THE ANALYST

THE ORGAN OF THE

Society of Public Analysts and other Analytical Chemists

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT OF ANALYTICAL CHEMISTRY

Publication Committee:

J. T. DUNN, D.Sc., F.I.C. (President).

A. L. BACHARACH, B.A., F.I.C.
E. RICHARDS BOLTON, F.I.C.
A. CHASTON CHAPMAN, F.I.C., F.R.S.
H. E. COX, M.Sc., Ph.D., F.I.C.
CECIL H. CRIBB, B.Sc., F.I.C.
BERNARD DYER, D.Sc., F.I.C.
B. S. EVANS, M.B.E., M.C., Ph.D., F.I.C.
J. T. HEWITT, M.A., Ph.D., D.Sc., F.R.S.
E. HINKS, M.B.E., B.Sc., F.I.C.
W. G. MESSENGER, B.Sc., F.I.C.
G. W. MONIER-WILLIAMS, O.B.E., M.C., Ph.D., F.I.C.
W. PARTRIDGE, F.I.C.
P. A. ELLIS RICHARDS, F.I.C.
W. H. SIMMONS, B.Sc., F.I.C.
J. AUGUSTUS VOELCKER, C.I.E., M.A., Ph.D., F.I.C.

Hon. Secretary:
F. W. F. ARNAUD, F.I.C.

Hon. Treasurer:
E. B. HUGHES, M.Sc., F.I.C.

Editor: C. AINSWORTH MITCHELL, M.A., D.Sc., F.I.C.

Abstractors:

J. W. BROWN, Ph.D., A.I.C.
S. G. CLARKE, Ph.D., B.Sc., F.I.C.
J. GRANT, Ph.D., M.Sc., F.I.C.
D. G. HEWER, B.Sc.
R. F. INNES, F.I.C.
T. H. POPE, B.Sc., F.I.C.
P. H. PRICE, B.Sc.
W. R. SCHOELLER, Ph.D.
W. P. SKERTCHLY, F.I.C.

VOL. LVI.

1931

PUBLISHED FOR THE SOCIETY BY
W. HEFFER & SONS LTD.
4, PETTY CURY, CAMBRIDGE, ENGLAND
1931

JANUARY, 1931. Vol. LVI., No. 658.

THE ANALYST

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

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 3rd, the President, Dr. J. T. Dunn, being in the chair.

Certificates were read for the first ime in favour of:—Kenneth Bullock, M.Sc., Ph.D., and Frederick Cecil Hymas, B.Sc. A.I.C.

Certificates were read for the second time in favour of:—Arthur Nicholls Ainsworth, B.Sc., Bertram Arthur Gough, William Henry Gough, M.Sc., A.I.C., and William Henry Shilling, B.Sc., A.I.C.

The following were elected Members of the Society:—Leonard Balmforth, B.Sc., F.I.C., Reginald Joseph Cole, B.Sc., Violet Dorothy Dudman, B.Sc., A.I.C., Frank George Edmed, O.B.E., B.Sc., A.R.C.Sc., F.I.C., Roy Gardner, D.Sc., F.I.C., William Victor Griffiths, B.Sc., A.I.C., Daoud Younis Haddad, B.Ph., Percy George Terry Hand, F.I.C., Magnus Herd, B.Sc., A.R.T.C., F.I.C., Gilbert Underwood Houghton, B.Sc., A.I.C., Archibald Robert Jamieson, B.Sc., F.I.C., William Jefferys Lesley, M.Sc., Ph.D., A.I.C., Allison Reginald Murray MacLean, B.A., M.Sc., Ph.D., Frederick Henry Newington, F.I.C., Colin Paterson, B.Sc., A.I.C.

The following papers were read and discussed:—"A Storage and Delivery Apparatus for Antimony Chloride and other Corrosive Reagents," by G. Middleton, B.Sc., A.I.C.; "Tests for Impurities in Ether," Parts II and III, by G. Middleton, B.Sc., A.I.C., and F. C. Hymas, B.Sc., A.I.C.; "The Determination of Small Quantities of Calcium in Magnesium Salts," by Norman Evers, B.Sc., F.I.C.; and "A New Method for the Detection of Nitro-Group in Organic Compounds," by P. K. Bose, D.Sc.

NORTH OF ENGLAND SECTION.

A MEETING of the Section was held on December 6th, the members, by kind invitation, being the guests of the Co-operative Wholesale Society.

In the morning the party, twenty-six in number, met in Manchester, and was conveyed to the C.W.S. works at Middleton Junction, where the processes of

manufacture of malt vinegar, jam, etc., were inspected. The party returned to Manchester and was entertained to lunch.

In the afternoon a meeting was held at which the following papers were read and discussed:—"The Reichert-Polenske-Kirschner Values of Rancid Butters and Margarines," by G. D. Elsdon, B.Sc., F.I.C., R. J. Taylor and P. Smith; "The Detection of Benzoic Acid in Food Stuffs," by A. N. Leather, B.Sc., F.I.C.

Prof. W. H. Roberts opened a discussion on the standards and definitions for jam recently agreed upon by the Food Manufacturers Federation and the Society of Public Analysts. An adjournment for tea was followed by a thorough discussion in which most of the members participated.

Death.

WITH great regret we record the death, on December 25th, of Dr. Henry Leffmann, who was a Vice-President of the Society in 1901-2.

The Determination of the Milk Proteins.

BY GEORGE M. MOIR, M.Sc., Ph.D., A.I.C.,
Pedler Research Scholar of the Institute of Chemistry, 1928–1930.

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

I. THE CHEMISTRY OF THE SEPARATION OF CASEIN.

INTRODUCTION.

A CERTAIN amount of confusion has arisen because of the fact that the substances described in continental and American literatures as "casein" and "paracasein" have sometimes been referred to in English literature as "caseinogen" and "casein," respectively. The first term in each case signifies the base-free protein as normally obtained from milk by acidifying, while the second is applied to the modified base-free protein obtained by the action of rennin on milk. The former terminology, which is adopted in this paper, has received much wider recognition, and it would be a great advantage if the term "caseinogen" were dropped.

Casein exists in milk not as a solution but as an ultra-microscopic dispersion of particles which consist of a compound of the protein with calcium, and this compound is often loosely referred to as "casein." It is highly probable that the colloidal calcium phosphate of milk is very closely associated, if not actually combined, with the dispersed protein. This colloidal material undoubtedly plays a

large part[1] in stabilising the fat emulsion of milk in a serum which contains two other proteins, albumin and globulin, which are considered to be actually in solution. It is very likely that a small amount of these two proteins is adsorbed upon the fat globules, thereby assisting the casein to stabilise the emulsion. The possibility, slight though it is, that the soluble proteins may be adsorbed upon the caseinate micelles, must not be overlooked. Owing to the intimate association of the fat and the casein it is impossible to separate the latter from the milk without removing the former at the same time. Consequently, any other protein matter associated with the fat may also be thrown down and remain with the precipitate unless it can be removed.

Some of the earlier methods used for estimating casein in milk (described by Richmond[2]) have long since been abandoned. However, I have used the principle of weighing the fat together with the casein (after drying) as the basis of a method which may be useful for estimating the value of milk for cheesemaking. Some of the other rapid processes for determining the casein after precipitation, such as Van Slyke and Bosworth's titration method,[3] Hart's centrifugal method,[4] Robertson's refractometric method,[5] and the iron alum titration method of Arny and Pratt[6] are, no doubt, capable of giving more or less satisfactory results if properly carried out, but they cannot be expected to yield results as accurate as those based on the nitrogen content of the precipitate. The same can be said of Harris's[7] potentiometric titration method for the total protein in milk.

When salts are used to precipitate the casein, not merely do they lack any solvent effect on the other proteins, but they usually have a tendency to render the latter more insoluble, with the result that unduly high values are obtained. That this is the case with potash alum, which has most frequently been used for casein determination, is clear from the extensive series of figures recently published by Danish investigators.[8] Howe[9] has also shown that saturated sodium chloride precipitates part of the globulin, while it has long been known that magnesium sulphate precipitates the casein and globulin together.

THE USE OF AN ACID PRECIPITANT.—The choice of a satisfactory and accurate method for separating the casein must therefore fall on the use of an acid reagent which will remove as much as possible of the material combined or associated with the protein as it exists in milk. Acetic acid has been much used for this purpose in the past, but Van Slyke and Winter[10] found that some latitude was permissible in the amount of acid that could be used with the highest quantitative results; also, that the higher the casein content of the milk (and therefore the greater the buffer value), the greater the amount of acid necessary.

The successful use of acetic acid depends on the fact that casein is a protein which is insoluble at its isoelectric point, which can be roughly attained by mixing definite quantities of milk and acid. Usually slight excess of acid is used to ensure complete precipitation and ease of filtration, but this involves the risk of redissolving some of the casein. This risk is evident from my analytical results, some of which will be given later, and also from the observations of others.[11]

The idea of precipitating the casein from milk as close as possible to its isoelectric point was first put forward by Waterman[12,13], but his method has proved unsuitable. With this objective it is necessary in the first place to have the *p*H of the point as definitely fixed as possible. Investigations have been made by Michaelis and his collaborators, who, as a result of their cataphoresis experiments, first stated the point as *p*H 4·74.[14] More careful experiments[15] subsequently gave a value of *p*H 4·6 ($H^+ = 2{\cdot}4 - 2{\cdot}5 \times 10^{-5}$). In a later paper[16] Michaelis showed by a series of nephelometric precipitation experiments that the point of optimum flocculation of casein was capable of being very considerably altered by the presence of different salts in the solution from which it was precipitated. In the presence of sodium acetate alone it lay between *p*H 4·4 and 4·7 (in these particular experiments his technique was developed with differences of 0·3 *p*H). In view of the possibility of such variations it is not surprising that Csonka, Murphy and Jones,[17] by solubility determinations in a series of buffer solutions, found the isoelectric point at *p*H 4·85. A further factor that is likely to cause variation in such determinations is that in the preparation of the "pure" casein employed for the experiments, changes may have been induced in the original material, especially if it has been subjected to a *p*H even faintly alkaline.[18,19] Recently Lebermann[20] treated skim milk with acetate mixtures of varied composition, and concluded (from what appear to be rather inadequate experiments) that the optimum precipitation of the casein occurred at *p*H 4·89.

Waterman[13] pointed out that the amount of acetic acid (1·5 ml. of 10 per cent.) usually used for 10 ml. of milk precipitated the casein at about *p*H 4·2, which is considerably below its isoelectric point. He recommended treating the milk with a definite amount of an acetate mixture (*p*H 4·61), so that the casein was precipitated at *p*H 4·7–4·8. To avoid the necessity of washing the precipitate, and also the prolonged Kjeldahl digestion due to the presence of the filter paper, he determined the nitrogen content of an aliquot portion of the filtrate. The casein nitrogen was then obtained by difference from the total nitrogen content of the milk found by a separate determination. This procedure neglected the volume of the fat, casein and other constituents of the milk, so that low results were to be expected—an expectation which I confirmed by comparison with direct determinations upon the washed casein precipitate. As a matter of fact, the Kjeldahl digestion is prolonged not so much by the filter paper as by the fat which is included in the precipitate.

The buffer mixture proposed by Waterman is not sufficiently acid and the casein is precipitated at too high a *p*H, with the result that it does not flocculate properly, but yields a cloudy filtrate. This is another reason for the low values which have been found by me and by others[21] when using his method.

Experiments with Buffer Mixtures.—With a view to finding a more suitable buffer mixture, a large number of experiments were carried out, but these can only be briefly mentioned. Owing to the very great natural variations which different samples of milk present to the analyst, and especially because of

the possible complication of souring (partial or complete), which may occur before analysis, it seemed desirable to investigate a number of different milks to see if it would really be satisfactory to propose the use of any particular buffer mixture for all cases. Trials were made of several mixtures containing acetic acid and sodium acetate in different proportions, and the final *p*H of the diluted milk mixture (as determined by means of the quinhydrone electrode) was always found to lie within narrow limits. In Table I appear the results obtained with one such

TABLE I.

Milk No.	Titratable acidity per cent. lactic acid.	*p*H of milk.	*p*H of filtrate.
	Per Cent.		
1.*	0·153	6·73	4·64
Same allowed to sour	0·43	5·41	4·53
2.	0·165	6·72	4·67
3.	0·165	6·70	4·59
4.*	0·185	6·63	4·68
5.*	0·12	6·89	4·64
6.*	0·153	6·72	4·74
7.	0·153	6·77	4·69
8.*	0·125	7·02	4·74
9.	0·165	6·66	4·73
Same allowed to sour	0·19	6·63	4·67
,, ,, ,, ,,	0·475	5·45	4·61
10.*	0·13	7·02	4·70
11.*	0·18	6·72	4·70
12.*	0·128	6·86	4·71
13.*	0·173	6·69	4·64

buffer which was made by mixing 90 ml. of $N/1$ acetic acid with 35 ml. of $N/1$ caustic soda, so that the acid and sodium acetate concentrations were respectively 0·44 N and 0·28 N. The *p*H of the mixture was 4·42, and 5 ml. (containing 132 mgrms. of free acid) were added to 10 ml. of milk, diluted first to about 50 ml. The majority of the milk samples used (those marked *) were from individual cows, as these usually provide a greater range of variation than bulk samples.

These results, together with others similarly obtained, showed that a buffer mixture of the type described could be used upon milk of widely varying composition in order to precipitate the casein within a comparatively narrow range of *p*H (0·15, excluding soured samples).

COMPARATIVE CASEIN DETERMINATIONS.—When comparative analyses were carried out by *combining before adding* to the diluted milk the same amount of acetic acid, with gradually increasing amounts of sodium acetate, greater amounts of casein were precipitated as the *p*H decreased (Table II). At the same time the opalescence of the filtrate decreased as increasing amounts of nitrogen were precipitated, but the filtrates were never quite clear like those obtained when

the acetic acid alone was used; yet the results from the acid alone were always appreciably low in this and other experiments.

TABLE II.

No.	Amounts used of: 10 Per cent. acetic acid.	Amounts used of: 0·28 *N* sodium acetate.	*p*H of filtrate.	Casein N per 100 ml. milk.	Average.
	Ml.	Ml.		Grm.	Grm.
A.i	1·5	—	4·24	0·3836	—
ii	,,			0·3804	0·3820
B.i	,,	1·5	4·41	0·3985	
ii				0·3999	0·3992
C.i	,,	3	4·53	0·3915	
ii				0·3993	0·3954
D.i	,,	5	4·66	0·3910	
ii				0·3890	0·3900
E.i	,,	8	4·80	0·3875	
ii				0·3883	0·3879
F.i	,,	11	4·91	0·3835	
ii				0·3834	0·3835

A considerable improvement was obtained when, instead of adding the acid and acetate combined, the acid was first added and then the acetate. After being allowed to stand for an hour to attain equilibrium, the filtrates obtained were usually quite clear over a considerable range of *p*H, provided the acidified mixture had not been too vigorously stirred. Tables III–V contain typical results, which warrant the conclusion that a maximum amount of casein is usually precipitated by acetic acid and sodium acetate at about *p*H 4·5–4·7—a range which agrees with the isoelectric point of this protein, as determined by Michaelis.

TABLE III.

No.	Amounts used of: 10 Per cent. acetic acid.	Amounts used of: 0·28 *N* sodium acetate.	*p*H of filtrate.	Casein *N* per 100 ml. milk.	Average.
	Ml.	Ml.		Grm.	Grm.
A.i	1·5	—	4·27	0·4476	
ii				0·4468	0·4472
B.i	,,	1·5	4·43	0·4355	
ii				0·4440	0·4398
C.i	,,	3	4·55	0·4495	
ii				0·4510	0·4503
D.i	,,	5	4·68	0·4498	
ii				0·4522	0·4510
E.i	,,	8	4·80	0·4470	
ii				0·4492	0·4481
F.i	,,	11	4·89	0·4475	
ii				0·4480	0·4478
G.i	,,	15	5·00	0·4468	
ii				0·4461	0·4465

TABLE IV.

No.	Amounts used of: 10 Per cent. acetic acid. Ml.	Amounts used of: 0·28 *N* sodium acetate. Ml.	*p*H of filtrate.	Casein *N* per 100 ml. milk. Grm.	Average. Grm.
A.i	1·5	—	4·22	0·3857	
ii				0·3865	0·3861
B.i	,,	1·5	4·37	0·3889	
ii				0·3868	0·3879
C.i	,,	3	4·51	0·3923	
ii				0·3920	0·3922
D.i	,,	5	4·62	0·3886	
ii				0·3892	0·3889
E.i	,,	8	4·75	0·3876	
ii				0·3904	0·3890
F.i	,,	11	4·86	0·3876	
ii				0·3887	0·3882
G.i	,,	15	4·98	0·3872	
ii				0·3881	0·3877

TABLE V.

No.	Amounts used of: 10 Per cent. acetic acid. Ml.	Amounts used of: 0·28 *N* sodium acetate. Ml.	*p*H of filtrate.	Casein *N* per 100 ml. milk. Grm.	Average. Grm.
A.i	2·5	—	3·97	0·3718	
ii				0·3687	0·3703
B.i	2·0	—	4·07	0·3844	
ii				0·3816	0·3830
C.i	2·0	—	4·07	0·3750	
ii				0·3795	0·3723
D.i	1·5	—	4·22	0·3966	
ii				0·3960	0·3963
E.i	0·5	—	4·91	0·4007	
ii				0·4028	0·4018
F.i	1·5	1·5	4·37	0·4028	
ii				0·4034	0·4031
G.i	,,	3·0	4·51	0·4019	
ii				0·4032	0·4026
H.i	,,	5·0	4·63	0·4049	
ii				0·4043	0·4046
K.i	,,	8·0	4·77	0·4047	
ii				0·4035	0·4041
L.i	,,	11·0	4·87	0·4023	
ii				0·3994	0·4011
M.i	,,	16·0	5·03	0·3962	
ii				0·3922	0·3941
N.i	,,	22·0	5·14	0·3616	
ii				0·3588	0·3602

In the experiment recorded in Table V, the filtrates of A, B, C, M, and N, were all quite opalescent, so that filtration and washing of these precipitates was very slow, lasting for more than thirty hours. The difference between B and C was due

to the use of a simply folded filter for C instead of the usual fluted folding, with the result that filtration took so long that before washing was complete the precipitate began to pass through the filter. It is noteworthy that E precipitated at *p*H 4·91 with a small quantity of acetic acid, gave practically the same result as L at 4·87, obtained in a different manner. The agreement of the duplicates (i and ii) was more satisfactory in most of the cases where clear filtrates were obtained.

In these, as in other experiments, only very slightly lower amounts of casein were precipitated at *p*H values on either side of the maximum point. The decrease became more definite, however, on reaching the *p*H obtained by the use of the usual quantity of acetic acid, which was found, as a rule, to give results 1–2 per cent. low. The slightness of the increase in solubility of casein on either side of its point of maximum flocculation has already been demonstrated by Sörensen and Sladek,[22] who published curves showing the effect of the salt content of casein solutions upon the point of minimum solubility of this protein. It is possible that the varying salt content of milk is the reason for slight variations in the *p*H at which the maximum amount of casein can be precipitated.

On the basis of the foregoing experiments (together with others which have yielded similar results) a modification of the A.O.A.C. "official" method (in which only 1·5 ml. of 10 per cent. acetic acid per 10 ml. of milk was used) seems justified. This consists in adding 4·5 ml. of 0·25 *N* sodium acetate (3·4 grms. crystals per 100 ml.) after the acid has been added, in the manner to be described in detail later. The use of these quantities of acetic acid and sodium acetate provides a buffer mixture of the same type as that which gave the results contained in Table I, but slightly modified so as to precipitate the casein from most samples of milk at a *p*H as close as possible to 4·6.

The foregoing procedure has been evolved for normal cows' milk. Owing to the different buffering powers of the milk of other animals, slight modifications may be required in the amount of sodium acetate needed to attain a *p*H of 4·6. For any particular type of milk the best procedure will be to carry out an experiment similar to that recorded in Table III, but without at first completing the nitrogen determinations. Having thus found approximately the right amount of sodium acetate to bring the *p*H to 4·6, the filtrate from a number of different samples of milk treated with the same quantity, should be examined to see if this *p*H is regularly attainable. Finally, complete experiments like that set out in Table III should be carried out, extending from *p*H 4·2 to 5·0, to make sure that the maximum amount of casein is precipitated at *p*H 4·6.

SUMMARY.—1. The chemistry of casein and the state in which it exists in milk have been briefly discussed in order to show the desirability of using an acid reagent for the purpose of its analytical separation.

2. Experiments have been carried out which show that by mixing definite quantities of milk and a suitable acetic acid and sodium acetate buffer solution a *p*H close to the isoelectric point of casein can be attained with milk of widely varying composition. Even when the milk has soured somewhat, the effect of this on the final *p*H of the mixture is slight.

3. Experiments have shown that in order to precipitate a maximum of casein from milk it is desirable to add the buffer solution in two parts, acid first and then sodium acetate. When this is done maximum casein values for milk are obtained between *p*H 4·5–4·7.

This paper represents part of the work carried out during my tenure of the Pedler Research Scholarship of the Institute of Chemistry, the assistance of which and the interest of the members of the Pedler Fund Committee is gratefully acknowledged. I should also like to add my appreciation of the facilities made available to me at the National Institute for Research in Dairying, and especially of the valuable advice of Capt. J. Golding, Head of the Chemical Department.

REFERENCES.

1. Titus, Sommer and Hart, *J. Biol. Chem.*, 1928, **76**, 237.
2. Richmond, "Dairy Chemistry," Chap. XI (Griffin, 1920).
3. Van Slyke and Bosworth, *N. York Agr. Expt. Sta. Tech. Bull*, 10 (1909).
4. Hart, *Wisconsin Agr. Expt. Sta. Bull*, 156 (1907).
5. Robertson, *J. Ind. Eng. Chem.*, 1909, **1**, 723.
6. Arny and Pratt, *Amer. J. Pharm.*, 1906, **78**, 121.
7. Harris, *Proc. Roy. Soc. Lond., B.*, 1925, **97**, 372.
8. *7de Beretning fra Stat. Forsogsmejeri, Hillerod*, Denmark (1929).
9. Howe, *J. Biol. Chem.*, 1922, **52**, 51.
10. Van Slyke and Winter, *J. Assoc. Off. Agr. Chem.*, 1915, 261.
11. Robertson, "Physical Chemistry of the Proteins," p. 96 (Longmans, Green & Co., 1924).
12. Waterman, *J. Assoc. Off. Agr. Chem.*, 1926, **9**, 247.
13. Waterman, *Id.*, 1927, **10**, 259.
14. Michaelis, *Biochem. Z.*, 1910, **28**, 193.
15. Michaelis, *Id.*, 1919, **47**, 260.
16. Michaelis, *Id.*, 1920, **103**, 178.
17. Csonka, Murphy and Jones, *J. Amer. Chem. Soc.*, 1926, **48**, 763.
18. Carpenter, *J. Biol. Chem.*, 1926, **67**, 647.
19. Cohn, *Physiol. Rev.*, 1925, **5**, 374.
20. Leberman, *Biochem. Z.*, 1929, **206**, 56.
21. Waterman, *J. Assoc. Off. Agr. Chem.*, 1928, **11**, 298.
22. Sörensen and Sladek, *Compt. Rend. Lab. Carlsberg*, 1929, **17**, No. 14, p. 29.

(*Part II. The Identity of the Caesin Precipitate will be published in the February issue.*)

The Determination of Unsaponified Oil in Soap or Fatty Acids.

By E. LESTER SMITH, M.Sc., A.I.C.

(*Read at the Meeting, October* 1, 1930.)

During the manufacture of a concentrate of fat-soluble vitamins by extraction of the unsaponifiable fraction from fish liver oils, it became necessary to have available a rapid method of detecting, and, if possible, of approximately determining, unsaponified oil in soap. Any oil which escapes saponification appears in the final extract and renders it unfit for use, besides causing difficulties in manufacture; re-saponification is troublesome, and may cause destruction of vitamin A. As

little as 0·1 per cent. of unsaponified oil in the soap corresponds to about 10 per cent. of oil in the unsaponifiable fraction of cod-liver oil, which is enough to be objectionable. The test should therefore be a sensitive one. Four methods have been so far available:—

(1) The apparent amount of unsaponifiable matter will be affected by any unsaponified oil in the fatty acids. This can be quantitatively determined, given a careful quantitative extraction and a knowledge of the unsaponifiable content of the oil. If an accurate method is employed, 0·05 per cent. of unsaponified oil is detectable (*cf.* ANALYST, 1928, **53**, 632).

(2) A test, known as the "Sodium Ethylate Test" has been devised in this laboratory and used as a routine test for the presence of saponifiable oil in concentrates of unsaponifiable matter. It involves a rough extraction of at least 50 grms. of the soap with ether, and the removal of the bulk of the sterols present by filtering an ice-cold alcoholic solution of the unsaponified matter. The sterol-free unsaponifiable matter, after removal of solvent, is tested as follows:—The material (0·2 ml.) is mixed with 0·2 ml. of 2*N* sodium ethylate in a small test-tube, and warmed in a water-bath at 70° C. for two minutes. The tube is then removed and cooled under the tap for a further two minutes, the appearance of the contents being noted. Any oil present is saponified, the soap causing a thickening of the mixture. The following grades are recognised:—(*a*) No thickening; (*b*) slight thickening on cooling (produced by 5 per cent. of oil); (*c*) setting to spongy mass (produced by 7·5 per cent. of oil); (*d*) setting solid in water bath (produced by 10 per cent. of oil). This test is sensitive to about 0·05 per cent. of oil in the fatty acid, but is tedious to carry out, except when examining final concentrates.

(3) The acid value of the fatty acids is reduced below the normal value by the presence of neutral oil. The course of a saponification may conveniently be followed by determinations of the acid value of the mixture of oil and fatty acids liberated on acidifying a portion of the saponification mixture. It is scarcely sensitive enough, however, to distinguish between 99.5 per cent. and 100 per cent. saponification, *i.e.*, to detect less than 0·5 per cent. of oil in the fatty acid.

(4) Lewkowitsch ("The Examination of Oils, Fats and Waxes" (1921), Vol. I, p. 112), describes the following "emulsion test":—Three c.c. of the fatty acid are mixed with 15 c.c. of 95 per cent. alcohol and 15 c.c. of concentrated aqueous ammonia; turbidity indicates unsaponified oil. Rutzler (*Oil and Fat Ind.*, 1929, **6**, [No. 9], 23; also, *Soap*, 1930, **4**, [No. 5], 31), has recently re-investigated this test and proposes a modification which renders it more sensitive. He found, when using the proportions Lewkowitsch suggests, that coconut oil fatty acids of low unsaponifiable content gave no cloudiness when they contained less than 1 per cent. of oil. He

therefore, proposes to add 1·2 per cent. of mineral oil to the fatty acid; this produces a turbidity perceptibly increased by 0·076 per cent. of coconut oil. The turbidity is measured in an "emulsometer," the depth of liquid in a Nessler glass being varied until the light of a lamp, shining through a pinhole at the end of a long iron tube beneath the Nessler glass, is just extinguished. It is necessary to standardise the time for which the mixture is allowed to stand, since turbidity varies with age.

Lewkowitsch's test is very insensitive, and Rutzler's modification is still not accurate enough. An examination of the principles on which the test is based, however, has suggested modifications which increase the sensitiveness of the test at least tenfold, without the use of mineral oil. Cod-liver oil fatty acids have been used as the test material, and every possible factor varied independently over wide limits to discover the conditions of maximum sensitivity. As a basis 1 grm. of fatty acid, containing 0·1 per cent. or less of cod-liver oil was used for the test, 1 ml. of aqueous ammonia of sp. gr. 0·880 diluted with an equal volume of water, instead of the enormous excess used by Lewkowitsch and Rutzler, and various volumes of mixtures of alcohol and water of different compositions. It was soon found that no turbidity was produced in very strong alcohol, as might be expected, owing to the distinct solubility of oil in this medium, or in water or weak alcohol; maximum turbidity was produced with aqueous alcohol containing about 65 per cent. of alcohol by volume. Moreover, strong solutions of the ammonium soap, of the order of 10 per cent., as used by Lewkowitsch and Rutzler, gave no turbidity; this appeared, however, on dilution with spirit of the same strength; the maximum appeared at about 1·7 per cent., *i.e.*, 1 grm. of fatty acid in 60 ml. of solution. Equivalent amounts of sodium hydroxide or potassium hydroxide in place of ammonia produced no turbidity with small percentanges of oil, and slowly destroyed the turbidity present if added to the ammoniacal solutions. Triethanolamine gave a turbidity of about the same intensity as ammonia. Varying the ammonia between 0·5 ml. and 2.0 ml. per grm. of acid made no noticeable difference. Under no conditions was the slightest haze observed with fatty acid free from oil, except after standing overnight, despite the presence of over 1 per cent. of unsaponifiable matter therein. Alterations in the order of mixing the reagents had no appreciable effect. With very small percentages of oil, the haze did not appear until after standing for some minutes, and gradually increased, even after some hours. Solutions could usefully be compared after fifteen minutes.

These observations may best be explained as follows:—The oil is always thrown out in the form of a finely dispersed emulsion when it is insoluble in the test solution; when no haze appears, the oil is either in molecular or colloidal solution; the former is the case in strongly alcoholic solutions; in solutions in water or dilute alcohol, and when the soap concentration is high, the oil is "dissolved by the soap," or adsorbed by the colloidal soap micellae. The ideal conditions, therefore, are those in which the soap is mostly in crystalloid form, *i.e.*, in dilute solution in strong alcohol, except that the alcohol must not be so strong as to dissolve the oil

appreciably, nor the dilution so great that the haze is invisible. Soda and potash give no turbidity, because the excess alkali present saponifies the trace of oil. If the exact equivalent of these alkalis is employed, turbidity occurs, as with ammonia, which is not a sufficiently powerful alkali to saponify the oil. The unsaponifiable matter present gives no turbidity, owing to its solubility in alcohol of the strength employed. In order to show that unsaponifiable matter has no great effect on the modified test, mixtures of synthetic glyceryl oleate with pure oleic acid, free from unsaponifiable matter, were tested; 0·05 per cent. of olein in the mixture gave a just perceptible haze, and 0·1 per cent. a marked cloudiness. Similarly, 0·05 per cent. of olive oil in pure palmitic acid, could be detected. At the other extreme the fatty acids from a "technical" fish-liver oil containing 6·7 per cent. of unsaponifiable matter gave only a slight haze, which was markedly increased by 0·1 per cent. of oil added to the fatty acid. Slight turbidity is best detected by looking through a column of the liquid in a Nessler cylinder held above a dark surface, in a good light. If the solution is illuminated with a beam of light in a dark room, a Tyndall cone effect is observed when oil is present, but this method of examination does not appear any more sensitive than the above; it is very easy to determine by inspection whether a liquid is quite bright or not.

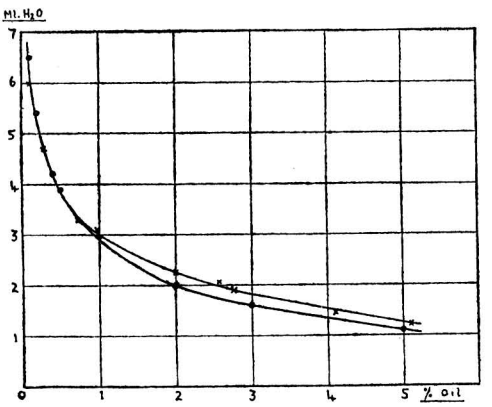
METHOD OF USING THE TEST.—The procedure finally adopted for the test is as follows:—The soap is decomposed by boiling with dilute hydrochloric acid, and the fatty acid skimmed off without any attempt to dry or otherwise to purify it. One grm. is weighed into a flask, melted if necessary by gentle warming, and 60 ml. of 65 per cent. alcohol (by volume) and 1 ml. of ammonia (0·880 sp. gr., diluted with water, 1: 1) added. At the same time a blank is prepared with pure fatty acid. The comparison is made as described above, after allowing the flask to stand for at least 10 minutes.

It was found in the case of cod-liver oil that 0·025 per cent. of oil in the fatty acid could just be detected. In the original Lewkowitsch test 0·5 per cent. of oil gives the faintest perceptible haze. Quantities of oil of 0·1 per cent. or more give with the modified test a cloudiness so obvious that no blank is necessary. This test is, therefore, at least as sensitive as any available, besides being simpler and quicker. We have found the sensitiveness to be of the same order for all natural oils examined, and practically independent of the amount of unsaponifiable matter, unless this is excessive, contrary to Rutzler's suggestion (*loc. cit.*). Mineral oil, however, gives a turbidity in the same way as vegetable oil.

Attempts to devise a quantitative test, which shall be independent of the nature of the oil, have not proved so successful. Nephelometric estimation of the turbidity is so complicated by the colour of the solution, by the dependence of degree of turbidity on time of standing, and by the considerable range of oil concentration over which the test can be used, that this method was abandoned. The emulsometer described by Rutzler gives surprisingly concordant results, considering its simplicity, and can be recommended for quantities of oil above 1 per cent. Below this, the column of liquid necessary to extinguish the light becomes impossibly long. Smaller quantities can, of course, be estimated by adding an extra

0·5 per cent. or 1 per cent. of oil to the fatty acid to be tested, but the accuracy is not greater than about ± 0·1 per cent. Results are not independent of the nature of the oil, so that a separate calibration curve must be constructed for each oil. Very small amounts of oil are best determined by comparison with standards made from pure fatty acids to which known percentages of the oil have been added; the solutions must be freshly prepared at the same time as the test solution.

QUANTITATIVE METHOD.—The test may be rendered quantitative by another modification. If 0·5 grm. of the fatty acid is dissolved in 20 ml. of 99 per cent. alcohol, and 0·5 ml. of ammonia added, no turbidity appears. If water is now added from a burette, the volume required to produce incipient turbidity is some indication of the amount of oil present. Unfortunately, the volume required is not independent of the speed at which it is added, which must be standardised in some way. The method finally evolved is as follows:—Two-and-a-half grms. of the fatty acid are weighed into a 100 ml. graduated flask and dissolved in alcohol, 2·5 ml.



X Olive Oil.
O Cod-liver Oil.

of ammonia are added (0·880 sp. gr., mixed with an equal volume of water), and the solution is made up to the mark with alcohol. It is important to standardise the strength of alcohol used. Four 20 ml. samples are pipetted into test-tubes of suitable size; the 20 ml. (approx.) remaining are titrated in the flask with water to incipient turbidity, to give an indication of the amount required; to the four tubes are added volumes of water slightly less than the volume required to give immediate turbidity, and varying by 0·1 or 0·2 ml. After having stood for 5 minutes the tubes are compared, and the volume of water which has just produced opalescence under these conditions is noted. It is necessary, of course, to prepare a calibration curve, using standard mixtures of oil and fatty acid, and the amount of oil present can then be read from the curve..

It was hoped that the curve would be independent of the nature of the oil and fatty acid; olive oil and cod-liver oil, mixed with their corresponding fatty acids, were compared, and gave nearly identical calibration curves, as shown in the Figure.

For most practical purposes, *e.g.*, in the soap industry, it would be sufficient to prepare such a curve for a typical soap stock, and to assume its validity for other oils. The method is simple and fairly rapid, and has the further advantage that its sensitiveness increases as the proportion of oil decreases. It is suitable for amounts of oil between 0·1 per cent. and 10 per cent.

SUMMARY.—Modifications of the "emulsion test," in which the presence of oil in fatty acid is indicated by the turbidity of a solution of the ammonium soap in dilute alcohol, are described.

As little as 0·05 per cent. of oil can be detected by the modified test, which is rapid and as sensitive as any other available.

The test may be rendered quantitative by a determination of the volume of water required to produce incipient turbidity in an alcoholic solution of the ammonium soap under standard conditions.

GLAXO RESEARCH LABORATORY,
56, OSNABURGH STREET, LONDON, N.W.1.

The Determination of Phosphorus in Steel, Alloy Steels and Cast Iron.*

BY A. T. ETHERIDGE, M.B.E., B.Sc., F.I.C.

PHOSPHORUS is oxidised to orthophosphoric acid in nitric acid solution and precipitated as ammonium phospho-molybdate, which was at one time weighed, but is now usually determined titrimetrically. The process is a very old one, the condition necessary for the formation of the precipitate having been investigated by Hundeshagen (*Z. anal. Chem.*, 1889, **28**, 141). Technical books on steel analysis show wide variations in describing the method as regards concentration of reagents, etc., as pointed out by Ridsdale (*Proc. Cleveland Inst. Engineers*, 1919, p. 155), most of which give fairly good results for medium or high phosphorus, but not all give correct figures for low phosphorus, or when arsenic is present. (High phosphorus = 0·1 per cent. or more; medium phosphorus = 0·05 per cent.; low phosphorus = 0·02 per cent. or less.)

The following is the method which I have used for some years and have found to be accurate even down to 0·002 per cent. of phosphorus in electrolytic iron. It is applicable to plain carbon steels, wrought iron and pure iron. Two grms. of steel are dissolved in a 300 c.c. Erlenmeyer flask in 45 c.c. of nitric acid (sp. gr. 1·2), and gently boiled for 5 minutes to oxidise carbides. Several drops of saturated

* Communication from the Research Department, Woolwich.

potassium permanganate solution are added to the boiling solution until a permanent precipitate of manganese dioxide is formed. After boiling gently for 5 minutes this precipitate is dissipated by careful addition of sodium nitrite crystals and freed from oxides of nitrogen by boiling for a short time. After cooling, 10 c.c. of dilute ammonia (1:1) are added, and the liquid shaken well to re-dissolve any iron hydroxide precipitated on the sides of the flask. The liquid is now heated to 80° C. (registered by a thermometer in the flask), the flask taken from the source of heat, 30 c.c. of molybdate reagent added, and the liquid well shaken to assist in the formation of the precipitate.†

After standing 10 minutes the precipitate is filtered on a pulp filter, washed twice with 5 per cent. nitric acid and six times with 5 per cent. potassium nitrate solution to wash all acid away (the washings are tested with litmus paper). The pulp and precipitate are placed in a beaker, 50 c.c. water added, and the mixture well shaken to disperse the precipitate through the liquid. Twenty c.c. of sodium hydroxide solution are now added from a pipette, and the flask well shaken.‡ If this does not dissolve the precipitate, as shown by the yellow colour disappearing (high phosphorus) a further 20 c.c. is added. It is very important to shake well to bring every particle of precipitate into contact with the alkali. The excess of alkali is now titrated with standard sulphuric acid, phenolphthalein being used as indicator.

The value of 20 c.c. of sodium hydroxide solution is found in terms of sulphuric acid by a separate titration in the presence of 50 c.c. of water. Thus, the phosphorus is expressed as a number of c.c. of the sulphuric acid, the exact value of which, in terms of phosphorus, must be found once for all. It is convenient to make up a large volume of this acid (about 5 litres) of approximately $N/10$ strength. It is standardised by a series of tests with standard sodium phosphate ($Na_2HPO_4.12H_2O$) solution (1 c.c.=·0001 grm. phosphorus) made from A.R. clear crystals and measured from a standard burette. In these experiments 2 grms. of electrolytic iron are added, and after the addition of the sodium phosphate solution, water and nitric acid (sp. gr. 1·42) are added to make 45 c.c. of nitric acid (sp. gr. 1·2), as in the method. It is convenient to use 10, 12 and 14 c.c., equivalent to 0·05, 0·06 and 0·07 per cent. of phosphorus, and to make a blank experiment with electrolytic iron alone. After correcting for the phosphorus in the electrolytic iron (usually 0·002 per cent.), the value of the acid, in terms of phosphorus, is calculated.

A few experiments conducted with the sodium phosphate in a similar manner, but in which the phosphorus is determined by the lead molybdate gravimetric process, are usually put through as a check on the sodium phosphate, and have always been found to agree. The sulphuric acid can also be standardised titrimetrically against hydrochloric acid ($N/10$), which has been standardised by the

† The molybdate reagent is made from ammonium molybdate, 160 grms., dissolved in a mixture of 300 c.c. of water and 120 c.c. of ammonia (sp. gr. 0·880), poured slowly, with stirring, into 1500 c.c. of nitric acid (sp. gr. 1·2).

‡ The sodium hydroxide solution is made from the solid sticks purified by alcohol and also contains barium to keep it free from carbonate. A soda-lime tube attached to the stock bottle prevents access of CO_2. The solution is approximately $N/10$ strength.

gravimetric silver chloride process. This titrimetric factor is based on the following equation:

$2[(NH_4)_3PO_4 \cdot 12MoO_3] + 46NaOH = 2Na_2HPO_4 + 21Na_2MoO_4 + 3(NH_4)_2MoO_4 + 22H_2O$.

This factor has been found to agree with the factor above.

NOTES ON THE PROCESS.—There is some danger of loss of ammonia at the stage where 10 c.c. of ammonia (50 per cent.) are added, if the liquid is not properly cooled, or if the ammonia is added too quickly.

It would be possible to add ammonium nitrate at this stage, but this would require less nitric acid to be used in dissolving the steel, which would be undesirable for rapid solution and oxidation of the carbides formed.

Clear crystals of sodium phosphate are used, not those which show signs of efflorescence, in order to ensure the correct composition, *viz.* $Na_2HPO_4 12H_2O$.

Oxidation with permanganate is necessary to destroy organic matter formed from carbon in the steel which is not completely decomposed by nitric acid. The omission of permanganate leads to low results, possibly due to the interference of organic substances with the formation of the yellow precipitate. The precipitate should not stand longer than 10 minutes, owing to the possibility of co-precipitation of arsenic (see later). From the equation given it will be observed that 1P=23NaOH, and hence the titration is capable of great accuracy, owing to the small titration factor. In fact, 1 c.c. of $N/10$ sulphuric acid equals 0·000135 grm. of phosphorus, equals 0·00675 per cent. on 2 grms. taken, so that errors in titration are almost negligible.

The agreement shown between the sodium phosphate method and the titrimetric method based on the equation given above proves the accuracy of the alkalimetric titration. This question was investigated by Nyssens (*Bull. Soc. Chim. Belge*, 1925, p. 232). He shows that there is no appreciable error in the use of phenolphthalein as indicator, although the ammonium radicle derived from the precipitate is present, so that it is not necessary to add excess of alkali and boil out the ammonia (as recommended by Richards and Godden for large precipitates, ANALYST, 1924, **49**, 565). This has been confirmed by Cameron and Dow (ANALYST, 1927, **52**, 576), who consider that it is also accurate for larger precipitates than obtained in steel analysis. Nyssens (*supra*) also showed that it is satisfactory to use the theoretical titrimetric figure for the standard acid, based on the equation given.

The metallurgical analyst is to-day ever increasingly called upon to determine phosphorus in alloy steels, in which it is not always possible to apply the standard procedure which has been described. In these cases it has been my aim to obtain the same conditions in the solution, prior to precipitation with molybdate, as exist in the standard method. Modifications which require the presence of ammonium chloride or sulphate, are undesirable. Ammonium chloride favours co-precipitation of arsenic, and ammonium sulphate hinders the formation of the yellow precipitate (this is markedly the case with low phosphorus steels)—hence, sodium nitrite is preferred to sulphurous acid in reducing manganese dioxide.

Also, it is by no means certain that the yellow precipitate has exactly the same composition with varying conditions, which is not unlikely in the case of such a complicated molecule.

MODIFICATIONS WITH PLAIN CARBON STEELS.—Before considering the alloy steels, etc., there is one modification which may be necessary in certain cases with plain carbon steels. This is due to the presence of arsenic, which is found in practically all steel. Usually arsenic is present only to the extent of about 0·03 per cent., and also if the phosphorus is not greater than 0·05 per cent., there is, in these circumstances, no co-precipitation. I have investigated the matter, and have found that with increasing phosphorus there is a slight but appreciable co-precipita tion, even with 0·02 per cent. of arsenic, and the higher the phosphorus the greater is the tendency. With high arsenic content (*e.g.* 0·10 per cent.) and phosphorus below 0·02 per cent., the tendency is very small, but beyond that point results are appreciably too high. The outcome of the work is that it is recommended to use a modified process where the ordinary method has given results greater than 0·05 per cent., unless it is independently found that the arsenic is less than 0·02 per cent., and in any case, if arsenic is greater than 0·10 per cent.

In the modified process the arsenic is removed. The ordinary process is followed as far as the precipitation of phosphomolybdate and washing with nitric acid, and one wash with potassium nitrate. From this point the process is as follows:—The precipitate is dissolved in 20 c.c. of ammonia (1 : 1), and after well washing the pulp with water, hot dilute hydrochloric acid (1 : 1) is run through the pulp, which is again washed with water. An excess of hydrochloric acid is added to the liquid, sufficient to react well with zinc dust, of which about 0·5 grm. is added. This reduces arsenic to the arsenious condition (also eliminates some as arsine). The liquid is now saturated with hydrogen sulphide and the flask closed and allowed to stand over-night. Arsenic is precipitated as As_2S_3, with some of the molybdenum as MoS_3. The precipitate is filtered and washed with ammonium chloride solution. The filtrate is boiled to drive out hydrogen sulphide and oxidised with nitric acid (sp. gr. 1·2 per cent.), which contains 0·1 grm. of electrolytic iron, previously dissolved in it.

After cooling a little, the iron is precipitated by ammonia in excess, which carried down all the phosphorus. This precipitate is filtered off, washed well with hot water and dissolved in 45 c.c. of nitric acid (sp. gr. 1·2), and the filter paper well washed. To the liquid is now added 1·9 grms. of electrolytic iron, and when this has dissolved the liquid is boiled down to 45 c.c., during which process practically only water is lost, owing to the fact that the constant-boiling mixture is approximately of 1·2 sp. gr.; in other words, the original condition has been arrived at. The ordinary process is now followed, and it only remains to correct for the phosphorus in the electrolytic iron (usually 0·002 per cent.).

This method has been tested both with sodium phosphate and standard steels, after adding 0·10 per cent. arsenic, and has given accurate results.

CAST IRON.—In regard to cast iron, there are two classes to be considered, *viz.* high-phosphorus cast iron (pig iron) and low-phosphorus cast iron (haematite

iron or haematite pig). In the high-phosphorus iron it is sufficient to take 0·25 grm. together with 1·75 grms. of electrolytic iron, and to use the ordinary process, ignoring graphite. The correction for the electrolytic iron is of no account in this case. With low-phosphorus cast iron it is necessary to take 2 grms. and to follow the ordinary process, ignoring graphite.

TITANIUM.—In these irons there is one element sometimes present which may cause trouble, *viz.* titanium. This was investigated by Ridsdale (*Proc. Cleveland Inst. Engineers*, 1920, p. 109), who showed that if titanium were present to the extent of 0·1 per cent., it seriously interfered. Titanium prevents or hinders the precipitation of phosphorus (for some obscure reason), as has been known for a long time. In fact, the technical books describe a process for overcoming the difficulty which Ridsdale (*loc. cit.*) calls the "long" process—an allusion to the many operations involved. He has improved on this by the use of cupferron, a full description of which is given (*loc. cit.*).

I have modified the method somewhat, preferring to collect the phosphorus in an iron precipitate, following the lines given in the discussion on arsenic, so as to apply the standard procedure for the final precipitation. The bulk of the iron is removed in the first place by the ether-extraction method rather than by the process given by Ridsdale, after which titanium (and the remainder of the iron) is removed by cupferron. It is fortunate that it is not usual to encounter low phosphorus iron with much more than 0·01 per cent. of titanium, which amount is too small to interfere with the ordinary process. With high-phosphorus irons, titanium is rarely of any consequence, since only 0·25 grm. is used.

SILICON.—Another element in low-phosphorus iron which has to be considered is silicon. It is convenient to consider high-silicon steels (2 or 3 per cent. of silicon) at this stage. On dissolving the iron in nitric acid a large amount of the silicon is thrown out of solution. If, however, this is filtered off, it will be found that more silicon is precipitated during subsequent opeations, seriously interfering with the filtration and washing of the yellow phospho-molybdate. There is also a possibility of silico-molybdate being co-precipitated, owing to the nitric acid solution being saturated with it. It has been found possible to remove the silica, practically quantitatively, from nitric acid solutions by dissolving as usual, adding about 6 drops of hydrofluoric acid (A.R. 40 per cent.), and boiling. Silicon fluoride is formed and hydrolyses at once; more silicon fluoride is formed and so on, the hydrofluoric acid thus acting catalytically. After filtering, washing and boiling down, no further trouble occurs in the ordinary operations.

If considered desirable, traces of phosphorus can be recovered from the silica by washing it off the paper into a platinum dish and evaporating down with hydrofluoric and nitric acids, driving off hydrofluoric acid by repeated evaporation with nitric acid, and finally taking up with a very small amount of dilute nitric acid and adding to the main filtrate.

ALLOY STEELS.—Nickel steels, nickel-molybdenum steels, nickel-chromium steels with low chromium and carbon, and manganese steels, give no trouble, and

the ordinary process can be followed. Chromium steels with low chromium (*i.e.* not greater than 3 per cent.) and medium or high carbon show a black residue (chromium carbide) on dissolving, and it is necessary to digest without losing much acid till this residue is dissipated. Otherwise no trouble is experienced and the ordinary process applies. It is a different matter with high chromium steels (15 to 20 per cent. chromium), the now well-known and much-used stainless irons and steels, heat-resisting and incorrodible steels, since these will not dissolve in nitric acid of any strength. Some of them do not dissolve at all quickly in *aqua regia* either; and furthermore, those with anything more than a low carbon content throw out a large quantity of carbide which is very resistant to the acid mixture, even on long digestion.

When silicon is also a constituent (2 or 3 per cent.) the position is worse, since the steel itself is often not completely attacked, owing to the particles being coated with gelatinous silica. Hydrochloric acid alone is the best solvent for these steels. However, this is obviously dangerous to use in this determination, owing to possible loss of hydrogen phosphide, but this is overcome by the use of the special apparatus described by Evans (ANALYST, 1929, **54**, 286). Hydrochloric acid is used to dissolve the steel (about 20 c.c. HCl and 20 c.c. of water for 2 grms. of steel), and brominated hydrochloric acid is used in the cylinder instead of nitric acid, in order to absorb any hydrogen phosphide which might be evolved.

As a matter of fact, some experiments which have been made appear to show that no loss of phosphorus occurs in hydrochloric acid alone, but this might not always be the case with different steels. When the steel has dissolved and the contents of the cylinder have been drawn over into the flask, as described by Evans, nitric acid is added to oxidise ferrous iron to ferric, and the liquid digested till the carbide has disappeared. The carbide which is thrown out by hydrochloric acid is much easier to dissipate than that given by *aqua regia*, which is another advantage in the use of hydrochloric acid instead of *aqua regia*. The same method is used for nickel-chrome alloys (*e.g.* nichrome wire), except that concentrated hydrochloric acid is used to dissolve the material, which is attacked too slowly by the 50 per cent. acid.

The contents of the flask are now transferred to a beaker and evaporated to dryness (but not baked), taken up with concentrated nitric acid (sp. gr. 1·42), and again evaporated to dryness. This is done several times to eliminate hydrochloric acid as completely as possible, and the residue is finally taken up with 25 c.c. of dilute nitric acid (sp. gr. 1·2) and 20 c.c. of water, since calculation has shown that this is approximately the equivalent of dissolving 2 grms. of steel in 45 c.c. of dilute nitric acid (sp. gr. 1·2), so that the ordinary process can now be followed.

It is necessary to use a very much larger amount of potassium permanganate to get permanent manganese dioxide, since all chromium must be oxidised to chromate first, and experiments appear to show that chromic acid is not effective alone (presumably in oxidising organic matter still remaining, but this point has not

yet been cleared up). It is convenient to add solid permanganate in small amounts at first, afterwards using the saturated solution as usual. It is necessary to use more sodium nitrite also, in order to reduce the chromate back to the trivalent condition, as chromate interferes with the formation of the yellow precipitate, causing too low results.

VANADIUM AND TUNGSTEN STEELS.—Vanadium interferes, partly by preventing the complete precipitation of phosphorus (like titanium), but also it is partly precipitated as a complex of similar constitution (like arsenic), recognised by the red colour imparted to the precipitate. These two effects have a compensating action, so that it is possible to obtain correct results by compensation with alloys of certain composition. Many steels are made with not much more than 0·2 per cent. vanadium, and this is too small to affect the result, so that in these cases the ordinary method can be used.

The colour of the precipitate is a criterion as to whether the ordinary method is applicable or not. As regards modifications of methods, those in which vanadium is reduced to the tetravalent condition and phosphorus precipitated at ordinary temperature have been suggested, but have not proved satisfactory. The method suggested by Johnson (*Analysis of Special Steels*, 1920, p. 41) is satisfactory, in which a large excess of nitric acid is used, and the precipitate allowed to stand for some time. Under these conditions vanadium is not precipitated. This is the only case where it is not possible to apply the standard procedure, since there is no satisfactory method for separating phosphorus and vanadium in the presence of a large amount of iron.

Johnson's method gives satisfactory results, tested with standards with or without vanadium added (several hours are required for precipitation). Tungsten interferes if tungstic oxide is precipitated in the ordinary method. Many steels are made with about 3 per cent. tungsten, which does not precipitate in the ordinary process and no trouble arises. With higher tungsten amounts (*e.g.* tool steels with 15 per cent.) some, but not all, of the tungsten is precipitated, and this always carries some phosphorus. Hence it is necessary to remove tungsten as the oxide and recover the occluded phosphorus.

A method of doing this was devised by me some years ago. It consists in obtaining tungstic oxide quantitatively from 2 grms. of steel by the ordinary hydrochloric acid method, dissolving the oxide in ammonia, and refiltering. The undissolved part appears to contain ferric phosphate and, in my opinion, all the occluded phosphorus is in this form, since attempts to recover more phosphorus from the clear ammoniacal filtrate by acidifying and addition of ferric nitrate (from electrolytic iron) and making alkaline with ammonia, have not yielded any more phosphorus.

It is, perhaps, safer to add a little ferric nitrate to the slightly acidified tungstate filtrate in the first place (the acid being run through the filter to dissolve the iron ferrous phosphate suspension remaining on it), and to precipitate with ammonia. The precipitates containing the recovered phosphorus are dissolved in

hydrochloric acid and added to the main filtrate. With high-tungsten steel it is difficult to eliminate tungsten, owing to the tendency to formation of ferric tungstate, which is carried down in the iron precipitate. A better plan is to pour the acid solution (if very slightly acid tungsten is not precipitated—nitric acid is better than hydrochloric acid in this respect) slowly into the excess of dilute ammonia. This method is very similar to that given by Rooney and Clark (*J. Iron & Steel Inst.*, 1925, **1**, 457). The hydrochloric acid is now replaced by nitric acid in the manner already given for stainless steels, and the ordinary method finally applied, or Johnson's method may be used if vanadium is present. It is necessary to remove the tungsten quantitatively in high-tungsten steels. It is far from being completely precipitated in nitric acid; and if the precipitate formed is filtered off, more tungsten is precipitated in the subsequent operations. Hydrochloric acid is necessary for quantitative precipitation.

RESEARCH DEPARTMENT,
WOOLWICH ARSENAL.

The Analysis of Ferro-Silicon.

BY G. H. GOODWIN, A.I.C.

THE primary object of this investigation was to examine the sources of error in the determination of silicon in high grade ferro-silicons, particularly those containing about 50 per cent. silicon. It is conceivable, however, that the information contained herein will be of use whenever the accurate estimation of silicon or silica is a *sine qua non*.

The chief sources of error in the analysis of silicon alloys (or silicates) are:

(1) The solubility of freshly precipitated silicic acid in sodium chloride.

(2) The solubility of freshly precipitated silicic acid in hydrochloric acid.

(3) Minor errors which can usually be avoided, such as (*a*) contamination from beakers, dishes, and reagents used, (*b*) loss of silica during ignition, (*c*) the absorption of moisture by the silica during weighing, (*d*) the effect of dehydration at too high a temperature, (*e*) incomplete dehydration.

Of these, (1) is probably the most important, as a comparatively large weight of flux is necessary. The effect of sodium chloride on the solubility of silicic acid has been investigated by A. B. Trickett (J. W. Mellor, *Treatise on Quantitative Inorganic Analysis*, **1913**, **174**), and attention has also been directed to it by others, *e.g.* V. Lenher and E. Truog (*J. Amer. Chem. Soc.*, **1916**, **38**, 1050), and F. G. Hawley (*Eng. Min. J.*, **1917**, **103**, 541).

The second error can be made negligible by using dilute acid and avoiding prolonged digestion in the hot or boiling solution.

After precautionary measures have been taken to eliminate the other sources of error the results tend to be too low.

The standard procedure, after fusion with sodium carbonate, evaporation and dehydration, is to filter off the silica and repeat the evaporation and dehydration of the filtrate, which contains the whole of the sodium chloride originally present in the solution.

It has been found, however, that on the addition of ammonium hydrate to the first filtrate, the remaining silica is completely precipitated, ***provided sufficient ferric chloride is present in the solution.*** The precipitate is then filtered off, washed and redissolved in hydrochloric acid, so that the subsequent operations are carried out in a solution free from sodium chloride.

The same process has previously been used for iron by A. Stadeler (*Arch. für Eisenhüttenwissen.*, 1929, 425), while a somewhat similar one is that employed in Berzelius' and Rose's method for the estimation of fluorides in which silicic acid is precipitated by an ammoniacal solution of zinc oxide (*v.* J. J. Berzelius, *Pogg. Ann.*, 1824, **1** 169, and H. Rose, *ibid.*, 1850, **79**, 115). W. F. Hillebrand and G. E. F. Lundell (*Applied Inorganic Analysis*, 1929, 722) also point out that traces of silica left in solution, after a double evaporation to dryness with an intervening filtration, "can be recovered later if an ammonia precipitation is made and a fair-sized precipitate is obtained," *i.e.* when the material under analysis contains appreciable quantities of (mainly) iron or aluminium. As, however, the process has not apparently been applied to the determination of silicon in ferro-silicons, the conditions necessary and limiting values of it have been determined by making up a number of "synthetic" ferro-silicons from "pure precipitated silica" and "Armco" iron drillings.

DETERMINATION OF SILICA AND SILICON IN MATERIALS USED.—The first step was to determine the actual percentage of silica and silicon in the materials used.

Pure Precipitated Silica.—The specimen contained about 13 per cent. of moisture, and hence it was ignited before use. One grm. of the ignited material was evaporated to dryness with sulphuric and hydrofluoric acids in a platinum crucible, and the residue ignited. The loss in weight gave 98·74 per cent. of silica. The residue in the crucible was fused with a weighed quantity of sodium carbonate, and the silica recovered amounted to 0·08 per cent. After subtraction of the blank for the weight of sodium carbonate taken, the final figure was 98·79 per cent.

"Armco" Iron.—The silicon as determined in platinum vessels was 0·002 per cent., and it was consequently ignored. The required weight of drillings was dissolved in hydrochloric acid, oxidised with nitric acid, taken to dryness, redissolved in hydrochloric acid and the solution used without filtration.

In the first series of experiments, 0·25 grm. quantities of the ignited silica were fused with 3 grms. of sodium carbonate, and the cake, after extraction, was decomposed by aqueous hydrochloric acid; varying weights of iron as chloride were

then added. The solution was made alkaline with ammonia, boiled and filtered, and the amount of silica passing into the filtrate determined as follows:

The solution was evaporated to dryness, and the residue baked for two hours at 110° C. The residue was taken up with 10 c.c. of hydrochloric acid (sp. gr. 1·1), warmed for a few moments on a water bath, diluted with cold water and filtered immediately, the precipitate being washed with cold 1 per cent. hydrochloric acid and treated as usual with sulphuric and hydrofluoric acids.

Experiments were then made to determine the effect on the amount of silica lost in the filtrate of the weight of silica present, 0·125 grm. quantities being used for this purpose.

Commercially Pure Iron (99·84 *per cent. of iron*).—The following results were obtained:

Weight of silica taken. Grm.	Weight of iron taken. Grms.	Ratio SiO_2:Fe.	Weight of silica recovered from filtrate. Grm.
0·25 ..	0·08	1 : 0·32	0·0418
	0·15	1 : 0·6	0·0256
	0·25	1 : 1	0·0168
	0·38	1 : 1·52	0·0086
	0·50	1 : 2	0·0065
	1·00	1 : 4	0·0046
	1·50	1 : 6	0·0030
	2·00	1 : 8	0·0010
0·125 ..	0·04	1 : 0·32	0·0276
	0·125	1 : 1	0·0112
	0·50	1 : 4	0·0014
	1·00	1 : 8	0·0002

Evidently the precipitation of silicic acid (probably as a ferric silicate) by addition of ammonium hydroxide to the filtrate from the first evaporation is complete, provided sufficient iron is present. This will be the case even in the higher grade ferro-silicons, as an experiment showed that the amount of silica passing into the filtrate after *one* evaporation was approximately 0·01 grm. For this purpose, 1 grm. of the silica and 0·5 grm. of iron were taken, as representing approximately a 50 per cent. ferro-silicon.

A further confirmation was obtained by fusing 1 grm. of silica and adding 0·5 grm. of iron as chloride (*i.e.* the approximate equivalent of a 1 grm. sample of 50 per cent. ferro-silicon), and taking it through the suggested method for the analysis of ferro-silicon outlined below. The 1 grm. of silica taken actually contained 0·9879 grm. of true silica, and 0·9878 grm. was recovered after the deduction of the blank.

Suggested Method of Ferro-Silicon Analysis.—Fuse 1 grm. of the finely divided sample with 10 grms. of sodium carbonate and 5 grms. of sodium peroxide

well mixed in a nickel crucible. Extract the cake with hot water, transfer to a basin and, when completely disintegrated, cover the basin with a clock glass and run in an excess of concentrated hydrochloric acid from a pipette through the lip of the dish.

When effervescence has ceased, rinse the underside of the clock glass into the basin and evaporate the liquid to dryness on a water bath. Break up the residue with a glass rod and bake for 2 hours in an air oven at a temperature not exceeding 110° C. Moisten the residue with 20 c.c. of hydrochloric acid (sp. gr. 1·1), and warm for 5 minutes on the water bath. Add about 100 to 150 c.c. of hot water and filter immediately through a No. 40 Whatman paper, washing with hot 5 per cent. hydrochloric acid. Add excess of concentrated ammonia to the filtrate, boil and filter, washing twice with hot water. Make a hole in the paper and wash the precipitate into the beaker from which it was precipitated.

Extract the paper with hydrochloric acid and hot water, adding more hydrochloric acid to the solution in the beaker and warming until completely dissolved. Evaporate and dehydrate as above, then take up the residue with 10 c.c. of hydrochloric acid (sp. gr. 1·1) warm for a few moments, dilute with *cold* water and filter through a No. 44 Whatman paper, washing with *cold* 1 per cent. hydrochloric acid (about six times). Transfer both papers to a platinum crucible and ignite in a *muffle*, retaining the lid in position until all volatile matter has been driven off. Heat as usual.

In conclusion, I wish to thank Mr. H. V. Thompson for suggestions and criticism during the course of this work.

RAMICOURT,
KINGSWAY, WEST,
NEWCASTLE-UNDER-LYME.

A New Method for Determining Traces of Chromium in Steel.*

BY W. J. AGNEW, B.A.

A METHOD for determining traces of chromium in steel has been described by Evans (ANALYST, 1921, **46**, 38). Although giving good results, this method of pouring the oxidised chromium into excess of sodium hydroxide solution, followed by excess of acetic acid, has some disadvantages, notably when nickel and cobalt are present, requiring a further separation of these two elements with sodium hydroxide before proceeding with the colorimetric estimation. Evans (ANALYST, 1921, **46**, 285) drew attention to the application of diphenylcarbazide, which gives

* Communication from the Research Department, Woolwich.

a purple colour with dichromate. This reaction is very sensitive, 17 parts per million being detected, and $N/1000$ potassium dichromate can be used as a standard.

An advantage of the method about to be described is that the determination can be made on a weight of 0·1 grm. of steel, if necessary. In most cases a weight of 1 grm. is a reasonably representative sample, from which, after dissolving, an aliquot portion is taken equal to 0·1 grm. of the original sample.

METHOD.—The method is as follows:—One grm. of the steel is dissolved in 15 c.c. of dilute sulphuric acid (1:3) and 20 c.c. of water and oxidised with 5 c.c. of nitric acid (sp. gr. 1·2).

The solution is boiled until free from nitrous fumes, cooled, and made up to a volume of 200 c.c. with distilled water. Forty c.c. of this solution, corresponding to 0·2 grm. of steel, are oxidised with 3 drops of saturated potassium permanganate solution, boiled for a few minutes, and the excess permanganate destroyed with a few drops of hydrochloric acid (sp. gr. 1·2), which is added, drop by drop, until the solution becomes quite clear; usually about 50 drops are required.

It is now immediately cooled, and the iron, etc., precipitated with a slight excess of sodium carbonate (saturated solution), diluted to 100 c.c. with distilled water, and filtered. Fifty c.c. of the filtrate, corresponding to 0·1 grm. of steel, are rinsed into a 600 c.c. flask, acidified with 20 c.c. of (1:3) sulphuric acid, 5 c.c. of a 0·1 per cent. solution of diphenylcarbazide added, and the whole transferred to a 100 c.c. Nessler glass. Into another Nessler glass are poured 20 c.c. of (1:3) sulphuric acid, 5 c.c. of the diphenylcarbazide solution, and about 70 c.c. of water, and the determination made by adding $N/1000$ dichromate solution to the standard until the solutions are matched in tint.

EXPERIMENTAL RESULTS.—The following figures were obtained for electrolytic iron to which known amounts of chromium had been added.

ELECTROLYTIC IRON WITH CHROMIUM.

Iron taken.	$N/1000$ potassium dichromate added. c.c.	$N/1000$ potassium dichromate found on 1/10 vol. c.c. × 10.	Chromium added. Per Cent.	Chromium found. Per Cent.
1·0	1	0·1	0·0017	0·0017
1·0	2	0·2	0·0034	0·0034
1·0	4	0·4	0·0068	0·0068
1·0	10	1·0	0·017	0·017
1·0	20	2·0	0·034	0·034
1·0	25	2·5	0·042	0·042
1·0	30	3·0	0·051	0·051

The following figures were obtained for electrolytic iron containing various amounts of other elements.

Iron with Copper and Chromium.

Iron taken. Grm.	Copper added. Per Cent.	Chromium added. Per Cent.	Chromium found. Per Cent.
1·0	1·0	0·0017	0·0017
1·0	1·0	0·0034	0·0034
1·0	1·0	0·0051	0·0051
1·0	1·0	0·0068	0·0068
1·0	1·0	0·0085	0·0085
1·0	1·0	0·017	0·017
1·0	1·0	0·026	0·026
1·0	1·0	0·035	0·035
1·0	1·0	0·050	0·050

Iron with Nickel and Chromium.

Iron taken. Grm.	Nickel added. Per Cent.	Chromium added. Per Cent.	Chromium found. Per Cent.
1·0	15·0	0·0017	0·0017
1·0	15·0	0·0034	0·0034
1·0	15·0	0·0050	0·0050
1·0	7·5	0·068	0·068
1·0	7·5	0·034	0·034
1·0	7·5	0·087	0·085
1·0	7·5	0·087	0·087

Iron with Molybdenum and Chromium.

Iron taken. Grm.	Molybdenum added. Per Cent.	Chromium added. Per Cent.	Chromium found. Per Cent.
1·0	2·70	0·0085	0·0085
1·0	2·70	0·0170	0·0170
1·0	2·70	0·068	0·068

Iron with Vanadium and Chromium.

Iron taken. Grm.	Vanadium added. Per Cent.	Chromium added. Per Cent.	Chromium found. Per Cent.
1·0	1·0	0·0017	0·0017
1·0	1·0	0·0034	0·0034
1·0	1·0	0·034	0·033
1·0*	1·0	0·0034	0·0026

* Colour in this case was a slightly different shade, due probably to vanadium.

Iron with Tungsten and Chromium.

Iron taken. Grm.	Tungsten added. Per Cent.	Chromium added. Per Cent.	Chromium found. Per Cent.
1·0	1·0	0·0017	0·0017
1·0	1·0	0·0034	0·0034
1·0	1·0	0·017	0·017
1·0	1·0	0·034	0·034

IRON WITH COBALT AND CHROMIUM.

Iron taken. Grm.	Cobalt added. Per Cent.	Chromium added. Per Cent.	Chromium found. Per Cent.
1·0	2·0	0·034	0·034
1·0	2·0	0·0017	0·0017
1·0	2·0	0·0050	0·0050

HIGH-CHROMIUM STEEL.

The following result was obtained on a steel containing a high percentage of chromium, compared with the percentage obtained by Evans's method:

Steel taken. Grm.	Chromium found. Per Cent.	Chromium found (Evans's method). Per Cent.
1·0	3·45	3·45

INFLUENCE OF HYDROCHLORIC ACID.—The following experiment was carried out to show that hydrochloric acid does not reduce the potassium dichromate under the conditions described. Each trial contained 2 c.c. of $N/1000$ potassium dichromate solution, to which was added 40 c.c. of distilled water, 3 c.c. of (1:3) sulphuric acid and 2 c.c. of nitric acid (sp. gr. 1·2); each was oxidised with potassium permanganate, and to A was added 30 drops of hydrochloric acid, to B 40 drops of hydrochloric acid, to C 50 drops of hydrochloric acid, and to D 100 drops of hydrochloric acid. They were then heated until clear, cooled, and diluted to 100 c.c. The colour in each case was the same on testing with diphenylcarbazide.

These results show that none of the dichromate was reduced, and as much as 15 per cent. of hydrochloric acid is permissible, provided the solution is not boiled too long.

INFLUENCE OF TIME OF BOILING.—The following experiments were carried out to show the influence of the time of boiling, after adding hydrochloric acid:

$N/1000$ potassium dichromate added. Drops.	Water added. c.c.	Hydrochloric acid added. Drops.	Time of boiling. Minutes.	Strength HCl. c.c. per 100 c.c.	$N/1000$ potassium dichromate found. Drops.
5	25	20	5	4·8	4
5	25	40	5	9·6	3
5	25	60	5	14·4	1
5	25	80	5	19·2	Trace
5	25	100	5	24·0	Nil
5	25	100	Just to boiling point	24·0	Nil
5	25	10	5	2·0	4
5	25	10	Just to boiling point	2·4	5

It will be observed from these results that prolonged boiling is fatal, since it leads to reduction of the potassium dichromate added.

CONCLUSION.—These test experiments show that chromium can be determined in steel by oxidising with potassium permanganate and reducing the excess of permanganate with hydrochloric acid, provided that the solution is cooled immediately the potassium permanganate is reduced; the experiments also prove that under those conditions the presence of as much as 15 per cent. of hydrochloric acid is permissible.

It should be mentioned that the chromium in all of these experiments was used in the form of potassium dichromate and was reduced before being added to the iron.

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 APPARATUS FOR THE DETECTION OF TRACES OF FLUORIDE BY THE ETCHING METHOD.

FOR the detection of small amounts of fluoride by the etch test, it is necessary to concentrate the acid vapours in a small space, sealed so as to permit of prolonged action without fear of loss. These requirements are met in the following simple and easily manipulated piece of apparatus.

It consists of a casting of lead, 2 inches across the foot, $1\frac{1}{2}$ inches across the mouth, and 2 inches high. The mouth is ground flat, and polished, and the cavity is about $\frac{1}{2}$ inch in diameter and 1 inch deep, having a capacity, therefore, of the order of 3 to 4 c.c.

The manipulation is as follows: The fluoride is concentrated into a small bulk of inorganic material, by precipitation or ashing with the usual precautions to avoid loss, and transferred to the leaden "test-tube." A moderately thick $\frac{3}{4}$-inch coverslip, preferably square for convenience in later handling, is covered on one side with high-melting paraffin wax, and the glass bared, in the centre of the slide, in a small but distinctive design, by means of a sharp splinter of wood, or a bone stylus (not metal). The material in the tube is rapidly and thoroughly mixed with a few drops of concentrated sulphuric acid, and the prepared coverslip taken up with forceps in one hand, while a few rapid strokes are made over the mouth of the tube with a Bunsen flame held in the other. The coverslip is then at once placed on the tube, waxed side down, when, if the manipulation has been correctly carried out, the wax melts just where it touches the warm metal, without encroaching on the design, and rapidly re-solidifies, thus hermetically sealing the cavity. The whole apparatus can then be placed in an incubator at 37° C. for as long as desired.

When the incubation is complete, the coverslip is melted off, the wax removed with ether, and the glass examined with a powerful lens, by means of light reflected from the etched surface. Under these conditions, a faint etching will be revealed as a dark shadow against the background of reflected light.

The apparatus was devised some years ago for the detection of traces of fluoride in fruit pulp, and I have found it possible to detect, with certainty, 2 mgrms. of sodium fluoride added to 100 grms. of pulp, with overnight incubation. Other workers, to whom the apparatus has been described, report a similar degree of sensitiveness. In my experience the detection of smaller quantities of fluoride could not be relied upon, and it would seem that some specimens of coverslip glass are more sensitive to the action of hydrogen fluoride than others.

R. E. ESSERY.

NUNEHAM, MAYPOLE LANE,
HOLLYWOOD, BIRMINGHAM.

BLACK DRAUGHT.

Mistura Sennae Composita, B.P., is an article which has been subjected to change with every new edition of the *British Pharmacopoeia*. In the 1914 edition, the alterations in the composition of Compound Tincture of Cardamoms and Infusion of Senna (two of the ingredients) involved some difference in the resulting Black But Draught.in both the 1898 and the 1914 editions, magnesium sulphate was, and is, incorporated in the proportion of five parts by weight in twenty fluid parts of the finished article. That is, the proportion of magnesium sulphate is 25 per cent. w/v. This means that the theoretical proportion of anhydrous magnesium sulphate is 12·2 per cent.

In 1902, the Local Government Board for Ireland, in proposing a "Schedule of Standards for Pharmacopoeial Preparations," included one that the ash of this preparation should be 9·5 per cent. It may be that (in spite of a concomitant declaration in the "standards" that the percentage of $MgSO_4$, $7H_2O$ was 25) the Local Government Board for Ireland had really based their standard, not on the 1898 *Pharmacopoeia*, but on that of 1885, where a smaller content of Epsom salts was directed. In any case, the ash figures detailed below show the results obtained on samples bought in four different counties during 1930. The ash figures were the results of igniting the total solids of five c.c. in porcelain milk dishes. The last sample is obviously not satisfactory.

Specific gravity at 15·5 °C.	Total solids per cent. (w./v.).	Ash per cent. (w./v.).
1·1216	21·63	11·23
1·1170	20·64	11·40
1·1118	19·62	11·44
1·1313	24·20	11·46
1·1146	22·02	11·52
1·1208	21·12	11·60
1·1183	21·68	12·08
1·1291	20·88	12·16
1·1283	20·52	12·62
1·1268	22·26	12·68
1·1375	23·50	14·20

WILLIAM PARTRIDGE.

10A, FEATHERSTONE BUILDINGS,
LONDON, W.C.1.

HOLDER FOR MERCURIC CHLORIDE PAPER IN GUTZEIT TEST.

SUGGESTIONS for holding the mercuric chloride paper have appeared in the journal from time to time (ANALYST, 1927, **52**, 699, 700, 701; 1928, **53**, 152; 1930, **55**, 503, 630), but the apparatus described below has the advantage of being easily and cheaply constructed, and of producing uniform stains with well-defined edges.

A tin screw cap arrangement is cut from a "Cardboard Screw Cap Post Box," and forced over a tightly fitting rubber bung. The bung has one hole in the centre, 8 mm. in diameter, and the tin screw cap also has a hole drilled through its centre, 8 mm. in diameter. The mercuric chloride paper is placed on the rubber bung covering the hole, the cap is screwed on, and the bung pushed on the end of the Gutzeit tube, so that the gas must pass through the paper. This apparatus, has been found efficient in this laboratory for some years. Its size is not important, so long as the 8 mm. holes in the rubber bung and the tin cap coincide.

G. H. DAVIS.

MAYNARDS LIMITED, VALE ROAD,
FINSBURY PARK, N.4.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1929.

THE number of samples analysed during the quarter was 1198, of which 51 were formal samples; of the total number 42 were incorrect.

CREAM.—Two samples (one formal, the other informal) from the same vendor were found to contain 0·12 and 0·15 per cent., respectively, of boric acid. A summons was taken out under the Food and Drugs Act, since no penalty is provided under the Preservative Regulations unless it is proved that the offence was *wilfully* committed. A fine of 10s. was imposed.

H. H. BAGNALL.

METROPOLITAN BOROUGH OF STEPNEY.

ANNUAL REPORT OF THE BOROUGH ANALYST FOR THE YEAR 1929.

OF the 1609 samples examined, 1537 were purchased under the Food and Drugs Act, 951 being formal (49 adulterated), and 586 informal (14 adulterated).

MILK.—One of the 923 samples examined was coloured with annatto. Formaldehyde (3 parts per million) was present in two samples taken during the hot weather. The vendor was fined £2 with £3 3s. costs.

ICE CREAM.—Four samples examined were genuine. Three samples contained in each case 2·6 per cent. of milk fat and were thickened with starch. One

sample contained 7·1 per cent. of fat and was free from starch filling. There is no legal standard controlling the composition of ice cream.

TABLE JELLY.—One sample (informal) containing 90 parts of sulphur dioxide per million was labelled in a misleading and unsatisfactory manner. An article of food may contain preservative if the constituents from which it is made are allowed to contain preservative. These constituents must not, however, in the final product, contain more than the maximum amount of preservative allowed in each constituent by the Regulations.

The Medical Officer of Health informed the retailers that the jelly contained preservative within the permitted amount, but that the notice created an impression that the jelly did not contain preservative, and that the notice should be withdrawn or altered in such a way as not to create a wrong impression. The retailers finally stated that the notice on the carton would be deleted in future (*cf.* ANALYST, 1930, **55**, 279).

CARBOLIC POWDER.—Eleven samples were examined for the Borough Engineer. Of these, 10 complied with the requirements of the specification, and one was unsatisfactory. The specification states that "carbolic powder must contain not less than 15 per cent. of tar acids calculated as cresylic acid, the base to consist of siliceous or other inert matter." During the period that these examinations have been made, the following unsatisfactory powders have been condemned: (1) Chalk containing 4 per cent. of tar acids; (2) flue dust mixed with wood tar creosote containing 9 per cent. of acidic oils of doubtful disinfectant value; and (3) spent gas lime containing 9 per cent. of naphthalene.

DOUGLAS HENVILLE.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

WARRANTIES AS TO CATTLE CAKE.

G. C. DOBELL & CO., LTD., *v.* BARBER AND GARRATT.

THIS was an appeal from the judgment of Mr. Justice Roche (ANALYST, 1930, **55**, 447), who had held that the plaintiffs, who were merchants, were entitled to a declaration on the question of warranty, but were not entitled to recover from the defendants the damages which they had had to pay to their buyers for injury caused to stock through the cattle cake containing castor seed. The plaintiffs appealed on the question of the measure of damages, and the defendants appealed on the question of liability.

Lord Justice Scrutton, in his judgment, agreed with Mr. Justice Roche that there was a sale by the defendants and a purchase by the plaintiffs of linseed cake, within the meaning of Sec. 2 (2) of the Act of 1926; and that the warranty of suitability was not excluded by Sec. 24. The defendants' cross-appeal must, therefore, be dismissed with costs.

On the question of the measure of damages, the plaintiffs were entitled to rely upon a statutory warranty, and they had statutory authority for disregarding any notice or contract to the contrary, and an analysis by a responsible firm that the cake was "castor free." The defendants said that they accepted no responsibility for the analysis. It was their only way of complying with the statutory obligation to give a correct statement as to the oil and albuminoids in the cake. Parliament had intended the vendors of cattle food to take responsibility for its fitness for the purpose, and if the vendor wished to escape his responsibility he should not sell food only used for that purpose. The appeal should be allowed, and the judgment by Mr. Justice Roche varied by declaring that the plaintiffs were entitled to include in their damages the damages and costs reasonably incurred in claims by their sub-purchases for breach of their statutory warranty.

Lord Justice Lawrence concurred.

Lord Justice Greer dissented. He held that Sec. 24 of the Act of 1926, excluded the operation of that Act in the circumstances of this case. He was not prepared to hold that Mr. Justice Roche was wrong.

REMOVAL OF MARKS FROM EGGS WITH ACETIC ACID.

On December 3rd, a shopkeeper was summoned, at the Levern Petty Sessions (East Yorkshire), for obliterating marks of origin from imported eggs in order to sell them as English.

An inspector under the Merchandise Marks Act gave evidence that he had visited a warehouse of the defendant in Hornsea. In one box he saw eggs bearing the mark "Holland," and in two other boxes damp eggs showing signs that the identification marks had been rubbed off. Samples of the eggs were taken and sealed in bottles for analysis, and a sample of liquid was also taken from a jar.

The Public Analyst's certificate showed that the eggs had been treated to remove the marks of origin, and that the liquid from the jar was strong acetic acid.

The Bench convicted and imposed a fine of £5.

Queensland.

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDING JUNE 30, 1930.

In his annual report Dr. J. B. Henderson states that 7947 samples were examined during the year, 2748 of which were for the Health Department. Of the total samples of foods and drugs submitted, 1511 were legal samples taken by the inspectors, in accordance with the provisions of the Health Act, and, of these, 305 were adulterated or not up to standard.

Lead Arsenate in Cabbage.—Ten samples of cabbage contained lead arsenate in quantities ranging from 3·2 to 9·3 grains per cabbage, showing that this dangerous menace is not yet removed.

SULPHUR DIOXIDE IN FRUIT AND MINCED MEAT.—Eight samples of preserved fruit contained sulphur dioxide at the rate of 8 to 18·9 grains per pound, whereas the maximum amount permitted to be present under the Food and Drug Regulations is 7 grains.

The use of sulphur dioxide is prohibited in minced meat, but eleven samples of minced meat received contained sulphur dioxide at the rate of 1·9 to 14·4 grains per pound. With cold storage so easily and cheaply available there is no excuse for adding preservatives to minced meat.

ORANGE BEVERAGES.—Out of thirty samples of orange beverages examined, 18 contained less than 3 per cent. of orange juice. It is important, from the standpoint of national health, as well as from that of the fruit-growing industry, that the minimum proportion of orange juice, namely, 5 per cent., required in an orange beverage, should be maintained.

POLICE DEPARTMENT.—For the Police Department, 208 samples were analysed, a distinct increase on the work of the previous year. In connection with 47 cases of death from suspected poisoning, 61 samples of viscera and 78 other samples of poisons, medicines, foods, etc., were examined. In 17 cases no poison was found, but in the other 30 cases poison was found as follows:—Strychnine, 21 cases; lysol, 2 cases; cyanide, 2 cases; carbon monoxide, sodium fluoride, arsenic, zinc chloride, and caustic soda, 1 case each.

Strychnine has of late years been gradually becoming more prominent in these cases, mostly suicides, and in 1929 was more than two-thirds of the total, probably because strychnine is now the most readily obtainable poison.

Sodium fluoride, which is used as a cockroach powder, provided its first recorded fatal case in Queensland. In connection with a case of attempted suicide, five exhibits were examined and strychnine found present. In 4 cases of alleged attempted food poisoning, 24 samples were submitted; strychnine was found in 2 samples, and cresol in 3 samples.

In 11 cases of suspected animal poisoning, 17 samples were examined, comprising viscera, opossum baits, dog baits, and water. In three cases poison was found, cyanide 1 case, strychnine 1 case, and arsenic 1 case; in the other eight cases no poison was found.

Government of Palestine.

ANNUAL REPORT OF THE DEPARTMENT OF HEALTH (CHEMICAL DIVISION) FOR THE YEAR 1929.

THE number of samples analysed during the year under the direction of the Government Analyst (Mr. G. W. Baker) was 6388, and much advisory work was undertaken for various departments, especially the Department of Customs, Excise and Trade.

MILK.—The control over milk supplies is of necessity decentralised, the analysis being carried out in 13 sub-districts with Gerber outfits; weekly returns from all sub-districts are scrutinised at the Central Laboratories. The question of equitable standards of composition is a difficult one, as some of the milk comes from well-kept herds of imported cattle, while much is a mixture of milk from wandering

herds of the small local cow and the goat. On the rather low standard of a minimum of 3 per cent. of fat and 8 per cent. of other solids, prosecutions were instituted in 3·7 per cent. of the 3892 samples taken.

EDIBLE OILS.—The analysis of 182 samples of edible fats and oils showed 18 per cent. of these to be adulterated. It has been found necessary to fix a limit to the acidity of edible olive oil supplied by contract to prisons. Provisionally, this maximum limit has been fixed at 15 per cent. This is, perhaps, somewhat high, but the local palate prefers a strong flavour. It might here be mentioned that the Customs tariff admits unrefined olive oil into Palestine free of duty, on the understanding that it is for soap-making, but there is little to prevent its being sold as edible oil to the prejudice of the consumer and the local oil producers.

LEGAL, JUDICIAL AND POLICE DEPARTMENTS.—The work undertaken for these Departments has involved the examination of 209 specimens and court exhibits, as compared with 164 last year.

Counterfeit Coins.—Of 78 coins submitted, 77 have been confirmed to be counterfeit. The outstanding features of most of these coins have been the same as those noted in last year's report, with the exception of two well-made 50 mil pieces containing approximately 57 per cent. silver. These coins are evidently struck and not cast, and are the first examples of struck counterfeit new currency to come under official notice. In one case in Haifa a large number of 100 mil pieces of pure tin were discovered by the police, together with iron moulds and sticks of pure tin.

Oil Stains.—In a case of burglary, where an iron bar on a window had been cut, a bottle containing a mixture of mineral oil and olive oil had been left on the window sill. Stains were noticed on the jacket of a suspect, and, on examination of these stains, the presence of freshly-cut fragments of iron and traces of oil of the same character as that in the bottle was discovered.

Firearms.—Much time has been spent upon the examination of firearms and ammunition in connection with murders committed during the disturbances. The laboratory investigation resulted in conclusive evidence that a cartridge case found on the premises where five persons were murdered had been fired in the rifle in possession of the accused person. As this case presents many interesting features from the scientific point of view it was decided to prepare a detailed account for publication elsewhere. (*Cf.* ANALYST, 1930, **55**, 738.)

DEPARTMENT OF CUSTOMS, EXCISE AND TRADE.—A total of 1572 samples has been examined for this Department, compared with 1291 last year.

Acid Oils for Soap-making.—If these contain not less than 30 per cent. free acidity (calculated as oleic acid) they are now exempt from import duty. This has necessitated the examination of samples from 277 consignments of such oils.

RAILWAYS AND HAIFA HARBOUR DEPARTMENT.—In the experience of the railways, boiler tubes are liable to be perforated after a few months' use with Haifa water. Magnesium chloride is apparently the cause of most of the corrosion, and in some of the wells this constituent (calculated as a "probable combination") amounts to as much as 35 parts per 100,000. Added to this there is a sodium chloride content high enough to give serious trouble.

The Composition of Fruits as used for Jam Manufacture in Great Britain.

A COMMUNICATION FROM THE BRITISH ASSOCIATION OF RESEARCH FOR THE COCOA, CHOCOLATE, SUGAR, CONFECTIONERY AND JAM TRADES.—T. MACARA, F.I.C., *Director of Research.*

DURING the past two years a joint committee of Public Analysts and representatives of the Jam Section of the Food Manufacturers' Federation have been engaged in discussing the question of Standards for Jams. Eventually agreement was reached, and a schedule of Standards and definitions was drawn up, copies of which were circulated to all members of the Society of Public Analysts and other Analytical Chemists (see ANALYST, **1930**, **55**, 694). These, of course, have at present no legal standing, as they have not been issued by a Government Department. In the absence of any such legal standards, however, analysts and manufacturers alike felt that the time had come when standards for jams were necessary, in the interests of both the public and the manufacturers themselves.

In order to assist analysts in the exceedingly difficult task of determining the fruit content of jams, the Council of the British Association of Research for the Cocoa, Chocolate, Sugar Confectionery and Jam Trades willingly consented to the publication of the results of a large number of analyses of jam fruits which its staff has made during the past seven years. This paper deals, therefore, with these analyses, describing the methods used and giving a summary of the results in detail in tables. Finally, suggestions are made as to how the figures given in the tables may be used in determining the fruit content of a jam.

THE SAMPLES OF FRUIT.—The samples of fruits were spread over a number of seasons, and were of varying origin, with a view to establishing not merely average figures for the composition of each kind of fruit, but also the extent of the variation likely to occur in those constituents which are of analytical interest. A certain proportion of Scottish fruits and fruits of foreign origin has been included. It should be emphasised that the selection could not be anything but an arbitrary one, so that in a sense the use of the word "average" is misleading—in fact, it does not seem possible to define anything that can be regarded as a true "average" composition of a fruit. The extreme figures, however, rest on a surer basis; they have been obtained once, and may be obtained again, or even exceeded. It is always possible that they may be extended in either direction by samples from fresh districts, by fresh varieties, or by the effects of an unusual season. In using them, discretion should be applied, in regard to the likely effect of condition of fruit, seasonal conditions, and so on.

Only those proximate constituents of the fruits which were of interest to the manufacturer or the analyst were determined. These were soluble solids, insoluble matter, pectin, sugars, and acidity. In some cases certain other features of interest were examined, mostly of a non-chemical nature; *e.g.* proportion of seeds in raspberries, etc.

ANALYTICAL DETAILS.

About 1 lb. of fruit, taken from a larger mixed sample, was passed through a mincer (care being taken to avoid any loss of juice), and 100 or 150 grms. of the well-mixed mass were weighed out, and boiled moderately for an hour with about 400 or 600 ml. respectively, of water in a large beaker, with occasional stirring and addition of water to maintain the volume. After cooling to room temperature, the mixture was transferred to a measuring cylinder, made up to 500 or 750 ml.

with water, and the whole thoroughly mixed by vigorous shaking. The extract was then strained off through a 120 mesh sieve or filtered through a large fluted paper, of a texture which permitted fairly rapid filtration. In some cases, for example, apples, it was necessary to interrupt the boiling after twenty minutes or half-an-hour, to rub the mixture through a coarse sieve, and then resume the boiling; this broke up lumps which otherwise would not have been thoroughly extracted. With cherries, a definite weight of whole fruit was boiled, and the stones were removed from the mixture before making up to volume. The same procedure was adopted for some of the plums; with others, it was possible to detach the stones beforehand, so that the analysis could be carried out on the minced flesh only, from the outset. The results were calculated back to 100 parts of the stoneless fruits, whether the stones were removed before or after boiling.

SOLUBLE SOLIDS.—The specific gravity and refractive index (by immersion refractometer) of this extract were determined, and from these figures the percentage of soluble solids was calculated by means of the ordinary sugar factors. The figures given in the tables are the means of the gravity and refractometric results.

SUGARS.—A suitable quantity of the extract was treated with lead subacetate, made to volume, filtered, and the excess of lead in a portion of the filtrate was removed with sodium phosphate. The final filtrate was then inverted at 60° C. with hydrochloric acid, cooled and neutralised with sodium hydroxide solution, and the reducing sugar was determined by copper reduction, either by the gravimetric method of Quisumbing and Thomas (in the earlier seasons) or by the volumetric method of Lane and Eynon. The results for total sugars may be considered to correspond to a sugar mixture more or less approximating to invert sugar in composition.

ACIDITY.—A quantity of extract, usually 50 ml., was diluted with several hundred ml. of distilled water and titrated with decinormal sodium hydroxide to the appearance of a colour with phenolphthalein. A blank titration of the distilled water was made at the same time, and deducted. The acidity is for convenience expressed as crystallised citric acid, except for apples, where it is given as malic acid (a figure not very different).

PECTIN.—In the earlier years this was determined in the extract (filtered through paper if only strained previously) by the method of Carré and Haynes (*Biochem. J.*, **16**, 63). In the later seasons it was found possible to handle a larger quantity of precipitate (up to 0·1 grm.) than was recommended by these workers. Consequently, the usual procedure adopted was to treat 50 c.c. of the 20 per cent. extract as described by Carré and Haynes, except that the time of saponification was shortened to 2 hours by keeping the volume of extract and alkali at about 100 c.c. After saponification this was diluted to 400 c.c. before precipitation of the pectate, which was afterwards filtered off on tared filter papers. The results are expressed as percentages of crude calcium pectate. A number of analyses were made in 1927, when the crude pectin was precipitated first by acetone and the true pectin determined in this precipitate. The percentage obtained in this way was generally within 0·1 per cent. of that obtained as crude pectate, except in a few fruits where the pectate was over 1 per cent. As it appeared that little was to be gained by elaborating the process in this manner, the work was continued by means of the direct process, which should, therefore, be used in the analysis of jams.

INSOLUBLE MATTER.—Ten or twenty grms. of the well-mixed minced material were weighed off, diluted with 100 to 200 ml. of distilled water, and boiled for half-an-hour. The mixture was poured on to a tared filter, the residue returned to the beaker and again boiled with a further quantity of water. The insoluble

matter was finally washed on the filter with plenty of boiling water and dried in the oven at 105° C. to constant weight.

REMARKS.—The figures obtained for the extracts were calculated back to percentage of the whole fruit except in the case of stone fruit, allowance being made for the effect of the volume of insoluble matter in causing the extracts to be not quite true "20 per cent." extracts. In most cases this effect was very small. The determinations were carried out on duplicate 20 per cent. extracts, and on duplicate portions for the insoluble matter.

The results, which are the mean of duplicates, have been expressed to the nearest 0·05 per cent. in the case of insoluble and soluble solids and sugars, as this represents about the probable limit of accuracy in these determinations.

Gooseberries and raspberries were analysed as received, but strawberries were "plugged" and currants had the "strigs" removed. Apples were analysed whole, *i.e.* were not peeled or cored.

VARIATIONS IN COMPOSITION.

The individual data have been summarised in the first Table, which shows the highest and lowest values found for each analytical figure, together with the averages (arithmetic means) for each type of fruit.

In order to afford a clearer view of the actual significance of the average figures, an analysis of some of the data has been made (Tables II to IV), so as to display the numbers of samples falling within definite ranges of values. In most cases, the average figure lies within the most frequently occurring range. The insoluble solids content of gooseberries, strawberries, and raspberries, however, occurs in greater frequency in a range a little below the average figure. The same applies to the acidity of Victoria plums, and to the pectin content of blackcurrants, Victoria plums, and damsons. The acidity of the cherries seems to fall into two groups, with the average figure dividing them.

The presentation of the data in this way may be useful also in showing the likelihood of occurrence of the extreme cases shown in Table I, some of which were undoubtedly abnormal (*e.g.* the very high figure of 1·31 per cent. pectin in apples; the high acid figure of 3·62 per cent. for damsons; and the high insoluble solids of 4·55 per cent. in gooseberries, and 5·95 per cent. in apples).

USE OF THE DATA IN THE INTERPRETATION OF JAM ANALYSES.

It should be emphasised that if it is desired to use the present data in interpreting the results of a jam analysis, the jam should be analysed in a manner similar to that adopted here for the fruits themselves. Thus, in making an extract of the jam, the sample should be boiled with a sufficient amount of water for about an hour. This is particularly important in regard to the pectin estimation in jams from fruits containing rather tough fibrous matter such as blackcurrants or blackberries.

In determining the fibre, pectin and acid in a jam, it is essential to use a proportion of water to jam, which is not less than that used in the analyses of the fruits, and to boil for a similar period. That is, the quantity of water used should be at least four times that of the sample, and the mixture should be boiled for about one hour, the volume of solution being maintained reasonably constant.

In sampling the jam the greatest care should be taken to see that the whole contents of the jar are thoroughly mixed as the fruit fibre invariably tends to float to the upper layers. The attention of Food and Drugs Inspectors, who are responsible for the division of samples, should be directed particularly to this point.

The portion used for analysis should be either ground in a mortar (soft fruit jams) or put through a small mincer (jams made with tough skinned fruits). *Stones*, *e.g.* those of plums, etc., should, of course, be removed and their proportion noted, though as a rule no conclusions can be drawn from the percentage found, as manufacturers frequently remove a considerable number before filling the jam into the jars.

Interpretation of the Analysis.

Generally the figures made use of in calculating the proportion of fruit in the jam are those for insoluble solids, acidity and pectin, all of which vary rather widely in different samples of the same fruit and render the exact determination of the fruit content almost an impossibility. Nevertheless it has been found possible, in the majority of cases of single fruit jams at least, to arrive at a fairly good approximation to the truth by a consideration of all three figures. Experience in the analysis of jams naturally is of great assistance, just as it is in the case of oils and fats.

It is suggested that in order to determine whether or not a jam is of a particular standard, the composition should first be calculated on the assumption that the fruit is of average composition. (See Table I.) Should the jam then fall below the standard it is advisable to use the three minima in this calculation. Should the jam still fall below the limits there can be little doubt that it has not been made with the standard weight of fruit and a certificate should be issued accordingly. Where it passes on this basis but does not come up to standard when using the average figures, it would be best to test further samples of the same make, and if all fall below the standard the manufacturer should be asked for an explanation.

Where the analysis is carried out on one sample only there are possibilities that a wrong conclusion may be drawn, for it is exceedingly difficult to ensure that the whole of the fruit in a boiling of jam will be evenly distributed throughout all the jars filled. When more than one jar is tested it will be found that while the insoluble solids may vary somewhat widely, the acid and pectin remain much the same in each. This is especially true of the acid, though the pectin may vary to a slight extent with the proportion of fibre. The acid figure will generally give a fair indication of the composition of the jam, except in those cases where acid has been added. A determination of the *p*H value of the jam will frequently indicate any marked addition of this sort, if compared with figures given by genuine full fruit standard jams.

Mixed Jams.

In the case of mixed jams the problem is naturally more complicated, and here it is useful to count the seeds, as in raspberry and gooseberry (see Table No. V), and, of course, a microscopic examination should also be carried out, comparing if possible with a jam of known composition or a known mixture of the fruits. In this way it has been found possible to detect adulteration with the seeds of raspberry in a raspberry and gooseberry jam. In one such case the quantity of raspberry was estimated to be about 10 per cent., although the seeds would have indicated nearer 40 per cent. The manufacturer afterwards stated that 12 per cent. had been used.

Mixtures of plums and apples are among the most difficult to deal with, but here a microscopic together with a macroscopic examination of the jam should help considerably.

Other Tests.

While it is recognised that the above methods of determining the fruit content of a jam leave much to be desired, the analyst will, as the result of his experience in analysing jams of undoubted standard quality, gain confidence in the results, but further methods of arriving at the fruit content are desirable. This fact has not been overlooked, and the staff of the Research Association has been engaged during the past fruit season in trying several new methods. Among these is one originally suggested by Mr. L. K. Boseley, which makes use of what is called the lead number. As originally described by Boseley the method did not give concordant results in all cases, but it has now been modified and developed as a routine method, and has already proved very helpful in many cases. When a sufficient number of figures for the various fruits have been collected, the method will be published.

Another figure which is of use in conjunction with others is the *p*H value, but here again a larger number of results is required before this can be applied with confidence to the estimation of the fruit content in jams.

TABLE I.

EXTREME AND AVERAGE COMPOSITIONS OF FRUITS.

	Insol. solids (fibre, etc.). Per Cent.	Soluble solids. Per Cent.	Total solids. Per Cent.	Total sugars. Per Cent.	Acid as crystallised citric. Per Cent.	Pectin as crude calcium pectate. Per Cent.
GOOSEBERRIES.						
Highest	4·55	11·35	15·25	7·1	3·00	1·19
Lowest	1·7	6·9	9·1	2·0	1·47	0·50
Average (86 samples) ..	2·61	8·45	11·06	3·51	2·22	0·81*
STRAWBERRIES.						
Highest	3·45	13·6	16·2	8·5	1·74	0·78
Lowest	1·3	5·4	7·3	3·2	0·46	0·36†
Average (47 samples) ..	2·14	8·98	11·12	5·48	0·93	0·53†
RASPBERRIES.						
Highest	9·2	11·9	20·65	7·85	2·68	0·87
Lowest	4·4	5·4	10·9	1·3	1·23	0·37‡
Average (54 samples) ..	6·17	7·98	14·15	3·58	1·73	0·53‡
REDCURRANTS.						
Highest	7·6	12·65	19·7	6·9	2·95	0·67
Lowest	4·05	9·1	13·75	4·05	2·16	0·44
Average (9 samples) ..	6·02	10·17	16·19	4·80	2·54	0·58
BLACKCURRANTS.						
Highest	7·9	16·7	22·4	8·25	4·32	1·67
Lowest	4·7	10·0	17·25	2·25	2·70	0·63
Average (20 samples) ..	5·69	14·25	19·94	6·44	3·48	1·08
CHERRIES (on stone-free fruit).						
Highest	2·7	14·75	17·45	10·6	1·65	0·40
Lowest	0·95	10·7	12·35	6·9	0·41	0·11
Average (12 samples) ..	1·88	12·41	14·29	8·33	0·88	0·24
VICTORIA PLUMS (on stone-free fruit).						
Highest	1·6	15·2	16·65	9·1	2·19	1·07
Lowest	0·9	9·6	10·5	5·9	1·15	0·61
Average (14 samples) ..	1·13	12·63	13·76	7·43	1·64	0·81
GREEN & GOLDEN PLUMS (on stone-free fruit).						
Highest	1·35	11·8	12·7	6·5	1·81	1·02
Lowest	0·85	9·1	9·95	4·5	0·97	0·67
Average (5 samples) ..	1·03	10·80	11·83	5·69	1·47	0·80
RED & MISCELLANEOUS PLUMS (on stone-free fruit).						
Highest	1·7	17·05	18·35	10·25	2·79	1·21
Lowest	0·75	9·35	10·35	3·95	0·54	0·54
Average (15 samples) ..	1·22	13·10	14·32	7·56	1·74	0·82
GREENGAGES (on stone-free fruit).						
Highest	1·35	17·25	18·3	11·3	1·44	1·03
Lowest	0·95	10·6	11·75	5·35	1·04	0·86
Average (5 samples) ..	1·16	14·05	15·21	8·00	1·20	0·95
APPLES.						
Highest	5·95	13·55	18·35	9·75	1·84§	1·31
Lowest	1·6	9·5	12·15	4·2	0·52§	0·49
Average (28 samples) ..	2·57	11·70	14·27	7·60	1·11§	0·75
DAMSONS (on stone-free fruit).						
Highest	2·8	22·65	24·95	11·45	3·62	1·52
Lowest	1·25	10·55	12·75	3·9	1·80	0·95
Average (18 samples) ..	1·96	16·03	17·99	7·53	2·48	1·15
BLACKBERRIES.						
Highest	13·55	10·4	23·0	6·7	1·24	0·85
Lowest	6·6	7·85	14·45	3·3	0·52	0·22
Average (11 samples) ..	9·64	9·06	18·70	5·10	0·85	0·59

* 63 samples.

† Excluding 3 sulphited samples.

‡ Excluding 10 sulphited samples.

§ As malic acid.

TABLE II.

SPREAD OF VALUES FOR INSOLUBLE SOLIDS CONTENT.

GOOSEBERRIES.

Range. Per Cent.	No. of samples.
1·55–2·0	7
2·05–2·5	36
2·55–3·0	28
3·05–3·5	12
3·55–4·0	2
4·05–4·5	0
4·55–5·0	1

Average 2·61 per cent.

STRAWBERRIES.

Range. Per Cent.	No. of samples.
1·05–1·5	3
1·55–2·0	18
2·05–2·5	17
2·55–3·0	7
3·05–3·5	2

Average 2·14 per cent.

RASPBERRIES.

Range. Per Cent.	No. of samples.
4·05–4·5	2
4·55–5·0	6
5·05–5·5	9
5·55–6·0	14
6·05–6·5	7
6·55–7·0	5
7·05–7·5	2
7·55–8·0	3
8·05–8·5	3
8·55–9·0	2
9·05–9·5	1

Average 6·17 per cent.

REDCURRANTS.

Range. Per Cent.	No. of samples.
4·05–4·5	1
4·55–5·0	1
5·05–5·5	1
5·55–6·0	1
6·05–6·5	2
6·55–7·0	1
7·05–7·5	1
7·55–8·0	1

Average 6·02 per cent.

BLACKCURRANTS.

Range. Per Cent.	No. of samples.
4·55–5·0	5
5·05–5·5	5
5·55–6·0	5
6·05–6·5	3
6·55–7·0	0
7·05–7·5	1
7·55–8·0	1

Average 5·69 per cent.

CHERRIES.

Range. Per Cent.	No. of samples.
0·55–1·0	1
1·05–1·5	2
1·55–2·0	4
2·05–2·5	2
2·55–3·0	3

Average 1·88 per cent.

VICTORIA PLUMS.

Range. Per Cent.	No. of samples.
0·55–1·0	5
1·05–1·5	8
1·55–2·0	1

Average 1·13 per cent.

GREEN & GOLDEN PLUMS.

Range. Per Cent.	No. of samples.
0·5 –1·0	3
1·05–1·5	2

Average 1·03 per cent.

RED & BLUE PLUMS.

Range. Per Cent.	No. of samples.
0·55–1·0	2
1·05–1·5	12
1·55–2·0	1

Average 1·22 per cent.

GREENGAGES.

Range. Per Cent.	No. of samples.
0·55–1·0	1
1·05–1·5	4

Average 1·16 per cent.

APPLES.

Range. Per Cent.	No. of samples.
1·55–2·0	7
2·05–2·5	8
2·55–3·0	9
3·05–3·5	3
3·55–4·0	0
4·05–4·5	0
4·55–5·0	0
5·05–5·5	0
5·55–6·0	1

Average 2·57 per cent.

DAMSONS.

Range. Per Cent.	No. of samples.
1·05–1·5	3
1·55–2·0	8
2·05–2·5	5
2·55–3·0	2

Average 1·96 per cent.

BLACKBERRIES.

Range. Per Cent.	No. of samples.
6·05– 7·0	2
7·05– 8·0	1
8·05– 9·0	0
9·05–10·0	3
10·05–11·0	3
11·05–12·0	0
12·05–13·0	1
13·05–14·0	1

Average 9·64 per cent.

TABLE III.

SPREAD OF VALUES FOR ACID CONTENT.

GOOSEBERRIES.

Range. Per Cent.	No. of samples.
1·41–1·60	1
1·61–1·80	6
1·81–2·00	14
2·01–2·20	19
2·21–2·40	24
2·41–2·60	11
2·61–2·80	7
2·81–3·00	2

Average 2·22 per cent.

STRAWBERRIES.

Range. Per Cent.	No. of samples.
0·41–0·60	2
0·61–0·80	13
0·81–1·00	15
1·01–1·20	13
1·21–1·40	3
1·41–1·60	0
1·61–1·80	1

Average 0·93 per cent.

RASPBERRIES.

Range. Per Cent.	No. of samples.
1·21–1·40	10
1·41–1·60	11
1·61–1·80	12
1·81–2·00	10
2·01–2·20	5
2·21–2·40	5
2·41–2·60	0
2·61–2·80	1

Average 1·73 per cent.

REDCURRANTS.

Range. Per Cent.	No. of samples.
2·01–2·20	1
2·21–2·40	1
2·41–2·60	4
2·61–2·80	2
2·81–3·00	1

Average 2·54 per cent.

BLACKCURRANTS.

Range. Per Cent.	No. of samples.
2·61–2·80	1
2·81–3·00	3
3·01–3·20	2
3·21–3·40	2
3·41–3·60	3
3·61–3·80	3
3·81–4·00	5
4·01–4·20	0
4·21–4·40	1

Average 3·48 per cent.

CHERRIES.

Range. Per Cent.	No. of samples.
0·41–0·60	4
0·61–0·80	3
0·81–1·00	1
1·01–1·20	0
1·21–1·40	3
1·41–1·60	0
1·61–1·80	1

Average 0·88 per cent.

VICTORIA PLUMS.

Range. Per Cent.	No. of samples.
1·01–1·20	1
1·21–1·40	1
1·41–1·60	7
1·61–1·80	2
1·81–2·00	0
2·01–2·20	3

Average 1·64 per cent.

GREEN & GOLDEN PLUMS.

Range. Per Cent.	No. of samples.
0·81–1·00	1
1·01–1·20	0
1·21–1·40	1
1·41–1·60	1
1·61–1·80	1
1·81–2·00	1

Average 1·47 per cent.

RED & BLUE PLUMS.

Range. Per Cent.	No. of samples.
0·41–0·60	1
0·61–0·80	0
0·81–1·00	0
1·01–1·20	1
1·21–1·40	2
1·41–1·60	0
1·61–1·80	5
1·81–2·00	2
2·01–2·20	1
2·21–2·40	1
2·41–2·60	1
2·61–2·80	1

Average 1·74 per cent.

GREENGAGES.

Range. Per Cent.	No. of samples.
1·01–1·20	3
1·21–1·40	1
1·41–1·60	1

Average 1·20 per cent.

APPLES.

Range. Per Cent.	No. of samples.
0·41–0·60	2
0·61–0·80	4
0·81–1·00	6
1·01–1·20	7
1·21–1·40	4
1·41–1·60	2
1·61–1·80	2
1·81–2·00	1

Average 1·11 per cent.

DAMSONS.

Range. Per Cent.	No. of samples.
1·61–1·80	1
1·81–2·00	1
2·01–2·20	1
2·21–2·40	5
2·41–2·60	6
2·61–2·80	1
2·81–3·00	1
3·01–3·20	1
3·21–3·40	0
3·41–3·60	0
3·61–3·80	1

Average 2·48 per cent.

BLACKBERRIES.

Range. Per Cent.	No. of samples.
0·41–0·60	2
0·61–0·80	2
0·81–1·00	2
1·01–1·20	3
1·21–1·40	1

Average 0·85 per cent.

TABLE IV.

SPREAD OF VALUES FOR PECTIN CONTENT.

GOOSEBERRIES.

Range. Per Cent.	No. of samples.
0·41–0·50	1
0·51–0·60	0
0·61–0·70	14
0·71–0·80	18
0·81–0·90	18
0·91–1·00	4
1·01–1·10	6
1·11–1·20	2

Average 0·81 per cent.

STRAWBERRIES.

Range. Per Cent.	No. of samples.
0·31–0·40	7
0·41–0·50	14
0·51–0·60	9
0·61–0·70	11
0·71–0·80	3

Average 0·53 per cent.

RASPBERRIES.

Range. Per Cent.	No. of samples.
0·31–0·40	3
0·41–0·50	16
0·51–0·60	18
0·61–0·70	3
0·71–0·80	3
0·81–0·90	1

Average 0·53 per cent.

REDCURRANTS.

Range. Per Cent.	No. of samples.
0·41–0·50	1
0·51–0·60	5
0·61–0·70	3

Average 0·58 per cent.

BLACKCURRANTS.

Range. Per Cent.	No. of samples.
0·61–0·70	2
0·71–0·80	1
0·81–0·90	2
0·91–1·00	5
1·01–1·10	1
1·11–1·20	3
1·21–1·30	2
1·31–1·40	1
1·41–1·50	1
1·51–1·60	1
1·61–1·70	1

Average 1·08 per cent.

CHERRIES.

Range. Per Cent.	No. of samples.
0·11–0·20	4
0·21–0·30	5
0·31–0·40	3

Average 0·24 per cent.

VICTORIA PLUMS.

Range. Per Cent.	No. of samples.
0·61–0·70	5
0·71–0·80	4
0·81–0·90	1
0·91–1·00	2
1·01–1·10	2

Average 0·81 per cent.

GREEN & GOLDEN PLUMS.

Range. Per Cent.	No. of samples.
0·61–0·70	2
0·71–0·80	1
0·81–0·90	1
0·91–1·00	0
1·01–1·10	1

Average 0·80 per cent.

RED & BLUE PLUMS.

Range. Per Cent.	No. of samples.
0·51–0·60	2
0·61–0·70	2
0·71–0·80	3
0·81–0·90	3
0·91–1·00	3
1·01–1·10	1
1·11–1·20	0
1·21–1·30	1

Average 0·82 per cent.

GREENGAGES.

Range. Per Cent.	No. of samples.
0·81–0·90	1
0·91–1·00	3
1·01–1·10	1

Average 0·95 per cent.

APPLES.

Range. Per Cent.	No. of samples.
0·41–0·50	2
0·51–0·60	3
0·61–0·70	6
0·71–0·80	8
0·81–0·90	6
0·91–1·00	1
1·01–1·10	1
1·11–1·20	0
1·21–1·30	0
1·31–1·40	1

Average 0·75 per cent.

DAMSONS.

Range. Per Cent.	No. of samples.
0·91–1·00	2
1·01–1·10	10
1·11–1·20	1
1·21–1·30	1
1·31–1·40	2
1·41–1·50	1
1·51–1·60	1

Average 1·15 per cent.

BLACKBERRIES.

Range. Per Cent.	No. of samples.
0·21–0·30	1
0·31–0·40	0
0·41–0·50	2
0·51–0·60	2
0·61–0·70	4
0·71–0·80	1
0·81–0·90	1

Average 0·59 per cent.

TABLE V.

SHOWING NUMBER AND WEIGHT OF SEEDS PER 100 GRMS.

	No. of seeds per 100 grm.	Wt. of seeds per 100 grm.
GOOSEBERRIES	990	1·83
	540	1·29
	730	0·97
	410	1·03
	320	0·97
Average	600	1·22
RASPBERRIES	3565	4·11
	3760	4·40
	4900	5·85
	4760	5·62
	4050	4·37
	4095	4·09
Average	4190	4·74
REDCURRANTS	865	3·56
	940	4·29
	1255	5·84
	738	3·10
	1055	3·86
Average	970	4·13
BLACKCURRANTS	3685	3·09
	5210	7·24
	4045	4·35
	4875	3·94
Average	4450	4·66
BLACKBERRIES	1930	4·34
	2700	5·57
	3765	7·31
	3450	8·01
	3780	7·65
	3460	7·63
Average	3180	6·75
BILBERRIES	13,200	2·31

Ministry of Agriculture and Fisheries.

STATUTORY RULES AND ORDERS, 1929, No. 1117.*

AGRICULTURAL PRODUCE (GRADING AND MARKING), ENGLAND.

THE AGRICULTURAL PRODUCE (GRADING) (POTATOES) REGULATIONS, 1929, DATED NOVEMBER 30, 1929, MADE BY THE MINISTER OF AGRICULTURE AND FISHERIES AS TO GRADE DESIGNATIONS FOR POTATOES.

In exercise of the powers conferred on him by the Agricultural Produce (Grading and Marking) Act, 1928, the Minister of Agriculture and Fisheries hereby makes the following regulations:—

1. Grade designations to indicate the quality of potatoes produced in England and Wales shall be as follows:—

E. & W. No. 1 Size
E. & W. No. 2 Size
E. & W. No. 3 Size

and the quality indicated by such grade designations shall be deemed to be as described in columns 2, 3, 4, 5, 6, 7 and 8 of the Schedule hereto.

2. These Regulations may be cited as the Agricultural Produce (Grading) (Potatoes) Regulations, 1929.

In Witness whereof the Official Seal of the Minister of Agriculture and Fisheries is hereunto affixed this thirtieth day of November, 1929.

(L.S.) CHARLES J. H. THOMAS.

* H.M. Stationery Office, 1930. Price 1d. net.

SCHEDULE.

Grade Designation.	Definitions of Quality.						
	General.	Applicable to Single Tubers.	Applicable to Quantities.				
			Tolerances.				
		Size (Minimum diameter).	Conformity to Variety, etc.	Undersize or Oversize.	Disease,* damage, etc.	Earth and/or extraneous matter.	*Maximum* aggregate of all defects under cols. 5, 6 and 7.
1.	2.	3.	4.	5.	6.	7.	8.
E. & W. No. 1 Size E. & W. No. 2 Size E. & W. No. 3 Size	Reasonably clean, healthy potatoes, free from serious defect and suitable for human consumption	1¾ in.† 1⅝ in. 1½ in.	At least 95 per cent., by count must conform to the variety as and when specified and to the type of soil on which grown, where such is declared.	Not more than 3 per cent. of the total weight may pass through a riddle or sieve having a square mesh of the minimum size‡ specified (in col. 3) for the grade, and, included in this, not more than 0·5 per cent. of the total weight may pass through a 1-in. mesh: potatoes which exceed 3¼ ins. in their smallest diameter shall be excluded. Otherwise, in regard to size, the potatoes shall be as grown.	Not more than 3 per cent. of the total weight may consist of appreciably diseased, damaged or unsightly potatoes, and, included in this amount, not more than 0·25 per cent. of the total weight may be obviously affected with soft rot.	Not more than 4 per cent. may be present in potatoes loaded up to November 1st in the year of harvesting, and 2 per cent. after that date the percentage to be calculated on the net weight of screened potatoes.	5 per cent. of the total weight.

* (i) Any disease or defect, the presence of which may be established by cutting open the potato, shall be taken into account, and potatoes having worm or slug holes penetrating into the flesh shall be regarded as damaged.

(ii) Potatoes affected by superficial disease or damage shall not be regarded as diseased or damaged unless more than one-tenth of the surface is so affected.

(iii) A potato shall only be regarded as being obviously affected with the soft rot if, at the time of inspection, it is squashy and/or the surface is at some part distinctly broken or wet owing to disease.

† When the potatoes have been passed over a riddle of greater mesh than 1¾ in., the minimum size may, at the seller's discretion, be appended to the grade name, *e.g.* E. & W. No. 1 Size (2 in.).

‡ As measured clear within the bounds of the mesh.

Merchandise Marks Act

MALT PRODUCTS.

STATUTORY RULES AND ORDERS, 1930, No. 566.*

THE MERCHANDISE MARKS (IMPORTED GOODS) NO. 5 ORDER, 1930.

At the Court of Buckingham Palace, the 26th day of June, 1930.

PRESENT,

The King's Most Excellent Majesty in Council.

Whereas by sub-section (1) of Section 2 of the Merchandise Marks Act, 1926 (16 & 17 Geo. 5. c. 53), it is provided that after an enquiry in relation to goods of any class or description has on a reference from the appropriate department been held by a committee appointed for the purposes of the said Act, and the report of the committee on the matter has been taken into consideration by the department, that department may, unless it appears to them that the trade of the United Kingdom or the trade generally of other parts of His Majesty's Dominions with the United Kingdom would be prejudiced if imported goods of that class or description for use or consumption in the United Kingdom were prohibited to be sold unless they bear an indication of origin, make a representation to His Majesty that it is desirable that an Order should be made under the said Section 2, and His Majesty in Council may thereupon, subject to the provisions of the said Act, make an Order prohibiting the sale or exposure for sale in the United Kingdom of imported goods of that class or description unless they bear an indication of origin:

And whereas in accordance with the provisions of the said section an enquiry in relation to imported Malt Products has, on a reference from the appropriate department, namely, the Minister of Agriculture and Fisheries, the Secretary of State for the Home Department and the Secretary of State for Scotland acting jointly (hereinafter called "the Department") been held by a committee appointed for the purposes of the said Act and the report of that committee has been taken into consideration by the Department:

And whereas it does not appear to the Department that the trade of the United Kingdom or the trade generally of other parts of His Majesty's Dominions with the United Kingdom would be prejudiced if Malt Products imported for use or consumption in the United Kingdom were prohibited to be sold unless they bear an indication of origin, and the Department has accordingly made representations to His Majesty that it is desirable that an Order should be made under the said Section 2:

Now, therefore, His Majesty, by and with the advice of His Privy Council, in pursuance of the powers vested in Him by the said Act, and of all other powers enabling Him in that behalf, is pleased to order, and it is hereby ordered, as follows:—

1. For the purpose of this Order, the expression "malt products" shall mean malt extract, malt flour, malt extract and cod liver oil, and malt extract blended with any other product so that malt extract comprises more than 50 per cent. by volume of the whole.

2. It shall not be lawful to sell or expose for sale in the United Kingdom any imported malt products unless they bear an indication of origin.

3. The indication of origin shall be printed, stencilled, stamped or branded on the container, or on a label securely attached thereto, indelibly and in a conspicuous manner, in plain block letters not less than one-twelfth of an inch in height when the greatest dimension of the container does not exceed six inches, not less than one-eighth of an inch in height when the greatest dimension of the container exceeds six inches but does not exceed fifteen inches, and not less than one-half of an inch in height when the greatest dimension of the container exceeds fifteen inches. For the purpose of this Order, the expression "greatest dimension" shall mean the height, length or breadth, whichever is the greatest, of a rectangular or approximately rectangular container, and the height or maximum diameter, whichever is the greater, of a cylindrical, oval or conical container.

* H.M. Stationery Office. Price 1d. net.

4. This Order shall apply on exposure for sale wholesale whether the person exposing the goods is or is not a wholesale dealer.

5. The provisions of this Order shall come into force at the expiration of three months from the date hereof.

6.—(*a*) This Order may be cited as "The Merchandise Marks (Imported Goods) No. 5 Order, 1930."

(*b*) The Interpretation Act, 1889,(a) shall apply to the interpretation of this Order as if it were an Act of Parliament.

M. P. A. HANKEY.

(a) 52–3 V. c. 63.

Ministry of Health.

REPORTS ON PUBLIC HEALTH AND MEDICAL SUBJECTS, No. 60.

THE EFFECT ON FOODS OF FUMIGATION WITH HYDROGEN CYANIDE.*

HYDROGEN cyanide is being increasingly employed as a fumigant for the destruction of insects and vermin pests in food. Its advantages are absence of taint, freedom from injurious effects on textiles, paint-work and metals, high toxicity to insects, and ease of removal subsequently by ventilation. On the other hand, the smell is not sufficiently strong to serve as a warning that it is present in dangerous amounts, especially as individuals vary in their power of detecting its presence by sense of smell.

METHODS EMPLOYED.—These were discussed in an earlier report (No. 19, 1923) by Stock and the author. The older "pot" method, in which the gas was generated by the action of acids on cyanides (*loc. cit.*), is now superseded in most countries by liquid hydrogen cyanide. The name "Cyclon," formerly applied to a mixture of 90 per cent. of methyl cyanoformate and 10 per cent. of methyl chloroformate, is now transferred to liquefied hydrogen cyanide adsorbed on kieselguhr or infusorial earth, and supplied in sealed tins in admixture with sufficient lachrymator (ethyl brom-acetate) to act as a warning.

The liquid gas may be transported in steel cylinders if stabilised with a little acid, and it is also supplied in strong glass bottles with crown corks, and in metal drums with screw caps.

"Cyanogas" is a dry, grey-black powder consisting essentially of calcium cyanide, cyanamide and a little calcium carbide, which evolves hydrogen cyanide in moist air. Betaine tablets, which evolve the gas when heated, and a mixture with aluminium chloride of an addition-product of ferric chloride and hydrogen cyanide (which is liberated by water) are also used.

RESIDUAL GAS IN FUMIGATED FOOD.—This depends on (1) strength of gas, (2) duration of fumigation, (3) moisture content of food, (4) state of subdivision of food, (5) method of packing, and (6) subsequent ventilation.

In most of the published work the data are incomplete, since the concentration of gas used is usually recorded in terms of the weight introduced per unit space, without correction for the capacity of the contents, failure to produce gas-tight

* By Dr. G. W. Monier-Williams. Obtainable at His Majesty's Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 6d. net.

conditions, condensation, absorption and, in the case of the "pot" method, side-reactions. The only reliable data are obtained from analyses at the beginning of and during the fumigation process. Tables of results of other workers show the "nominal" concentration of gas, periods of exposure and ventilation, and parts of residual HCN per million. The last figures vary from 12 to 100 (water in open dish), 22 to 100 (milk), 8 to 1632 (cheese), 2 to 618 (oils and fats), 5 to 530 (meat and fish), 1 to 206 (cereals, flour), 3 to 580 (fresh fruit), 11 to 480 (dried fruit), traces in fresh vegetables (except 500 to 1100 in peas and beans), nil to 970 (tea, coffee, etc.). The author found nil to 3 in samples of grain from ships, and 63 to 102 and 24 to 47 for the top and centre layers respectively, of boxes of sultanas exposed for a few hours.

The variations are due to the widely different conditions used, but, in general, the results indicate the effectiveness of ventilation in removing excess gas (except in the cases of dried and liquid milk, dried fruit and, possibly, cheese). Absorption is greatest for moist, finely-divided unwrapped foods. Orange and apple skins resist absorption, whilst peaches and bananas are more readily penetrated. Cooking removes almost all the absorbed gas. In general, foods treated with less than 1 volume of hydrogen cyanide in 200 volumes of air, and subsequently exposed to air, retain less than 20 parts per million.

Toxicity.—The fatal dose (Lehmann, *Chem. Ztg.*, 1915, **39**, 573) is 60 mgrms. of hydrogen cyanide, though foods containing cyanogenetic glucosides have been known to produce death in quantities corresponding with 10 to 12 mgrms. It is difficult to suggest a limit, but there is no reason why a maximum of 20 parts per million should be exceeded for foods which are eaten raw, except in special cases (*e.g.* dried fruit), or when excessive local absorption may occur.

Chemical Compounds Formed. Analysis.—Hydrogen cyanide may be retained in foods by laevulose, with which it forms a cyanhydrin. Dextrose cyanhydrin, however, forms only when the food is alkaline, whilst potassium cyanide disappears rapidly from foods containing either dextrose or laevulose. This is attributed to the formation first of the cyanhydrin, and then, by hydrolysis, in the presence of alkali, of hydroxy acids and ammonia, the latter reaction being favoured by the presence of alcohol (*cf.* Fischer, *Annalen*, 1892, **270**, 64). There is little evidence, however, that glucose is a practical antidote to prussic acid poisoning. The toxicity of the cyanhydrins probably depends on the extent to which they may dissociate into sugar and hydrogen cyanide; but their formation is of importance, since it may serve as a means of storage in the food of hydrogen cyanide produced during fumigation.

These conclusions also indicate that, probably, the most satisfactory method of analysis is to promote dissociation by addition of water, and to distil in steam in a neutral or slightly acid medium. The author used 25 grms. of sample in 250 c.c. of water, and titrated the distillate with 0·02 *N* silver nitrate solution in the presence of sodium hydroxide and potassium iodide, the results being checked colorimetrically by means of the copper benzidine acetate reagent. The first 100 c.c. of distillate usually contained the whole of the hydrogen cyanide.

Influence of Hydrogen Cyanide on Sulphur Dioxide Determinations.—Attention is directed to the fact that the determination of sulphur dioxide in dried fruits, etc., is quite unreliable if the food has been fumigated for the destruction of insects and contains residual hydrogen cyanide.

Deterioration of Food on Fumigation.—Over-treatment may interfere with the natural respiration-processes of fruits and vegetables essential to their value as foods and so cause serious damage, and instances are given of softening

and discoloration. Since, under certain conditions, the gas has a stimulating effect on growth, there is evidence that a short exposure to a high concentration is preferable to prolonged exposure at low concentrations. The injurious effect is ascribed to the inhibitory action on the oxidation-reduction enzymes concerned with plant-respiration rather than to any direct action on the tissues themselves. Fermentative and proteolytic enzymes are less affected.

Fertile hens' eggs are killed by fumigation with 1 per cent. hydrogen cyanide (by volume) at 3° C. for 4 hours, although the amount actually absorbed is small.

ACTION ON BACTERIA, MOULDS, ETC.—These are relatively resistant to the gas, and are affected permanently only by excessive quantities, the use of which is precluded by other considerations.

J. G.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Determination of Aldose Sugars by Titration with Standard Iodine and Alkali Solutions. G. M. Kline and S. F. Acree. (*Ind. Eng. Chem.*, [*Anal. Ed.*], 1930, **2**, 413–415.)—A quantity of the sugar solution which will react approximately with 20 c.c. of 0·1 *N* iodine solution is neutralised, aqueous phenolphthalein solution being used as indicator; 5 c.c. of 0·1 *N* iodine solution are added, followed by 7·5 c.c. of 0·1 *N* sodium hydroxide solution. These additions are repeated until 22 c.c. of iodine solution and 35 c.c. of sodium hydroxide solution have been introduced. A definite quantity of 0·1 *N* hydrochloric acid is then added, and the liberated iodine is titrated with thiosulphate solution. After the addition of phenolphthalein solution the acidity is titrated with 0·1 *N* sodium hydroxide solution. If the liberated iodine requires more than 3 c.c. of 0·1 *N* thiosulphate solution, too much iodine has been added resulting in over-oxidation of the sugar; if less than 1·5 c.c. is required, insufficient iodine has been added. In either case, the determination must be repeated, adding more or less iodine as indicated; 0·15 grm. of xylose is equivalent to 20 c.c. of 0·1 *N* iodine solution or 30 c.c. of 0·1 *N* sodium hydroxide solution. W. P. S.

Chemistry of the Products of Cocos Nucifera. Part I. J. P. C. Chandrasena. (*Biochem. J.*, 1930, **24**, 1493–1495.)—In this paper, the first of a proposed series on the chemistry of the various products of the coconut palm, the author deals with the examination of the kernel and the oil at various stages of development of the nut, and also the constituents of the haustorium; no investigation has hitherto been carried out on the nature of the oil obtained. The following results were obtained with bunches of ripe nuts ready for harvest (*i.e.* nuts picked about a year after the complete setting of the fruit) from each of four trees, one from Colombo (Kitulwatta), the second from a suburb of Colombo

(Dehiwala), and the third and fourth from Moratuwa and Panadura, two coast towns 13 and 16 miles respectively south of Colombo.

	Kernel.			Oil.	
	Water. Per Cent.	Oil. Per Cent.	Residue. Per Cent.	Sp. gr. at 29° C.	n_D
Kitulwatta ..	48·1	40·0	18·7	0·9152	1·4559
Dehiwala ..	45·5	36·0	20·0	0·9297	1·4538
Moratuwa ..	42·1	38·5	20·7	0·9190	1·4540
Panadura ..	42·0	42·7	20·8	0·9170	1·4550

	Oil.			Residue.	
	Acid value.	Sap. value.	Iodine value.	Ash Per Cent.	Pentosans Per Cent.
Kitulwatta ..	0·42	234·1	6·84	5·87	2·89
Dehiwala ..	0·73	268·4	3·37	5·79	1·96
Moratuwa ..	0·23	260·3	6·48	4·86	1·91
Panadura ..	0·12	249·8	5·78	6·19	2·10

The haustorium (coconut apple), which is yellowish on the surface but white inside with fibres running longitudinally, contained 84·9 per cent. of moisture, and the dried material yielded 18·9 per cent. of an oil which had sp. gr. 0·9177 at 29° C., saponification value 238·7, iodine value 16·1, and acid value 1·46. The press-juice of the fresh haustorium was an opaque liquid of sp. gr. 1·040, from which was extracted 0·62 per cent. of an oil with sp. gr. 0·9171, saponification value 248·0, iodine value 10·1, and acid value 1·47. The dry residual material, after extraction of the oil, contained: pentosans 9·49 per cent., lignin 27·0 per cent., and ash 4·05 per cent. The percentage of the water in the kernel was found to diminish with age, the iodine and acid values were high in the oils from the youngest bunches, and the iodine value was even higher in the oil from the haustorium. P. H. P.

Variation in Colour-Test Value of Commercial Samples of Cod-liver Oil. F. J. Dyer and F. Wokes. (*Quart. J. Pharm.*, 1930, **3**, 417–426.)—Colour-test value is defined as the intensity of the blue colour produced by a saturated solution of antimony trichloride in chloroform on the oil under given conditions. Ninety grms. of antimony trichloride are rapidly weighed and transferred to anhydrous chloroform to make about 270 c.c., and the solutions used then have a sp. gr. of 1·626 to 1·627. The oil to be tested is dissolved in anhydrous chloroform to give a solution producing an initial blue colour between 4 and 8 Lovibond units (1·5 to 4 c.c. for the cod-liver oils used). To 0·2 c.c. of the freshly-made oil solution in a test tube of 1 cm. internal diameter are added at a given time 2 c.c. of the antimony solution, mixing is carried out by twirling, and the reading made in the tintometer exactly 30 seconds after mixing. If fading has commenced, readings are taken at 60 and 90 seconds, and by the curve of rate of fading the blue colour at maximum intensity is calculated. The values obtained on 24 commercial samples of cod-liver oil as sold to the public, and from various sources, ranged from 3·0 to 9·0, with an average of 5·7. From a study of these figures and others for oils as imported, the consumer in this country is apparently receiving an article

containing, on the average, only two-thirds of the activity (as measured by the colour test) of the satisfactory samples imported. The readings for oils stored under different conditions show that cod-liver oil is best preserved in completely filled amber-coloured bottles. A satisfactory sample of cod-liver oil should not give a colour-test value below 4·0. The practice of attempting to convert colour-test values into so-called biological units is regarded as unjustifiable. D. G. H.

Fatty Acids in the Liver of the Sheep. K. Turner. (*Biochem. J.*, **1930, 24, 1327–1336.**)—The fatty acids that can be isolated from the liver and other organs of animals differ from those that are found as glycerides in the adipose tissue, where reserve fat is held in store, but the precise nature of the unsaturated acids in these organs has been defined only in the case of certain acids from the liver of the pig. Hartley (*J. Physiol.*, **1909, 38, 353**) isolated an oleic acid from pig's liver in which he proved that the double bond was between C_{12} and C_{13}, and a linolic acid with double bonds between C_9 and C_{10} and between C_{12} and C_{13}. No evidence of the presence in pig's liver of the ordinary $\Delta^{9,10}$-oleic acid was obtained, though this appeared to be the only oleic acid present in the adipose tissue fat of the pig. In a re-investigation of the nature of the oleic acid in pigs' livers containing about 4·5 per cent. of fat certain data have been obtained which point to the presence of both oleic acids in the organs used. An investigation has been made on the fatty acids obtained from the liver of the sheep. The ethyl esters prepared from these fatty acids were oxidised by the method of Armstrong and Hilditch (*J. Soc. Chem. Ind.*, **1925, 44, 43** T.), and a mixture of pelargonic and caproic acids was obtained. Oxidation of the mixed fatty acids with hydrogen peroxide according to the method described by Hilditch (*J. Chem. Soc.*, **1926, 1828**) gave rise to dihydroxystearic acid, but not to tetrahydroxystearic acid. Dilute alkaline permanganate, however, produced a mixture of both these acids. The dihydroxystearic acid and tetrahydroxystearic or sativic acid were then oxidised separately. From the data obtained the oleic acid present in sheep-liver fat has been identified as the $\Delta^{9,10}$-modification which is commonly found in adipose tissue fat. Linolic acid (the same as Hartley obtained from pig's liver) is present, and also arachidonic acid, but there is no evidence of a linolenic acid. The occurrence of the linolic acid in the liver, but not in adipose tissue fat of the sheep, lends itself to the same interpretation as that given by Hartley for $\Delta^{12,13}$-oleic acid and linolic acid in pig's liver, *viz.* that it is formed from the $\Delta^{9,10}$-oleic acid by the introduction of a new double bond between C_{12} and C_{13}. P. H. P.

National Mark Malt. (*Pharm. J.*, **1930, 125,** 224.)—The contents of 32 jars selected at random (except that no recognisable brands were duplicated), from some hundreds of 1 lb. jars of malt extract with cod-liver oil, bought as "the kind generally sold," were analysed in the Government Laboratory for (1) protein content, (2) sp. gr., (3) diastatic activity of the malt extract, (4) volume of cod-liver oil, (5) and freedom from adulteration. (1) Two-fifths of the samples were below National Mark standard (5 per cent.) (see p. 45), two containing less than 4, nine between 4 and 5, and fifteen 5 per cent. and over, with a maximum of 6·9 per cent.

(2) Fifteen samples were below standard (1·4). (3) Only five samples conformed to the standard (25); nine samples were between 10 and 20, nine between 5 and 10; six below 5, and in two there was no diastatic activity. Only one sample complied with all the National Scheme requirements, not counting country of origin of the grain. (4) More than 50 per cent. were below National Mark standard; nine contained less than 13 per cent., and one only 10·8 per cent. of cod-liver oil.

D. G. H.

Behaviour of Natural and Artificial Fruit Essences towards Sodium Paratoluene-sulphonchloramide (Heyden Chloramine). A. Miermeister. (*Z. Unters. Lebensm.*, 1930, **59**, 585–594.)—One c.c. of essence, 20 c.c. of water, 50 c.c. of a 0·01 *N* solution of chloramine-T reagent (Tillmans and Hollatz, *id.*, 1929, **57**, 489), and 0·5 c.c. of acetic acid are kept for 4 hours in diffused daylight, potassium iodide and dilute sulphuric acid added, and the iodine titrated with 0·01 *N* sodium thiosulphate solution and starch indicator (*A*). Another 1 c.c. portion is shaken with 100 c.c. of water and 80 c.c. of ether, the filtered ethereal extract evaporated at the ordinary temperature, and the residue dissolved in 2 c.c. of alcohol and 20 c.c. of water, and the chloramine value (*B*) found as described above, the blank given by the reagent being deducted. The values *A* were determined for 22 natural and artificial essences, and with anise, vanilla, strawberry, raspberry, and mandarin, the ratios of the values for the natural to those for the artificial products were 12·3: 0·9, 24·7: 38·9, 6·8: 29·0, 1·8: 17·0, and 10·0: 35·2, respectively. With volatile aromatic liquids the chloramine values of five 12 c.c. fractions, distilled from 1 c.c. of essence and 100 c.c. of water, were found. With essences of natural citrus fruits, apple, mandarin and orange, and artificial apple, banana, pear, apricot, anise and mandarin essences, the sum of the chloramine values of the fractions (which were always greatest for the first fractions) equalled the direct value *A*, but in the other cases *A* was the greater, the balance being accounted for by the chloramine value of the residue after distillation. The difference between the values *A* and *B* is, therefore, taken as the chloramine value of the non-volatile reducing substances. The results indicate that natural cocoa, coffee, anise, vanilla, currant, strawberry, and raspberry, and artificial strawberry, gooseberry, raspberry and vanilla essences contain only a small proportion of steam-volatile matter. Further directions are given for the treatment of various beverages containing these essences. The liquids should be filtered, and carbon dioxide removed by tossing. The reagent, $CH_3.C_6H_4SO_2(Na):NCl$, is obtained from *p*-toluene sulphonic chloride, a by-product of the manufacture of saccharin, and is sold as a disinfectant under the names "aktivin," "mianin," "chlorazene," or "tolamine." It may also be prepared by sulphonation of toluene, treatment of the sodium salt of the sulphonic acid with phosphorus pentachloride, and conversion of the resulting sulphonic chloride into the sulphonamide by means of ammonia. The action of a slight excess of an alkaline 1·5 *N* solution of sodium hypochlorite then produces chloramine-T, which crystallises from the liquor. It forms colourless solutions stable for a month, but is decomposed by acid or alkaline hydrolysis into sodium chloride and oxygen. J. G.

Determination of Total Alkaloids in Cinchona Bark. P. A. W. Self and C. E. Corfield. (*Quart. J. Pharm.*, 1930, **3**, 410–416.)—The assay of cinchona bark, both by the B.P. and German Pharmacopoeia methods, is unsatisfactory, whilst that of the U.S.P. gives low and variable results. Extraction by ammoniacal alcohol is not recommended without preliminary treatment. The proposed method is to mix 10 grms. of bark (in about No. 60 powder) with a mixture of 7·5 c.c. of strong lead acetate solution and 12·5 c.c. of water, and leave for 1 hour. Fifty c.c. of ammoniacal alcohol (alcohol 97·5 and ammonia 2·5 parts) are then added, and, after standing for another hour, the mixture is extracted for 3 to 4 hours in a continuous extractor with boiling ammoniacal alcohol. The greater part of the alcohol is then distilled off, and 10 c.c. of *N* sulphuric acid and 40 c.c. of water added, and the mixture boiled and cooled. After filtration through cotton wool into a separator the mixture is treated with 10 to 20 c.c. of boiling 0·1 *N* sulphuric acid, cooled and filtered, and the flask and wool washed with cold acidified water until a few drops of filtrate show no opalescence with Mayer's reagent. Chloroform (20 c.c.) is added to the separator, the contents shaken for 2 minutes, and the chloroform layer run into another separator containing a mixture of 5 c.c. of *N* sulphuric acid and 15 c.c. of water. After shaking, the chloroform layer is rejected. The liquid in the first separator is shaken with two further quantities of chloroform, which are washed as before. The acid washings are transferred to the first separator, made alkaline with ammonia, and completely extracted with chloroform, the extract washed with water, the chloroform distilled off, 5 c.c. of alcohol added, and evaporation completed. The extract is then dried and weighed. It is of a high degree of purity, and results obtained by this method are accurate. D. G. H.

Extract of Colocynth. E. M. Smelt. (*Quart. J. Pharm.*, 1930, **3**, 433–437.)—Extracts of colocynth were prepared with 60 per cent. alcohol and with diluted U.S.P. alcohol (48·4 to 49·5 per cent. by vol. C_2H_5OH). The directions of the U.S.P. were followed, but the preparations could not be completed, since the amount of extract exceeded the final weight specified, *i.e.* 25 per cent. of the drug taken. Extracts were then made with 8 samples of colocynth pulp, and of these, 5 samples yielded over 25 per cent. of extract when 60 per cent. alcohol was used, and 6 samples over 25 per cent. with diluted U.S.P. alcohol. The samples giving lower values were an Egyptian colocynth several years old, and two brownish samples. It is suggested that the U.S.P. (10th Rev.) monograph requires revision. D. G. H.

Assay of Stramonium Leaves and Tincture of Stramonium. C. M. Caines. (*Quart. J. Pharm.*, 1930, **3**, 342–348.)—The U.S.P. (10th Rev.) process for the assay of stramonium leaves is rapid and complete in the initial extraction, but the use of 0·2 *N* solutions throughout is regarded as preferable. The German Pharmacopoeia method is not recommended, nor are the methods of van Itallie, Eder, or the author regarded as satisfactory. A modification of the B.P. (1914) process (Caines, *Quart. J. Pharm.*, 1929, **2**, 271) is suggested to overcome the

formation of obstinate emulsions, and this method is regarded as good. Ten grms. of the leaves, in No. 60 powder, are moistened with 5 c.c. of a mixture of 4 vols. of ether and 1 of chloroform, 2 c.c. of ammonia diluted with 3 c.c. water added, the whole packed into a small percolator, the resulting percolate distilled till the volume is 15 c.c., transferred to a separator, the flask washed with two quantities each of 5 c.c. of chloroform, 12·5 c.c. of 90 per cent. alcohol added, and the liquid extracted with successive quantities of 0·02 *N* sulphuric acid. The combined acid extracts are washed with 10 c.c. of chloroform (which is rejected), the liquid made distinctly alkaline with ammonia, and the alkaloids completely extracted with chloroform. The extracts are washed with 5 c.c. of water, the chloroform distilled off, and the residue dissolved successively in 3 c.c. of ether and 2 c.c. of absolute alcohol. The dried residue is dissolved in 1 c.c. of absolute alcohol, 5 c.c. of 0·2 *N* sulphuric acid added, and the excess acid titrated with 0·2 *N* sodium hydroxide solution, with methyl red as indicator, 1 c.c. of 0·2 *N* sulphuric acid being equivalent to 0·005785 grm. of alkaloid. The tincture (1 in 5) may be assayed by evaporating 100 c.c. to 10 c.c., transferring to a separator, and washing the dish with 2 c.c. of 45 per cent. alcohol, followed by 3 quantities of 5 c.c. of water, and then with 2 c.c. of ammonia, and finally with 4 quantities of 5 c.c. chloroform. After shaking, the chloroform layer is separated, the extraction repeated with two more portions of 10 c.c. of chloroform, 15 c.c. of 90 per cent. alcohol added, the chloroform solutions extracted with 0·02 *N* sulphuric acid, and the process completed as above. D. G. H.

Determination of Nicotine in Oriental Tobaccos. J. Burmann. (*Helv. Chim. Acta*, 1930, **13**, 785–787.)—The following semi-micro-method demands extremely pure reagents, exact standard solutions, and accurately graduated burettes. The moisture in the tobacco is determined by heating 10 grms. of the tobacco, spread on a sheet of paper, in a ventilated steam oven at 100° C. for 3 hours, cooling and weighing. The dried tobacco is immediately ground to about the fineness of snuff and stored in a sealed vessel. To determine the nicotine, 3 grms. of the powder are triturated for some minutes in a porcelain dish about 10 cm. in diameter, with 3 c.c. of 30 per cent. sodium or potassium hydroxide solution by means of a glass rod. After 3 grms. of gypsum have been mixed in, the resulting dry powder is transferred to a 150 c.c. flask closed with a rubber stopper carrying a three-way tap. The flask is evacuated by a water pump, air being then re-admitted and the flask again evacuated, so that the bulk of the ammonia liberated is withdrawn. After addition of 75 grms. of absolute ether (freshly distilled over phosphorus pentoxide) the powder is shaken at intervals during an hour, then left for an hour or two and filtered rapidly through a pleated filter covered with a watch-glass. From 50 grms. of the clear liquid in a 150 c.c. Erlenmeyer flask the ether is distilled, by heating on a water-bath at about 50° C. The residue is treated with three successive quantities of 5 c.c. of the pure ether, each of which is distilled off. After all traces of ammonia have been expelled in this way, the residue is dissolved in 20 c.c. of pure ether, which is distilled off after addition of 50 c.c. of distilled water. The cold liquid is titrated with 0·01 *N*

hydrochloric acid in presence of 1 drop of a 1 per cent. solution of bromocresol purple in alcohol, using as comparison 50 c.c. of water containing one drop of the indicator and one drop of 0·01 *N* acid. Multiplication of the number of c.c. of the acid used by 0·081 gives the percentage of nicotine in the tobacco. The result may be checked gravimetrically by filtering the titrated liquid, washing on the filter, and making the volume of filtrate up to 100 c.c. This is mixed with 2 c.c. of concentrated hydrochloric acid (sp. gr. 1·19) and 3 c.c. of 12 per cent. silicotungstic acid solution. After the lapse of 24 hours the liquid is decanted off, and the precipitate collected, with the help of a pump, on a weighed Gooch crucible, and washed several times with water and then with alcohol and absolute ether. The weight of the precipitate, determined after drying at 100° C. and cooling in a desiccator over sulphuric acid, is multiplied by 0·0506 to obtain the percentage of nicotine in the tobacco. T. H. P.

Biochemical.

Biochemistry of Aluminium. I. Excretion and Absorption of Aluminium in the Pig. K. Mackenzie. (*Biochem. J.*, 1930, **24**, 1433–1441.)—The biological significance of aluminium is at present an unsolved problem; even when aluminium occurs in the diet in a readily available form, animals do not seem to utilise it in the metabolic processes to any extent. The utilisation of aluminium by young pigs has now been examined, and the path of excretion has been determined. An attempt has been made to ascertain if the excretion of urinary phosphorus is disturbed by the use of aluminised diets, and the amount of aluminium present in various organs has been determined. From the data obtained it is concluded that the intake and excretion of aluminium in the pig are equal (within the limits of experimental error). Aluminium excretion is confined solely to the alimentary tract. The absorption of aluminium from normal diets containing moderate amounts of available aluminium, as determined by the analysis of the organs, is small. Diversion of phosphates from the urine to the faeces does not occur on such diets; the urinary excretion of phosphate, therefore, disposes of the very doubtful assumption that aluminium may affect the metabolic processes by combining with available phosphate in the intestinal tract and thereby immobilising it. No harmful effect on general growth and metabolism results from feeding the pigs with comparatively large amounts of aluminium. The method does not take account of small quantities which might be absorbed and excreted without appreciably affecting the results. P. H. P.

Manganese in Relation to Nutrition. M. B. Richards. (*Biochem. J.*, 1930, **24**, 1572–1590.)—The manganese content of a large number of substances of vegetable or animal origin has been determined. The analyses were carried out by a procedure based on the Willard and Greathouse periodate method, described by Richards (ANALYST, 1930, **55**, 554). The manganese content of plant reproductive organs has been investigated. Wide differences are found in different

plants, but there is little difference as regards manganese content between the male and female organs of the same plant. Analysis of lupin seeds at various stages of development shows that there is a marked increase in total manganese as the seed grows to maturity. This increase seems to bring further evidence that manganese may be regarded as an essential element for the development of the plant. The reproductive organs of water-loving plants, such as willow and sedge, show a high manganese content; it is of interest to note that a very high percentage of manganese has been reported in many true water-plants, such as *Zostera marina*. The data for the manganese content of foodstuffs indicate that, whilst soil conditions may have influence in determining manganese absorption by the plant, samples of a foodstuff from different sources show in general approximately the same content of manganese. From a consideration of the data for the manganese content of animal organs, the author concludes that, whilst we may be still in ignorance of the actual function of manganese in nutrition, there is a considerable amount of evidence in favour of regarding this element as one of the essential constituents of the animal organism. Direct proof of the indispensability of manganese for normal growth and development has not yet been furnished, and, in considering the possibility of its importance, it has to be remembered that manganese may behave in the animal body like silver, mercury, lead and other heavy metals, and that its presence in organs and tissues may have no real physiological significance. On the other hand, the steady increase of manganese in the developing egg, the invariable presence of the element in such tissues as the reproductive organs, and the constancy of the amount not only in these organs, but also in those most closely connected with the processes of assimilation (a constancy which is fairly well maintained when large amounts of manganese salts are added to the diet) are facts which suggest that manganese is no accidental constituent of the organism, but may have some intimate relationship to the vital processes. P. H. P.

Manganese in Foodstuffs. A. E. Boycott and G. R. Cameron. (*Lancet*, 1930, 959.)—In seaching for manganese as a possible cause of cirrhosis of the liver in drunkards, many foods and condiments were analysed for their contents of manganese. Manganese was absent from cockles, whelks and limpets; from marmite, tomato ketchup, essence of anchovy salad dressing, chutney, pickles (3 sorts), lobster paste, mustard, capers, and caraway seeds. Winkles contained, as mgrms. in 100 grms. of dried material, trace to 16; *Crepidula fornicata*, 10 to 17; oyster, 4; mussel, *nil* to 4; scallop, *Pecten opercularis*, trace to 40, *Pecten maximus*, 5; shrimp (bottled), *nil* to 4; prawn (bottled), *nil*; tea, 27 to 43; coffee, trace or *nil*; cocoa, trace; mixed spice, 14; cinnamon, 2; ginger, 4 to 12; coriander, 10; cloves, 48 to 50; vinegar, 1; curry powder, 4; olives (flesh), 6; pepper, 10 to 20; cayenne pepper, 2 or less. It is concluded that a vegetarian teetotaller would probably take in more manganese than a heavy drinker. D. G. H.

Destruction of Diastatic Enzymes in Honey on Heating. H. W. Boer. (*Chem. Weekblad*, 1930, **48**, 646–648.)—Honey may be heated for 24 hours at 60° C.

without destroying the diastatic enzymes, but at 65° C. the diastase value* is reduced by 3 to 4 points, an average of 1 unit in 7 hours. Usually 12 hours' heating at 65° C. of a honey containing all the enzymes will not affect them much, but a similar heating of a honey which has been previously heated might destroy them all. The smaller the diastase value, the greater the risk that it will disappear on heating. Heating at 70° C. reduces the diastase value, on an average, 1 unit in 4 to 5 hours; at 75° C., 1 unit in 2 to 2½ hours; at 80° C., 1 unit in 10 minutes; at 90° C., 1 unit in 2 minutes; and at 95° C., 1 unit in ¾ minute, and the fall is most rapid at the beginning. (*Cf.* Lampitt, Hughes and Rooke, ANALYST, **1930**, **55**, 666.) D. G. H.

* Gothe defines the diastase value of honey as the amount of 1 per cent. starch solution hydrolysed in 1 hour by 1 grm. of honey under the optimum conditions. The diastase values of the Dutch honeys examined ranged from 29·4 to 53.

Vitamins of Olive Oil and the Effect of Refining. G. Bertrand. (*Compt. rend.*, **1930**, **191**, 725–727.)—Virgin and refined olive oils were introduced into the diets of rats showing stationary weight curves for several days. An immediate rise in the curves was produced, but the weight increased much more rapidly with virgin than with refined oil. The difference is clearly manifest with the addition of as little as 3 per cent. of the oils, showing that the refining process impoverishes the olive oil of its vitamins. D. G. H.

Question of the Identity of a Bacterial Growth-Promoting Factor with Vitamin B_1. J. G. Davis and J. Golding. (*Biochem. J.*, **1930**, **24**, 1503–1506.)—An investigation has been made of the vitamin B_1 content and bacterial growth-promoting properties of three commercial peptones. The test organism used was a lacto-bacillus requiring for good growth, not only the intermediate products of protein degradation, but also some factor present in all tissues containing vitamin B_1. The vitamin B_1 contents of the peptones were compared by feeding tests on rats. The results showed that commercial peptones contain only negligible amounts of vitamin B_1. There is no relation between the vitamin B_1 content of peptones and their ability to stimulate the growth of an organism requiring a vitamin *B*-like factor. Vitamin B_1 concentrates of the same order of potency for rat protection had widely different effects on the growth of the test organism. Since some had no effect at all, it may be concluded that vitamin B_1 itself has no influence on the metabolism of the organism. Therefore, the bacterial growth-stimulating substance and vitamin B_1 are not identical. P. H. P.

Vitamin B_2 Content of Cereals and the Supposed Connection between Human Pellagra and Deficiency of this Vitamin. W. R. Aykroyd. (*Biochem. J.*, **1930**, **24**, 1479–1488.)—Aykroyd and Roscoe (*Biochem. J.*, **1929**, **23**, 483) examined cereals and other foodstuffs for their vitamin B_2 content, with the use of the method of determination described by Chick and Roscoe (*Biochem. J.*, **1928**, **22**, 790). This work has now been further extended in order to continue the investigation of the relation between the epidemiology of human pellagra and vitamin B_2 deficiency. One of the most striking (and hitherto unexplained) facts

about human pellagra is its almost exclusive occurrence among maize-eating populations. In the previous experiments it was found that whole maize, though low in vitamin B_2 when compared with foods containing animal protein, was by no means devoid of the vitamin, and that maize endosperm compared well with wheat flour in this respect. Two other staple cereals, rice and millet, have now been included, and their vitamin B_2 content compared with that of maize. Two samples of whole rice and two samples of milled rice "raw" and "parboiled," were found to be poor sources of vitamin B_2. Whole millet is a poor source of vitamin B_2. Maize is a rather better source of vitamin B_2 than millet or rice. Control rats from each litter were fed on the basal diet complete except for vitamin B_2. All remained practically stationary in weight, but skin symptoms did not consistently develop. Curative tests were made on two rats suffering from dermatitis. Diets which contained 65 per cent. of maize endosperm and 50 per cent. of whole rice respectively did not alleviate the symptoms. It is pointed out that, since neither rice nor millet shows any superiority over maize as a source of vitamin B_2, it is difficult to accept vitamin B_2-deficiency as the sole cause of human pellagra, as this disease is almost invariably associated with the consumption of maize. At present the association, if any, of vitamin B_2 and human pellagra is obscure. The general distribution of vitamin B_2 corresponds well with that of Goldberger's P-P (pellagra-preventive) factor, and the dietary factor which prevents "black-tongue" in dogs, as far as all three are known, and with the foodstuffs known from clinical observation to be preventive and curative of human pellagra, but the distribution of vitamin B_2 as worked out on the rat, leaves the association of pellagra with maize unexplained, and gives no support to the theory that the dermatitis produced in rats by vitamin B_2-deficiency is the analogue of human pellagra. No satisfactory evidence has so far been obtained of the presence of a toxin in maize.

P. H. P.

Bacteriological.

Pyruvic Acid in Bacterial Metabolism with an Account of the Methods used for the Detection and Determination of Pyruvic Acid. R. P. Cook. (*Biochem. J.*, 1930, **24**, 1526–1537.)—For the qualitative detection of pyruvic acid the most sensitive and specific test is that of Posternak (*C. R. Soc. Phys. Hist. Nat. Genève*, 1927, **44**, (1), 519), in which the solution is treated with an equal volume of concentrated hydrochloric acid and a few crystals of phloroglucinol; a positive reaction (red colour) is obtained with 1 in 5000 pyruvic acid. For the quantitative determination the method of Wieland (*Liebig's Ann.*, 1924, **436**, 233) is the only one of use for small quantities. A new method is described for the determination which gives better results; it depends on the bisulphite-binding capacity of pyruvic acid. It may be used to determine acetaldehyde and pyruvic acid in a single sample. Friedemann, Cotonio and Shaffer (*J. Biol. Chem.*, 1927, **73**, 355; ANALYST, 1927, **52**, 418) applied it to the determination of acetaldehyde from the oxidation of lactic acid in the quantitative determination of the latter; the method for pyruvic acid is essentially the same. The method consists in

titration of the excess sodium hydrogen sulphite with iodine, and liberation of the bound sulphite with sodium carbonate. The liberated sulphite is then titrated with standard iodine solution, 1 c.c. of *N*/10 iodine being equivalent to 4·4 mgrms. of pyruvic acid. If acetaldehyde or other bisulphite-binding substance is present, the total bound sulphite is determined. Acetaldehyde or any substance of a volatile nature may be distilled off after hydrolysis with acid, and collected in bisulphite solution. The acetaldehyde may then be determined in the distillate. The pyruvic acid in the original solution may be determined by difference, and the result can be checked by very careful neutralisation of the original solution, addition of fresh bisulphite solution, and titration again of the bound sulphite. Pyruvic acid, even in small amounts, is quite stable in acid solution. For this method the use of ammonia-free water in the manipulations is absolutely necessary. Quantities as low as 0·2 mgrm. of pyruvic acid may be determined. Pyruvic acid is produced in the aerobic oxidation by *B. coli* of various substrates, if the reaction is checked by the use of fixatives for pyruvic acid. Pyruvic acid (as pyruvate) is not decarboxylated by *B. coli*. Evidence is brought to show that pyruvic acid is broken down by *B. coli* to a mixture of formic and acetic acids. P. H. P.

Haemolytic Properties of Micro-Organisms belonging to the Paratyphoid Group. C. P. Eliot and W. W. Ford. (*Amer. J. Hyg.*, 1930, **12**, 681–684.)—In an examination of 200 young rats infected with the virus of rat anaemia (*Bartonella muris*), 18 strains of paratyphoid bacilli have been isolated and identified by cultural and serological reactions, all the strains being Gärtner's *B. enteriditis*. They produce characteristic haemolytic colonies of the Alpha type of Smith and Brown on blood-agar plates made with rabbit erythrocytes. Haemolysins (haematoxins) are also found in broth cultures and in sterile neutralised Mandler filtrates of these cultures, and prove resistant to a temperature of 90° C. Haemolytic colonies have been observed also with other members of the paratyphoid group, including *B. paratyphosus B*, certain strains of *B. enteriditis* Gärtner, *B. aertrycke* De Nobele, *B. typhi murum* of Loeffler, and certain strains of Salmon and Smith's *B. cholerasius*. Some strains of *B. paratyphosus A* gave little or no haemolysis, whilst others gave the Alpha type. Haemolytic colonies were produced by two strains of *B. typhosus* and by strains of *B. coli* of human origin.

T. H. P.

Toxicological.

Methyl Alcohol. (*Pharm. J.*, 1930, **125**, 234.)—At a conference on methyl alcohol in June at the U.S. Prohibition Bureau, Dr. Doran stated that the only jurisdiction the U.S. Treasury Dept. has over methyl alcohol (methanol) is as an ingredient of denatured alcohol, and alcohol containing as much as 10 per cent. of methanol has been consumed by the public. In the case of death from alcoholic poisoning the trouble appears to be due to ethyl alcohol until the mixture reaches 30 or 35 per cent. of methyl alcohol. Synthetic methyl alcohol now coming on

the market as a solvent, and as a 75 per cent. ingredient of certain anti-freeze solutions (of which some 40 to 45 million gallons per annum are used in the U.S.) seems likely to increase the danger. D. G. H.

Poisoning by Seeds of *Datura stramonium* (Thorn-Apple). A. Sartori. (*Chem. Ztg.*, 1930, **54**, 890.)—The stomach, stomach contents, duodenum, and alimentary canal (total weight 135 grms.), in a case of suspected poisoning, were found to contain 54 brownish kidney-shaped seeds, 2–3 mm. in size, with wrinkled surface, these being identified as thorn-apple seeds. The following procedure served to isolate and identify the atropine: 150 grms. of a mixture of the organs supplied (including spleen, kidneys, liver and blood) were slightly acidified with tartaric acid and digested with alcohol for 24 hours at a moderate temperature. The alcoholic extract, showing green fluorescence, was evaporated on a water-bath and the residue purified by solution in water and alcohol alternately, with filtration of the various solutions. The final aqueous solution, which was almost clear, was shaken with ether and then, after over-saturation with sodium carbonate, with chloroform. The pale yellow residue resulting from evaporation of the united chloroform extracts at a low temperature was then tested as follows: (1) A drop of the neutralised solution of part of the residue in water containing a trace of sulphuric acid was introduced into the eye of a cat, the pupil showing dilation shortly afterwards. (2) Part of the residue was evaporated to dryness with a few drops of fuming nitric acid in a porcelain dish. Addition of a few drops of alcoholic potassium hydroxide solution to the cold residue yielded a violet coloration, soon changing to cherry-red. (3) A solution of the remainder of the residue in concentrated sulphuric acid exhibited frothing and emitted an odour of flowers when heated and treated with water. T. H. P.

Organic Analysis.

Combustion of Methane by Means of Copper Oxide. J. R. Campbell and T. Gray. (*J. Soc. Chem. Ind.*, 1930, **49**, 432–437T.)—Methane, prepared by the hydrolysis of magnesium methyl iodide, was passed through a 20 cm. column of closely-packed, fused, granulated sieved copper oxide (77·8 grms.). Since this occupied 18·9 c.c., the time of contact of gas and oxide could be calculated from the rate of flow of the former, the reduced oxide being regenerated in air after each experiment and used again. Circulation of the methane gave discordant results, and it was, therefore, passed over the oxide, maintained at the desired temperature, at a constant speed, the time of flow being noted, and the volume of gas determined from the volume of saturated magnesium chloride solution expelled from an aspirator. Since the products of reaction are carbon dioxide and water only, the percentage of the total methane oxidised is given by $100\ K\ (K+M)$, where M is the volume of methane in the gas after combustion and K the ratio of the amount of carbon dioxide (V) to M. The results obtained by this and a method in which the gas was heated in intimate contact with the oxide in a closed tube and the reaction followed from the changes in pressure, showed that below 280° C. V is

almost negligible for moderate periods of contact. From 280° to 400° C. the rate of oxidation is slow, but at higher temperatures the amounts of methane oxidised tend to a maximum for any one temperature, and are influenced relatively little by the period of contact, so long as this is not small. Above 700° C. combustion is rapid, being complete in 7 minutes. Hence, when analysing gases by the fractional combustion method, it is necessary to oxidise hydrogen and carbon monoxide at temperatures not exceeding 300° C., if methane is the only other combustible gas present (*cf.* following abstracts, and Burrell and Oberfell, *J. Ind. Eng. Chem.*, 1916, **8**, 228). J. G.

Influence of Various Catalysts in Promoting the Oxidation of Methane by Means of Copper Oxide. J. R. Campbell and T. Gray. (*J. Soc. Chem. Ind.*, 1930, **49**, 447–450T.)—A mixture of nitrogen and 5 per cent. of methane was passed over copper oxide, the resulting carbon dioxide determined by absorption in alkali, and the amount of methane burned thence calculated. The oxidising agents used were: (1) copper oxide (8 to 32 mesh) activated by alternate reduction and oxidation. (2) copper oxide mixed with an aqueous suspension of cuprous chloride, and dried so as to contain 13·8 per cent. of Cu_2Cl_2; (3) copper oxide and vanadium pentoxide, prepared by mixing the copper oxide with a suspension of ammonium vanadate in water, drying the mixture and igniting the residue; (4) copper oxide with 2 per cent. of cobaltous oxide; (5) copper oxide with 2 per cent. of nickelous oxide; (6) copper oxide with 2 per cent. of manganese dioxide. From the results the following conclusions were drawn:—(1) The rate of combustion is appreciable at 560° C. and complete at 705°C. (*cf.* preceding abstract) provided the contact-time is 2·4 to 3 minutes. The results at 808° C. indicate that an increase in rate of flow above a certain minimum produces a progressive decrease in the amount of methane burned, though very little methane is unoxidised even at the rate of 42·3 c.c. per minute. At 592° C. rates of 18·2 and 1·41 c.c. per minute produce oxidation of 21·6 and 94·1 per cent. of the methane, respectively. (2) Oxidation commences at 400 °C. and is complete at 475° C. Cuprous chloride loses its activity after prolonged use, probably as a result of fusion (m.pt. 430° C.), and hydrochloric acid is produced above 660° C. (3) Oxidation commences at 445° and 475° C., and is complete at 675° and 690° C. for 4·2 and 1 per cent. of V_2O_5, respectively, and the activity is not impaired by use. For (4), (5) and (6) the respective temperatures are 290°, 395° and 215° C. for commencement of combustion, and 650°, 675° and 675° C. for complete combustion, the contact times being 3 to 3·5 minutes. The mechanism of the action of cuprous chloride therefore differs from that of the other catalysts, and this catalyst may be considered ideal for the Dumas method of nitrogen determination (*cf.* following abstract). J. G.

Oxidation of Various Gases by Means of Copper Oxide, Lead Chromate and Cobalt Oxide. J. R. Campbell and T. Gray. (*J. Soc. Chem. Ind.*, 1930, **49**, 450–453T.)—Addition of hydrogen or ethylene to methane lowers the external furnace temperature required for complete oxidation of methane in the presence

of copper oxide (*cf.* preceding abstracts), probably owing to the local generation of heat by the combustion of the more easily oxidised gas. The effect of ethylene, consequently, is greater than that of hydrogen, whilst its action as a negative catalyst or poison is not apparent in this reaction. Fused lead chromate is inferior to copper oxide in combustion analyses, since it may cause carbon monoxide to be formed as a result of incomplete combustion of the methane; moreover, lead chromate cannot be regenerated by oxidation *in situ*, even at 808° C. Cobalt oxide alone is equal in efficiency as an oxidising agent to copper oxide, whilst, in the presence of copper oxide, it has a positive catalytic effect (*cf. loc. cit.*). J. G.

Separation of Alkyl and Aryl Halogen. Q. Landis and H. J. Wichmann. (*Ind. Eng. Chem.* [*Anal. Ed.*], 1930, **2**, 394–397.)—Detailed methods are described for the determination of halogens in insecticides containing such substances as carbon tetrachloride, *p*-dichlorobenzene, etc. The Stepanow process for organic halogen is modified by heating a solution of the sample in kerosene or xylene with an excess of sodium; a small quantity of amyl alcohol is also added, and the heating is carried out under an efficient reflux apparatus. Benzenoid halogen is decomposed completely by this treatment. Aliphatic halogen in the presence of aryl halogen is determined by decomposition in kerosene solution with a concentrated potassium hydroxide solution in *n*-butyl or amyl alcohol. The mixture is heated at 100° C. in a pressure bottle for two hours, or at 115° C. for fifteen minutes. Total halogen in this case is determined by heating the mixture with sodium.

W. P. S.

Pyrolysis of Vegetable Oils of Pronounced Acetyl Value (Grapeseed, Castor, Para Rubber Seed Oils). R. Delaby and R. Charonnat. (*Compt. rend.*, 1930, **191**, 1011–1012.)—The absence of ricinoleic acid from grapeseed oil is shown by the fact that, when decomposed by heating it under reduced pressure, such oil yields only traces of unsaturated aldehyde; saturated and unsaturated fatty acids of high average molecular weight (303–339) are obtained in 20 per cent. yield under these conditions. Pyrogenic decomposition of the sodium soap of castor oil gives sebacic acid, methylhexylcarbinol and the corresponding ketone, whilst similar treatment of grapeseed oil yields an insignificant alcoholic fraction forming an oily acid phthalate. Hence grapeseed oil contains no appreciable amount of ethylenic acid-alcohol capable of splitting into saturated aldehyde and unsaturated acid. Pyrolysis in a vacuum of oil from seeds of *Hevea brasiliensis* obtained from Indo-China yielded about 1 per cent. of liquid (b.pt. 80–140° C. at 14 mm. pressure) giving a faint coloration with Schiff's reagent, the bulk of the product being fatty acids, b.pt. 200–230° C., of mean molecular weight 312.

T. H. P.

Para Rubber Seed Oil. G. S. Jamieson and W. F. Baughman. (*Oil and Fat Ind.*, 1930, **7**, 419–421, 437.)—The kernels of a sample of rubber seed (*Hevea brasiliensis*) yielded 42·53 per cent. of a dark red oil having the following characteristics:—Sp. gr., 25/25° C., 0·9185; $n_D^{20°}$ C., 1·4737; saponification value,

191·8; iodine value (Hanus), 135·2; Reichert-Meissl value, 0·3; Polenske value, 0·2; acid value, 40·9; unsaponifiable matter, 0·8 per cent.; thiocyanogen number, 88·8; hexabromide value, 15·7; saturated acids, corrected, 16·0, unsaturated acids, corrected, 78·4 per cent. of iodine value, 163·8. The proportions of oleic (27·3), linolic (31·5) and linolenic acid (19·6 per cent.) in the oil were calculated by the Kaufmann method from the iodine value and the thiocyanogen iodine value of the oil. At least two isomers of linolenic acid are present. The saturated acids were separated by the lead salt and ether method and esterified, and six final fractions were analysed, showing the presence in the original oil of 7·3 per cent. of palmitic, 9·1 of stearic, and 0·3 of arachidic acid. The poor drying properties of commercial samples of rubber seed oil are regarded as due, at least partly, to the high acidity. D. G. H.

Para Rubber Seed Oil. Y. Iwamoto. (*J. Soc. Chem. Ind. Japan*, 1930, **33**, 409B.)—Fallen Para rubber seeds, collected from Malaya, were extracted with ether, and the oil tested for its acid value. That from fresh seeds was sweet to the taste, and had an acid value of 7·2, that from seeds not so fresh was somewhat bitter and of higher acid value, whilst that from putrified seeds was very bitter, and had an acid value of 110·86. Cold pressing gives a 28 per cent. yield of sweet edible oil, but hot pressing yields only 17 per cent. of a bitter oil from which the bitter taste may be removed by treatment with sodium hydroxide. The constants of the oil extracted from fresh seeds were found to be as follows:—Sp. gr. at 15°/4° C. 0·9234; $n_D^{20°}$ C., 1·4757; solidif. pt., 2° C.; acid value, 7·2; iodine value, 138·8; Reichert–Meissl value, 2·28; acetyl value, 2·41; unsaponifiable matter, 1·62 per cent.; liquid fatty acids, 80 per cent.; and solid fatty acids, 17·8 per cent. The liquid acids consisted largely of oleic, linolic and linolenic; the solid acids of 70 per cent. of stearic and 30 per cent. of palmitic acid. Various samples of crushed kernels were kept at room temperature for about three months and then extracted with ether. The acid value of the extracted oil was about six times as high as that extracted from the same kernels which had been previously heated for 5 hours at 105° C. The author concludes from this and other observations that the seeds contain a lipolytic enzyme. R. F. I.

Determination of Wax in Shellac. A. G. Stillwell. (*Ind. Eng. Chem.*, [*Anal. Ed.*], 1930, **2**, 387.)—Five grms. of the powdered shellac are dissolved in 150 c.c. of boiling water containing 3 grms. of sodium carbonate, the solution cooled, and the insoluble matter collected on a filter consisting of alternate layers of cotton-wool and asbestos, washed with 50 c.c. of 70 per cent. alcohol, and dried. The filter and its contents are then extracted with carbon tetrachloride in a Soxhlet apparatus, the extract is evaporated, and the residue of wax weighed. W. P. S.

Inorganic Analysis.

Analytical Applications of the Reaction of Ammonia on Resorcinol in the Presence of Cations. L. Bey. (*Bull. Soc. Chim.*, 1930, **47-48**, 1192–1193.) —*Cadmium.*—A 5 per cent. solution of resorcinol in ether is added carefully to the

solution which has previously been treated with just sufficient ammonia to redissolve the hydroxide. A blue ring is produced at the junction of the liquids in 25 minutes in the presence of 0·001 per cent. of $CdCl_2,2H_2O$, but after 5 minutes it turns to the non-characteristic violet colour, also produced with smaller quantities of cadmium. Large amounts of copper inhibit the reaction, and, in the presence of small amounts, sufficient potassium cyanide should be added to remove any blue colour due to cadmi- and cupri-ammonic ions. *Tin.*—The solution is oxidised by means of bromine water, shaken with 2 c.c. of 5 per cent. ammonia, and 2 c.c. of a 5 per cent. aqueous solution of resorcinol added. The liquid above the precipitated stannic hydroxide appears blue in 2 to 20 minutes. With less than 0·0015 per cent. of stannous chloride a non-characteristic green-grey colour results. Antimony chloride does not affect the result, unless the proportion of antimony is 400 times that of the tin; in that case the antimony should be separated with hydrogen sulphide in the usual way (*cf.* ANALYST, 1929, **54**, 561). J. G.

Titration of Lead Salts. R. C. Wiley, P. M. Ambrose and A. D. Bowers. (*Ind. Eng. Chem.* [*Anal. Ed.*], 1930, **2**, 415–416.)—The lead solution to be titrated should not contain other metals which form insoluble molybdates. It should be neutralised with ammonia, and any precipitated lead hydroxide dissolved by boiling the solution after the addition of ammonium nitrate. The solution is boiled until it is neutral and, while still hot, titrated with standardised molybdate solution. The end-point is indicated when a drop of the mixture yields a brown coloration with a drop of pyrogallol and chloroform solution. W. P. S.

Detection of Tellurium in Bismuth. H. Töpelmann. (*Z. anal. Chem.*, 1930, **82**, 284–295.)—The spark spectrum of tellurium gives few sensitive lines; the two strongest (2385·8 and 2383·3Å) are in the ultra-violet. The most delicate reaction is the stannous chloride test, which detects 0·002 mgrm. of tellurium in 1 grm. of bismuth; an almost immediate brown discoloration is produced. Arsenic interferes, as it gives the same reaction (Bettendorff's test); selenium gives a red precipitate. Hence the stannous chloride test is not sufficiently specific. The author combines the above two reactions, thereby obtaining a specific and more sensitive test. The metal is dissolved in nitric acid, the solution evaporated to dryness on the water-bath, and the residue heated with sulphuric acid till white fumes are evolved. The mass is taken up in hydrochloric acid of sp. gr. 1·13 (10 c.c. for 1 grm., 50 c.c. for 10 grms. of bismuth). 0·001 grm. of arsenic as arsenite (collector for tellurium), and 5 c.c. of 10 per cent. stannous chloride solution in hydrochloric acid (sp. gr. 1·13) are added; the dark precipitate is left to deposit overnight, collected, washed with 1 per cent. stannous chloride solution followed by water, and dissolved in strong nitric acid. The solution is concentrated by evaporation, rinsed into a 4 c.c. beaker, and taken to dryness. The residue is dissolved in a drop of hydrochloric acid and this transferred to a hollow carbon electrode, the beaker being washed twice with a drop of acid. The spark is then passed and the appearance of line 2383·3 in the spectrograph observed (exposure

15 minutes). Proceeding in this manner the author was able to detect 0·00005 per cent. of tellurium in 10 grms. of bismuth. W. R. S.

Electrometric Titration of Chromium in Steel and Ferro-chrome. F. Spindeck. (*Chem. Ztg.*, 1930, **54**, 890.)—With steels containing high percentages of chromium, determination of the latter by reduction with ferrous sulphate and titration with permanganate does not give trustworthy results, and iodimetric titration is more costly. The following electrometric method gives satisfactory results. The apparatus required consists of a Fischer's electrical stirrer, two platinum electrodes, an Emich filter rod or a leg cut from an electric plug, which is easier to fill than the filter rod, and a micro-ammeter with resistance. The filter rod is filled with a solution prepared by dissolving 2·926 grms. of ammonium vanadate and 4·9 grms. of ferrous ammonium sulphate in water acidified with 50 c.c. of sulphuric acid (1:5) and making up to 500 c.c. From 0·3 to 0·5 grm. of the metal is dissolved in 1:5 sulphuric acid, the solution being then oxidised with silver nitrate and ammonium persulphate solution, and the permanganic acid reduced with 1:1 hydrochloric acid. After cooling, the liquid is treated with manganese sulphate solution and titrated with ferrous ammonium sulphate solution. The whole of the resistance is inserted at first, so that the galvanometer needle reaches about the zero point of the scale. The resistance is then cut out to give the greatest sensitivity and the titration carried out dropwise to the end-point, where the needle shows a large deflection. The end-point may be confirmed by again inserting the resistance; the needle then travels back over the scale and scarcely moves when 1–2 drops of the ferrous ammonium sulphate are added.

Material difficult to dissolve is fused with sodium peroxide, dissolved in water, and the solution made up to a definite volume. An aliquot part is filtered off, acidified with sulphuric acid, and at once titrated with ferrous ammonium sulphate. Tungsten, nickel, and cobalt do not interfere with the titration.

T. H. P.

Identification of Aluminium and Magnesium in Printing Inks. L. M. Larsen. (*Ind. Eng. Chem.* [*Anal. Ed.*], 1930, **2**, 416–417.)—The ink is mixed with a quantity of linseed oil varnish and a small amount of cobalt drier, and the mixture spread evenly on paper which has not been treated with alum during its manufacture. When the ink is quite dry, strips of the paper are boiled for one minute with 2 *N* hydrochloric acid, and the solution is decanted and cooled. If not more than a trace of iron is present, the solution is treated with an equal volume of "aluminon" reagent (250 grms. of ammonium acetate, 10 grms. of glacial acetic acid and 1 grm. of aurin tricarboxylic acid in 1000 c.c. of water), the mixture boiled for one minute, and cooled. A deep red flocculent precipitate indicates the presence of aluminium. The precipitate remains unchanged when the mixture is shaken with an equal volume of ammoniacal ammonium carbonate solution. To test for magnesium, strips of the paper are boiled for two minutes with 5 per cent. acetic acid, the extract is decolorised, if necessary, by heating it with the addition of a few drops of 2 per cent. chloramine-T solution, cooled, and treated with an

equal volume of 5 per cent. sodium hydroxide solution. One drop of an aqueous 0·025 per cent. benzopurpurin 4*B* solution is then added. A rose-red precipitate indicates the presence of magnesium. W. P. S.

Determination of Calcium and Magnesium in Dolomitic Limestones by means of Saccharate Solutions. A. C. Shead and B. J. Heinrich. (*Ind. Eng. Chem.* [*Anal. Ed.*], 1930, **2**, 388–389.)—The method depends on the solubility of calcium hydroxide in sucrose solution and on the insolubility of magnesium hydroxide or oxide in this solvent. About 0·5 grm. of the sample is ignited at 900° to 1000° C. until the weight is constant, the oxides are then transferred to a flask and heated to boiling with 25 c.c. of water; the mixture is cooled while the flask is closed to prevent the entrance of carbon dioxide, 100 c.c. of 30 per cent. sucrose solution are added, and the mixture is shaken thoroughly. The insoluble magnesium hydroxide (oxide) is collected on a paper-pulp filter under conditions which exclude atmospheric carbon dioxide, washed several times with dilute sucrose solution, then transferred to a flask, boiled with the addition of an excess of 0·2 *N* acid, and the excess of acid is titrated, phenolphthalein being used as indicator. The calcium is determined indirectly by boiling a weighed quantity of the sample with an excess of 0·2 *N* acid, titrating the excess of the acid, and deducting the alkalinity due to the magnesium hydroxide as found in the first titration. W. P. S.

Determination of Beryllium in Aluminium. H. V. Churchill, R. W. Bridges and M. F. Lee. (*Ind. Eng. Chem.* [*Anal. Ed.*], 1930, **2**, 405–407.)—One grm. of the alloy is dissolved in 25 c.c. of 1:1 hydrochloric acid, the solution is treated with hydrogen sulphide, filtered, the filtrate is evaporated until crystals appear, an equal volume of ether is added and dry hydrogen chloride is introduced until the two phases are completely miscible. The precipitate is collected on a filter, washed with a mixture of concentrated hydrochloric acid and ether saturated with hydrogen chloride, dissolved in a small quantity of water, and reprecipitated with hydrogen chloride as before. This precipitation may be repeated once more if necessary. The combined filtrates are evaporated, the residue is heated with 5 c.c. of 1:1 sulphuric acid until white fumes are given off, cooled, dissolved in water, filtered, and the filtrate neutralised with ammonia, rosolic acid being used as indicator. The mixture is boiled, filtered, the precipitate washed with ammoniacal ammonium chloride solution, dissolved in hydrochloric acid and reprecipitated, again dissolved, the solution nearly neutralised with ammonia, heated at 60° C., and treated with an excess of 8-hydroxyquinoline and ammonium acetate solutions. The mixture is filtered, the filtrate treated at 60° C. with a slight excess of ammonia, cooled, the precipitate collected, washed with ammonium acetate solution, dried, ignited, and weighed as beryllium oxide. W. P. S.

Determination of Nitrous and Nitric Acids in Sulphuric Acid. H. A. J. Pieters and M. J. Mannens. (*Z. anal. Chem.*, 1930, **82**, 218–224.)—The subject was re-investigated. Lunge's nitrometer, which gives excellent results with large

quantities of nitrogen, is no longer reliable when the nitrogen concentration is less than 0·0005 grm. per c.c. *Nitrous acid.*—The best results are obtained by the colorimetric *m*-phenylenediamine method; permanganate titration is reliable if no other reducing substance is present, but this does not seem to be the case with crude chamber acid. *Nitric acid.*—The authors reject colorimetric determination with brucine and favour the following reduction method. The acid (50 c.c. for 0·0001 to 0·0005 grm. nitrogen per c.c.) is introduced into a small separating funnel, the tube of which dips into 200 c.c. of water in a conical flask well cooled in running water; the acid is allowed to run slowly into the flask containing the water, followed by an excess of potassium hydroxide in strong solution. After addition of 3 grms. of Devarda's alloy, the flask is immediately connected with a receiver through a cooler, and the ammonia distilled into a measured excess of standard acid. This operation gives total nitric and nitrous nitrogen; the latter is given by the phenylenediamine process, and the former computed by difference. W. R. S.

Microchemical.

Colorimetric Micro-reactions of the Glutogenic Protides and Cellulosic Gels of the Wheat Grain. P. Bruère. (*Compt. rend.*, 1930, **191**, 792–794.)—Treatment of a transverse section of a wheat grain with a 0·1 per cent. solution of bromocresol green (yellow for values of *p*H below 3·6 and blue for those above 5·2) in neutral 60 per cent. alcohol reveals compact blue masses of glutogenic protides in the cells fused to the innermost of the six membranes of the skin, termed the seat of the enzymes by Bertrand. In the middle of the corn, these masses become less compact. When a flour is used, the blue glutogenic masses, starch granules and cellulosic débris may be squeezed out by means of the cover-glass, blue, pasty, amoeboid lumps, corresponding with the peptised gel known as moist gluten being then observed. When use is made of bromocresol purple, which is yellow for *p*H values not exceeding 5·2 and purple-violet at the neutral point, the colorations obtained indicate, with the ripe corn, increase in acidity from *p*H 6·8 at the periphery to *p*H 5·6 at the centre, the mean being about 6·2. Flour recently milled shows the value 6, although this value varies with the degree of extraction, chlorination, ageing, etc. T. H. P.

Erratum.—In the abstract of the paper by Wagenaar (ANALYST, **1930**, **55**, 349), for "cystine" read "cytisine."

Physical Methods, Apparatus, etc.

Emulsification. Part III. A Factor Inhibiting the Emulsification of Cod-liver Oil. E. Lester Smith. (*Quart. J. Pharm.*, 1930, **3**, 373–374.)—A substance which stabilises water-in-oil emulsions and inverts or reduces the stability of oil-in-water emulsions is produced in cod-liver oil during oxidation or

drying. The extent to which the oxidation has been carried in an oil may be found by the "drop weight method," which is a measure of the interfacial tension. A small pipette, with very fine capillary constriction above and below the bulb, but terminating in a fairly coarse jet, is filled to the upper constriction with water, and the jet lowered into a beaker of oil. The flow of water is started by blowing, and the number of drops formed while the pipette empties to the lower capillary is counted. This number (which is inversely proportional to the surface tension) divided by the volume of the pipette, gives the number of drops per mil. Figures recorded for a number of oils varied from 4 to 23. Most good oils give values of 9 or under. D. G. H.

Quantitative Spectral Analysis. P. Urbain. (*Bull. Soc. Chim.*, **1930, 47-48**, 1183–1188.)—The method depends on the electrolytic deposition of the trace of metal to be determined on a rod or wire of metal giving no spectral lines which may interfere with those due to the ultimate rays of the metal to be determined. If, in addition, a known quantity of a substance is added which produces lines close to the ultimate rays of the metal sought, the spectrograph then shows (1) the ultimate rays of the metal sought, (2) the principal rays of the comparison metal, and (3) rays due to the electrodes and impurities in the electrolyte, etc. Pairs of lines (doublets) may then be made up from a line of the metal sought and the nearest line of the comparison metal, and their intensities compared from the depths of the corresponding serrations in the curve obtained when the plate is examined micro-photometrically. The line of total opacity given by the points of commencement and conclusion of the photometric curve is taken as the reference-line. Since the quantity of comparison metal deposited simultaneously with the metal sought is constant, the ratio of the degrees of blackening of the plate for the doublets concerned is a measure of the amount of the latter metal. The error depends on the efficiency of electrolytic deposition, and micro-photometric measurement, and is usually less than 10 per cent. The technique for the determination of gold with silver as comparison metal (or *vice-versa*) is described. Solutions containing (say) 0·05 mgrm. of silver and 1 to 50×10^{-3} mgrm. of gold are deposited from 0·1 N potassium cyanide solutions on carbon rods 2 mm. in diameter, with platinum anodes (3 volts, and 1 milliamp. per sq. cm.), the containing vessels being rotated to ensure thorough mixing. After 4 hours, spectrographs are taken with a discharge of 10,000 volts across electrodes 2 mm. apart, and the spectrograph plates divided into several sections, each of which corresponds with a doublet, *e.g.* λ (2676, 2660), (2428, 2438), (3123, 3281), etc., for gold and silver, respectively. Typical photometric curves of such plates are shown and discussed. J. G.

Reviews.

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Fifth Edition. Edited by C. AINSWORTH MITCHELL, M.A., D.Sc., F.I.C. Volume VIII. Pp. x+761. London: J. & A. Churchill. 1930. Price 30s.

The new "Allen," when complete, will apparently consist of nine volumes instead of eight, as in the previous edition. Most readers will probably agree that the arrangement of articles in this edition has been improved, but naturally in the last two volumes the more or less miscellaneous groups are bound to accumulate, and so we pass from the homogeneous volumes VI (Dyes and Colouring Matters) and VII (Alkaloids) to this rather heterogeneous volume, which deals with groups so diverse as bitter principles, enzymes, cyanogen compounds and proteins, and the editor has made the best arrangement possible of this variegated material.

The first three chapters are by Dr. Julius Grant on glucosides, bitter principles, and enzymes. Although a great deal of work has been done on all three subjects in the sixteen years that have elapsed since the previous edition was prepared, Dr. Grant has been able to fit the new material neatly into the old framework, except in the case of enzymes, where it has been necessary to expand the article from fifteen to forty-two pages, and to add much new matter.

The chapter on bitter principles has needed less revision, except as regards hops, which, in view of recent work, has been largely re-written. It would be interesting to know whether there is any real evidence of the presence of even traces of morphine in American wild hops (p. 117). It is almost fifty years since the statement was made, and nobody seems to have verified it.

The section on glucosides has been largely extended and, as in the two sections just alluded to, the revised and added matter is all of a kind to make the chapter more useful to the analyst, particularly such new matter as the biological standardisation of the heart-stimulating glucosides (p. 40), the summary of information on the estimation of prussic acid yielded by plant-products containing cyanogenetic glucosides (p. 14), and the resumé of recent work on saponins (p. 52). It is not easy to see what kind of a glucoside could be isolated by the following process (p. 10). "Sometimes it is quicker to steam-distil an aqueous extract of the bark and to precipitate the distillate with lead chloride and lead oxalate."

Though Dr. Grant is clearly aware of the useful English and American practice of calling the crystalline glucoside of *Strophanthus gratus*, ouabain, and so distinguishing it from amorphous strophanthin ex *S. Kombe*, he does not make this distinction clear in his description of strophanthin (p. 48), which is the place where it is most wanted.

Professor Barger suggests that putrefaction bases should no longer be called ptomaines, and provides, in thirteen pages, a brief but clear summary of information on these interesting substances.

The publishers have been generous, almost lavish in fact, in the space allocated to constitutional formulae in Dr. Falk's article, on "Animal Bases," and the reproductions of photomicrographs of crystals with which he has replaced some of the more diagrammatic illustrations of the previous edition are particularly good. This article, like that by Drs. Hawk and Bergeim on "Animal Acids," has clearly been revised with great care. Mr. Buchanan's article on "Cyanogen Compounds" not only admirably fulfils its primary purpose of catering for the needs of the analyst, but, incidentally, provides an interesting illustration of the immense part played by such compounds in modern civilisation, and the meticulous care with which chemists have devised means for the control of the various agricultural and industrial applications of these dangerous substances.

The last two chapters on "Proteins" and "Digestion Products of the Proteins" were started by the late Prof. Schryver and finished by his collaborator Dr. H. W. Buston. They consist of the informative and practical articles, which Dr. Schryver contributed to the previous edition, thoroughly revised and brought up-to-date, and they will undoubtedly be of great value to anyone who has to deal with analytical problems in this complex and difficult group of products.

This is a volume on which the Editor and his collaborators can be cordially congratulated.

T. A. HENRY.

COCOA AND CHOCOLATE MANUFACTURE. By H. W. BYWATERS, D.Sc., F.I.C. Pp. xii+316. London: J. & A. Churchill. Price 21s.

As the author remarks, books dealing with cocoa and chocolate are unusually scarce; they are also very incomplete. We have here, however, a work which publishes a large amount of useful information, especially as to methods and machinery. The book is the culmination of many years' observations from an important vantage point, and the laboratory evidently had a satisfactory link with manufacture. The independent setting out of cocoa powder and chocolate manufacture into two sections, complete in themselves, enables the non-expert reader to grasp the real sequence of the complex operations and their various alternatives.

To the works' chemist and analyst the most disappointing feature is the devotion of a mere 11 pages out of 307 to the laboratory tests and figures for cocoa products. These omissions make the book much less useful for reference in the chemists' library than it might have been; no doubt, many interests are involved. Considering first the laboratory applications: one hoped for a full set of figures recording the many physical and chemical values of varieties of cocoa butter, which subject has practical application. We have, however, to be content with a quotation of the values published by an allied laboratory. The general statement

as to the differences of Arriba and Accra cocoa butters would be of more interest if specifications of production were given.

Like most of us, the author seems to have overlooked the significance of the work of H. Fincke (1921) on the phosphoric anhydride variation (*i.e.* lecithin) in cocoa butter, although the fact is now made use of in manufacture. The repetition here of the high average fat content (53 to 55 per cent.) for cocoa mass, and roast nib, has not been confirmed in the writer's laboratory, where the best Soxhlet determinations have given the lower range 52–54 per cent. The rather high melting point recorded for cocoa butter (93°–96° F.) must be due to the method used—a cold-filled capillary tube.

The big subject of cocoa butter substitutes receives a very slight description. These fats are in large and permanent use, and their control requires the constant aid of the laboratory.

It is a reflection on our chemical knowledge of cocoa that only thirteen pages are here allotted to the constituents and their changes. Even so, we are glad of some authoritative details of tannin-body investigations. The reviewer, however, cannot accept the repetition of the very low tannin determinations of Adams (1·9–2 per cent.), without proof that extraction was complete.

The analyst will look in vain for those figures of ash composition of varied cocoas which are useful for identification and for determining adulteration, process, etc. Public analysts and others will note the author's decisive views as to cocoa alkalisation, which he denies is injurious in the slightest degree. Even so, it is scarcely necessary to claim that such alkaline action on protein "cannot be other than helpful to their digestion." Alkalisation is, in fact, an advantage to the consumer, and is carried out by the manufacturer at a substantial cost.

It is very notable that for shell determinations reliance is placed on crude fibre determination, the eccentricities of levigation not being accepted. It is not quite clear what is meant by the statement that only a fraction of shell present may be detected by any known "chemical" method after super-grinding.

Considering now the main theme of the book, manufacture—as might be expected, the sections on cocoa powder production—roasting, alkalising, pressing and grinding—are of great value, and even the advanced practices of uniform roasting after husk stripping, and continuous roasting, are described. Valuable basic data are given throughout. The "liquoring" of cocoa powder, with cold mixing and milk addition, for testing as a beverage, is not the only method used by experts. Although solvent fat extraction is noted, the technical use of absolutely fat-free cocoa for certain food purposes is not mentioned.

In the manufacture of chocolate the somewhat opposed aims of fineness and optimum flavour production are also discussed in all their bearings. Some of us, who are aware of the older technique of many English manufacturers, will not be cheered at the thought of competing with the advanced machine products of the

Continent and the United States. The physical condition of chocolate is throughout well treated, although some numerical values for the viscosity changes would have been appreciated.

In addition to the usual views on the effects of conching, the author makes the further suggestions that loss of bitter (?) taste, occurs with improvement in colour, as a result of full conching. The reviewer, however, cannot confirm these changes. Some chemical analyses of the possible tannin changes, presumed both by the reviewer and the author, would be useful knowledge. The writer is able to confirm Dr. Bywaters' lack of preference for cane sugar in chocolate, and is of opinion that good beet sugar answers every requirement of the palate.

The extreme abbreviation of the technology of milk chocolate is unfortunate, as it is the most important home product. Neither the stages nor the variations are given with the fullness which is essential for so sensitive a manufacture. The technical data given as to enrobing are satisfactory, so far as they go, but they overlook other practices used in the attainment of fine and stable surface. As indicated, a great deal of information may be obtained as to radical improvements in manufacture—especially by those competent to develop them. Finally, one may envy the author the concise and natural way in which he sets out his knowledge for our benefit. To the expert the book is indispensable.

H. R. JENSEN.

HANDBUCH DER KAUTSCHUK-WISSENSCHAFT. By Prof. K. MEMMLER with Coworkers. Pp. 747 and Index. Leipzig: S. Hirzel. Price: Stitched, M.57.50; bound, M.60.

This work is, perhaps, the most comprehensive which has yet appeared on the various aspects of the technology of rubber. The subject-matter is treated mainly from the theoretical standpoint. It is the work of seven experts in their own branches of the subject, and is accordingly divided into seven sections dealing, respectively, with (A) Botanical and Cultural Aspects, (B) Chemistry, (C) Vulcanisation, (D) Chemical Analysis, (E) Physics, (F) Physical or Mechanical Methods of Testing, and (G) Microscopic Examination.

Speaking broadly, the book is well up-to-date, and the subject-matter of each section is fully treated, with very few omissions. Some of the sections are excellent. Sections "A" and "B," by Prof. Zimmermann and Prof. Pummerer and Dr. Koch, respectively, strike me as being particularly good. In section "E," by Professor Hock, we have, for the first time, a succinct account of the more recent physical work on rubber from the pen of one who has himself contributed several papers in recent years on this subject. Sections "D" and "F" are those of most interest to readers of our journal. Section "D," by Prof. Kindscher, is perhaps the least satisfactory in the book. It is rather of the nature of a catalogue of methods of analysis, and it does not read as if the author were in the habit of making frequent use of the operations he describes. In this respect it is much less interesting than the previous section "C" by the same author.

In contrast to section "D," section "F," by Profs. Memmler and Schob, dealing with the mechanical tests, does read as if the authors were perfectly familiar with the details of design and working of the machines and appliances described. They have definite opinions, boldly stated, which command attention, although one may not in all cases see eye to eye with them. Thus, they describe the figure for "tensile product" as a false measure, as it takes no account of the character of the load-stretch curve. It may be at once admitted that this criticism is perfectly valid. On the other hand, the "tensile product" as an approximate figure is of considerable value, and the relative figures for similar types of rubber approach very closely those of "proof resilience," which is admittedly a more accurate representation. The latter, however, necessitates the determination of an area bounded by a curve which must be plotted, and it is easy to see that, even with autographic records, the time taken in working out the figures for the large number of determinations which are necessary in technical work would hardly be possible. This section, particularly, is worthy of careful study. The last section, by Dr. Pohle, is one of the most interesting. In spite of obvious difficulties, this method of attack may become increasingly important.

There are, as might be expected, the usual defects of treatises of this type. Some overlapping occurs which, however, could hardly be avoided, and disproportion in the space allotted to different subjects, although, naturally, different portions of a book with such a wide range will interest different persons to a widely varying extent. There are occasionally misprints, particularly with the initials of authors, but, on the whole, the work is well arranged, clearly printed, and packed full of references. The only complaint on this score is the weight of the paper, and consequently the book is too heavy to support in the hands; unbound, it tends to fall to pieces.

H. P. STEVENS.