.

* *Abstractor's Note.*—Glass-wool mixed with ascarite also serves this purpose.

Determination of Nitrogen by Pregl's Micro-Dumas Method.—Air-free carbon dioxide is obtained from the action of sulphuric acid (20 per cent. by volume) on lumps of sodium carbonate. As, occasionally, a negative pressure may occur in the combustion tube, the apparatus must be tested from time to time to see that it is air-tight. *Determination of Sulphur.*—High results with the Pregl method were found to be due to the use of gas burners. When an electric heater was used satisfactory results were obtained. J. W. M.

Micro-analysis of Cholesterol. I. Investigation of the Liebermann-Burchardt Reaction. K. Šilink. (*Mikrochem.*, 1934–35, **16**, 45–66.)—In the Liebermann–Burchardt reaction 2 ml. of acetic anhydride and 3 drops of conc. sulphuric acid are added to 5 ml. of a chloroform solution of cholesterol, and the green colour is compared with a standard after a suitable time-interval. It was found that the development (I) and fading (II) of colour are two independent reactions, and the conditions were investigated. Traces of water retard stage I of the reaction, but do not affect II. At a temperature of 16° C. the maximum colour-intensity persists longer, at 22° C. the fading begins immediately the maximum is reached. Errors are unavoidable, even with careful manipulation, but may be kept down to 4 to 8 per cent. A large number of time-curves are given for readings in various conditions; from which it appears that several readings are advisable, as the correct concentration may be calculated from the time-curve for a given temperature. J. W. M.

Collected References. Micro-Technique in Testing Manufactured Products. I. 1918-1928. E. Gründsteidl. (*Mikrochem.*, 1934–35, **16**, 247–320.)—The sampling problem is discussed (3 references) and the general methods applicable to all kinds of commercial testing, such as methods of filtration, work in impregnated threads, crystallographic methods, boiling-point determination, vacuum sublimation, capillary analysis, volumetric work with the centrifuge, hydrogen-ion determination, work with borax beads, measurement of minute volumes of liquid, surface tension measurement, micro colorimetry and turbidity measurement are briefly described (40 references). The methods of analysis of metals and alloys (18 references), glass and pottery (20 references), dyes and lakes (22 references), mineral fuels (14 references), fermentation industry problems (44 references), foods (86 references), preservatives (26 references), drugs and pharmaceutical products (42 references), textiles (27 references), cellulose and paper (20 references), and various (16 references), are all described in some detail. J. W. M.

Physical Methods, Apparatus, etc.

Photometric Method for the Determination of Melting-points. P. Woog, J. Givaudon, R. Sigwalt and J. Lienhart. (*Bull. Soc. Chim.*, 1936, V, **5**, 439–442.)—The apparatus is based on the principle of the Bunsen photometer. Since a stain formed on a screen by the material whose m.p. is to be determined is rendered visible when the two faces of the screen are unequally illuminated, it is possible by suitable unequal illumination of the faces to arrange that the stain appears

when the sample melts. The method is particularly suitable for waxes and fats, and it requires a mg. or less of the sample; with small particles (*e.g.* crystals) a halo appears around the fragment when melting starts, completion being marked by the disappearance of the particle and the formation of a uniform stain. A viewing tube, in the base of which is a lens or glass disc, is inserted in the top portion of a vertical cylindrical chamber (diameter 28 mm., depth 60 mm.) in the centre of a cylindrical aluminium block (diameter 90 mm., height 60 mm.). Below the end of the tube is a diaphragm with a circular central opening (diameter 16 mm.), on which is placed a cover slip (18 × 18 mm.) with a frosted top surface. At right angles to the vertical hole are two parallel horizontal holes, the outside ends of which are closed by glass or mica discs and adjustable diaphragms. A source of light is placed so as to illuminate these diaphragms equally, and by adjustment of the latter it is possible to control the intensities of illumination entering the central chamber above and below the cover-slip; the horizontal base only of the latter portion of the central chamber is painted matt black. A thermometer is inserted horizontally into the aluminium block, so that the bulb projects into the lower central chamber near the base, and the whole apparatus is supported on an electric-heater with a variable resistance. The apparatus is set by inserting a cover-glass on which is an oily stain (the viewing-tube being removed for this purpose), and arranging the diaphragms so that the stain is easily visible; the cover-slip is then replaced by another slip which carries the material to be investigated, and the temperature is gradually raised. J. G.

Examination of Chalks under Ultra-violet Light. W. E. Naylor and A. Surfleet. (*Pharm. J.*, 1936, **136**, 261.)—Genuine samples of B.P. prepared chalk had a peach- or flesh-coloured fluorescence in filtered ultra-violet light, whilst with genuine B.P. precipitated chalks a "smoky" greyish-violet colour was produced. A sample alleged to be prepared chalk was shown in this way to be precipitated chalk, and the results were confirmed by the micro-crystalline structure usually associated with the precipitated variety. The fluorescence method may be applied satisfactorily to distinguish chalks used in preparing MacLean's powder (*cf.* Grant, *Proc. Technical Sec. Paper Makers' Assoc.*, 1935, **16**, 97). J. G.

Reviews

REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY. Vol. XX. 1935. Issued by the Society of Chemical Industry. Pp. 753 (excluding Indexes). Price to members, 7s. 6d.; to non-members, 12s. 6d.

The industrial, or other of the many varieties of chemist, faced with the necessity of keeping himself informed of developments in branches of the science other than his own particular line of work, is confronted with the alternative of abstracting abstracts for himself or making use of an annual résumé, such as that under review. In this, the year's progress is recorded under twenty-five headings, each written as a connected account by a recognised authority on the subject

treated, and each capable of being read as a connected story, without causing that attack of mental indigestion so liable to follow a conscientious attempt to keep pace with the weekly output of Abstracts B.

The various subjects are discussed critically, and a good standard of literary style is maintained. Amongst those most likely to appeal to members of this Society may be mentioned Oils, Fats and Waxes, by T. P. Hilditch; Soils and Fertilisers, by E. M. Crowther; Sugars, by Lewis Eynon and J. H. Lane; Foods, by H. E. Cox; and Sanitation and Water Purification, by C. Jepson.

All these articles contain references to the analytical chemistry of their subject-matter, some in the text and others under separate sub-headings.

Analytical chemistry as a separate subject is dealt with in the Chemical Society's Annual Report, and so this Report contains no separate section on progress in analytical chemistry, but analysis is by no means entirely neglected in articles other than those mentioned above; this is what was to be expected from a list that contains eight members of this Society out of a total of forty-two contributors.

The work is characterised by clarity of style and freedom from errors and misprints. The usual full bibliography is supplied as footnotes.

The reviewer would like to suggest that a table of the abbreviations employed in the references would form a useful addition. Its inclusion might well mark the "Coming of Age" number next year. F. L. OKELL

ORGANIC SOLVENTS—PHYSICAL CONSTANTS AND METHODS OF PURIFICATION. By A. WEISSBERGER and E. PROSKAUER, translated from the German MS. by R. G. A. NEW. Pp. 212. Published by Humphrey Milford, Oxford, Clarendon Press. Price 15s. net.

It is no mere cliché to say that this is a book which should be in every type of laboratory and within easy access of every student. The increased range of organic solvents available both for research and for industrial use fully justifies the publication of a reference book devoted solely to their physical properties and to their purification. There has been a tendency for recent books on solvents to be written with an eye to their specialised use in certain branches of industry, and this has necessarily involved some curtailment of general usefulness. The present work is free from this limitation and deserves nothing but praise.

It is obviously impossible for the writers to have tested for themselves the innumerable methods of purification described in the book; though more indication of the relative value of alternative methods might have been useful, it must be remembered that research workers seeking abnormally exacting standards of purity must, in any case, refer to the original literature. An exhaustive bibliography with over 1400 references is appended, and a number of these are as recent in date as 1935.

The book is excellently arranged and, as far as we can see, compiled with meticulous care. Among the few omissions we notice aldehydes, and they are, at any rate potentially, as valuable as certain of the other solvents described. Furfural and furfuryl alcohol, neither of which is described, are now available commercially in the United States. The former, mentioned as an impurity in

ethyl alcohol, is spelt on pp. 118–119 with the disused spelling, furfur*ol*. Ethylene glycol is described, but trimethylene glycol, which we understand is available commercially in the United States, is not mentioned.

Careful search has revealed very few errors. *o*-Nitroanisole is incorrectly described as a nitro-alcohol instead of as a nitro-ether on p. 7, and on p. 113 "sense and direction" of rotation is used where "sense and magnitude" is obviously intended. Indiscriminate use of alternatives such as tribrom-benzoic acid (p. 117) and tribromobenzoic acid (p. 122) has occasionally escaped the proof reader. The translator is to be congratulated on his excellent work.

The authors have wisely included in their scope the toxicity of many of the solvents and have quoted several important references. The value of future editions would be increased still further if mention of toxic properties in the general text were somewhat amplified and placed on a more quantitative basis, for the book will undoubtedly find its way into the hands of many chemists responsible for the health and safety of operatives. For example, it is not generally known that, according to Safety Circular No. 51 of the Association of British Chemical Manufacturers, prolonged exposure to benzene vapour in concentrations below those detectable by odour may be considered harmful. E. W. PATES

THE CHEMISTRY OF MILK. By W. L. DAVIES, PH.D., M.SC., F.I.C. Pp. xii + 552. London: Chapman & Hall. Price £1 5s.

"Richmond," that old-time mine of information, has been out of date for many years, and with most dairy chemists has been superseded by "The Fundamentals of Dairy Science," edited by L. A. Rogers. One is inclined to ask, therefore, whether a further text-book is required so soon after the publication of the second edition of the latter. The author in his preface seems to have no doubt as to the value which this book will have to those interested in milk and its problems, and so we will leave it at that. It is not possible for any one man to be a specialist in all the sections of milk chemistry, physics and technology, and therefore Dr. Davies has not been able to give us what is badly needed, a critical monograph.

By putting each section and even sub-sections in the hands of specialists the Americans have more nearly approached what should be the ideal way of composing such a treatise.

Another feature the reviewer would like to see in a monograph is a few blank sheets at the end of each section on which to note down ideas, additional references, and so on. This could easily have been arranged by reducing or leaving out some of the unnecessarily long tables; *e.g.* no good purpose is fulfilled by giving all the figures quoted for the composition of milk on p. 19; further, nothing is gained by giving the numerous figures for copper and iron on pp. 223 and 224. All that is required are figures which a critical examination of the method and technique of analysis suggest as nearest the truth; anything more is misleading.

The description of the work of Lampitt and Bushill on p. 85 is erroneous—it is spray powders that have the fat-particles surrounded by a membrane of amorphous lactose which prevents the extraction of the bulk of the fat by solvents; if, however, moisture is absorbed until the lactose crystallises, the particle is ruptured and the fat is then readily extracted.

Again, the statement on p. 99, that on heating lactose hydrate to 110° C. no change occurs, is contrary to the fact that it starts to lose water at 80° C., as shown by Herrington, and is contradicted by the author himself on p. 106, where he says, "when the moisture is determined by the oven method (100° C.) all the water of crystallisation is slowly driven off."

In the chapter on the Enzymes of Milk—a subject on which much work remains to be done—there are several statements of doubtful validity. The method described on p. 181 for detecting lipase is not satisfactory, as organisms can grow in the cream saturated with sucrose, and there is no doubt that such bacteria as the staphylococci and micrococci ordinarily contaminating milk have fat-splitting properties. The reviewer is also unable to understand the statement on p. 203 concerning the re-activation of catalase, where the conditions described are quite likely to lead to the production of bacterial catalase, nor can this enzyme be regarded as "fairly heat resistant," as it is destroyed at a lower temperature than phosphatase.

As regards this latter enzyme, the statement on p. 358, that it does not appear in the ordinary flora which would proliferate in pasteurised milk, is not borne out by experiments in the reviewer's laboratory. It is doubtful whether anyone who has had practical experience of milk-condensing would support the author's faith in the alcohol test. There is also considerable doubt whether Greenbank and Holmes's statement, that tallowiness develops more readily in milk powders of very low moisture-content, is correct; it certainly is not of general application.

It is surprising that under Dried Whey no reference is made to the pioneer work of Harding published in 1913. Despite these errors, to which attention is called in order to emphasise the necessity for critical reading, there is a mass of useful material in the book, and the bibliography is excellent; one must echo, therefore, the editor's quotation from Goethe that "higher aims, even if unfulfilled, are in themselves more valuable than lower aims quite attained," and hope that what has been said will stimulate the author to do what he undoubtedly can—write a critical monograph on sections of the subject with which he has first-hand acquaintance.

E. B. ANDERSON