THE ANALYST

THE JOURNAL OF THE

Society of Public Analysts and other Analytical Chemists

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT OF ANALYTICAL CHEMISTRY

Publication Committee:

W. H. ROBERTS, M.Sc., F.I.C. (President).

F. W. F. ARNAUD, F.I.C.
A. L. BACHARACH, M.A., F.I.C.
R. C. CHIRNSIDE, F.I.C.
H. E. COX, D.Sc., Ph.D., F.I.C.
BERNARD DYER, D.Sc., F.I.C.
F. W. EDWARDS, F.I.C.
G. D. ELSDON, D.Sc., F.I.C.
B. S. EVANS, M.B.E., M.C., D.Sc., F.I.C.
E. HINKS, M.B.E., B.Sc., F.I.C.
G. ROCHE LYNCH, O.B.E., M.B., B.S., D.P.H., F.I.C.
G. W. MONIER-WILLIAMS, O.B.E., M.C., Ph.D., F.I.C.
A. MORE, I.S.O., A.R.C.S., A.R.T.C., F.I.C.
J. R. NICHOLLS, B.Sc., F.I.C.
W. H. SIMMONS, B.Sc., F.I.C.
ERIC VOELCKER, A.R.C.S., F.I.C.
K. A. WILLIAMS, B.Sc., F.I.C.

Hon. Secretary:
L. EYNON, B.Sc., F.I.C.

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

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

Secretary and Assistant Editor: J. H. LANE, B.Sc., F.I.C.

Abstractors:

S. G. CLARKE, Ph.D., B.Sc., A.I.C.
E. B. DAW, B.Sc., A.I.C.
J. GRANT, Ph.D., M.Sc., F.I.C.
D. G. HEWER, B.Sc.
A. O. JONES, M.A., F.I.C.
J. W. MATTHEWS, Ph.D., F.I.C.
E. M. POPE, B.Sc.
F. A. ROBINSON, M.Sc.Tech., F.I.C.
W. R. SCHOELLER, Ph.D., F.I.C.
D. R. WOOD, F.I.C.

VOL. 64

1939

PUBLISHED FOR THE SOCIETY BY
W. HEFFER & SONS LTD.
4, PETTY CURY, CAMBRIDGE, ENGLAND
1939

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, December 7th, 1938, the President, Professor W. H. Roberts, in the chair.

Certificates were read in favour of G. Carter, B.Sc., A.I.C.; O. B. Darbishire, B.Sc., A.R.C.S., D.I.C., A.I.C.; F. M. Dyke, B.Sc., F.I.C.; A. A. Eldridge, B.Sc., F.I.C.; Prof. F. Feigl, Dr. Ing.; G. H. Fraser; M. B. Ichaporia, M.Sc., Ph.D., A.I.C.; R. Porter; A. C. Ratcliff, B.Sc.; W. H. Templeton, B.Sc., F.I.C.

The following were elected members of the Society:—W. A. Alexander, B.Sc., A.I.C.; D. R. A. Davies, B.Sc.; E. R. Jones, B.Sc., Ph.D., F.I.C., M.D., Ch.B., D.P.H.; H. A. Jones, A.I.C.; Dr. B. A. Macola; J. M. Malcolm, A.I.C.; Mrs. S. M. L. Tritton, M.P.S., F.I.C.; S. A. Ullah, B.Sc., Ph.D., A.I.C.

The following papers were presented and discussed:—"The Selective Oxidation of Animal and Vegetable Fats: A New Constant," by W. A. Alexander, B.Sc., A.I.C.; "The Determination of the Essential Oils of White and Brown Mustards," by R. C. Terry, M.Sc., A.I.C., and J. W. Corran, Ph.D., F.I.C.; "The Electrolytic Determination of Bismuth," by F. G. Kny-Jones, M.Sc.

NORTH OF ENGLAND SECTION

A meeting of the Section was held in Manchester on October 22nd, 1938. The Chairman (Prof. T. P. Hilditch) presided over an attendance of thirty-seven, which included the President (Professor W. H. Roberts), who introduced a discussion on the Food and Drugs Act, 1938, in which many members took part.

The following communications were made and discussed:—"A Note on Nigerian Ginger," by P. H. Jones, F.I.C., and a paper on the "Quantitative Determination of Mercury in its Compounds with Special Reference to the Assay of Solution of Mercuric and Arsenious Iodide," by H. Brindle, B.Sc., F.I.C., Ph.D., and C. E. Waterhouse, A.I.C., Ph.D.

A Meeting of the Section was held in Manchester on December 10th, 1938. The Chairman (Prof. T. P. Hilditch) presided over an attendance of thirty-nine.

The following papers were read and discussed:—"The Estimation of Vitamins and Hormones," by R. A. Morton, Ph.D., D.Sc., F.I.C.; "A Note on the Behaviour

of Rice Bran," by C. Louden, B.Sc., F.I.C., and F. L. Kinsella; "A Convenient Method of Estimating the Hydrocyanic Acid generated by Linseed Cake," by C. Louden, B.Sc., F.I.C., and H. Antrobus.

Resolutions were passed congratulating Mr. U. A. Coates on the occasion of the diamond jubilee of his wedding day, and Mr. H. Humphreys Jones on his appointment as a Justice of the Peace.

SCOTTISH SECTION

AN Ordinary Meeting of the Section was held in the Central Station Hotel, Glasgow, on November 18th, 1938. The meeting was of an informal nature and the following subjects were discussed:—"American Food and Drugs Act," introduced by R. G. Thin; "Copper Content of Tomato Purée," introduced by A. Dargie; "Memorandum on the Food and Drugs Act, 1938," introduced by M. J. Robb; "Determination of Alumina in Water," introduced by R. T. Thomson; "Determination of Lactose and Sucrose in Milk Chocolate," introduced by H. C. Moir; "Air Raid Precautions," introduced by J. W. Hawley.

A new Colour Reagent for Lead and its Use as an Indicator in the Titration of various Cations and Anions*

(Pb, Zn, WO_3, MoO_3, V_2O_5, P_2O_5, As_2O_5)

BY B. S. EVANS, M.C., M.B.E., D.SC., F.I.C.

(Read at the Meeting, October 5, 1938)

COLOUR reactions for lead, due to the formation of soluble compounds with the range of stability necessary for indicator purposes, are rare.[11] The well-known colour formed with diphenyl thiocarbazone[1,9] is intense and easily produced, but it is so stable as to preclude its use as an indicator. Carbazones give relatively intense colours with many metals, including lead, copper,[9] iron, nickel, cobalt, zinc, mercury,[10,2,3] thallium[4] and others, but here again the lead colour is so stable that it is not readily destroyed by most precipitants. It was observed that if an acetone solution of diphenyl carbazide is added to a solution of lead nitrate containing pyridine nitrate a very pale pink colour is produced; if the solution is allowed to stand the colour slowly deepens, becoming eventually (after about 20 hours) a dark red, proportional in depth to the amount of lead present. After a considerable amount of work a reagent was evolved which immediately developed the full colour.

REAGENT.—The reagent used in the work done for this paper was prepared as follows:

Solutions required.—(*a*) A 1·5 per cent. solution of diphenylcarbazide in alcohol (this solution seems to keep its properties indefinitely, although it darkens and

* Communication from the Research Department, Woolwich.

the carbazide is probably converted into carbazone); (*b*) purified pyridine (*vide infra*); (*c*) dilute nitric acid (sp.gr. 1·2).

A mixture of 10 ml. of (*a*) with 30 ml. of (*b*) was diluted with 120 ml. of cold water, 2 ml. (carefully measured) of (*c*) were added, and the liquid was heated to boiling and allowed to stand on the bench overnight, after which it was ready for use. It has subsequently been found that the heating is entirely unnecessary, and it has consequently been discontinued; the reagent is now prepared as follows:

Preparation.—A mixture of (*b*), (*c*) and water in the correct proportions is made up in bulk, and to the required volume of this mixture an amount of (*a*) is added to produce the strength indicated above. The liquid is allowed to stand overnight and is then ready for use. With a fairly new (*a*) solution the colour directly after mixing will probably be very pale; if a test is made with it on a lead nitrate solution the colour produced is almost imperceptible at first, but gradually deepens to the full shade if allowed to stand for some hours. After the reagent has stood for its appointed time its colour is a fairly deep orange-brown, and on being mixed with lead nitrate solution it should develop its full colour (a cherry-red with 1·0 mg. of lead nitrate in 100 ml. of water) immediately. The reagent keeps fairly well for several days, but it slowly deteriorates and eventually ceases to give any red colour whatever with lead. Since the completion of the work for this paper, however, I have found that an alcoholic solution of diphenyl carbazide which has been made up for several weeks (in one instance five) produces a reagent which can be used without any standing (presumably because the carbazide has been oxidised to carbazone). If only fresh carbazide solution is available the lead and zinc colours can be developed by the cautious addition, drop by drop, of bromine water to the liquid after the addition of the reagent (for lead, until the full colour is produced ; for zinc, 5 drops). A satisfactory reagent seems also to be produced by warming 2 ml. of the carbazide solution with 1 drop of hydrogen peroxide (20 vols; stabilised with sulphuric, *not* with phosphoric acid) until the brown colour ceases to deepen, and then mixing with 30 ml. of the pyridine-nitric acid-water mixture. These oxidising agents, however, are very liable to destroy the properties of the reagent altogether if used in slight excess, and on the whole it is better to prepare the reagent by the method given above.

THE TEST.—If a small amount of lead nitrate solution is neutralised and diluted to about 100 ml., and 10 ml. of the reagent are added, the red colour developed is proportional to the amount of lead present; with 0·002 g. of lead nitrate the colour should be a fairly dark cherry-red; a blank test done in the same way, but without lead, gives a pale orange-brown due to the colour of the reagent. The colour difference is made more apparent by adding acetone, which seems to eliminate the reddish factor from the reagent colour without disturbing that due to the lead; the colours are now a permanganate tint and a very pale yellow, respectively. If, to the solution containing the developed lead colour, successive additions of very dilute nitric acid are made, it first turns paler and then at a certain point is entirely bleached; if, instead of nitric acid, dilute ammonia is added, the colour first darkens and then at a certain point is replaced by the orange-brown shade characteristic of alkaline solutions of diphenylcarbazide. There is thus a *p*H range over which the colour is effective and a fairly limited one

at which it is at an optimum; this is the reason why the 2 ml. of nitric acid added to the reagent must be carefully measured and why the lead solution has to be neutralised before making the test. The colour seems to be destroyed by anything liable to precipitate lead under the *p*H conditions prevailing; thus phosphates, arsenates, tungstates, vanadates, molybdates and citrates destroy it promptly, and sulphate in any appreciable amount weakens it. It is this fact that makes the colour reaction interesting, because so many other metals give a similar colour (*vide infra*) that it is not of much use as a test for lead; but if the colour can be progressively removed by addition of small amounts of any of the reagents mentioned above (*i.e.* by titration), it can obviously be made the basis of a volumetric process for minute amounts of lead; on the other hand, it should equally be possible to use it as an indicator in the titration of these reagents with lead nitrate solution. The following method has been worked out for the volumetric determination of lead:

VOLUMETRIC PROCESS FOR LEAD.—The solution of lead as nitrate, neutralised (to litmus paper) with ammonia, is placed in a flask and diluted to 100 ml.; 100 ml. of distilled water are placed in a similar flask; 10 ml. of reagent are added to each, followed by 30 ml. of acetone. The titrating liquid is prepared in the following manner:—Ten ml. of syrupy phosphoric acid are made up to 100 ml. (A); 20 ml. of (A) are made up to 250 ml. (B); 10 ml. of (B) are diluted, boiled, cooled and made up to 1000 ml. (C).

The lead colour is titrated away with solution (C) until the colours of the supernatant liquids in the two flasks match. The colour at first diminishes rapidly, but towards the end-point the change becomes slower; there is no difficulty with the titration up to within about 0·4 ml. of the end-point; from then onwards the colour change is very slight and gradual; the presence of the slightly brownish precipitate of lead phosphate somewhat complicates the matching, and when matching becomes difficult it is desirable to allow the liquid to stand for a minute or two after each addition. The end-point, however, can be determined with reasonable speed and certainty. The titration can be performed as accurately in the absence of acetone, but it then becomes much slower as, towards the end, the precipitate has to be left to settle for a considerable time after each addition; an additional function of the acetone is to prevent adsorption of the colour on the precipitate, making the latter a mauve colour and so masking the end-point. The phosphoric acid standard must be standardised against lead nitrate. The method was tested, with the following results:

(*a*) *With Acetone.*

Lead nitrate taken g.	Titration ml.	Lead nitrate found g.
0·0090	16·10	0·00907
0·0080	14·40	0·00812
0·0070	12·30	0·00694
0·0060	10·70	0·00603
0·0050	8·85	0·00499
0·0040	7·00	0·00395
0·0030	5·20	0·00293
0·0020	3·65	0·00206
0·0010	1·75	0·00099
0·0100	17·75	0·01002

The first nine of these results were calculated from the factor (1·0 ml. ≡ 0·0005645 g. of $Pb[NO_3]_2$) obtained by the tenth titration; the tenth result was calculated from the mean of the factors obtained from the other nine (1·0 ml. ≡ 0·0005640 g. of $Pb[NO_3]_2$).

(*b*) *Without Acetone.*

Lead nitrate taken g.	Titration ml.	Lead nitrate found g.
0·0100	9·15	0·01006
0·0090	8·10	0·00891
0·0080	7·30	0·00802
0·0070	6·35	0·00698
0·0060	5·45	0·00600
0·0050	4·55	0·00500
0·0040	3·65	0·00401
0·0030	2·70	0·00297
0·0020	1·80	0·00198
0·0010	0·95	0·00104

For these determinations a stronger phosphoric acid solution was used whose factor was 1·0 ml. ≡ 0·00110 g. of $Pb(NO_3)_2$.

The precipitate formed in the course of titration appears to have the composition $PbO(Pb_3[PO_4]_2)_2$.

Titration with Ammonium Vanadate.—Lead can be titrated in the same manner with ammonium vanadate. The following results were obtained by the use of a solution containing 0·0184 g. of $NH_4VO_32H_2O$ in 1000 ml. (1·0 ml. ≡ 0·00008 g. of V).

Lead nitrate taken g.	Titration ml.	Lead nitrate found g.
0·0100	13·80	0·00998
0·0090	12·45	0·00900
0·0080	11·05	0·00799
0·0070	9·70	0·00701
0·0060	8·32	0·00601
0·0050	7·00	0·00506
0·0040	5·55	0·00401
0·0030	4·20	0·00304
0·0020	2·80	0·00202
0·0010	1·37	0·00099

The factor (1 ml. ≡ 0·000723 g. of $Pb[NO_3]_2$) was calculated from the mean of the first four results. The titration is somewhat sharper than with phosphate, but the composition of the precipitate does not appear to correspond with any simple relationship of Pb:V. Probably a mixture of meta- and ortho-vanadate is formed (*cf.* Calliere and Guiter's work).[15]

Determination of Acid Radicles.—Many acid radicles are precipitated by lead salts at or near the neutrality point. The difficulty in using these reactions volumetrically, apart from the lack of an internal indicator, is the tendency of lead to form basic salts, thus rendering the composition of the precipitate uncertain. The reagent proposed, besides being a good internal indicator, provides a very efficient buffer, thus keeping the *p*H value within narrow limits; consequently

several volumetric processes of very fair accuracy have been evolved. The acids dealt with are the following:—molybdic, tungstic, vanadic, phosphoric and arsenic.

None of these acids, with the exception of vanadic, gives any marked colour with the reagent (molybdic acid gives a pale orange); consequently, if a solution of lead nitrate is run into a solution of one of their salts containing the reagent, no marked colour change takes place until the lead is in excess, when the liquid begins to turn red. The end-point is very similar to that of a titration with alkali, using phenolphthalein as indicator.

Molybdates.—The solution is neutralised with ammonia or nitric acid, as the case may be (it is desirable that it should be on the alkaline rather than the acid side), and diluted to 100 ml.; 10 ml. of the reagent and 30 ml. of *alcohol* are added. The mixture is titrated with lead nitrate solution (1 g. of $Pb[NO_3]_2$ made up to 1000 ml.) to the appearance of the first permanent pink flush. The lead solution should be standardised in the same way against ammonium molybdate. Tested in this manner on a solution of ammonium molybdate the method gave the following figures:

Molybdenum taken g.	Titration ml.	Titration (calc. from the 0·004 Mo. figure) ml.
0·0100	36·00	36·10
0·0050	18·05	18·06
0·0040	14·45	—
0·0030	10·80	10·84
0·0020	7·25	7·23

The titration results therefore are strictly proportional within the limits of experimental error; they are not quite comparable with those next to be cited, as an old lead nitrate solution, probably slightly concentrated, was used.

The process was tried on a sample of MoO_3 obtained in the course of a molybdenum determination. The sample, which weighed 0·0527 g. (this included the weight of the filter-ash) was dissolved in sodium hydroxide and made up to 250 ml.; portions were neutralised separately with nitric acid and titrated as described above.

	Volume taken ml.	Titration ml.	≡	MoO_3 g.	Calculated total weight of MoO_3 g.
(*a*)	25·0	12·30		0·00519	0·0519
(*b*)	25·0	12·30		0·00519	0·0519
(*c*)	50·0	24·70		0·01042	0·0521
(*d*)	20·0	9·80		0·00414	0·0518
*(*e*)	10·0	5·00		0·00211	0·0527
(*f*)	10·0	4·90		0·00207	0·0518
(*g*)	10·0	4·95		0·00209	0·0522
(*h*)	10·0	4·95		0·00209	0·0522
†(*i*)	10·0	4·95		0·00209	0·0522

* Neutralisation rather too much on acid side.
† Faintly alkaline.

It will be noted that, leaving out of consideration (*e*), the neutralisation of which was at fault, the results group themselves closely round their mean 0·0520; the excess, 0·0007 g., is presumed to be the weight of the filter ash contained in the sample.

Details of the standardisation are as follows:

Molybdenum taken g.	Titration ml.	Titration (calc. to 0·010 g. of Mo) ml.	Mean ml.
0·0050	17·8	35·6	
0·0040	14·2	35·5	35·575
0·0030	10·7	35·7	
0·0020	7·1	35·5	

Hence 1·0 ml. ≡ 0·0004218 g. of MoO_3.

From the foregoing figures it appears that the reaction is not quite stoichiometric for the formula $PbMoO_4$

1 atom of Pb ≡ 1·03 instead of 1·00 atom of Mo.

Phosphates.—The following titrations were carried out on the phosphoric acid solution used for titrating lead (*vide supra*). In view of the very faint acidity of the solution, no neutralisation was attempted. The titration was performed in exactly the same manner as for molybdates, except that 30 ml. of acetone were used instead of 30 ml. of alcohol.

H_3PO_4 solution taken ml.	Titration, $Pb(NO_3)_2$ ml.	P_2O_5 found calc. from formula $PbO(Pb_3[PO_4]_2)_3$ g.	P_2O_5 present, calc. from NaOH filtration g.
10·0	6·9	0·000888	0·000898
5·0	3·5	0·000450	0·000449
4·0	2·8	0·000360	0·000359
3·0	2·2	0·000283	0·000274
2·0	1·5	0·000193	0·000180
1·0	0·7	0·000090	0·000090

It will be noted that the compound formed when lead nitrate is run into excess of phosphoric acid appears to be $PbO(Pb_3[PO_4]_2)_3$ instead of the $PbO(Pb_3[PO_4]_2)_2$ formed when the phosphoric acid is run into excess of lead.

Arsenates.—The following titrations were carried out exactly as for phosphates; the solutions titrated were very slightly on the alkaline side of neutrality.

As^{V} taken g.	Titration ml.	Calc. factor 0·001 As^{V} ≡ $Pb(NO_3)_2$ g.	As^{V} found, calc. from mean factor g.
0·00100	7·5	0·0075	0·001000
0·00080	6·0	0·0075	0·000800
0·00060	4·5	0·0073	0·000600
0·00050	3·8	0·0076	0·000506
0·00040	3·0	0·0075	0·000400
0·00030	2·3	0·0077	0·000308
0·00020	1·5	0·0075	0·000200
0·00010	0·75	0·0075	0·000100
	Mean	0·0075	

The atomic ratio As^{V}:Pb, calculated from the mean factor, is 1:1·70, which lies about half-way between the two ratios given for phosphates (4:7 and 6:10 *vide supra*). Arsenites do not appear to influence the titration.

Vanadates.—The acids so far dealt with give little or no colour with the reagent; with vanadium this is not so. $Vanadium^{V}$ gives a colour almost identical with that of lead, V^{iv} gives a very intense violet; in a titration with lead V^{iv} does not come into consideration, but it will obviously be necessary to ensure that all vanadium is in the highest stage of oxidation. If a neutral solution of a vanadate to which the reagent has been added is titrated with lead nitrate solution the cherry-red colour of the V^{V} fades as lead vanadate is precipitated till only the colour of the reagent itself is left; an excess of lead then causes the lead colour to appear. The titration is therefore very easy to perform; it is carried out in exactly the same way as that for phosphates (*i.e.* neutral solution, volume 100 ml., 10 ml. of reagent and 30 ml. of acetone).

A series of titrations carried out on ammonium vanadate gave the following results:

			Vanadium^{V} found	
Vanadium^{V} taken g.	Titration ml.	Factor calc. from result 0·001 V ≡ ml. $Pb(NO_3)_2$	Calc. from mean of factors 0·0008 – 0·00056	Calc. from formula $3PbO[Pb(VO_3)_2]_2$
0·00160	12·40	7·75	0·001544	0·001527
0·00120	9·40	7·84	0·001171	0·001158
{0·00080	6·40	8·00}	0·000797	0·000788
{0·00072	5·80	8·05}	0·000722	0·000714
{0·00064	5·15	8·05}	0·000641	0·000634
{0·00056	4·50	8·04}	0·000560	0·000554
0·00048	3·90	8·12	0·000485	0·000480
0·00040	3·20	8·00	0·000398	0·000394
0·00032	2·60	8·12	0·000324	0·000320
0·00024	1·95	8·12	0·000243	0·000240
0·00016	1·25	7·81	0·000156	0·000154
0·00008	0·65	8·12	0·000081	0·000080

It will be noted that results above 0·001 g. tend to be low, although those below that amount show very good agreement; for this reason the method is not recommended for amounts of vanadium in excess of 0·001 g. Hence the factor from which the results in column 4 were calculated was the mean of the first four within the accepted range (those enclosed in brackets); this factor is 1·0 ml. ≡ 0·0001245 g. of V; from this the atomic ratio of V: Pb in the precipitate can be deduced, giving 1:1·236, roughly corresponding to $3(PbO)(Pb[VO_3]_2)_2$, which requires an atomic ratio of 1:1·25 and gives a factor of 1 ml. ≡ 0·0001232, or possibly a mixture of meta- and ortho-vanadate is formed (*vide supra*). A paper has recently been published (ANALYST, 1938, **63**, 870) in which is described a volumetric method for determining amounts of vanadium from 0·01 to 0·001 g., covering the interval between this method and the ordinary permanganate process. The whole range of amounts of vanadium down to below 0·08 mg. can therefore

now be determined volumetrically. When it is remembered that 0·2 mg. of vanadium gives only a very faint, and 0·1 mg. an almost imperceptible, colour with hydrogen peroxide in the ordinary colorimetric process[5] the significance of the process just described becomes apparent.

Tungstates.—The last member of the series of acids under consideration is exceedingly difficult to determine in small amounts. We are not here concerned with its separation from other elements (*cf.* Schoeller,[6] Yagoda and Fales,[7] Halberstadt[8]); the present research was undertaken primarily to provide the necessary step of an accurate means of determining the small amount when separated. Lead tungstate is precipitated very completely from neutral solution, but it readily dissolves in either acid or alkali; from pyridine-buffered solution, however, precipitation appears to be as complete as one could wish. It seemed obvious that, if the constitution of the precipitated lead tungstate could be regulated, the method of titration already described for phosphates, etc., should be available also for tungstates. The first experiments were made by adding a known excess of lead nitrate to the buffered solution and titrating the excess of lead away with phosphoric acid, as described already. The results obtained were only approximate and tended to be high (*i.e.* they were not very consistent among themselves and an excess of lead over that required by the formula $PbWO_4$ was used up). Apparently, basic compounds (or adsorption complexes) were being precipitated and these, as might be expected with tungsten, were of uncertain composition; it was felt that with this particular element an attempt must be made to produce a precipitate of the theoretical composition, $PbWO_4$. After many experiments it was found that the addition of boric acid seemed to prevent the adsorption of lead (basic compounds did not appear to be formed); in fact, too much boric acid swung the results over slightly in the opposite direction. The following figures illustrate this effect:

Tungsten taken g.	Boric acid added, saturated solution ml.	Titration, standard $Pb(NO_3)_2$ ml.	Tungsten found, calc. from formula $PbWO_4$ g.
0·003	nil	20·00−13·95=6·05	0·00336
0·003	10	10·00− 4·82=5·18	0·00288
0·003	10	11·00− 5·80=5·20	0·00289
0·003	5	10·00− 4·82=5·18	0·00288
0·003	2	10·00− 4·65=5·35	0·00297

A series of titrations was accordingly made in which 2 ml. of saturated boric acid solution were added to the neutralised tungstate solution diluted to such a volume that, with the lead nitrate solution to be added, the volume would be about 100 ml., the excess of standard lead nitrate was next run in, followed by 10 ml. of the reagent and 30 ml. of acetone; the excess of lead was then titrated with standard phosphoric acid exactly as described at the beginning of this paper. The following figures were obtained:

Tungsten taken g.	Titration, H_3PO_4 ml.	$Pb(NO_3)_2$ solution added ml.		$Pb(NO_3)_2$ solution equiv. to H_3PO_4 ml.		$Pb(NO_3)_2$ solution required for WO_3 ml.	Tungsten found, calc. from $PbWO_4$ formula g.
0·0100	2·40	20·00	—	2·12	=	17·88	0·00994
0·0090	4·15	20·00	—	3·67	=	16·33	0·00907
0·0080	1·00	15·00	—	0·88	=	14·12	0·00785
0·0070	2·80	15·00	—	2·48	=	12·52	0·00696
0·0060	4·70	15·00	—	4·16	=	10·84	0·00602
0·0050	6·60	15·00	—	5·85	=	9·15	0·00508
0·0040	3·15	10·00	—	2·79	=	7·21	0·00401
0·0030	5·25	10·00	—	4·65	=	5·35	0·00297
0·0020	1·45	5·00	—	1·28	=	3·72	0·00207
0·0010	3·65	5·00	—	3·23	=	1·77	0·00098

Standardisation: 1 ml. of H_3PO_4 solution ≡ 0·885 ml. of $Pb(NO_3)_2$ solution.

Repeated attempts to filter out the lead tungstate before titration invariably gave high results. It would seem that lead is withdrawn as a loose adsorption complex which is broken down during the titration.

Some titrations were also carried out on amounts of tungsten unknown to the operator. The results were as follows:

Tungsten given g.	Titration, H_3PO_4 ml.	$Pb(NO_3)_2$ solution added ml.		$Pb(NO_3)_2$ solution equiv. to H_3PO_4 ml.		$Pb(NO_3)_2$ solution required for WO_3 ml.	Tungsten found, calc. from PbWO formula g.
0·00370	15·05	20·00	—	13·32	=	6·68	0·00371
0·00610	10·50	20·00	—	9·12	=	10·88	0·00604
0·00550	11·40	20·00	—	10·09	=	9·91	0·00551
0·00085	21·10	20·00	—	18·67	=	1·33	0·00074
0·00122	20·20	20·00	—	17·90	=	2·10	0·00117
0·00188	19·00	20·00	—	16·80	=	3·20	0·00178

Standardisation: 1 ml. of H_3PO_4 solution ≡ 0·85 ml. of $Pb(NO_3)_2$ solution.

The foregoing work was carried out before the direct titration process for phosphates, etc., was discovered (*vide supra*); it seemed worth while therefore to ascertain if this process was also available for tungstates. The titration was performed in the manner described for vanadium, but 40 ml. of acetone, instead of 30, were added; as the end-point was rather difficult to observe 1 ml. of the lead nitrate standard was added to a blank and the tungsten solution was titrated

until the colours matched, 1 ml. being deducted from the result. The following results were obtained:

Tungsten taken g.	Titration ($Pb[NO_3]_2$) solution ml.	Tungsten found, calc. from $PbWO_4$ formula g.
0·0100	18·9−1·0=17·9	0·00995
0·0050	10·0−1·0= 9·0	0·00500
0·0040	8·3−1·0= 7·3	0·00405
0·0030	6·4−1·0= 5·4	0·00300
0·0020	4·6−1·0= 3·6	0·00200
0·0010	2·9−1·0= 1·9	0·00106
Unknown to operator		
0·0041	8·0−1·0= 7·0	0·0039

Owing to the production of a slight mauve tint, due presumably to adsorption of the lead colour on the precipitate, it is as well to allow the vessel to stand for a few minutes before the final matching.

Somewhat contrary to expectation, therefore, tungstic acid alone amongst the acids dealt with appears to throw down the normal lead salt. The addition of acetone is more important in titrations of tungstates than of the other acids, as without it the lead colour is adsorbed on the lead tungstate, making the end-point very difficult to observe.

Other Volumetric Methods for Tungsten.—A paper published in 1936[11] contains an account of various diamine scarlets used as indicators for lead in a lead-tungstate titration somewhat similar to that given here. The dyes act as adsorption indicators, and the results given are excellent, but the quantities dealt with are not as small nor as varied as those which form the subject of this paper; also, titration has to be carried out at the boiling-point. Another published volumetric method for tungsten appears to rely on some form of acidimetry.[12]

Dotreppe's reduction method[13] has been severely criticised by Holt.[14]

Neutralisation.—In view of the fact that carbonates seem to act in the same way as phosphates, etc., in destroying the lead colour which is the subject of this paper, it is necessary to bear in mind their possible introduction during neutralisation. For this reason it is best to boil the solution, neutralised with sodium hydroxide, and then make faintly acid with nitric acid, and, after cooling, to bring it back to neutrality or faint alkalinity by cautious addition of dilute ammonia (*not* sodium hydroxide solution). The exact *p*H value does not matter very much except where tungstates are being titrated, as then the colour is being matched and the intensity of the colour is extremely sensitive to *p*H value. In this instance it is best to add 10 ml. of 20 per cent. ammonium nitrate solution to both the sample and the blank (the latter must not be omitted because ammonium nitrate distinctly lightens the colour) before adding the reagent. The titration of tungstates is being investigated further.

Other Acids.—The titration should theoretically work with chromates, but when this was tried a dark brown colour developed during the titration and

entirely obscured the end-point. Many organic acids (*e.g.* citric) are precipitated by lead in neutral solution, and the titration should undoubtedly be available for them. In all the work hitherto described the strength of the titrating solution was 1·00 g. of lead nitrate per 1000 ml. It is desirable always to standardise it against the particular ion to be titrated and to use the same batch of reagent.

BEHAVIOUR OF THE REAGENT WITH DIFFERENT IONS.—The reagent gives colours with a number of ions; its behaviour is summarised in the following table:

ION	REACTION	ION	REACTION
Cu^{II}	Red colour immediately fading and replaced by the pyridine blue colour.	Mn^{II}	Slight reddish brown (impurity ?).
		V^{V}	Red colour.
Cr^{VI}	No effect.	V^{IV}	Intense violet colour.
Cr^{III}	No effect.	W^{VI}	No effect.
Fe^{III}	$Fe(OH)_3$ precipitated; no colour.	Ti^{IV}	No effect.
Fe^{II}	Red colour.	Mo^{VI}	Pale orange brown.
Hg^{II}	Intense violet colour.	U^{VI}	Slight yellow colour.
Hg^{I}	Intense violet colour.	Sn^{II}	Red colour.
Zn^{II}	Purple red colour tending to precipitate.	Sn^{IV}	No effect.
Co^{II}	Purple red colour tending to precipitate.	Tl^{I}	No effect.
Ni^{II}	Purple red colour tending to precipitate.	Ag^{I}	Slight brownish-red.
Pb^{II}	Red colour.	Bi^{III}	Slight red colour (probably impurity).
Cd^{II}	Red colour.		

Cl' SO_4'' NO_3' PO_4''' AsO_4''' AsO_3''' SO_3'' No action.

The red colour of vanadium^{v} is not interfered with by titanium^{iv}, which gives no colour itself. Citrates and tartrates appear to destroy the colour not only of the lead complex but of that of vanadium^{v} and vanadium^{iv} as well. Many of the coloured compounds, notably those of zinc, nickel and cobalt, are extractable with chloroform; that of lead seems to be partially and with difficulty extracted but slowly destroyed, the reagent passing into the chloroform. The action of copper (*vide supra*) appears to destroy the reagent, as the solution no longer gives a red colour with lead; copper must therefore be eliminated. Some of the colours are probably merely those given with carbazones.

It seemed worth while to attempt titrating away the colours of some of these cations in much the same way as was done for lead. Zinc and nickel were tried, but only with zinc was success achieved; the nickel complex seems to be too stable for its ready titration.

ZINC.—To obtain a satisfactory colour with this metal a rather higher *p*H is needed than for lead; consequently, if one attempts to form it in the same manner as with lead the appearance of the colour is somewhat uncertain. Chloroform appears to catalyse the formation of the coloured compound, which dissolves in it; this has the additional advantage of concentrating the colour and making the titration sharper.

The following process was tried:—The neutralised zinc solution was diluted to 100 ml., 30 ml. of acetone were added, followed by 5 ml. of the reagent, and lastly 5 ml. of chloroform; it was shaken and then titrated with $M/1000$ potassium

ferrocyanide solution with vigorous shaking after each addition until the chloroform showed only the colour of the reagent. Results thus obtained were:

Zinc taken g.	Titration ($M/1000$ $K_4Fe[CN]_6$) ml.	Zinc found, calc. from the 0·001 Zn titration figure g.
0·0010	8·30	0·000997 (calc. from mean factor of the other results)
0·0005	4·10	0·000494
0·0004	3·35	0·000403
0·0003	2·50	0·000301
0·0002	1·70	0·000205
0·0001	0·85	0·000102

If the titration figures are calculated on the ordinary basis, on the assumption that $K_2Zn_3(Fe[CN]_6)_2$ is precipitated, the results are about 20 per cent. too low. The ratio Zn : $K_4Fe(CN)_6$ is approximately 2 atoms of Zn : 1 molecule of $K_4Fe(CN)_6$. Subsequent determinations have shown that if, in the neutralisation, an excess of pyridine is added to the faintly acid solution, the exact ratio is obtained and therefore the theoretical factor (1 ml. of $M/1000$ $K_4Fe(CN)_6 \equiv 0{\cdot}0001308$ Zn) for $Zn_2Fe(CN)_6$ can be used. The only modification required in the process described above is that neutralisation should be carried slightly to the acid side of neutrality, and 1 ml. of 20 per cent. pyridine should then be added.

It has since been found that minute traces of nickel are exceedingly liable to be introduced in the course of an analysis and that these entirely upset the titration by producing a pink colour which cannot be titrated away. This can be counteracted by adding 2 drops of 10 per cent. potassium cyanide solution immediately after the pyridine and allowing to stand for 2 or 3 minutes before adding the reagent. The titration should then be completed without delay, as the nickel colour tends to recur. The blank liquid is treated in the same manner.

PYRIDINE.—The question of the supply of pyridine for these experiments was one of some difficulty. Commercial pyridine is exceedingly impure and the reagent prepared from it gave no colour at all, but a white precipitate, with lead; other supplies of alleged "pure" pyridine gave a reagent which produced a lead colour that almost immediately faded. AnalaR grades of pyridine were not tried. Satisfactory samples were supplied by both Messrs. Hopkin & Williams and British Drug Houses, and doubtless the requirements could easily be met by any manufacturer who knew them. The interfering substances would seem to be ammonia or homologues or derivatives of pyridine; water apparently has no effect whatever. It was found that if commercial pyridine is distilled from lead nitrate and the distillate subsequently boiled for 10 minutes in an open vessel the product can be used to prepare a very fair reagent; it however does not keep nearly as long, and on the whole is not so satisfactory, as that made from Messrs. Hopkin & Williams' or the B.D.H. product. The use of other organic

bases (*e.g.* cinchonine and aniline) is being investigated with fairly promising results up to the present.

REFERENCES

1. N. L. Allport and G. H. Skrimshire, ANALYST, 1932, **57**, 440.
2. C. Miller, *Chemist Analyst*, 1930, **25**, No. 1.
3. P. Krumholz and F. Hönel, *Microchimica Acta*, 1937, **2**, 177.
4. B. S. Evans, unpublished work.
5. B. S. Evans and S. G. Clarke, ANALYST, 1928, **53**, 480.
6. W. R. Schoeller, *Analytical Chemistry of Tantalum and Niobium*, Chapman & Hall, 1937, p. 80.
7. H. Yagoda and H. A. Fales, *J. Amer. Chem. Soc.*, 1936, **58**, 1495; 1938, **60**, 640.
8. S. Halberstadt, *Compt. rend.*, 1937, **205**, 987.
9. H. Fischer, *Mikrochem.*, 1930, **8**, 319.
10. E. S. Vassermann and I. Suprunovitch, *J. Chim. Ukraine*, 1934, **9**, 330.
11. Z. Raichinstein and N. Korobow, *Z. anal. Chem.*, 1936, **104**, 192.
12. A. del Campo and F. Sierra, *Anal. Fis. Quim.*, 1933, **31**, 356.
13. G. Dotreppe, *Chim. et Ind.*, Special Number 173 (March, 1931).
14. M. L. Holt, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 476.
15. E. Carrière and H. Guiter, *Compt. rend.*, 1937, **204**, 1339.

RESEARCH DEPARTMENT
WOOLWICH

September, 1938

Quinaldinic Acid as a Reagent for Copper, Zinc and Cadmium

BY R. J. SHENNAN, M.Sc., A.I.C.

QUINALDINIC acid has been proposed as an analytical reagent for the quantitative determination of a number of metals,[1,2,3,4,5] and has been recommended as being suitable for the separation of copper from cadmium.[1,4]. The following investigation was undertaken to establish the *p*H range over which complete precipitation could be effected for the metals copper, zinc and cadmium, and so to define more precisely the conditions for determination.

DETERMINATION OF COPPER.—Copper sulphate, AnalaR (15 g.) was dissolved in water and the solution was diluted to 2500 ml. The copper-content of this solution was determined by the sodium anthranilate[6] method (found: copper, 0·03842 g. per 25 ml.).

To 25 ml. of the standard copper solution were added 25 ml. of sodium acetate solution (5 g.), a measured quantity of glacial acetic acid, and water to make up 150 ml. The solution was boiled and 20 ml. of reagent solution (5 g. of sodium quinaldinate in 250 ml. of water) were added slowly. After 45 minutes the precipitate was collected on a No. 4 sintered glass crucible, and the filtrate was reserved for subsequent *p*H determination by means of a hydrogen electrode. The precipitate was washed well with water, dried at 125° C. and weighed. The results are given in Table I.

Complete precipitation was obtained over the *p*H range 2·5 to 6·96. Attempts to extend the range above *p*H 7 resulted in the precipitation of copper hydroxide. In the absence of sodium acetate it was found possible to attain *p*H values below 2 and to extend the range of copper precipitation to *p*H 1·5.

TABLE I

Copper taken in each Experiment = 38·42 mg.

Acetic acid ml.	*p*H	Wt. of ppt. mg.	Copper found mg.
125*	0·69	nil	nil
100*	0·93	131·5	19·66
40*	1·43	251·7	37·54
35*	2·20	257·0	38·43
100	2·05	124·4	18·61
75	2·34	210·8	31·52
50	2·60	255·7	38·23
5	3·59	257·2	38·46
0·05	5·69	256·8	38·41
nil	6·96	256·8	38·41

* No sodium acetate buffer used in these experiments.

DETERMINATION OF CADMIUM.—Cadmium sulphate, AnalaR (9·6 g.), was dissolved in water and the solution was diluted to 2 litres. The cadmium was determined with anthranilic acid[8] (found: cadmium 55·17 mg. per 25 ml.).

The procedure adopted for the cadmium determinations was identical with that employed for copper. The results are given in Table II.

TABLE II

Cadmium taken in each Experiment = 55·17 mg.

Glacial acetic acid ml.	*p*H	Wt. of ppt. mg.	Cadmium found mg.
20	3·15	nil	nil
10	3·37	54·1	13·32
5	3·95	223·9	55·13
0·1	5·92	223·8	55·11
0·05	6·47	223·8	55·11
nil	6·82	223·9	55·13
0·05 2*N* NaOH	7·17	224·2	55·21

It will be observed that complete precipitation is obtained over the *p*H range 3·9 to 7·2.

DETERMINATION OF ZINC.—Zinc, AnalaR (2·7 g.), was dissolved in the minimum quantity of nitric acid; the solution was made just alkaline with sodium carbonate and then just acid with acetic acid and diluted to 2 litres. The zinc was determined by the method of Funk and Ditt.[8]

The method of precipitation, washing and drying of zinc quinaldinate was similar to that employed for copper and cadmium. The results, shown in Table III, indicate that complete precipitation occurs over the range *p*H 2·3 to 6·5.

The foregoing series of precipitations were also expressed graphically. The results show that copper-zinc separations are impossible by adjustment of *p*H, and that if any separation of copper from cadmium or of zinc from cadmium is possible it should be over the *p*H range 2·7 to 3·1. When sodium acetate buffer was employed it exerted a pronounced solubility effect; a parallel case is that of copper anthranilate.[7]

TABLE III

Zinc taken in each Experiment = 33·82 mg.

Glacial acetic acid ml.	*p*H	Wt. of ppt. mg.	Zinc found mg.
100	1·72	nil	nil
75	1·96	145·7	22·27
50	2·10	207·8	31·77
25	2·30	221·7	33·89
10	2·75	221·6	33·88
5	3·09	221·2	33·82
1	3·52	221·6	33·88
nil	5·43	221·1	33·80
0·1 2*N* NaOH	6·45	221·6	33·88

Experiments to separate copper from cadmium and zinc from cadmium were made. The conditions of precipitation, washing and drying were essentially those employed in the separate determinations. The results are recorded in Table IV.

TABLE IV

Cadmium taken in each Experiment = 55·17 mg.

Zinc or copper taken mg.	Glacial acetic acid ml.	*p*H	Wt. of ppt. mg.	Corresponding to copper or zinc mg.
38·42 Cu.	30	3·11	268·8	40·20 Cu.
38·42 Cu.	40	2·93	262·0	39·18 Cu.
38·42 Cu.	48	2·69	259·0	38·74 Cu.
33·82 Zn.	25	2·85	240·0	36·70 Zn.
33·82 Zn.	30	2·60	239·1	36·56 Zn.
33·82 Zn.	40	2·30	235·9	36·07 Zn.

High results were obtained in all experiments owing to co-precipitation of cadmium quinaldinate. In the separation of copper from cadmium, co-precipitation varied from 0·8 to 4·5 per cent. over the *p*H range 2·7 to 3·1. In the separation of zinc from cadmium the results were inaccurate to the extent of 8 per cent.

It is to be concluded from these results that while quinaldinic acid offers a convenient, rapid and highly accurate method of determining copper, zinc or cadmium separately, it is unsuited for separation of these metals from one another.

In conclusion I should like to thank Dr. A. J. Lindsey for the interest he has shown in this work.

REFERENCES

1. P. Rây and M. K. Bose, *Z. anal. Chem.*, 1933, **95**, 400.
2. P. Rây and A. K. Majundar, *Id.*, 1935, **100**, 324.
3. P. R. Rây and M. K. Bose, *Mikrochem.*, 1935, **17**, 11.
4. P. R. Rây and J. Gupta, *Id.*, 1935, **17**, 14.
5. P. Rây and M. K. Bose, *Id.*, 1935, **18**, 89.
6. M. Funk and M. Ditt, *Z. anal. Chem.*, 1933, **93**, 242.
7. R. J. Shennan, J. H. F. Smith and A. M. Ward, ANALYST, 1936, **61**, 395.
8. H. Funk and M. Ditt, *Z. anal. Chem.*, 1933, **91**, 332.

THE SIR JOHN CASS TECHNICAL INSTITUTE
JEWRY STREET, LONDON, E.C.3

July, 1938

The Vitamin A and Vitamin D Contents of Butter: II. Seasonal Variation

By H. WILKINSON, B.Sc., Ph.D.

(*Read at the Meeting, November* 2, 1938)

In a previous paper from this Laboratory (Morgan and Pritchard[1]) on the vitamin A and D contents of butter, the assays of part of a series of Scottish butters were reported. This series has now been completed and the assay results, together with those on a series of Danish butters, form the basis of the present paper. The variation during the year in the vitamin A and D contents of butter was shown in the previous paper, but the data were incomplete in that the dietary regime of the cows supplying the butter was not known, and indeed in many cases the origin of the butter was also unknown. The present results are of interest in that in the Scottish series the rough feeding details and the origin and time of manufacture are known, whilst in the Danish series the time and place of manufacture are known, although no feeding details are available.

Experimental Technique.—The vitamin A content of each butter was determined directly by means of the biological technique described by Morgan.[2]

The vitamin D content of some of the higher potency butters was determined directly on the butter. The method due to Morgan[3] was used. The basal vitamin D-free diet has been slightly modified as shown below:

	(Morgan)	New diet
Maize flakes (ground) ..	72	84
Meat meal (extracted) ..	5	12
Salt mixture	4	4
Wheat gluten	19	—

Where the vitamin D potency was expected to be very low, assays were made by means of the Bechdel–Hoppert alcohol-extraction method,[4] but it has been found that this method does not give complete extraction of the vitamin D, a finding supported by other workers.

Attempts were therefore made to determine the vitamin D content directly by incorporating the butter in the diet in place of part of the maize flakes. This method has proved satisfactory, and has been used towards the end of the series.

Scottish Butters.—Arrangements were made with a creamery in Ayrshire to send us a monthly sample of butter, representative of the churning during 48 hours, and dispatched to us as soon as possible. Details of the feeding practised by the farmers during the month represented by the sample were also sent to us.

The district in which the creamery is situated lies between Rothesay, Renfrew and Dumfries. To calculate the hours of sunshine daily at the farms mentioned in this study, the average of the average number of hours of sunshine daily for

each of the three places, mentioned above, has been calculated and taken as representative of the district. The values used in the calculation have been obtained from the Weekly Weather Report, Volume LIII (Meteorological Office), for the period March 1st, 1936, to February 27th, 1937. These figures are shown graphically in Fig. 1.

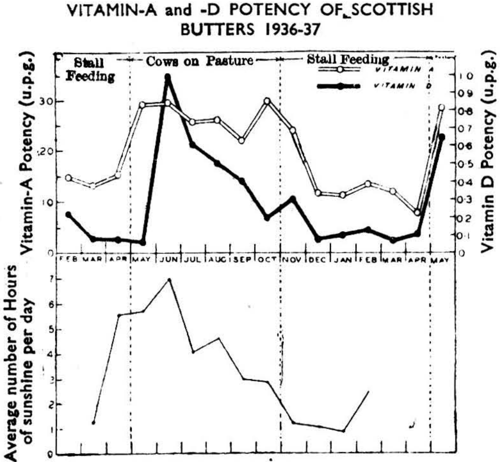


Fig. 1

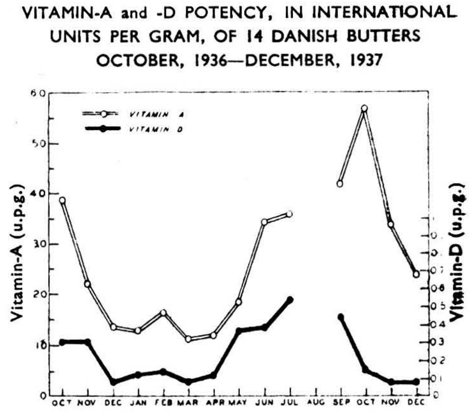


Fig. 2

The vitamin A and D contents of the butters are given in Table I, and shown in graphical form in Fig. 1. The feeding details are gathered together in Table II.

TABLE I

VITAMIN-A AND VITAMIN-D POTENCIES OF SCOTTISH BUTTERS, 1936/37

	Vitamin A (International units, per g. of butter)	Vitamin D (International units, per g. of butter)
February, 1936 ..	14·8	0·22
March ,, ..	13·2	0·08
April ,, i	15·3 } 15·3	0·07 } 0·08
ii	15·3	0·08
May ,, ..	29·1	0·60
June ,, ..	29·5	0·99
July ,, ..	25·6	0·60
August ,, ..	26·0	0·50
September ,, ..	22·0	0·40
October ,, ..	29·9	0·20
November ,, ..	24·1	0·30
December ,, ..	11·8	0·08
January, 1937 ..	11·4	0·11
February ,, ..	13·6	0·13
March ,, ..	12·2	0·08
April ,, ..	8·0	0·12
May ,, ..	28·6	0·65

TABLE II

The number of farms supplying milk to the creamery each month and the number of farms on which the different foodstuffs were fed during the month.

	1936										1937				
	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May
Total No. of Farms	9	8	6	6	6	7	6	7	9	9	7	9	7	7	7
Grass	–	–	4	6	6	6	6	4	–	–	–	–	–	–	7
Concentrates ..	8	8	6	2	2	5	6	7	9	8	7	9	7	7	7
Straw	8	6	–	–	–	–	–	–	7	6	5	6	6	6	–
Hay	9	6	–	–	–	–	–	–	6	7	5	6	6	6	–
Turnips	3	1	–	–	–	–	–	–	4	6	3	4	5	2	–
Crushed oats	2	1	–	–	–	–	1	1	–	–	–	–	–	–	–
Beet pulp	4	5	–	–	–	–	–	–	3	3	3	4	2	4	–
Bean meal	1	–	–	–	–	–	–	–	3	3	3	4	3	2	–
Maize	1	–	–	–	–	–	–	–	–	–	–	1	–	–	–
Malt culms	1	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Lentil meal	1	–	–	–	–	–	–	–	1	1	1	1	1	1	–
Barley meal	1	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Screw pressed G.N.O. cake	1	–	–	–	–	–	–	–	–	–	–	–	–	–	
Cabbage	–	–	–	–	–	–	–	1	–	–	–	–	–	–	–
Green cut hay ..	–	2	–	–	–	–	–	–	1	1	1	1	1	–	–
Potatoes	1	–	–	–	–	–	1	1	1	1	1	1	2	–	–
Marrow stem kale ..	–	–	–	–	–	1	1	3	4	–	–	–	–	–	–

DISCUSSION.—*Vitamin A.*—The highest and lowest vitamin A potencies encountered in this study are 29·9 u.p.g. in October, 1936, and 8·0 u.p.g. in April, 1937, respectively. The average vitamin A potency during the summer months, when the animals received grass, is 27·2 u.p.g., and the winter level is 13·8 u.p.g. The average value of the 16 samples assayed is 19·7 units of vitamin A per g. This value does not differ significantly from the average value reported by Morgan and Pritchard.[1] The seasonal variation, reported previously by many workers, is amply confirmed.

It is evident that the vitamin A content of these butters undergoes a considerable increase immediately after the beginning of pasture feeding. The high level reached in June falls away in July, August, and September, probably owing to deterioration in the quality of the pasture. However, in October there is obtained a significantly increased vitamin A potency, compared with the two previous months. This is due most probably to the flush of young grass that would occur in the pasture at that period. This rise in the vitamin A potency of butter has been reported before.[1] The cattle were taken from pasture at the end of October, and the November sample shows an immediate and rapid fall, which is continued through to December. This sample possesses about the normal vitamin A potency of winter butter. In 1937 there is again shown the sudden and rapid rise in the vitamin A potency of the butter when the cows go out to grass.

In Table II are given the rough feeding details, and various indications may be obtained from them:

(i) Only during grass feeding is the vitamin A potency of the butter significantly increased.

(ii) Although the peak in the vitamin A potency occurred in October, only 4 out of 7 farms were feeding grass, whilst in September all farms had their cows on pasture. The most probable explanation is that in October there occurs a flush of young grass in the pasture, coupled with the feeding on the other 3 farms of marrow stem kale and green-cut hay, both probably richer in carotene than the grass obtainable in September. The high value in November is due possibly to the feeding, on 4 farms, of marrow stem kale.

(iii) The winter feed is noticeably deficient in carotene, the precursor of vitamin A. This applies especially to all materials except the concentrates, the carotene and vitamin A contents of which are not known, and the green-cut hay.

Definite conclusions are difficult to draw, since the amounts fed per cow, the milk yield, and the amount of milk supplied to the creamery by each farm are unknown. However, the effects of the feeding regime are well demonstrated.

Vitamin D.—The variations in the vitamin D content of this series of Scottish butters are perhaps even more profound than the vitamin A variations. The highest potency was obtained in the June, 1936, sample (0·99 unit of vitamin D per g.), and the lowest of 0·08 u.p.g. in March, April and December, 1936, and March, 1937. The average summer value (*i.e.* while cows are out on grass) is 0·56 u.p.g., and the average winter value is 0·13 u.p.g. The average vitamin D content for the 16 samples is 0·32 u.p.g.

Consideration of Fig. 1 demonstrates quite clearly that the influence of the food on the vitamin D potency of the butter is negligible; the fall away is almost as rapid as the rise in potency, although almost the same feeding regime was practised for a further 4 months after the peak in June.

Campion *et al.*[5] have demonstrated that the vitamin D potency of butter varies directly with the amount of solar radiation which the cow receives. For this reason the approximate number of hours of sunshine per day have been calculated for the district around the farms supplying the milk. In Fig. 1 these values are shown graphically. The following points are of interest:

(i) Although the hours of sunshine in April and May in 1936 were high, the vitamin D potency of the butter was low. The reason for the low April sample is that the cows were being stall-fed (*i.e.* indoors) during this month and did not go out to grass until the beginning of May. It is most probable that the increase in vitamin D potency of the butter lags behind the beginning of the solar radiation, and this possibly accounts for the low vitamin D content of the May sample. The rapid increase in the May sample 1937 is due to the animals going out to grass about a fortnight earlier than in 1936.

(ii) The peak of the vitamin D potency in 1936 corresponds with the maximum number of hours of sunshine per day.

(iii) The falling away in the vitamin D potency is very closely related to the drop in the number of hours of sunshine per day.

It may be concluded, therefore, in confirmation of the results of Campion *et al.*,[5] that the vitamin D content of milk is due almost entirely to the ultra-violet irradiation that the cows receive.

DANISH BUTTERS.—These are authoritative samples representative of Danish butter churned in the Jutland district of Denmark. No data about feeding, or hours of sunshine, are available.

The vitamin A and D potencies are collected together in Table III and shown graphically in Fig. 2.

TABLE III

VITAMIN-A AND VITAMIN-D CONTENT OF DANISH BUTTER

Date		Vitamin A (International units, per g. of butter)	Vitamin D (International units, per g. of butter)
October,	1936 ..	38·8	0·3
November	,, ..	22·0	0·3
December	,, ..	13·4	0·08
January,	1937 ..	12·7	0·12
February	,, ..	16·9	0·14
March	,, ..	10·8	0·08
April	,, ..	11·7	0·12
May	,, ..	18·4	0·36
June	,, ..	34·2	0·38
July	,, ..	36·1	0·54
August	,, ..	—	—
September	,, ..	41·8	0·44
October	,, ..	56·7	0·15
November	,, ..	33·8	0·08
December	,, ..	23·7	0·08

DISCUSSION.—*Vitamin A.*—The vitamin A content of this series of butters varies more widely than that of the Scottish butters. The highest potency was found in the October 1937 sample, with 56·7 u.p.g. of butter. Incidentally, this is by far the highest potency that has been obtained for butter in this laboratory, the next highest being 41·8 u.p.g. shown in the previous month's sample (September, 1937). The lowest potency (10·8 u.p.g.) was shown in the sample of March, 1937. The average winter vitamin A potency is 18·1 u.p.g. (8 samples), which is higher than that reported for the Scottish butters (13·8 u.p.g.). This is due to the very high potencies of the last 2 samples received in November and December, 1937. The average vitamin A potency of the 14 samples is 26·5 u.p.g., which is higher than the averages of the 16 samples of Scottish butter described earlier in this paper and of the 75 samples of various butters described by Morgan and Pritchard.[1]

No feeding details are available, so that discussion of the results from this angle is impossible. The rise in potency in October, noted previously in our work on butter, has been obtained, but unfortunately the August sample was not received, so that it is not possible to tell whether there was a fall in potency in September before the October increase. However, the general trend of the results follows previous experience.

Vitamin D.—A variation in vitamin D content similar to that previously reported has been obtained in this series of butters. The range, however, is not

as wide as in the Scottish butters, the lowest level being the same (0·08 u.p.g. in December, 1936 and 1937, March and November, 1937), but the highest level (0·54 u.p.g.) is only about half the highest Scottish level, and is reached in July, 1937. The amount of sunshine may, of course, have been less in Jutland in 1937 than in Scotland in 1936. The average winter level is 0·12 u.p.g., and the summer level 0·36, with an average over the year (14 samples) of 0·23 u.p.g.

CALCULATION OF ERRORS*.—Each assay is calculated from the mean of the "pair differences." The standard deviation (σ) of the pair differences of each assay is given by:

$$\sigma = \sqrt{\frac{\Sigma(x - M)^2}{n - 1}},$$

where x = a pair difference, n = number of pairs, M = mean,

the limits on either side of the mean within which two-thirds of the pair differences could be expected to lie being given by $M \pm 6$.

Similarly, the standard deviation of a group of m assays will be:

$$\sqrt{\frac{\Sigma\Sigma(x - M)^2}{N - m}}$$

where N = total number of pair differences ($= \Sigma n$)

This value can be used to estimate the "probable error" *of the assays themselves, i.e.* the percentage limits of the assay within which there is 1 chance in 2 that the true assay lies, by combining it with the growth/dosage equation in the case of the vitamin A tests and the healing/dosage equation in the case of the vitamin D tests.

Besides the probable error (P.E.), two other standards are in common use, *viz.* 2 × P.E., which gives the limits within which there are 21 in 22 chances of truth, and 2·576 × P.E., which gives the limits of 99 in 100 chances. This latter error, written usually as "limits of error ($P = 0·99$)," has been adopted in the British Pharmacopoeia Addendum, 1936.

All three methods of expression are given below for the four groups of assays. Although the average number of pairs used per test was 9, the errors have been calculated on 10 pairs, this being the standard number.

TABLE IV

PERCENTAGE ERROR

WITH 10 PAIRS OF RATS PER TEST

Vitamin-A Assays

	Scottish butters		Danish butters	
P.E.	+7	−6	+7	−7
3 P.E.	+21	−17	+24	−19
P = 0·99 ..	+28	−22	+31	−24

Vitamin-D Assays

	Scottish butters		Danish butters	
P.E.	+9	−8	+9	−8
3 P.E.	+29	−22	+28	−22
P = 0·99 ..	+39	−28	+38	−27

Cf.* Coward, ANALYST, 1934, **59, 681.

For biological tests, these errors may be considered very satisfactory. They are considerably smaller than the representative "limits of error (P = 0·99)" quoted by the B.P. Addendum, which are:

For vitamin A assays (10 pairs) + 239 per cent. − 70 per cent.
" " D " (10 ") + 115 " " − 51 " "

SUMMARY.—Two series of butters taken at monthly intervals, one in Scotland and the other in Denmark, have been assayed for vitamin A and vitamin D. The typical monthly variation is shown in both series, the highest vitamin A value being obtained when the cows are on grass. One sample (October, 1937) in the Danish butter series has a vitamin A potency of 56·7 u.p.g., which is the highest potency recorded in this laboratory.

The variation in the vitamin D potency of the Scottish butters has been related to the variation in the amount of sunshine received by the cows on pasture. It has not been possible to do this for the Danish butters owing to lack of the necessary data.

The percentage error of the assays has been calculated.

I wish to thank the directors of Lever Brothers & Unilever, Ltd., for permission to publish these results.

REFERENCES

1. R. S. Morgan and H. Pritchard, ANALYST, 1937, **62**, 354.
2. R. S. Morgan, *Biochem. J.*, 1934, **28**, 1178.
3. ——, *Id.*, 1932, **26**, 1144.
4. H. E. Bechdel and C. A. Hoppert, *J. Nutrition*, 1936, **11**, 537.
5. J. E. Campion, K. M. Henry, S. K. Kon and J. Mackintosh, *Biochem. J.*, 1937, **31**, 81.

FOOD RESEARCH LABORATORY
LEVER BROS. & UNILEVER, LTD.
PORT SUNLIGHT

May, 1938

The Determination of Cobalt in Animal Tissues

BY K. J. McNAUGHT, M.Sc.

(*Read at the Meeting, October* 5, 1938)

THE importance that cobalt has assumed in recent years in the treatment of certain types of wasting disease in sheep and cattle, in Western and South Australia,[1,2] in different parts of New Zealand,[3,4] and in Florida,[5] has focussed attention on the determination of the very small amounts of this element normally present in animal tissues.

Bertrand *et al.*,[6,7] using α-nitroso β-naphthol reagent, succeeded in determining the cobalt content of various animal organs and tissues, but their method requires very large amounts of material. Stare and Elvehjem,[8] using Van Klooster's nitroso-R-salt reagent, developed a colorimetric method sensitive to 0·01 mg. of cobalt, but were unable to demonstrate the presence of this element in the bodies of normal rats and pigs.

The nitroso-R-salt reagent is, however, much more sensitive than the work of Stare and Elvehjem would indicate. A modification of their method that I made[9] was found applicable to rat tissues,[10] with as little as 0·0002 mg. of cobalt available for the determination. By still further refinement, a method sensitive to 0·00005 mg. of cobalt has been attained, making possible the investigation of this element in "bush-sick" pastures in New Zealand,[11] and in various animal organs.[12,13]

For animal tissues experience has shown that a modified nitric and sulphuric acid digestion method, which has been generally used for toxicological work in this laboratory for several years past, is preferable to ashing. The method is detailed below:

REAGENTS USED.—(1) Conc. nitric acid distilled from glass. (2) Conc. sulphuric acid of analytical reagent quality. (3) Hydrochloric acid of constant b.p., distilled from glass. (4) Ether of analytical reagent quality. (5) Hydrated sodium acetate (analytical reagent quality). (6) A 0·2 per cent. solution of phenolphthalein in 50 per cent. alcohol. (7) Potassium hydroxide of analytical reagent quality (about 30 per cent. solution). (8) A 0·1 per cent. solution of nitroso-R-salt. (9) Cobalt chloride of analytical reagent quality (0·4037 g. of $CoCl_2.6H_2O$ per litre gives a standard containing 0·1 mg. of cobalt per ml.).

PREPARATION OF THE TEST SOLUTION.—The sample (10 g. of dry tissue may conveniently be used) is moistened with about 20 ml. of water and 10 ml. of nitric acid, and the mixture is gently boiled. The flame temperature is raised and the boiling continued to reduce the volume to about 15 ml. The resulting partly digested mixture is allowed to cool for several minutes and 20 ml. of sulphuric acid are added. A rather vigorous reaction, with evolution of nitrous fumes, usually ensues and the solution finally chars. It is allowed to cool for a further few minutes, a few ml. of nitric acid are added, and the solution is heated, gently at first, but gradually more strongly, until the brown fumes cease and further charring begins. The nitric acid treatment is repeated until the solution, after being heated until white fumes have appeared, and then cooled, is quite colourless.

This digestion process can be conveniently completed in three to six hours, depending on the amount and nature of the sample being analysed, whereas digestion in the normal way with addition of the sulphuric acid at the initial stage is a much more prolonged process owing to the intense charring that results. The method has the further advantage that frothing is avoided, and, provided that the solution is allowed to cool sufficiently before the addition of further amounts of nitric acid, the consumption of this acid is greatly reduced (for 10 g. of dried liver the average requirement is about 40 ml.).

The sulphuric acid is driven off in a basin over an Argand burner, and the residue is heated for five minutes in the muffle furnace at 500° C. to destroy any residual traces of organic matter. The residue is taken up on the steam-bath with hydrochloric acid of constant b.p. Most of the iron is removed from such a solution by shaking with successive portions of ether until the ethereal layer is no longer yellow, and copper is removed by means of hydrogen sulphide. The dissolved hydrogen sulphide is expelled, a few drops of strong nitric acid are added, and the solution is evaporated just to dryness on the steam-bath. The residue is taken up

in about 15 ml. of water on the steam-bath, and the resulting solution is transferred to a 50-ml. beaker and evaporated to about 7 to 8 ml.; it is then ready for the determination of cobalt.*

DETERMINATION OF THE COBALT.—One g. of sodium acetate and a drop of phenolphthalein indicator are added. The solution is warmed and treated with strong potassium hydroxide solution until the reaction is just alkaline, and then diluted with hydrochloric acid to make it faintly acid again. One ml. of a 0·1 per cent. solution of nitroso-R-salt is added and the solution is boiled for half-a-minute. To the boiling solution 1·5 ml. of conc. nitric acid is added, drop by drop, with constant stirring. The rate of addition should not exceed one drop per second and the boiling should be continued for a further half-minute after the acid has been added. The solution is allowed to cool for half-an-hour, protected from sunlight, and then made up to 10 ml. and matched in 10-ml. narrow graduated tubes (14 cm. deep by less than 1 cm. in diameter) against standards developed in the same way. If the volumes and conditions of the standard and test solutions are kept as nearly alike as possible, very satisfactory matching of the colours may be attained with amounts down to 0·05γ of cobalt or even less.

The refinements introduced in this modification of the Stare and Elvehjem method for the determination of cobalt are as follows:

(1) Precautions in preparation of the test solution to ensure the absence of interfering substances. Copper and iron in amounts up to 100γ and 1000γ, respectively, do not interfere with the determination of 1γ of cobalt in such solutions.

(2) Neutralisation of the solution before addition of the nitroso-R-salt. As the reagent is highly coloured, the neutralisation of the solution is usually difficult in its presence and large amounts of phenolphthalein indicator may be required. Furthermore, although the final cobalt complex with nitroso-R-salt is very stable to boiling nitric acid, the reagent itself is readily attacked in hot acid solution by oxidising agents and even by mild reducing agents, such as citric acid.[9] Neutralisation before addition of the reagent avoids any such difficulty.

(3) Reduction in the amount of reagent used.

(4) Reduction in the final volume of the solution to 10 ml.

(5) Use of special deep tubes of narrow bore for the colour matching.

Another modification[14,15] of the Stare and Elvehjem method, claimed to be sensitive to 0·0001 mg., has been described, but in this method the objectionable practice of adding the reagent before neutralisation has been retained.

The sensitivity of the present method is shown by the analysis of individual rat livers (Table I).

These results may be compared with a value of 0·14 p.p.m. obtained previously from the analysis of a composite sample of seven normal rat livers.[13]

The reliability of the above figures is indicated by recoveries of cobalt (0·2γ)

* This wet digestion process was thought at the time to be novel, but it has since been found that the essential procedure of the preliminary treatment with nitric acid before the addition of sulphuric acid is similar to that described in the First Report of the Sub-Committee on the Determination of Arsenic Lead and other Poisonous Metals in Food Colouring Materials (ANALYST, 1930, 55, 107).—K. J. McN.

TABLE I

COBALT (Co) IN LIVERS OF NORMAL RATS

Sample No.	Total weights: Wet wt. g.	Dry wt. g.	Taken for analysis Dry wt. g.	Co found: mg.	p.p.m. on dry weight
1	3·782	1·079	0·768	0·00017	0·22
2	3·146	0·913	0·644	0·00013	0·20
3	3·177	0·904	0·646	0·00014	0·22
4	4·321	1·244	0·918	0·00018	0·20
5	3·875	1·135	0·832	0·00014	0·17
6	3·871	1·054	0·770	0·00018	0·24
7	3·440	0·965	0·712	0·00012	0·17
				Average	0·20

added to a similar weight of a sample of dried sheep liver of approximately the same cobalt-content (Table II).

TABLE II

RECOVERIES OF COBALT (Co)

Weight taken g.	Cobalt added mg.	Cobalt found mg.		Recoveries Per Cent.
1·00	—	0·00024	Av. 0·00022*	—
,,	—	0·00020		—
,,	—	0·00022		—
,,	0·00020	0·00040		90
,,	,,	0·00043		105
,,	,,	0·00041		95
			Average	97

* Duplicate analyses of 10-g. samples gave an average value in exact agreement with this figure (0·22 p.p.m.). The much lower cobalt-content of the livers of sheep and cattle suffering from cobalt deficiency (about 0·01 to 0·06 p.p.m.) necessitates the digestion of a larger amount of tissue.

SUMMARY.—(1) A rapid and convenient method for the wet digestion of animal tissue, involving preliminary treatment with nitric acid before the addition of sulphuric acid, and avoiding intense charring, is described.

(2) A delicate method sensitive to 0·05γ for the determination of cobalt is detailed and illustrated by the analysis of individual liver samples from some normal rats.

(3) With the procedure described good recoveries of added cobalt are obtained.

REFERENCES

1. E. J. Underwood and J. F. Filmer, *Australian Veterinary J.*, 1935, **11** [3], 84.
2. E. W. Lines, *J. Council Sci. and Ind. Res. (Austral.)*, 1935, **8**, 117.
3. H. O. Askew and J. K. Dixon, *N.Z. J. Sci. and Tech.*, 1936, **18**, 73.
4. E. M. Wall, *N.Z. J. Sci. and Tech.*, 1937, **18**, 642.
5. W. M. Neal and C. F. Ahmann, *J. Dairy Sci.*, 1937, **20**, 741.
6. G. Bertrand and M. Mâcheboeuf, *Compt. rend.*, 1925, **180**, 1993.
7. G. Bertrand and H. Nakamura, *Id.*, 1927, **185**, 321.

8. F. J. Stare and C. A. Elvehjem, *J. Biol. Chem.*, 1932–33, **99**, 473.
9. K. J. McNaught, *N.Z. J. Sci. and Tech.*, 1937, **18**, 655; Abst., ANALYST, 1937, **62**, 467.
10. S. W. Josland, *N.Z. J. Sci. and Tech.*, 1936, **18**, 474.
11. K. J. McNaught, *Id.*, June, 1938.
12. S. W. Josland, *Id.*, 1937, **19**, 31.
13. S. W. Josland and K. J. McNaught, *Id.*, 1938, **19**, 536.
14. E. B. Kidson, H. O. Askew and J. K. Dixon, *Id.*, 1936, **18**, 601.
15. H. O. Askew and J. K. Dixon, *Id.*, 1937, **18**, 707.

CHEMISTRY SECTION
DEPARTMENT OF AGRICULTURE
WELLINGTON, NEW ZEALAND

August 9, 1938

Erratum.—December issue, p. 869: *For* "Present-day fertilisers contain very little chloride," *read* "Present-day fertilisers containing nitrate contain very little chloride."

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.

THALLOUS CARBONATE AS A STANDARD IN VOLUMETRIC ANALYSIS

THE requirements of a suitable standard for volumetric work may be stated very briefly. The substance should be readily obtainable in a high degree of purity, it should have a high equivalent weight, and it should be of such a nature as to be weighable with certainty. On this account hygroscopic substances and substances that contain water of crystallisation are to be avoided. Substances that can react both as acids and as oxidising agents have certain obvious advantages. Potassium bi-iodate can be obtained in a high degree of purity, and it enables acidimetric and iodimetric determinations to be correlated. Similar considerations apply to potassium quadroxalate, which can serve as a standard for permanganate as well as for alkalis. Potassium quadroxalate, however, crystallises with two molecular proportions of water, and may be open to objection on that account.

So far as I am aware, the claims of thallous carbonate have not yet received the attention they deserve. This compound was first prepared by Crookes and by Lamy more than seventy years ago, and it appears to have received little study since that time. The compound is easily prepared by saturating a solution of thallous hydroxide with carbon dioxide. Crookes made a few determinations of its solubility, and found that 100 parts of water dissolved 4·2 parts of the salt at 15·5° C. and 27·2 parts at 100° C. Similar figures were published about the same time by Lamy. The compound is readily obtained in highly pure condition by recrystallisation from water which must contain excess of carbon dioxide to suppress hydrolysis.

Preparation of Thallous Carbonate.—Granulated thallium was covered with water and gradually converted into a solution of thallous hydroxide by aspirating air through the solution. The solution was then filtered and saturated with carbon dioxide. Thallous carbonate crystallised out, but after prolonged passage of the gas the crystals gradually redissolved as thallous bicarbonate. A small sparingly soluble residue, obviously consisting of carbonates of other metals, was rejected. On adding fresh thallous hydroxide solution to the concentrated

solution of the bicarbonate, a fine crystalline precipitate of thallous carbonate again separated. Purification was effected by evaporating a concentrated filtered solution of the bicarbonate to small bulk. Carbon dioxide was freely evolved during the evaporation, and the thallous carbonate was finally obtained in almost colourless crystals. The salt was then dried by exposure over soda lime in a desiccator.

The following observations on the stability and non-hygroscopic character of the compound are relevant to its use in analytical work. Thallous carbonate (8·4902 g.) was exposed in an open weighing tube to the atmosphere of the laboratory for 24 hours. The weight was then 8·4907 g. The salt was transferred to a desiccator containing soda lime and left for two days, after which its weight was 8·4905 g. It was then heated at 100° C. for two hours and cooled in the desiccator for three hours; the final weight was 8·4900 g. The extreme change of weight under these varied conditions was therefore less than one part in ten thousand.

Qualitative and quantitative comparison with extremely pure sodium carbonate as regards the behaviour with different indicators showed that the preparations were free from bicarbonate, and therefore suitable for preparing accurate standard solutions.

Standardisation of Acids.—As an example, the use of thallous carbonate for standardising nitric acid may be cited. Fifty ml. of a solution of thallous carbonate, containing 23·207 g. of Tl_2CO_3 per litre, required 43·2 ml. of nitric acid, the end-point being determined with methyl orange screened with xylene cyanol FF, as recommended by Hickman and Linstead (*J. Chem. Soc.*, 1922, **121**, 2502). The *p*H at the end-point was 3·8. The concentration of nitric acid was therefore 7·22 g. per litre.

By way of comparison a determination was carried out with AnalaR potassium bicarbonate under identical conditions. Fifty ml. of potassium bicarbonate solution (9·779 g. of $KHCO_3$ per litre) required 42·7 ml of nitric acid. The concentration of nitric acid was thus 7·21 g. per litre.

Standardisation of Potassium Iodate.—I have previously shown (ANALYST, 1926, **51**, 137) that thallous salts can be oxidised quantitatively by potassium iodate in presence of a high concentration of hydrochloric acid. The reaction with thallous carbonate takes place as follows:

$$Tl_2CO_3 + KIO_3 + 8HCl = 2TlCl_3 + KCl + ICl + 4H_2O + CO_2.$$

Ten ml. of a solution of thallous carbonate (23·207 g. of Tl_2CO_3 per litre) required 30·2 ml. of a solution of potassium iodate, the end-point being determined with the aid of chloroform. The concentration of potassium iodate was therefore 3·516 g. per litre.

This result was checked by titrating AnalaR potassium iodide under identical conditions. Fifty ml. of potassium iodide (5·223 g. of KI per litre) required 47·9 ml. of potassium iodate solution. The concentration of potassium iodate, as thus determined, was 3·516 g. per litre.

It will be evident that thallous carbonate has much to recommend it as a standard substance. The equivalent weight is unusually high—234 as an alkali and 117 as a reducing agent in an Andrews titration—and, as has been mentioned, the compound is easily prepared in a high degree of purity. At the same time no substance will command general satisfaction as a standard until it has received prolonged experimental study in the hands of a large number of independent workers. It is therefore much to be desired that chemists should subject the compound to the most careful scrutiny.

A. J. BERRY

THE UNIVERSITY CHEMICAL LABORATORY
CAMBRIDGE

THE EXCRETION OF BISMUTH AND ITS ESTIMATION IN URINE AND FAECES

A FEMALE patient, 57 years of age, was admitted to hospital suffering from severe polyneuritis, and died 19 weeks later from hypostatic pneumonia resulting from the polyneuritis. Both lead and bismuth were detected in the urine, the amounts present being determined 31, 43, and 59 days after the patient's admission. The lead and bismuth were extracted and separated by combining the Allport and Skrimshire method (ANALYST, 1932, **57**, 440), and the S.P.A. method for determining lead (ANALYST, 1935, **60**, 541). Each was estimated colorimetrically, as sulphide, in alkaline solution. The bismuth was identified by the tests used by Lynch, Slater and Osler (ANALYST, 1934, **59**, 787). Alternatively, the S.P.A. method, only, was used.

The following results were obtained with samples of the urine:

Days after admission	Lead mg. per litre	Bismuth mg. per litre
31	0·09	1·09
43	0·25, 0·25	2·00, 2·00
59	0·05, 0·05, 0·06	1·52, 1·48, 1·60

A specimen of faeces, taken 60 days after admission, contained 6·0 mg. of bismuth and 2·3 mg. of lead per 100 g. of dried material.

A. HOULBROOKE
C. H. MANLEY

CITY ANALYST'S LABORATORY
1, SWINEGATE, LEEDS, 1

USE OF THE LOVIBOND TINTOMETER FOR THE COLORIMETRIC ESTIMATION OF FORMALDEHYDE BY THE PHLOROGLUCINOL METHOD

COLLINS and Hanzlik (*J. Biol. Chem.*, 1916, **25**, 231; Abst., ANALYST, 1916, **41**, 283; Hanzlik, *J. Biol. Chem.*, 1920, **42**, 411) based a method of estimating formaldehyde in dilute aqueous solution on its colour reaction with a phloroglucinol reagent, the colour being compared after 3 minutes with the colours of mixtures of Congo red and methyl orange. Spoto (*Diagnostica Tec. Lab.* (*Napoli*) *Riv. mensile*, 1931, **2**, 362) found that mixtures of alizarin yellow R with methyl orange made better colour standards; he allowed 5 minutes for the colour to develop.

In experiments on the influence of volume and temperature of the reagent, we have found that with a volume of 0·6 ml. for concentrations of formaldehyde between 1·6 and 32 p.p.m., and of 0·9 ml. for concentrations between 32 and 65 p.p.m., an error of 5 per cent. in measuring will only slightly affect the maximum colour. Variations of temperature between 15° and 30° C. have no effect upon the maximum colour, but a large influence on the rate of development and fading.

METHOD.—The experimental conditions for accurate estimation are embodied in the following outline of the method:—Measure 25 ml. of the formaldehyde solution (at 15° to 30° C.) into a 50-ml. measuring cylinder previously washed out with some of the solution. Add the phloroglucinol reagent (1 g. in 100 ml. of 10 per cent. sodium hydroxide solution) in the proportion of 0·6 ml. for concentrations of formaldehyde between 1·6 and 32 p.p.m. or 0·9 ml. for 32 to 65 p.p.m. After stirring the mixture, use it to rinse and fill a tintometer cell of suitable thickness. Begin the observation of colour within two minutes from the time the reagent was added and continue until the maximum is passed, *i.e.* for about 4 minutes longer, depending on the temperature. The tintometer is always set with 1·0 unit of brightness (neutral tint). Calculate the concentration of the

formaldehyde solution from the maximum colour (red units) developed, by means of the following equation:

$$R = 0{\cdot}414tC + 1{\cdot}2$$

$$\text{or } C = \frac{R - 1{\cdot}2}{0{\cdot}414t}$$

where R represents the colour in Lovibond red units, t the thickness of the cell in inches, and C the concentration of formaldehyde in parts per million.

In test experiments with solutions containing from 1·6 to 65 p.p.m. of formaldehyde the red units observed agreed with the calculated values within ±0·1 to 0·2 unit (+0·4 with 1·6 p.p.m.).

The colour produced in the reaction is almost a pure orange, but it was found that the red could be observed much more accurately than the yellow. For this reason only red units are used in the equations and yellow units are disregarded. It was found that 1·0 unit of brightness (neutral tint) was generally required.

We wish to express our thanks to the Directors of the British Xylonite Company, Ltd., for permission to publish this note.

R. C. Hoather
P. G. T. Hand

Laboratory, Lactoid Works
The British Xylonite Co., Ltd.
Hale End, London, E.4

September, 1938

Official Appointments

The Minister of Health has approved the following appointments:

Hugh Childs as a Public Analyst for the County of Nottingham, in addition to John Evans (November 15, 1938).

Hugh Childs as a Public Analyst for the County Borough of Rotherham, in addition to John Evans (November 16, 1938).

Hugh Childs as a Public Analyst for the County Borough of Doncaster, in addition to John Evans (November 21st, 1938).

Hugh Childs as a Public Analyst for the County Borough of Sheffield, in addition to John Evans (November 23rd, 1938).

The Ministry of Agriculture and Fisheries has approved the following appointments since May 20th, 1938:

E. R. Andrews as Agricultural Analyst for the County of London, vice E. T. Shelbourne.

C. J. Regan as Deputy Agricultural Analyst for the County of London.

H. Childs as Deputy Agricultural Analyst for the County of Nottingham and, for the six months ending April 29th, 1939, for the County Borough of Sheffield.

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.

LONDON COUNTY COUNCIL

Annual Report of the Chemical Branch for 1937

The Report* of the County Medical Officer of Health includes a section on the work of the Chemical Branch. In addition to statistical information of analyses, mainly of materials bought by the Council for use in its numerous institutions or for its other activities, the Report gives details of a number of chemical investigations.

School Meals.—In connection with the provision of meals for necessitous children, 107 samples were examined during the year. Included in this total were samples taken from 51 complete two-course meals. The standard adopted is that each meal shall contain not less than 25 g. of protein and have a heat value of not less than 750 calories. The average of the samples examined was 28·6 g. of protein and 732 calories. Where the requirements were not fulfilled, suggestions were made as to the steps that should have been taken to avoid the deficiencies.

Toxicity of Products from the Use of Fire Extinguishers.—At the request of the chief officer of the London Fire Brigade, an investigation was carried out as to the relative toxicity of the products from the use of fire extinguishers of the carbon dioxide, carbon tetrachloride, and methyl bromide types. A "standard" fire was generated in a small room by ignition of wood wool and high tension cable. The fire was then extinguished by the use of one of the extinguishers and samples of the atmosphere in the room at different levels were collected at once, and after an interval, by aspiration through glass gas tubes. The contents of the tubes were analysed to determine the proportions of various toxic gases present, such as carbon monoxide, carbon dioxide, chlorine, bromine, hydrochloric acid, hydrobromic acid, carbonyl chloride and carbonyl bromide. Taking into consideration the results of the analyses and information gained from a research into the available scientific literature on the toxicity of these substances, it was concluded that methyl bromide and carbon tetrachloride under the conditions of test could produce acid vapours of such a concentration as would be dangerous in an enclosed space unless a mask were worn. Although carbonyl chloride (phosgene) and carbonyl bromide were not found in appreciable quantity, the possibility of their formation under special circumstances must be borne in mind. In order to extinguish a fire with carbon dioxide it appears that a concentration of this gas is required which must be regarded as a possible danger in a confined space unless a mask is worn; the time required to extinguish a fire by this means is also longer than when using methyl bromide. The final opinion expressed was that there is no more risk involved in the use of methyl bromide and carbon tetrachloride extinguishers than when carbon dioxide alone is used. With each it would be necessary to use a mask if the fire were in a confined space.

Action of Sulphates on Concrete.—Much discussion has taken place in professional circles, and many papers have been published, on the question of the effect of sulphates, in water or subsoil, on Portland-cement concrete. The matter has been investigated during the year, and work is still being continued in connection with one of the Council's housing estates where the clay has been found to

* Public Health, No. 3380. 1938. To be obtained from P. S. King & Son, Ltd., 14, Great Smith Street, Westminster, S.W.1. Price 1s.; post free 1s. 2d.

contain a small amount of sulphuric anhydride present as soluble sulphates, and also appreciable quantities of pyritic matter and selenite which may cause damage to Portland-cement concrete especially in the presence of water. A sample of water from this site was found to contain soluble sulphate considerably in excess of that found in normal surface water.

THE ATMOSPHERE IN VEHICULAR TUNNELS.—The systematic investigations, begun in 1928, on the condition of the air in Blackwall and Rotherhithe tunnels, were continued during 1937; 101 and 104 samples of air, respectively, from these tunnels were examined for carbon monoxide content and 26 from each for black suspended matter. The increase in motor traffic using the tunnels has continued at the same considerable rate at which it has been occurring since this work was started. However, on the whole, the atmospheric conditions can be said to have been no worse than in the previous year. The chief engineer has in hand works that will effect a large increase in the ventilating capacity of the plant at Blackwall tunnel.

Ministry of Health

LEAD IN FOOD*

IN this Report, Dr. Monier-Williams collects and examines the information available on the subject, with a view to arriving at some conclusions as to the significance of traces of lead in food and suggesting the best methods for its determination.

ABSORPTION, EXCRETION AND STORAGE OF LEAD IN THE BODY.—Lead may be taken into the system from many sources—through the lungs from dust, through the skin from grease paints and cosmetics containing lead, and through the alimentary canal from food. From a consideration of the published results (quoted in detail) the conclusion is drawn that under certain conditions lead may be quickly eliminated from the intestinal tract. Much of this lead is probably excreted by the liver into the small intestine and eliminated in the faeces. Some of it reaches the systemic circulation, whence it is partly excreted in the urine and partly stored in a comparatively innocuous form in the skeleton.

A normal person may excrete daily 0·05 mg. in the urine and 0·3 to 0·4 mg. in the faeces. Normally, systemic blood contains about 0·2 p.p.m. of lead, and the amount rises to 0·6 to 0·7 p.p.m. in the blood of persons suffering from lead poisoning.

The bones of a normal person may contain from 50 to 100 p.p.m. of lead, equivalent to 0·75 to 1·5 g. in the whole skeleton. It seems probable that under certain conditions lead may be released from the store in the bones into the systemic circulation and give rise to symptoms of lead poisoning. The tissues of the body, other than the skeleton, do not retain lead in any considerable amount.

THE LEAD-CONTENT OF FOOD.—Results previously recorded are summarised with references to the original publications. Among the foods and food ingredients that have been found to contain excessive quantities of lead are tartaric and citric acids, acid calcium phosphate, food colours, cider, tea, curry powder, aerated waters and sardines. The amounts of lead in various foods were determined in the Foods Laboratory of the Ministry of Health, and the following table gives some of the principal results obtained with certain individual samples (one, except where

* Reports on Public Health and Medical Subjects. No. 88. By G. W. Monier-Williams, O.B.E., M.C., Ph.D., F.I.C. Pp. 51. 1938. H.M. Stationery Office, York House, Kingsway, London, W.C.2. Price 1s. net.

otherwise mentioned). They are not to be taken as representative but only as a general indication. In view of Chapman's finding of 1·5 and 6·4 p.p.m. of lead in two samples of lobster flesh (ANALYST, 1926, 51, 564), it was unexpected not to find any in the flesh, although appreciable amounts were present in the shell.

	Lead p.p.m.
Fruits	
Strawberries (stalks removed)	0·4
Cherries (stalks removed)	0·5
Gooseberries	0·3
Redcurrants (stalks removed)	0·2
Blackcurrants	nil
Black grapes (imported)	0·5
Peaches	0·9
Pears (imported)	0·4
Oranges (pulp)	0·5
Bananas (as eaten)	0·6
Apples (as purchased)	0·3
Vegetables	
Tomato purée (2)	nil
Tomato juice	nil
Canned peas (imported)	nil
Canned peas (home-grown)	0·8
Runner beans (fresh)	0·3
Green peas (fresh)	0·2
Dried peas	1·1
Milk foods	
Malted milk	0·4
Chocolate milk (2)	1·2
Condensed milk (unsweetened)	nil
Butter	nil
Wrapped cheese (2)	nil
Meat foods	
Beef paste	nil
Corned beef (canned)	nil
Beef bone (imported)	6·8
Chicken and ham paste	nil
Meat extract	1·6
Meat cubes (2)	2·0, 2·4
Condiments	
Black pepper	2·0
White pepper	1·0
Curry powder	1·8
Curry powder	21·6
Mustard	nil
Ground ginger	0·4
Ground cloves	4·0
Ground nutmeg	0·2
Sauces (2)	nil
Gravy (dried)	4·4
Canned and bottled fruits	
Pears (imported)	nil
Peaches (imported)	nil
Apricots	0·2
Pineapple	0·3
Dried and crystallised fruits	
Apple rings	0·2
Prunes	0·6
Raisins	nil
Figs	nil

	Lead p.p.m.
Cereals	
Cake mixture	0·5
Oatmeal	nil
Corn flakes	nil
White bread	0·2
Rice	0·4
Self-raising flour	2·4
Fish foods	
Salmon and shrimp paste	0·4
Sardine paste	8·3
Brisling (2)	0·3, 0·5
Shrimp (aluminium container)	0·3
Silds (aluminium container)	5·1
Silds (in tinned can)	0·3
Herring roes	0·4
Lobster flesh (2)	nil
Lobster shell	3·4
Crab	0·3
Oysters	0·2
Whelks	0·2
Whelks	2·1
Winkles	1·5
Beverages	
Lemonade crystals	nil
China tea (loose, as bought)	1·9
China tea (in lead foil)	4·4
China tea (in lead foil)	6·1
Indian tea (loose, as bought)	10·2
Ground coffee	0·4
Coffee essence	0·3
Stout	nil
Miscellaneous	
Turmeric root	282·5
Turmeric root	10·0
Liquid saffron (colour)	5·2
Apricot yellow (food colour)	44·0
Damson blue paste (food colour)	337·0
Apple green paste (food colour)	85·0
New-laid eggs	nil
Dried eggs	nil
Tap water (Westminster)	0·03
Baking powder (alum and phosphate)	7·1
Baking powder (tartrate)	1·1
Demerara sugar	0·6
Blackcurrant jam	nil
Plum jam	nil
Lard	nil
Margarine	0·3
Gelatin (powdered)	2·0
Custard powder	nil
Custard powder	1·2
Blanc mange powder	1·0

LIMITS FOR LEAD IN FOOD FROM THE PUBLIC HEALTH VIEW-POINT.—From a consideration of these figures and results previously recorded the following conclusions are drawn: It would appear that, normally, about 0·2 to 0·25 mg. of lead is likely to be ingested daily with food, but that if certain items of high lead-content are added to the diet, the total amount of lead ingested may become excessive. The total daily intake of lead from all sources, including water, is normally about 0·5 mg. An intake of 1 mg., or possibly even less, must be regarded with suspicion.

In discussing permissible limits for lead in various articles of food the important point is not whether the limits themselves are "safe," but what their effect would be on the total intake of lead.

In all probability there is a wide range between the limit for toxicity and a lower limit for safety below which the harmfulness of lead may be assumed to be negligible. This lower limit of safety is unknown and it is therefore desirable to reduce the lead in food to the lowest amount possible.

DETERMINATION OF LEAD IN FOOD.—The more important methods that have been used at various times for determining lead in foods and biological material are summarised and critically discussed under the following heads:—(i) Destruction of organic matter. (ii) Separation as sulphide. (iii) Precipitation as oxalate. (iv) Extraction and determination with dithizone. (v) Separation with sodium diethyl-dithiocarbamate. (vi) Separation by electrolysis. (vii) Precipitation as sulphate. (viii) Colorimetric determination as sulphide. (ix) Determination as chromate. (x) Nephelometric determination as sulphate. (xi) Special methods for calcium phosphate. (xii) Separation of iron and bismuth as thiocyanates. (xiii) Spectrographic methods. (xiv) Use of radio-active lead in physiological research. (xv) Nitrite test.

GENERAL METHOD.—The method used in obtaining the results in the foregoing table was practically the same as that of Allport and Skrimshire (ANALYST, 1932, **57**, 440), with the addition of lead sulphate precipitation as carried out by Francis, Harvey and Buchan (ANALYST, 1929, **54**, 725). The method of Allport and Skrimshire, without precipitation of lead sulphate, does not differentiate between lead and bismuth, and it is not always safe to assume that bismuth is absent from foods. A further advantage of lead sulphate precipitation is that it ensures that a perfectly colourless solution is obtained for the colorimetric determination.

For the determination of lead in samples that contain much calcium phosphate (*e.g.* bone or baking powder), a method similar to that of Roche Lynch, Slater and Osler (ANALYST, 1934, **59**, 787) was used.

By the combination of the methods described satisfactory results were obtained in presence of as much as 1000 p.p.m. of tin, iron or magnesium. With certain synthetic food colours, containing very large quantities of tin, and possibly other metals, it may be necessary to use the special method of the S.P.A. (ANALYST, 1935, **60**, 541) or that given by Allport and Skrimshire (*loc. cit.*).

The Report concludes with 11 pages of references to papers published (with a few exceptions) during the last 12 years. In each instance the subject matter of the paper is indicated.

Department of Scientific and Industrial Research

REPORT OF THE CHEMISTRY RESEARCH BOARD FOR THE TRIENNIAL PERIOD ENDED DECEMBER 31, 1937*

THE Report reviews the progress of the research undertaken at the Chemical Research Laboratory during the three years that have elapsed since the publication of the last Report (*cf.* ANALYST, 1935, **60**, 613), and includes the Report of the Director (Sir Gilbert Morgan). Much of the work described is of a long-term character, as for instance, the researches on the corrosion and tarnishing of metals, the study of coal and tar, and the investigation of the rarer elements found within the British Empire. Other investigations of more immediate industrial application have been carried out at the request of, and mainly at the expense of, the industries concerned. References are given to over 70 papers dealing with the work published in scientific and technical journals and to 16 patents covering results of various aspects of the work, including the fundamental patents on the use of synthetic resins in water purification.

CORROSION OF METALS.—A prolonged enquiry into the causes of corrosion and their prevention is in progress, and concurrently with this research, investigations of a technical character, such as the corrosion of locomotive boiler-tubes, have been carried out in co-operation with the London, Midland and Scottish Railway.

Corrosion of Locomotive Boiler Tubes.—Preliminary experiments showed that localised pitting was unlikely to be caused by impurities in the metal, nor could intercrystalline corrosion due to attack by alkalis at high pressures and temperatures be detected in corroded tubes. The corrosion products at boiler temperature consist largely of nearly black ferroso-ferric oxide which may be precipitated either in a loose sooty condition, or as a coherent varnish-like scale, or in intermediate forms. The particular form is influenced by the composition of the water and probably other factors. The tube thus becomes covered with a more or less continuous layer of oxide which overlies the very thin film of "mill-scale" formed in the last stages of tube manufacture, and the layer may contain calcium or magnesium salts, or both, precipitated from solution. Pits form where the conditions are locally unsuitable for the formation of this layer in a protective form. Corrosion is mainly of the oxygen absorption type, but small amounts of hydrogen are probably evolved, and the evolution centres may perhaps give rise to pits. The condition of the mill-scale determines to some extent the area over which general corrosion (roughening) occurs.

Protection of Magnesium Alloys by the Selenium Process.—Magnesium alloys are particularly susceptible to corrosion by chloride solutions, and their use for aircraft, etc., exposed to marine atmospheres or to sea-water is dependent on adequate protection by some form of corrosion-resisting film or layer. The best results were obtained by depositing a film of selenium produced by immersing the alloy for 5 to 10 minutes in a solution containing 10 to 15 per cent. of selenious acid and 0·5 per cent. of sodium chloride. Protective films have also been formed by rubbing the alloy with cotton-wool saturated with the solution. The protection afforded by the selenium film may be increased by over-coats of suitable paints.

Corrosion of Magnesium Alloys by Leaded Petrol Fuels.—The attack is probably caused by hydrolysis of the tetraethyl lead in the presence of ethylene dibromide and water to form lead bromide or ethylated lead bromides which deposit low over-voltage cathodes of metallic lead on the alloy. Of the large number of inhibitive substances examined, the best results were obtained by adding quinoline to the fuel. The addition of 1 per cent. suppressed corrosion in a test of six months' duration.

* H.M. Stationery Office, York House, Kingsway, London, W.C.2 1938. Price 3s. net.

Production of Green Patina on Copper.—Thionyl chloride, applied in the form of a spray, to copper roofs, especially those blackened by exposure, produces a coating which improves in appearance with subsequent exposure and yields a satisfactory patina after only a few months (B.Pat. Appl., No. 28541/37).

HIGH-PRESSURE RESEARCH.—The technique of high-pressure operations has been studied for several years at the Laboratory, and the Report gives details of experiments on the synthesis of acetic acid from methyl alcohol and carbon monoxide, and of studies in the production of higher aliphatic acids.

Acetic Acid Synthesis.—Further experiments have confirmed the previously reported yield of approximately 80 per cent. It would appear to be impracticable to make acetic acid from water-gas without isolating methyl alcohol as an intermediate product.

COAL, TAR AND RUBBER RESEARCHES.—A research on the constitution of coal has been initiated recently, and an extended study of coal tars, especially of those derived from low-temperature carbonisation, has been in progress for several years and has resulted in a valuable extension of knowledge of tar constituents. Catechol, a product for which this country is now dependent on imports and which is used as a starting point in the preparation of several important drugs and fine chemicals, has been found in low-temperature tar. Technical methods have been devised which should lead to the industrial production of this compound from liquors that have hitherto been a waste product. Attention has also been directed to tars to improve their value as road materials.

The possibility of compounding rubber and tar with a view to establishing its use on the roads and for other industrial purposes is also being investigated in co-operation with the rubber-growing industry.

Tar Stills.—The introduction of vertical retorts for the carbonisation of coal has led to the production of tars which are considerably more corrosive to tar stills than tars derived from horizontal retorts. Since the introduction of vertical retort tar, the life of certain stills has diminished from 16,000 to 30,000 tons to an average of 7000 to 8000 tons when dealing with tars composed approximately of 75 per cent. of vertical and 25 per cent. of horizontal retort material. It was calculated that this reduction in the life of a still by 50 per cent. was equivalent to 5d. per ton of tar distilled and that the total cost to the tar distillation industry was of the order of £25,000 annually. A detailed inquiry into the causes of corrosion of stills has been made at the request of the industry and has resulted in suggestions for reducing the activity of the corrosive elements.

Chlorinated Rubber.—The different types of products that can be made with chlorinated rubber have received attention. Sheets of linen were impregnated with a solution of chlorinated rubber in benzene or carbon tetrachloride and the solvent was removed when the sheets were submitted to pressure at 140° C. If the materials were allowed to cool under pressure, hard, dense boards were obtained, but if the pressure was released when the ingredients were hot, very light laminated materials of a cell-like structure resulted. Chlorinated rubber can be used with various fillers, such as asbestos, woodmeal, etc., as a moulding material giving products of considerable strength. The most striking of its properties is that it can be utilised as a plastic without the addition of any filler. When compacted under pressure of one ton per square inch at 115° C. to 120° C. for a short period, an opaque moulding is produced when the pressure is released at this temperature. If, however, the pressure is retained while the mould is cooled to about 70° C., a completely transparent moulding is obtained. Transparent films of chlorinated rubber are readily obtained by slow evaporation of benzene or carbon tetrachloride solutions. Chlorinated rubber unites with basic colouring matters in a remarkable manner. When the carbinol base of rosaniline or of brilliant green is dissolved in the benzene solution of chlorinated rubber, the colour of the dye is rapidly developed. On evaporation of the solvent, coloured

films remain from which the dye is not readily extracted by water, dilute acids or alkalis. Such coloured material could be utilised in the production of transparent moulded articles.

SYNTHETIC RESINS.—Investigations, such as that on the structure of phenolic resins, have been continued in conjunction with efforts to develop more immediate applications of resinous materials, notably those resins that possess base-exchange and acid-exchange properties. The remarkable properties of these substances were discovered at the Teddington laboratory (*cf.* ANALYST, 1935, **60**, 614; 1936, **61**, 33; 1937, **62**, 302). In the present Report an account is given of the pyrolysis and structure of phenolic resins, their X-ray examination, and their electrical properties. The use of natural phenolic substances, such as catechin and gambier, as a cheap component in the manufacture of resins in place of phenols derived from tar, has received attention. These resins can be used in the industrial preparation of laminated boards. Investigations have also been made on ketone resins of the transparent, glass-like variety which are becoming of increasing interest, notably in the motor-car and aircraft industries.

CHEMOTHERAPY.—An investigation of new bases of the pyridine series that may be of service in chemotherapy is in progress. A new series of heterocyclic derivatives has been discovered, to which the generic name of 1:3-diazalines has been given.

Neocryl.—A new drug, succinanilomethylamide *p*-arsonic acid, now known as "neocryl," has been discovered and is being clinically tested by the Therapeutic Trials Committee of the Medical Research Council, for the treatment of syphilis and African sleeping sickness. Present indications are that it is less toxic than drugs already in use.

RARE METALS.—Successful attempts have been made to extract some of the rarer metals known to exist in coal or coal ash and also found in the flue dusts which accumulate in the producer gas mains and waste gas flues of gas works. Gallium, germanium, indium, cerium, thallium, lanthanum and silver were all recognised and recovered, in varying but mostly very small amounts, and further attention will be directed to the utilisation of certain of these metals, for example, gallium and germanium.

In these investigations a quantity of Australian molybdenite was treated for the rhenium it contained, and use was made of the di- and tri-pyridyls obtained by the dehydrogenation of pyridine. Dipyridyl has proved to be a valuable reagent for the study of the constitution of complex metallic salts, and specimens of the base have been supplied to other British laboratories for this purpose. Furthermore, dipyridyl, when combined with salts of ruthenium, gives rise to an exceptionally stable orange red trisdipyridyl ruthenous chloride which has been resolved into its optically active components. Tripyridyl, which has hitherto been prepared exclusively in the Laboratory, may be used as a very delicate reagent for ferrous iron in sea water (at a dilution of one part in two million parts of water), and a specimen was employed in this way in a recent expedition to the Indian Ocean.

Recently two higher polypyridyls, tetrapyridyl and a hexapyridyl, have been isolated; these new bases develop characteristic colours with metallic salts.

MICROBIOLOGY.—Bacterial investigations were called for in dealing with problems as diverse as the preservation of ropes and cordage against decay, the discoloration of paintwork, the origin of an unpleasant bacterial odour in beer, the corrosion of water mains and petrol storage tanks, and the cause of an earthy flavour in salmon. In all these problems bacteria have played a destructive part, but acetic acid bacteria, especially *B. suboxydans*, are utilised constructively in the preparation of sorbose, an essential step in the production of synthetic vitamin C from glucose. One common disadvantage attending the employment of bacteria is the excessive time they sometimes take in effecting their transformations. With the acetic acid bacteria, however, it has been shown that the period can be

reduced substantially by blowing fine bubbles of air through the fermentation liquid. In this way the time required for one stage of the process has been reduced from 12–15 days to less than 2 days.

Investigations on the biochemistry of the lower fungi are now being conducted under the direction of Professor Raistrick. Earlier work on the subject has shown that many new organic compounds can be made economically from sugar by the use of different species of fungi, and, although these new products of mould metabolism are at present of purely academic interest, future work may well lead to developments of industrial importance.

New Zealand

Department of Agriculture

Annual Report of the Chemistry Section for 1937–1938

The activities of the Chemistry Section, under the direction of Mr. R. E. R. Grimmett, M.Sc., are closely co-ordinated with those of other Divisions of the Department and of the Department of Scientific and Industrial Research, and a certain measure of amalgamation with the Dominion Laboratory has been brought about. In addition to investigation related to advisory work, a number of special problems have been studied.

Deficiency Diseases of Livestock.—*Bush Sickness.*—The demonstration of the importance of cobalt to livestock has been followed by developments in other directions through the co-ordinating activity of the Cobalt Committee. The Chemistry Section is undertaking work in the North Island and the Cawthron Institute in the South Island. A comprehensive series of soil and pasture samples has been collected, and McNaught's successful application of the "R-salt" method (*cf.* Analyst, 1939, p. 23) has provided valuable confirmation of field evidence. Under conditions of spring growth, with ordinary but not extreme precautions to avoid soil contamination, it has been found that pastures that are bush sick for both cattle and sheep contain from 0·01 to 0·04 p.p.m. of cobalt, those sick for sheep but not for cattle from 0·04 to 0·07 p.p.m., and healthy pastures from 0·07 to 0·3 p.p.m. or more. Pastures from specially enclosed plots on extremely bush-sick country, as at Kopaki, may contain less than 0·01 p.p.m. of cobalt. In experiments with cobalt top dressing, in which 1/4 to 2 lb. of cobalt sulphate was used in admixture with superphosphate or cobaltised superphosphate, very definite results in improved health and increased weight of sheep and lambs have been obtained, and analyses indicate that the cobalt-content of the pastures may be increased after several weeks of top dressing by as much as tenfold, and that amounts above the critical value for stock health are still maintained six months later. Bush-sick pastures show a slight rise, and healthy pastures a much greater rise in cobalt-content in late summer.

Phosphorus Deficiency in Cases of Osteomalacia.—In several cases of pica, osteomalacia, etc., it was suspected that the disease was associated with deficiency of phosphorus or an unbalanced ratio of phosphorus to calcium. On a property at Onewhero, near Tuakau, Raglan County, very persistent bone and stick chewing had occurred among dairy cows, and over a number of years young cattle and sheep failed to thrive. Analyses at the Veterinary Laboratory had demonstrated low levels for inorganic phosphorus in the blood. Samples of soil and pasture, when analysed, supported the contention that deficiency of phosphorus was the cause of the trouble. The soils were leached volcanic ash loams with high lime requirements, high soluble alumina probably resulting in strong phosphate fixation, and with very low contents of total and available phosphoric acid. The pastures contained

approximately 1 per cent. of calcium oxide, but only about 0·4 per cent. of phosphoric acid. It was subsequently demonstrated that feeding with bone-meal, when persisted in long enough, would overcome the stock trouble.

In connection with an outbreak of bandiness in hoggets near Balclutha, turnips on which the animals were being fed were submitted for analysis. The roots from Balclutha contained 0·43 per cent. of calcium oxide and 0·75 per cent. of phosphoric acid on the dry weight, whilst other turnip roots from Ruakura for comparison contained from 0·6 per cent. to 0·7 per cent. of calcium oxide and 0·4 per cent. of phosphoric acid.

MINERAL DEFICIENCIES AND FRUIT TREE GROWTH.—A considerable number of citrus-tree leaves have been analysed in connection with a chlorotic condition of the leaves and general unhealthiness of the trees. Some indications of positive response to zinc spraying have been obtained by the Horticulture Division in the Tauranga area, and analyses point to a zinc-content of the young leaves of from 5 mg. to 20 mg. per kilo. of dry matter being associated with such conditions, while healthy trees usually have a higher zinc-content.

In the Auckland district joint investigations by the Horticulture Division and the Department of Scientific and Industrial Research indicate a deficiency of manganese as a contributing factor to chlorotic conditions, and leaves of the affected trees were found to vary in zinc-content from 16 mg. to 31 mg. per kilo., and in manganese-content from 5 mg. to 12 mg. per kilo.

Samples of leaves taken under a standard system have been obtained from manurial trials in apple orchards. The analytical results will be compared with those indicated from qualitative and quantitative observations on the yield and vigour of the trees.

TOXICITY OF ZINC TO PIGS.—Two further experiments in which pigs were fed with pure zinc lactate showed that an intake of 0·05 to 0·005 per cent. in the milk fed were associated with death and with a non-specific arthritis. High amounts of zinc have been found in the organs. The total amount of zinc required to cause death has been as low as 37 g. given over two months. Several cases of suspected poisoning of pigs from milk passed through galvanised-iron pipe lines have again occurred, and analyses have confirmed the presence of excessive zinc in the milk and in the organs of the pigs.

POISONING DUE TO ARSENIC SULPHIDE IN THE SOIL.—A case requiring intensive investigation occurred in the Reporoa district. This isolated farming community lies to the south of the Waiotapu thermal area and also has a number of thermal and mineral springs scattered over it. Dairying, dry stock, and sheep farming are all carried on, but results, both in stock health and production, have never been as good as might have been anticipated. Continued unthriftiness and mortality of dairy stock on one farm led to an analysis being made of mud and water from a drain; arsenic was found in both. Further investigation revealed that the mud deposited by the Waiotapu River was arsenical and that the swamp soils formed from this mud contained arsenic. The arsenic appears to be present both in combination with iron and as sulphide. Orpiment occurs in massive form in the sinters around some springs, and as a finely divided precipitate in pools receiving the overflow from the Champagne Pool at Waiotapu, the waters of which contain arsenic in solution. A large number of samples have been collected, and a survey of the whole settlement is in progress. Among samples so far analysed up to 3·75 mg. of As_2O_3 per 100 ml. have been found in some drainage waters, 2·5 per cent. in muds, 0·3 per cent. in soils, 2·3 mg. per 100 g. in dry matter of grass, and 0·6 mg. and 0·25 mg. per 100 g., respectively, in the dry marrow and femur bone of a cow that had died under suspicious circumstances.

CHEMICAL CONTROL OF RAGWORT.—The Agricultural Chemist (Mr. F. B. Thompson) has investigated the conditions for the most successful use of sodium chlorate. Chlorate injury could be traced by the red colour imparted to the

affected roots of the plants. All the experiments indicated that the ragwort plant has great difficulty in absorbing and translocating within its tissues sufficient sodium chlorate to kill the whole length of the roots, but that very little chlorate will completely defoliate it. To kill the plant completely the doses had to be considerably larger than was first anticipated. Analyses of treated soil showed that the chlorate tends to remain on the top few inches. Atlacide, a proprietary sodium chlorate weedkiller, behaved in the same way as the pure salt. Comparative tests with other weed-killers, *e.g.* the sulphates and nitrates of copper and zinc, showed that approximately 15 g. of these compounds were required to produce an effect similar to that obtained with 1 g. of sodium chlorate. Dichromates, thiocyanates and bisulphites were also less effective than sodium chlorate. Much of the re-growth that has been attributed to fresh seeding is undoubtedly the result of incomplete killing of the roots.

British Guiana

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1937

UNDER the Food and Drugs Ordinance various authorities are permitted to submit samples for analysis. According to the Government Analyst (Mr. Kenneth Wallis) 5129 samples were submitted, mainly by the Police Department, the Government Public Health Departments, the Mayors and Town Councils of Georgetown and Berbice, and the Superintendent of the Alms House. Of the 4238 samples of milk examined, 325 were adulterated. Special raids are unexpectedly made by the Police Department and Public Health Departments on Sundays, Public Holidays and after official hours. Of 983 samples thus taken, 120 were adulterated, the percentage rate being 12·2 as compared with 6·0 on ordinary week-days.

CRIMINAL INVESTIGATION.—Three hundred and forty-seven exhibits were examined, including 10 in cases of arson, 91 in 23 cases of alleged poisoning, and 150 in 23 cases of counterfeiting coins and notes.

Poisoning Cases.—The chief poisons found were arsenic, datura, sulphuric acid, mercuric chloride, belladonna liniment and ground glass.

Counterfeit Coins and Currency Notes.—The 150 exhibits examined included various coins, currency notes, moulds and crucibles. The moulds were made of plaster of Paris, and several showed excellent impressions of two and one shilling pieces. In some, flaws were found and photographed (enlarged), which corresponded with flaws in silver pieces previously examined. The composition of the fused masses in the crucibles agreed in most instances with that of the counterfeit coins. Several pieces of metal were also analysed in connection with these cases to ascertain if they could be used in counterfeiting.

Palestine

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1937

THE Government Analyst (Mr. G. W. Baker) reports that 12,330 samples have been examined, as compared with 9188 in 1936; the increase was mainly due to more intensive sampling made possible by the appointment of additional inspectors.

FOOD AND DRUGS.—Of the 7465 samples examined, 3985 were of milk (290 adulterated) and 2120 of semni (140 adulterated). Very large quantities of fat similar in appearance and flavour to, but containing no butter-fat, are imported from Europe. This fat is labelled in accordance with the provisions of the Ordinance, but there is no doubt that much of it is used as a substitute for, or adulterant of, semni.

Standard for Cream.—Under the Foods Ordinance a minimum of 35 per cent. of fat is required for cream, but this is now being reconsidered as the result of representations that the manufacture of tinned cream with so high a percentage of fat is impracticable.

Standards for Honey.—During the year standards for honey have been added to the regulations under the Foods Ordinance. They are as follows: "Honey means the nectar and saccharine exudation of plants gathered, modified and stored in comb by honey bees, without the addition of any colouring, flavouring, or other substance. Honey shall be laevorotatory and shall contain not more than 25 per cent. of water, not more than 0·25 per cent. of ash, and not more than 8 per cent. of sucrose."

Of the 30 samples of honey examined, 14 were adulterated.

Hypersensitivity to Iodine.—Among the 2260 biochemical specimens examined were the blood and urine of a patient who was hypersensitive to iodine. The blood contained 1·27 mg. per 100 g. and the urine 5·8 mg. per 100 ml.

POLICE DEPARTMENT.—*Poisoning Cases.*—In connection with 9 cases of suspected human poisoning, 33 specimens were examined. In five cases poison was found: arsenic in 2, mercury in 1, veronal in 1, and carbon monoxide in 1.

Shooting and Bombing.—Seventy-nine exhibits were examined. Most bullets and cartridge cases are now examined in the C.I.D., and it is only when a second opinion or chemical analysis is required that they are submitted to the Government Analyst.

Finger-prints on a Time Fuse.—The finger-prints on a time fuse were photographed with the aid of the specially constructed "cold stage" described in the 1936 Report (*cf.* ANALYST, 1938, **63**, 115). They corresponded with those of an arrested suspect.

Spreading of Ink as Evidence of Forgery.—In a case in which a will had been forged evidence of later additions was provided by the spreading of the ink into the creases of the paper in the added portions, and absence of such spreading in the rest of the document.

"ACTIVE ALUMINIUM" IN THE SOIL.—In an investigation to determine the relation of exchangeable cations to "active aluminium" in the soil it was found that there is a close relation between the valence of an adsorbed cation and the amount of "active" aluminium present. Potassium and sodium tend to decrease, whilst lithium and magnesium salts increase the aluminium toxicity of the soil.

Georgia Experiment Station

FIFTIETH ANNUAL REPORT, 1937–1938

THE Georgia Experiment Station was founded in 1887 by Act of the United States Congress, and is under the control of the University System of Georgia. During its 50 years of service the Station has issued 50 annual reports, 199 bulletins and 115 circulars, and has made many discoveries of benefit to agriculture.

RAPID CHEMICAL SOIL TESTS.—More than ten thousand rapid chemical tests have been made on 1200 soil samples taken from fields of known fertiliser treatment and crop response, and correlation studies between the laboratory data and response to fertilisation are in progress. In addition to showing the approximate amount of available nitrogen, phosphorus and potassium necessary to produce good crops on Georgia soils, the quick tests have indicated soil abnormalities other than deficiencies in any of these three elements. There are indications that aluminium toxicity is prevalent in parts of the State. The following data, obtained by rapid soil tests on two soils of widely different nature and location, suggest aluminium toxicity. The results are expressed in pounds per acre.

	Crop	Condition	*p*H	NO_3	P	K	Al	NH_3	Fe	Ca
Soil 1*a* ..	Corn	Fair	4·65	0	15	426	100	75	20	200
,, 1*b* ..	Corn	Dying	3·95	0	10	336	500	125	200	200
Soil 2*a* ..	Wheat	Fair	5·30	10	40	205	100	75	5	150
,, 2*b* ..	Wheat	Poor	4·55	15	15	111	500	50	5	100

COLCHICINE TREATMENT OF SEEDS.—This method holds interesting possibilities for the production of new varieties of pasture and forage plants. Seeds of the more important pasture and forage plants have been treated for varying periods of time, and approximate effective time-concentrations for some plants have been determined. Even rather light treatment of the seeds of some species so weakened and retarded the growth of the seedlings that an unusually high proportion died. It was surmised that the colchicine treatment may destroy or inhibit the production of the plant hormones needed for root and shoot development, and that treatment with Hormodin (or individual plant hormones) might overcome the retarding effect. Some of the legumes, but none of the grasses, responded definitely to hormone treatment. Alfalfa seedlings were much more vigorous when treated with Hormodin. This favourable reaction was used later for getting a greater survival of seeds of the creeping-rooted alfalfa, seeds of which were obtainable in only a limited quantity. Subterranean clover also reacted favourably to the Hormodin treatment subsequent to the colchicine treatment.

MANGANESE REQUIREMENTS OF COTTON.—Large well-fruited cotton plants have been grown repeatedly in nutrient solutions containing 0·1 p.p.m. of added manganese. It was found that cotton seedlings grown in a medium without added manganese developed deficiency symptoms in about three weeks. Under certain conditions a medium containing 0·01 p.p.m. of manganese produced almost as much vegetative growth as those containing larger amounts of the element.

PEACH STORAGE STUDIES.—Peaches stored at 33° to 36° F. in an atmosphere containing 10 per cent. of carbon dioxide were better preserved than in any other combinations of gases tried. Even at this concentration, however, the fruit had an undesirable flavour at the end of several weeks.

TOXICITY OF PEANUT MEAL FOR SWINE.—Swine fed for several days with large quantities of peanut meal developed toxic symptoms and some of them died. Preliminary investigation of this problem indicates that the effects are due, at least in part, to the comparatively high potential benzoic acid content of peanut meal. Although the amount of benzoic acid found in the urine of pigs fed on this material was considerably less than has been reported for cattle fed on the meal, it appeared to be high enough to cause a severe drain on the glycine supply of the animals.

New International Standard for Vitamin B_1

THE Medical Research Council has requested us to publish the following statement:

It is announced that the first International Standard for Vitamin B_1, which consisted of an adsorbate of the antineuritic vitamin, made from rice polishings, on fullers earth, has now been replaced by a preparation of crystalline Vitamin B_1 hydrochloride. In recent years progress in the study of the antineuritic vitamin has been rapid, and this change in the form of the International Standard has been made possible by the synthetic preparation of the vitamin in pure crystalline form.

Through the generosity of four manufacturers, an adequate quantity of the new crystalline material was placed at the disposal of the National Institute for Medical Research, Hampstead, to enable a new standard to be prepared consisting of the pure crystalline substance. Extensive international investigations of the properties of this material, and, in particular, the determination of its potency in terms of the original international standard by a variety of methods have now been completed, and the members of the International Conference on Vitamin Standardisation have unanimously recommended that the sample be adopted as the Second International Standard for Vitamin B_1, and that the International Unit be defined as the antineuritic activity of 3 microgrammes of the international standard preparation. This recommendation has been adopted by the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations.

As in the case of the other International Vitamin Standards, the new standard for Vitamin B_1 is held, on behalf of the Health Organisation of the League of Nations, at the National Institute for Medical Research, Hampstead, N.W.3, and is distributed therefrom to national control centres established in other countries for local distribution to laboratories, institutes and research workers; and to workers resident in countries in which the establishment of national control centres has not yet been completed.

With regard to the supply of the new standard for Vitamin B_1 to those requiring it in the United Kingdom, samples have already been sent to the laboratories, institutes and research workers who have hitherto received the standard adsorption product. Others requiring the standard are asked to make application to the Department of Biological Standards, the National Institute for Medical Research, Hampstead, N.W.3.

18th November, 1938

National Physical Laboratory

FEES FOR TESTS ON VOLUMETRIC GLASSWARE

THE Director of the Laboratory (Sir Frank E. Smith) has requested us to call attention to the issue of a new schedule of fees for tests on volumetric glassware, which came into operation on December 1st, 1938.

The new fees are on a nett basis and, generally speaking, are equal to less than the old fees, less the 33⅓ per cent. discount previously only obtainable on batches of one dozen or more vessels of the same type and capacity sent together for test.

The new schedule covers a considerably larger range of apparatus than the old schedule. Thus it now includes volumetric glass ware for testing milk and milk products.

British Standards Institution

THE following Standard Specifications have been issued*:

No. 647—1938. BRITISH STANDARD METHODS FOR TESTING GLUES. (BONE, SKIN AND FISH GLUES.)

This Specification, first published in December, 1935, and revised in September, 1938, is in two parts.

Part I.—General.—(1) Preparation of Sample. (2) Concentrations. (3) Testing of Liquid and Jelly Glues.

Part II—Methods of Test.—(A) Method for the Determination of Moisture-Content. (B) Determination of Jelly Strength. (C) Determination of Jelly Strength, using the Bloom Gelometer. (D) Viscosity. (E) Melting-point. (F) Foam. (G) Water Absorption. (H) Keeping Quality. (I) Joint Strength in Shear. (J) Reaction (*p*H). (K) Grease. (L) Ash. (M) Chloride. (N) Sulphur dioxide.

Diagrams are given of a test piece, a clamping device for retaining a joint under pressure, and the Bloom gelometer, and there is an appendix with notes on the use of apparatus described. These are not to be taken as excluding other manufacturers of chemicals or apparatus.

No. 809—1938. BRITISH STANDARD METHODS FOR THE SAMPLING OF DAIRY PRODUCTS.*

These Methods of Sampling form part of a series of British Standards for Use in the Dairying Industry, the preparation of which was authorised by the Chemical Divisional Council in 1933.

The methods include the sampling of milk, cream, butter, condensed milk, cheese, and milk powder, and include sampling both for chemical analysis and for bacteriological examination.

The standard also includes a description of various types of apparatus that have been found suitable for obtaining samples of various dairy products.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Chemical Evaluation of Spoilage in Canned Fish. F. Hillig. (*J. Assoc. Off. Agr. Chem.*, 1938, **21**, 688–695.)—The traces of volatile fatty acids normally present in fresh canned fish consist mainly of formic and acetic acids. As decomposition proceeds there is a progressive increase in the volatile acid content and formation, in increasing amounts, of higher members of the series. The identity of all the higher members formed has not been established, but in tuna fish the highest member is normal butyric acid, and in salmon iso-butyric acid. The method consists in the determination of the "volatile acid number" and the "formic acid number." The finely minced fish (50 g.) is suspended in 100 ml. of water and treated with 15 ml. of 2 *N* sulphuric acid and 15 ml. of 20 per cent. phosphotungstic acid solution (with tuna fish 25 ml. of each reagent are used). The mixture is diluted to 250 ml., shaken, allowed to stand for 5 minutes, and filtered. The filtrate (150 ml.) is distilled at the rate of about 200 ml. per hour in Dyer's apparatus (*J. Biol. Chem.*, 1917, **28**, 445; Abst., ANALYST, 1917, **42**, 149), as modified by Clark and Hillig (*J. Assoc. Off. Agr. Chem.*, 1938, **21**, 684) after the

* Obtainable from the Publication Department, British Standards Institution, 28, Victoria Street, London, S.W.1. No. 647, price 3s. 6d. net, post free 3s. 8d. No. 809, price 2s., post free 2s. 2d.

addition of 0·5 ml. of 50 per cent. sulphuric acid (1 ml. for tuna fish) until two 100-ml. portions have been collected. Each portion is titrated with 0·01 *N* barium hydroxide solution, phenolphthalein being used as indicator, until the colour matches that of a buffer solution of *p*H 8·6 containing the same amount of indicator. After deduction of the result of a blank titration, the total number of ml. of 0·01 *N* acid corresponding with 100 g. of fish is termed the "volatile acid number." The two titrated liquids are combined and, after the addition of two drops of saturated barium hydroxide solution, evaporated to dryness. The residue is treated with 5 ml. of water and 1 ml. of *N* hydrochloric acid in excess of the amount necessary to liberate the volatile acids, and the solution is filtered. The combined filtrate and washings, the volume of which must not exceed 30 ml., are treated with 5 ml. of 10 per cent. aqueous sodium acetate solution, 5 ml. of 5 per cent. sodium chloride solution and 10 ml. of 5 per cent. mercuric chloride solution, and the mixture is heated beneath a reflux condenser on the steam-bath for two-and-a-half hours. The precipitate of mercurous chloride is weighed in a tared Pregl filter-tube counterpoised by a similar tube prepared and treated in the same manner. The weight of the precipitate $\times 0{\cdot}0975$ gives the weight of formic acid in the sample, and $3\frac{1}{3}$ times this figure gives the weight of formic acid in 100 g. of fish. This value (mg. per 100 g.) is the "formic acid number." The following figures were obtained with canned mackerel in three stages of decomposition, the first figure being for the fresh, and the third for the badly tainted product:—volatile acid number, 12·3; 21·5; 48·7; formic acid number, 0·82; 1·85; 3·60. With fish packed in sauce containing acetic acid, the volatile acid number is of little value, but the formic acid number may be used as a reliable index of the condition of the sample.

A. O. J.

Analysis of some North American Indian Food Plants. E. Yanovsky and R. M. Kingsbury. (*J. Assoc. Off. Agr. Chem.*, 1938, **21**, 648–665.)—Analyses of 119 food plants belonging to 66 species and 28 natural orders are recorded. All these plants have been used as food by the aboriginal North American Indians. The methods employed are mainly those described in *Assoc. Off. Agr. Chem., Methods of Analysis* (4th Ed., 1935). Sugars were determined by the Munson and Walker method after preliminary preparation of the sample (*op. cit.*, p. 341). Polarimetric readings taken before and after inversion indicated the nature of the sugars present and served for the detection of inulin, which has a negative rotation changed by inversion to a higher negative value. Differences in the determination of starch by the acid and the diastatic methods were recorded as hemicellulose. For liquorice plants crude glycyrrhizin was determined by extraction with alcohol, precipitation with dilute sulphuric acid after the removal of alcohol, purification by solution in ammonia, and re-precipitation with dilute sulphuric acid. Of the 66 species examined, 6 contained inulin as reserve carbohydrate material. These were the bulbs of *Allium nuttallii* S. Wats; the bulbs of *Quamasia spp.* (Camas bulbs); the roots of *Balsamorhiza spp.*; the tubers of *Helianthus tuberosus* L. (Jerusalem artichoke); the roots of *Leontodon taraxacum* L. (dandelion) and the roots of *Wyethia spp.* Lichenin is present as reserve material in *Alectoria jubata* (L.) Ach. Hackberries (*Celtis occidentalis* L.) have an abnormally high calcium-

content amounting to 25 per cent. by weight (as calcium carbonate) of the dry fruit. Some foods, *e.g.* the nuts of *Aesculus californica* (Spach) Nutt. (Californian buckeye), which are considered poisonous or obnoxious by white peoples, were made into palatable food by the Indians. Samples of *Glycyrrhiza lepidota* Pursh contained from 7·7 to 14·8 per cent. of crude glycyrrhizin (on dry basis), but none had the sweet taste of the officinal plant, *G. glabra* L. The percentage composition of the ash (4·4 per cent.) of *Glycyrrhiza lepidota* is as follows, the figures in brackets being the corresponding figures for *G. glabra* (ash, 6·2 per cent.):—potassium oxide, 12·9 (18·4); phosphoric anhydride, 8·1 (4·0); calcium oxide, 40·2 (22·4); magnesium oxide, 4·9 (7·1); manganic oxide, 0·025 (0·052); iron and aluminium oxides (mainly iron oxide), 6·1 (11·3). A. O. J.

Analysis of the Fruit and Leaves of *Bauhinia reticulata* D.C. The Presence of Large Quantities of *l*-Tartaric Acid. J. Rabaté and A. Gourévitch. (*J. Pharm. Chim.*, 1938, **28**, 386–397.)—The pericarp of the fruit contains 16 per cent. of a balsam extract soluble in acetone, 1·1 per cent. of reducing sugars, 2·7 per cent. of sucrose and 6 per cent. of pectin. The whole fruit contained 1·4 per cent. of free *l*-tartaric acid and 3·9 per cent. of *l*-tartaric acid as acid potassium tartrate (4·9 per cent. of tartrate) and 1·3 per cent. of K_2O; allowing for the solubility of the tartrate in the mother liquors, the quantity of *l*-tartaric acid in the fruit must be about 6 per cent. The dry leaves contained 1·5 per cent. of free *l*-tartaric acid, 3 per cent. of *l*-tartaric acid as potassium tartrate, and 1·4 per cent. as neutral calcium tartrate. The fruit and leaves of *Bauhinia reticulata* D.C. are the only natural source of *l*-tartaric acid and could easily supply considerable quantities of the material (40 to 50 g. per kg. of dry matter). E. M. P.

Malic Acid in Bordeaux Musts and Wines. E. Peynaud. (*Ann. Falsif.*, 1938, **31**, 332–347.)—Hitherto the proportion of malic acid in wine has had to be determined by difference, but a method is now put forward which depends on the manganic oxidation of a molecule of malic acid to acetaldehyde. The distillation apparatus used carries a capillary funnel which allows a dilute (0·01 *N* or 0·005 *N*) solution of potassium permanganate to fall at the rate of 1 drop per second on to the surface of the boiling solution of malic acid; the acetaldehyde is collected in the distillate. The proportion of malic acid present should be small—about 0·05 to 2 mg.-equivalents (1 mg.-equivalent is 67 mg.). The *p*H of the malic acid solution should be adjusted to about 3·2 with a buffer solution (150 g. of potassium dihydrogen phosphate and 5 ml. of syrupy phosphoric acid per litre). Oxidation, which should be slow, is catalysed by the addition of a few mg. of manganese sulphate. Boiling should be brisk and pumice used to prevent bumping. The acetaldehyde is determined either by the method of Jaulmes and Espezel (*Ann. Falsif.*, 1935, **28**, 325; Abst., ANALYST, 1935, **60**, 703), as already applied by the authors to the determination of lactic acid, acetal, etc., or by titration with iodine in alkaline medium. Ethyl alcohol, and probably its esters, lactic acid, glycollic acid, glycerol in acid medium, and certain sugars yielding formaldehyde, may be eliminated by precipitating the malic acid, but at *p*H 3·2 the production of acetaldehyde from substances such as these is almost negligible. Corrections must be made for the production of acetone from citric acid

and a small amount of acetaldehyde from tartaric acid, but with musts and wines such corrections are small. With fruits such as peaches, apricots, etc., containing citric and malic acids, both acids may be determined in one oxidation after precipitation. Half the distillate is used for the determination of aldehyde and acetone. In the other half the aldehyde is oxidised with permanganate (0·5 *N* sulphuric acid, 0·1 *N* potassium permanganate solution) at ordinary temperature, the excess of oxidising agent is reduced after 45 minutes with ferrous sulphate, and the acetone (which has not been affected) is separated by distillation and titrated with iodine in alkaline medium, giving the proportion of citric acid; the difference between the two titration figures, corresponding with the acetaldehyde, gives the malic acid. The malic acid in musts and wines is determined as follows:—Ten ml. of the wine or must are neutralised with ammonia solution, diluted to three times its volume, and treated with 5 ml. of *N* barium chloride solution and 60 ml. of 90 per cent. alcohol saturated with barium malate. The mixture is left in a refrigerator for 2 or 3 hours, and the voluminous precipitate (containing all the tartrate and citrate and part of the succinate) is filtered off and washed with two 25-ml. portions of 72 per cent. alcohol saturated with barium malate. It is then transferred with warm water to a beaker, and the mixture is boiled and treated with 5 ml. of *N* sulphuric acid, which liberates the acids. After cooling, the volume is made up to 100 ml., the liquid is filtered, and 10 ml. of the filtrate are used for the oxidation. The liquid is boiled for a few minutes before the oxidation in order to get rid of traces of alcohol. Errors of experiment for artificial wines, musts and wines to which malic acid had been added in varying quantities did not exceed 2 mg.-equivalents per litre. During the progress from grape to non-sulphited wine the proportion of malic acid gradually diminishes during maturation until the zero point may even be reached, but the actual proportion of malic acid found in various vintages differs considerably. Alcoholic fermentation of various musts at 25° C. for 14 days resulted in a loss of about 10–15 per cent. The proportion of malic acid in some of the chief white Bordeaux wines of the years between 1914 and 1937 varied between 3·30 g. per litre in a 1936 wine from Illats, Graves, and 0·28 g. in a 1933 wine from Plassac Blayais; for red Bordeaux wines, from 0·53 g. per litre in a 1935 wine from Pomerol, St. Emilionnais, to 0·00 in a wine of 1926 from St. Julien, Médoc. D. G. H.

Detection of Horse-fat in Admixture with Lard, Beef-fat or Mutton-fat. B. Paschke. (*Z. Unters. Lebensm.*, 1938, **76**, 476–478.)—The method officially recommended in Germany for the detection of horse-fat in the presence of other fats by means of the refractive index and the iodine value is not reliable. The new method depends upon the presence in horse-fat of 1 to 2 per cent. of linolenic acid and its relative scarcity (0·1 per cent.) in the other animal fats. The procedure is an adaptation of that of Rossmann (*Fette u. Seif.*, 1936, **43**, 224) for the determination of linolenic acid by conversion into its hexabromide. The fat (10 g.) is saponified under reflux (½ hour) with 100 ml. of 0·5 *N* alcoholic potassium hydroxide and, after the removal of alcohol and dilution with water, the soap solution is shaken with about 15 ml. of 5 *N* sulphuric acid, 250 ml. of saturated sodium chloride solution and 50 ml. of ether. The separated ethereal

layer is washed three times with salt solution and filtered. A portion (5 ml.) of the filtrate is cooled to −15° C. in an ice-and-salt mixture simultaneously with 5 ml. of pure ether. Bromine (0·45 ml.) is added from a burette to the cooled pure ether, and this solution is added gradually in five or six portions to the fatty acid solution, the temperature being kept below 0° C. The mixture is allowed to remain in the freezing-mixture for ten minutes, and then left at 5° to 10° C. for 15 to 18 hours. Before filtration of the precipitated hexabromide, the mixture is allowed to stand for a short time in a warm room at 13 to 15° C. in order that any precipitated free fatty acids may be re-dissolved. The precipitate is collected in a weighed filter-tube (Allihn) and washed twice with 3 ml. of ether cooled to −10° C., and it is important that the precipitate should remain covered with liquid during the filtration and washing. The precipitate is dried at 100° C. and, when cold, is again washed at room temperature with 5 ml. of ether. (The hexabromide is less soluble in ether when dry than when freshly precipitated.) Finally the precipitate is dried at 100° C. and weighed. The amounts of hexabromide yielded by 1 g. of fat were:—horse-fat, 41·2 mg.; lard, 2·8 mg.; beef-fat, 3·0 mg.; mutton-fat, 3·3 mg. When mixed with 30 per cent. of horse-fat the other fats yielded (mg. per g.):—lard, 8·2; beef-fat, 10·8; mutton-fat, 11·0.

A. O. J.

Fatty Acids in the Lecithin and Glyceride Fractions of Egg-yolk. R. W. Riemenschneider, N. R. Ellis and H. W. Titus. (*J. Biol. Chem.*, 1938, **126**, 255–263.)—An examination by the usual methods was made of the fatty acids of the lecithin and glycerides of egg-yolk. The findings of previous workers were substantially confirmed, except that the evidence indicated the presence of clupanodonic acid rather than of arachidonic acid, and that no evidence was obtained of the presence of isopalmitic and margaric acids. The following table shows the composition of the lecithin and glyceride fatty acids:

	Lecithin fatty acids		Glyceride fatty acids	
Acid	Per cent. by weight	Molecular per cent.	Per cent. by weight	Molecular per cent.
Myristic	—	—	0·7	0·8
Palmitic	31·8	34·6	25·2	27·0
Stearic..	4·1	4·0	7·5	7·3
Palmitoleic	—	—	3·3	3·6
Oleic	42·6	42·0	52·4	51·0
Linolic..	8·2	8·2	8·6	8·4
Clupanodonic ..	13·3	11·2	2·3	1·9
Total saturated ..	35·9	38·6	33·4	35·1
,, unsaturated ..	64·1	61·4	66·6	64·9

F. A. R.

Composition of the Wax-like Substance Extracted from the Coffee Berry. Part II. H. Wagner. (*Z. Unters. Lebensm.*, 1938, **76**, 449–475.)—In continuation of the previous work (*Z. Unters. Lebensm.*, 1938, **76**, 1; Abst., ANALYST, 1938, **63**, 667), other methods for the separation of the constituent fatty acids of this substance have been investigated. Meyer and Eckert have reported the possibility of separating the individual acids by differences in the solubilities

of their methyl esters. The petroleum spirit extract of the wax was saponified with lithium hydroxide and the mixed acids obtained by decomposition of the lithium salts were converted into their methyl esters. These esters were separated into fractions according to their solubilities in methyl alcohol, and the fatty acids obtained from them by saponification were purified by recrystallisation from glacial acetic acid and other solvents. Further separations of these acids were effected by precipitation with lithium acetate or conversion into their lead salts. Fractions of approximately equal m.p. were united and further separations were made by similar methods. By another method the petroleum spirit extract of the wax was esterified directly by heating with methyl alcohol and sulphuric acid under reflux and the esters were subsequently extracted with ether. The purified esters were fractionally distilled *in vacuo*. By a third method the original wax was saponified with alcoholic potassium hydroxide solution in the presence of toluene. The fatty acids obtained by decomposition of the soap were converted into their methyl esters which were fractionally distilled *in vacuo*. The various fractions of mixed fatty acids obtained by these methods were investigated. According to Meyer and Eckert the solid fatty acids contain capric, daturic, palmitic and carnaubic acids; according to Heiduschka and Kuhn (*J. prakt. Chem.*, 1934, **139**, 270), capric, palmitic, stearic and carnaubic acids, and according to Bengen and Anderson (*J. Biol. Chem.*, 1932, **97**, 99; Abst., ANALYST, 1932, **57**, 579) palmitic, stearic and carnaubic (but not capric) acids. By investigation of the behaviour of capric acid and its salts in the presence of other acids, a method was devised whereby capric acid, if present in the mixture of fatty acids, could be detected. Capric acid was not detected in any of the appropriate fractions. From certain of the fractions of the esters separated by distillation *in vacuo* a fatty acid fraction was finally obtained which corresponded with the "daturic acid" of Meyer and Eckert, and which could not be separated further by precipitation with lithium acetate. Although this fraction simulated a single substance it was proved to be a mixture separable by fractional precipitation with magnesium acetate into palmitic acid and an acid of higher molecular weight. By fractional precipitation of mixed acid fractions of m.p. above 60° C. in the form of their lithium salts, pure palmitic acid was isolated and identified. Methods designed to isolate stearic acid, if present, were not successful, but evidence was obtained of the presence of an acid of approximate molecular weight 310 to 314 which resembled arachidic acid. A. O. J.

Extractives and Mineral Matter in Chicory. L. Hoton. (*J. Pharm. Belg.*, 1938, **40**, 760–762; 777–780.)—An extensive investigation has been carried out to determine if any modification is advisable of the limits fixed in Belgium for mineral matter (maximum 10 per cent.) and hot-water-soluble extractives (minimum 50 per cent.) of chicory, *Cichorium intybus*. Before limits can be fixed for chicory as sold, the composition and variations in the original root and the industrial processes concerned in the preparation must be taken into account. The fresh root contains about 75 per cent. of water, and in the drying process loses about 75 per cent. in weight; in the roasting process the dried product loses about 25 per cent. in weight. Published figures for the ash of roasted chicory vary from

3 to 5 per cent., averaging about 4·5 per cent., which means about 1 per cent. on the original root. Washing and drying of the root does not remove every particle of adherent soil. A classification of the cut root according to size with the proportion of mineral ash commonly found in each (*Rapport du Syndicat français des Fabricants de Chicorée*) is as follows:—Cossettes, "grosses" 50–52 per cent. of the roots, with ash 7–8 per cent.; "moyennes," 10–15 per cent., ash 7–8; "fines," 25–30 per cent., ash 7–9. The remainder, called "touraillons," is further classified according to size—"gros," 2–3 per cent., ash 8–10 per cent.; "moyens," 1–2 per cent., ash 10–12 per cent.; "fins," 1 per cent., ash 15–25 per cent., "pellicules," 1–2·5 per cent., ash 35–45 per cent. Normal industrial cossettes, however, never have an ash over 6 per cent., nor the next grade, over 7 per cent. Much of the extraneous mineral matter from the soil will be separated during drying and roasting, and sieving or winnowing will remove it. From a study of factory conditions 8 per cent. of ash is regarded as a maximum, and there should be no difficulty in keeping below it. In the manufacture of chicory extract in the form of powder most of any extraneous mineral matter will pass into the powder, but if all the adherent soil is previously removed the ash of the powder will not exceed that of the original root. An actual experiment gave the following percentages of ash; cossettes, 4·8; "grosse semoule," 4·3; "moyenne semoule," 4·4; "petite semoule," 4·5; powder, 5·6 per cent. The proportion of extract in hot water is at present fixed in Belgium at a minimum of 50 per cent., but this is regarded as too low, since the roasting, which raises the proportion of soluble matter, can easily be adjusted to give a product with 60 per cent. of soluble matter. Ordinarily, chicory sold in Belgium is not allowed to contain more than 15 per cent. of water.

D. G. H.

Determination of Cocaine in Coca Leaves. A. W. K. de Jong. (*Rec. Trav. Chim. Pays-Bas*, 1938, **57**, 1218–1222.)—A method of extracting cocaine from its 0·1 *N* hydrochloric acid solution is suggested, which differs somewhat from that published in the *Bulletin of the Health Organisation of the League of Nations* (*cf.* ANALYST, 1938, **63**, 828). Instead of neutralising the 45 ml. of the acid solution with 1 g. of sodium bicarbonate and then shaking three times with 30 ml. of a mixture of 2 parts of ether and 1 part of light petroleum, it is proposed to neutralise the solution with 5·5 ml. of *N* sodium carbonate solution and extract three times with 30 ml. of ether. This makes the extraction more rapid and avoids the use of the mixed solvent. On adding sodium bicarbonate to a solution of cocaine hydrochloride, no precipitate is formed, for the cocaine remains in solution as its bicarbonate. Such a solution tends to lose carbon dioxide, with the formation of free cocaine. Extraction of such a solution with ether disturbs the equilibrium and leads to more or less complete dissociation of the bicarbonate. By adding sufficient sodium carbonate, however, the free bases are at once liberated and can thus be extracted much more rapidly and completely than by the use of bicarbonate. Unfortunately, other bases such as hygrines and amino-acid esters are also extracted under these conditions, which leads to high results. Correct results can be obtained by re-dissolving the bases in hydrochloric acid and again neutralising and extracting with ether. To avoid the necessity for this re-treatment or, alternatively, the

application of a correction, an amount of sodium carbonate has been deliberately chosen "by which a quantity of bases is obtained equal to that of the cocaine." This condition is satisfied by adding 5·5 ml. of *N* sodium carbonate solution to the 45 ml. of cocaine solution. F. A. R.

Semen Strychni. **E. Le Coultre and P. Van der Wielen.** (*Pharm. Weekblad,* 1938, **75**, 1329–1332.)—The dimensions specified for *Semen Strychni* (Nux vomica) by Pharmacopoeias representing 17 nations and by other authorities, are compared. The diameter is usually given as 2·0 to 2·5 cm., but figures of 1·0, 1·5 and 3·0 occur in some instances. The value for the minimum thickness is usually 0·3 cm. and the maximum 0·5 cm., but in some specifications dimensions up to 0·5 cm. and approximately 0·5 cm. are specified, whilst one Pharmacopoeia (Austria, 1906) does not specify any value at all. Tschirch (*Handbuch der Pharmakognosie,* 1923, Vol. III, p. 450) states that the diameters vary according to the origin of the seeds; thus, values for Bombay seeds range from 2·0 to 2·2; Cochin, 1·9 to 2·8; Madras, 1·2 to 2·1; Ceylon, 1·3 to 2·5; Malabar, up to 3·4 cm. (thickness, 5 to 6 mm.). Data are given for a large number of commercial samples of the seeds, which were divided according to size into large, medium and small grades. The respective average diameters were 2·20, 1·80 and 1·52; weight, 1·731, 1·181 and 0·820 g.; fat-content, 5·62, 6·27 and 6·6 per cent.; alkaloid-content (determined by the method of the Dutch Pharmacopoeia, 5th Ed.), 2·62, 2·82 and 2·88 per cent.; brucine and strychnine in the alkaloids (determined by the method of the Dutch Pharmacopoeia Commentary, Pt. IV, p. 129), 0·86, 0·91 and 1·02 per cent. (all percentages being calculated on the dry substance). These last figures are lower than those given in the Dutch Pharmacopoeia, although, according to the literature, the strychnine-content may fall within the range 0·54 and 1·54 per cent. Only the U.S., British and Brazilian Pharmacopoeias specify minimum strychnine-contents (1·15, 1·2 and 1·25 per cent., respectively), but no mention is made of brucine, which is associated with strychnine, but is much less toxic. A minimum strychnine-content of 1 per cent. is to be expected. J. G.

Senecio vulgaris **(and its Pharmacological Properties). J. Van der Meer.** (*Pharm. Weekblad,* 1938, **75**, 1169–1177.)—Although *Senecio vulgaris* (common groundsel) has recently been introduced for treating uterine troubles, the nature of the active principle responsible for its effects is not known. Existing work comparing the nature and effects of the alkaloids present in the different varieties of *Senecio* is summarised. In the months of April and September the only alkaloid found in *S. vulgaris* is senecionine, $C_{18}H_{25}O_5N$, although other alkaloids are present during the summer months. Varieties of *Senecio* found around London (*viz. S. vulgaris* and *S. jacobaeae*) are not toxic, but these same varieties from New Zealand and S. Africa have been known to cause wasting, sickness, gastric haemorrhage, diarrhoea, cirrhosis of the liver, and even death when eaten by cattle. *S. jacobaeae* contains the alkaloid jacobine, $C_{18}H_{23}O_5N$. *S. latifolius* contains the alkaloids senecifoline, $C_{18}H_{27}O_8N$, and senecifolidine, $C_{18}H_{25}O_7N$, and in small quantities it produces haemorrhagic effects, especially on the liver; larger quantities affect the central nervous system. *S. silvaticus* (which contains the alkaloid silvasenecine, $C_{12}H_{21}O_4N$) acts similarly, whilst *S. illicifolius* and

S. burchelli have found their way into bread for human consumption, and have then caused diarrhoea and vomiting with loss of blood, and emaciation. The pharmacological experiments were carried out by comparing the effects of extracts and decoctions of powdered *Radix Senecionis vulgaris* on the horn of an isolated uterus weighing 250 to 300 g. with that of a standard preparation of histamine; the Storm van Leeuwen technique was used. Subsequently a standardised extract of *S. vulgaris* was used to check the histamine, and so to eliminate any change in its activity. Approximately 2 ml. of an extract in water was equivalent in its effect to 1 ml. of a 0·002 per cent. solution of the histamine; the small quantity of nipagin used as a preservative was shown to have no influence on the results. A decoction in water was less effective than the extract. Although alcohol inhibits the test, its effect is negligible compared with the reverse effect exerted by alcoholic extracts of *S. vulgaris*. Thus an extract in 30 per cent. alcohol was 25 per cent. more effective than the extract in water, the extracts in 70 and 90 per cent. alcohol being both approximately 100 times more effective than the 30 per cent. extract. An extract of *Radix S. jacobaeae* in 70 per cent. alcohol was more effective than a similar extract of *Radix S. vulgaris*; extracts of *Herba S. jacobaeae* and *Radix S. jacobaeae* were similar in effect; *Herba S. vulgaris* was much weaker in its action. The action on the heart of a frog was then tested; the aqueous extract acted powerfully, the extract in 70 per cent. alcohol being much weaker. Attempts were made to isolate the constituent responsible for the action on the uterus. The extract in 70 per cent. alcohol was acidified with hydrochloric acid, diluted with an equal volume of water, evaporated to its original volume (to remove the alcohol) and filtered. The residue from the filtration was washed with acidified water, which left a green mass, consisting mainly of the hydrochlorides of the alkaloids. It was made alkaline with ammonia and extracted with chloroform (until Bouchardat's reagent gave a negative reaction for alkaloids in the aqueous layer), and the chloroform was removed by evaporation. Although a solution in alcohol of the green mass gave an active uterus test equivalent in activity to that of the original extract, the solution remaining after extraction with chloroform and a solution of the alkaloid hydrochlorides in water were inactive. The green mass had a characteristic odour which was removed by steam-distillation, and the resulting distillate gave an active uterus test. The distillate was salted-out and extracted with ether, and the extract on evaporation left a white solid which was inert towards the uterus, although the residue of the green mass was active. Solutions of the green mass in various alkalis were also tested, but gave negative results; this may have been due to the inhibiting action of the alkali. Solutions prepared from other organic solvents, or by heating, were also inactive. When the solution of the green mass in alcohol was decolorised with activated carbon it yielded a liquid which, on evaporation, proved very active; treatment with silica gel or diatomaceous earth was less effective. Dilution with water produced a precipitate; this was extracted with ether, the extract was dried with anhydrous sodium sulphate, and the residue left on evaporation was dissolved in alcohol; the solution was very active. The solution remaining from the extraction with ether was extracted with chloroform, and a solution of the residue left on evaporation of the solvent was found to be inactive, as was also the aqueous solution remaining

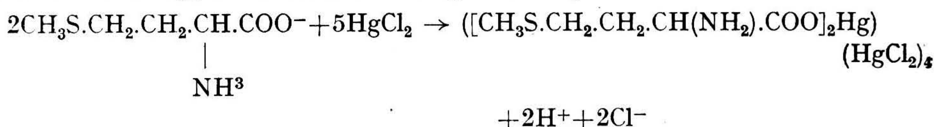
after extraction with chloroform. When a solution of the green mass in alcohol was diluted with water and extracted with ether, the extract was more easily decolorised than the original solution and, when dried and evaporated under reduced pressure, yielded a colourless viscous liquid. A similar product was obtained by extracting the original *Radix Senecionis vulgaris* with 70 per cent. alcohol, and then extracting the diluted and acidified extract with petroleum spirit. This new extract, when decolorised and evaporated, yielded 2·3 g. of a viscous pale yellow liquid (n_D^{20} 1·4830, setting p. 11° C.) from 5 kg. of the original preparation. It had a characteristic odour, was insoluble in water and most organic solvents, and contained 79·09 per cent. of carbon and 11·37 per cent. of hydrogen. Nitrogen, halogens, sulphur and phosphorus were absent, but tests for unsaturated carbon linkages and aromatic aldehyde groups were positive. The pharmacological strength was more than double that of histamine. J. G.

Biochemical

Study of Sulphaemoglobin. H. O. Michel. (*J. Biol. Chem.*, 1938, **126**, 323–348.)—Sulphaemoglobin, with an absorption band at 620$m\mu$, is formed by treating a solution of haemoglobin with sodium hydrosulphite solution, adding a drop of ammonium sulphide solution, and then a drop of hydrogen peroxide solution. Sodium perborate, or any other substance yielding hydrogen peroxide in water, can be used instead of hydrogen peroxide. Other oxidising agents, such as potassium ferricyanide, potassium chlorate, potassium permanganate or bromine, fail to produce sulphaemoglobin. In the same way sulphide sulphur is essential for the formation of sulphaemoglobin, other forms of sulphur, such as thiourea, cystine, thiosulphate, sulphite or elementary sulphur, being without action. The solubility, resistance to alkali, molecular weight and cataphoretic mobility of sulphaemoglobin are not appreciably different from those of haemoglobin. It can be prepared from artificial haemoglobins containing porphyrins other than protoporphyrin, so that the latter possesses no special structure essential to its formation. One atom of sulphur for each atom of iron present is necessary in the conversion of haemoglobin into sulphaemoglobin, and the latter contains one atom of sulphur easily oxidisable by bromine to sulphate; this sulphur is not present as a free sulphydryl group. Sulphaemoglobin combines with carbon monoxide, one molecule of the latter being bound for each atom of iron present. Reduced sulphaemoglobin is very stable, but the oxidised form is unstable. A sulphaemoglobin can also be prepared from muscle haemoglobin; this has a greater specific absorption than blood sulphaemoglobin and is more stable; it also forms a carbon monoxide compound.

It is suggested that the condition of sulphaemoglobinaemia depends on the formation of hydrogen sulphide in the organism together with the administration of acetanilide or related derivatives. Although *in vitro* neither acetanilide nor aniline is capable of catalysing the formation of sulphaemoglobin from oxyhaemoglobin and sulphide, *p*-aminophenol, which has been shown to be formed from acetanilide in tissues, can do this. It is readily autoxidisable to a quinone form, with the formation of hydrogen peroxide; this is probably the active agent in producing sulphaemoglobin. F. A. R.

Reaction of Methionine and other Amino Acids with Mercuric Chloride. G. Toennies and J. J. Kolb. (*J. Biol. Chem.*, 1938, **126**, 367–379.)—The factors governing the precipitation of methionine with mercuric chloride were studied. The substances appear to react according to the equation:



$$2CH_3S.CH_2.CH_2.\underset{\displaystyle NH^3}{\underset{|}{CH}}.COO^- + 5HgCl_2 \rightarrow ([CH_3S.CH_2.CH_2.CH(NH_2).COO]_2Hg)(HgCl_2)_4 + 2H^+ + 2Cl^-$$

free acid being formed corresponding to one equivalent per molecule of methionine. Complete precipitation was favoured by neutrality, by the absence of chloride ion, by the removal with mercuric acetate of free chloride ion formed in the reaction, and by the presence of alcohol. Basic amino-acids, which form precipitates with mercuric chloride, and acid amino-acids, which form precipitates with the mercury ion of mercuric acetate, interfere with the precipitation of methionine. Neutral amino-acids do not interfere by precipitate formation, but they react with mercuric chloride to form soluble compounds, probably thus:

$$R(NH_3^+)COO^- + HgCl_2 \rightarrow R(NH_2)COOHgCl + H^+ + Cl^-$$

Consequently an excess of mercuric chloride must be added to compensate for that required by this reaction, and also mercuric acetate and alkali to remove the chloride ion. F. A. R.

Occurrence of Nicotinic Acid in Ox-liver. D. Ackermann and H. G. Fuchs. (*Z. physiol. Chem.*, 1938, **256**, 90–94.)—The presence of nicotinic acid in liver, reported by previous workers, has been confirmed by the isolation of the acid in a quantity (0·85 g. from 69 kg. of liver) adequate for a detailed examination to be made. Analyses of the free acid and of its flavianate gave figures in close agreement with the theoretical values. Moreover, the acid had the same m.p. and crystalline form, and gave the same characteristic colour reactions as nicotinic acid. It gave no depression in m.p. with an authentic specimen. The method employed in isolating the acid did not involve any stages sufficiently drastic to have hydrolysed any nicotinamide present, and it therefore seems unlikely that the acid was derived from amide. Neither trigonellin nor betaine could be detected in the appropriate liver fractions, and it seems equally unlikely that either of these could be the precursor of nicotinic acid. It is concluded that the acid is derived from the food, and is stored as such in the liver. F. A. R.

Antirachitic Provitamin from Wheat-germ Oil. A. Windaus and F. Bock. *Z. physiol. Chem.*, 1938, **256**, 47–48.)—The provitamin D content of wheat-germ oil sterols was increased from 1·2 to 85 to 90 per cent. by repeated chromatographic adsorption on alumina and elution. The provitamin was identified as ergosterol by a mixed m.p. determination and analysis of its acetate and 3:5-dinitrobenzoate, and by the mixed m.p. of the following derivatives with the respective authentic specimens:—α-dihydroergosterol and its acetate, α-ergostenol and its acetate, ergopinacone and its acetate. The irradiated provitamin possessed the biological activity of irradiated ergosterol and not of irradiated 7-dehydro-sitosterol or 7-dehydrostigmasterol. F. A. R.

New Vitamin D in Cod-liver Oil. C. E. Bills, O. N. Massengale, K. C. D. Hickman, and E. Le B. Gray. (*J. Biol. Chem.*, 1938, **126**, 241–244.)—The most volatile antirachitically-active fraction of cod-liver oil, prepared by molecular distillation, was assayed for vitamin D on both rats and chickens. Rat unit for rat unit, this fraction was only one-half to one-quarter as effective for chickens as the total vitamin D of cod-liver oil. This evidence supports the hypothesis formulated to explain the results obtained by molecular distillation, *viz.* that several vitamins D exist in cod-liver oil. F. A. R.

Toxicological and Forensic

Action of Nicotine on the Human Organism. W. Brandt. (*Chem.-Ztg.*, 1938, **62**, 851–852.)—The fatal dose of nicotine is not known with certainty, but 2 to 3 drops (30 to 60 mg.) of the pure alkaloid will cause death to man, whilst if a glass rod is dipped in nicotine and held under the beak of a bird, death will result in a few seconds. The tolerance of a moderate but habitual smoker towards nicotine in the form of vapour is 16 to 20 mg. per hour. Although 5 g. of tobacco (*i.e.* one average cigar or 5 cigarettes) contain about 60 mg. of nicotine, only about 10 and 40 per cent. of this, respectively, are evolved with the smoke, and only 20 per cent. of this fraction finds its way into the system, except perhaps when the smoke is inhaled, when the percentage may rise to 80. The actual amount of nicotine entering the system will vary considerably with the method of smoking and the type of tobacco (*e.g.* from 1·2 to 19 mg. from 5 g. of the original tobacco), but a normal figure appears to be 8 mg. or less per hour, and apparently this produces no manifest symptoms of nicotine poisoning. Such symptoms include an increase in blood-pressure, catarrh of the throat and larynx, heart and eye troubles and possibly, gastric ulcers and diuresis. Thus the urine excreted by a female occasional smoker in 3 hours was increased from 340 to 975 ml. as the result of smoking one cigarette 30 minutes before the first sample was taken, whilst a male habitual smoker was unaffected under similar conditions. From the point of view of effects on the human organism, nicotine is the most important constituent of tobacco. Cigars and cigarettes are roughly equivalent in this respect, because inhalation is more customary with cigarettes and they are smoked in larger numbers. Cigars can contain up to 3·5 per cent. of nicotine, cigarette tobacco contains on an average 1 to 2 per cent., and "low-nicotine" brands of cigars 0·6 to 1·0 per cent. The saliva and other body fluids that come into contact with tobacco smoke cause the suspended particles to be deposited, so that the nicotine is more easily carried into the system. An irritant effect on the mucous membrane also results, although this is not attributed to the nicotine present. Attempts to remove nicotine from tobacco smoke (*e.g.* by means of wads of cotton wool or of tannin or silica gel filters in the end of the cigarette) or to remove it from (*e.g.* by extraction) or fix it in the tobacco beforehand have not proved entirely satisfactory, either because the reduction in nicotine-content is insignificant, or because the flavour and aroma of the tobacco are affected. More promising results may be expected from experiments which are being carried out on the breeding of strains of tobacco plant which have low nicotine contents (*cf. ibid.*, 1938, **62**, 841;

and Wenusch, *Z. Unters. Lebensm.*, 1934, **68**, 412; 1937, **74**, 492, 497; *cf.* ANALYST, 1927, **52**, 728; 1929, **54**, 164; 1931, **56**, 753; 1932, **57**, 181, 727; 1933, **58**, 44, 165, 625; 1935, **60**, 260, 829). J. G.

Technique for the Determination of Alcohol in Blood. Anon. (*Chem.-Ztg.*, 1938, **62**, 852.)—In the determination of alcohol in blood by Widmark's method (*cf. Biochem. Z.*, 1922, 407, 473; "*Pharmakol. Beiträge z. Alcoholfrage,*" Pharmakol. Inst., Jena, 1938, Vol. 8) the potassium dichromate solution used should not only be stored in the dark, but also prepared and used in the dark. The distillation flask should be filled in a darkened room, and the titration should be carried out with only the titration flask illuminated, the daylight lamp of the Pulfrich photometer being suitable for this purpose. The temperature should be controlled by means of a thermostat, and not by a water-bath as suggested, and it should not exceed 50° C., as the titre of the potassium dichromate solution then varies considerably. Details of technique for the transference of the sample to the distillation-flask are also given; the outlet of the apparatus should be carefully cleaned with a mixture of potassium dichromate and conc. sulphuric acid and thoroughly washed, and the formation of bubbles should be avoided. When a series of determinations is being made the titrations should be carried out, so far as possible, in rapid succession, and each titration should take less than 1 minute. The potassium iodide solution should be colourless (as a yellow colour indicates the presence of free iodine), and the determinations should be made only by practised workers. Maximum, minimum and average "fasting values" recorded for the alcohol-content of blood are 0·05074, 0·0029 and 0·0286 parts per thousand, respectively. J. G.

Identification of Traces of Alcohol. Determination of Alcohol in Urine. J. M. Hambersin. (*J. Pharm. Belg.*, 1938, **20**, 741–746.)—The iodoform and oxidation methods for the determination of alcohol are not specific, particularly when blood or urine is being examined. A modification of Rosenthaler's method (*Chem.-Ztg.*, 1912, **36**, 830; *Z. anal. Chem.*, 1914, p. 196; Abst., ANALYST, 1912, **37**, 407) is preferred because, although it determines all primary alcohols, the colour obtained from methyl alcohol is negligible in intensity, and it is unlikely that alcohols containing more than 3 carbon atoms will be found in urine. Four ml. of a solution of 1 g. of sulphanilic acid in a mixture of 150 ml. of water and 50 ml. of 0·2 *N* hydrochloric acid, are mixed with 1 ml. of a 0·7 per cent. aqueous solution of sodium nitrite. One ml. of a 0·5 *N* solution of sodium hydroxide and then 1 ml. of the sample are added and the mixture is warmed; in the presence of alcohol a blood-red colour develops. The alcohol is oxidised by the diazo-compound, which reacts with the aldehyde so formed to produce the red compound, the chemical nature of which is not known. The colour is matched against standards prepared from solutions containing known amounts of alcohol, allowance being made for a blank determination. As the colour is unstable it must be developed simultaneously in the standards and sample. If urine is to be examined, 100 ml. are distilled in a small flask having a side-tube; the first 10 ml. of distillate are collected, and 1 ml. of this is treated as described above. Experiments have shown that distillation is essential in order to avoid errors due to the colour of

the urine or to interference by other substances present in it; and that urine free from alcohol then gives negative results. In test experiments in which known quantities of alcohol were added to urine it was found that with concentrations ranging from 0·8 to 0·008 g. per 100 ml., the whole of the alcohol was obtained in the first 10 ml. of the distillate, and that the method was sensitive to 8 mg. of alcohol per 100 ml. of urine. Curves show the relationship between the amount of alcohol found in the urine and the time that elapses after consuming 10 to 75 ml. of 94 per cent. alcohol. It is concluded that the alcohol-content of the blood or urine is unreliable by itself as an indication of drunkenness; factors such as the age and physical condition of the subject and the concentration of the alcohol absorbed must also be taken into account. J. G.

Bacteriological

Essentiality of Gallium to the Growth and Reproduction of *Aspergillus niger*. R. A. Steinburg. (*J. Agric. Res.*, 1938, **57**, 569–74.)—The effect of traces of gallium on the growth of *Aspergillus niger* has been investigated, special precautions being taken to prevent contamination with other elements. Transparent quartz vessels were used, and the distilled water for the culture medium was distilled successively in an Acree metal still, a Pyrex glass still and a transparent quartz still. The sucrose, which contained only 0·0014 per cent. of ash, was purified by extraction with 95 per cent. alcohol for 6 hours, and the chemicals used were spectroscopically pure. The fungus was grown on 5 per cent. sugar solution to which all necessary salts had been added in approximately optimum concentrations. Each litre contained the following ingredients: sucrose 50 g. ammonium sulphate 3·4 g., potassium dihydrogen phosphate 0·55 g., magnesium 0·025 g., iron 0·2 mg., zinc 0·2 mg., copper 0·05 mg., manganese 0·025 mg., and molybdenum 0·02 mg. Inoculation was made with a spore suspension and, after incubation at 37° C. for 4 days, the mycelial felts were filtered off on 1G3 Jena glass filters, dried overnight at 103° C. and weighed. The experimental results are given in tables. Experiment 1 showed a maximum yield of 847·1 mg. under conditions apparently optimum, whereas with unextracted sugar and reagent chemicals the yield was usually approximately 1150 mg. Tests with the salts of 77 elements led to the selection of gallium as the element capable of eliminating the decrease in yield most effectively, the addition of only 0·02 mg. of this element per litre resulting in a weight of 1123 mg., or almost maximum yield. The tables also record the effect of omitting the elements iron, zinc, copper, manganese and molybdenum. The omission of zinc and manganese had the most pronounced effect, the omission of copper had a medium effect, and that of iron or molybdenum only a slight effect. The conclusion is drawn that, in addition to iron, zinc, copper, manganese and molybdenum, the element gallium at concentrations of 0·01 to 0·02 mg per litre is essential to the growth and reproduction of *Aspergillus niger* in the medium described above. D. R. W.

Light as a Factor in the Production of Pigment by Certain Bacteria. J. A. Baker. (*J. Bacteriology*, 1938, **35**, 625–31; *Bull. Hyg.*, 1938, **11**, 907.)—In order to encourage pigment production it is customary to incubate the culture

in the usual way and then to leave it on the bench exposed to diffused daylight. The author has studied the conditions governing the effect of light on the production of pigment, observations being made on an acid-fast saprophytic bacillus producing a pink pigment. He exposed fully-developed cultures to various types of light for different periods and then kept them in the dark and noted the pigment production. He found that exposure of the cultures to sunlight for 15 minutes, to a 100 watt Mazda incandescent lamp at 2 feet distance for 30 minutes, and to a mercury vapour lamp at 3 inches distance for 1 minute caused them to develop maximum pigmentation within 48 hours; the best results were obtained when the cultures were exposed at 37° C. and afterwards kept at 24° to 37° C. He concludes that the production of pigment is a metabolic phenomenon, for cultures killed by exposure at 60° C. for 30 minutes develop no pigment, nor do cultures exposed to light so long as to be killed, and exposure of an alcoholic extract of the unpigmented culture (the pigment in his experiments being readily soluble in alcohol) to light did not lead to pigment formation. D. R. W.

Organic

Simplified Procedure for Analytical Oxime Formation with Aldehydes and Ketones. S. Sabetay. (*Bull. Soc. Chim.*, 1938, **5**, 1419–1422.)—For use in the analysis of perfume ingredients, when an accuracy of 95 per cent. is sufficient, the author recommends the following methods, in each of which use is made of a reagent prepared by dissolving 50 g. of hydroxylamine hydrochloride in 90 ml. of hot water, adding 20 ml. of bromophenol blue solution and making up to a litre with 90 per cent. alcohol. The indicator is prepared by grinding 0·1 g. of bromophenol blue with 3 ml. of $N/20$ sodium hydroxide solution and making up to 25 ml. with water; methyl orange may be used instead of bromophenol blue. In each titration the colour should be compared with that of a standard containing one or two drops of $N/2$ potassium hydroxide solution. (*Cf.* S.P.A. Method, ANALYST, 1932, **57**, 773; 1934, **59**, 105).

Carbonyl compounds that combine with hydroxylamine hydrochloride in the cold.—Exactly 1 g. of fine calcium carbonate, 0·5 to 5 g. of the carbonyl compound or essential oil, and 25 ml. of the reagent are allowed to stand in the cold for 1 to 3 hours, with occasional shaking, in a 150-ml. flask. A control is similarly treated. To each is added 25 ml. of N hydrochloric acid, and the liquids are titrated, immediately after the decomposition of the calcium carbonate, with $N/2$ potassium hydroxide solution, a standard indicator colour being used for comparison. The results are calculated from the formula: Percentage of aldehyde = molecular weight × (ml. of KOH for sample − ml. of KOH for control) / (20 × weight taken). The initial acidity can be neglected.

Carbonyl compounds that form oximes with difficulty in the cold.—With compounds such as pulegone and camphor, oxime formation in the cold gives low values, and the reaction must be effected by heating on a boiling water-bath for 1 hour, in the presence of calcium carbonate, by the method of Vandoni and Desseigne (*Bull. Soc. Chim.*, 1935, **2**, 1685; Abst., ANALYST, 1935, **60**, 776); a control must be used. After cooling, 25 ml. of hydrochloric acid are added, and the titration is carried out as for compounds which react in the cold.

E. M. P.

Inorganic

Electrolytic Determination of Antimony. S. L. Jovanovitch. (*Z. anal. Chem.*, 1938, **114**, 415–425.)—Antimony can be deposited from its solution in strong (*e.g.* 1:1) sulphuric acid, as shown by Sand (ANALYST, 1908, **33**, 411). In more dilute acid precipitation occurs owing to hydrolysis of the normal sulphate, but it has now been found that this does not prevent quantitative deposition of the antimony under suitable conditions. The metal sample (*e.g.* 1 g. or less) is dissolved in 12 ml. of hot conc. sulphuric acid. The cooled mass is dissolved in a little water, and gradually diluted to 150 ml. The suspension of the precipitate formed by hydrolysis of the normal sulphate is warmed to 85° to 90° C., agitated mechanically, and electrolysed at 2·4 volt with a current of 3 amp. In about 20 minutes the precipitate dissolves, and the voltage is then reduced to 2·2, the current decreasing to 0·3 amp. The precipitation is complete at this stage, but the electrolysis is continued for another 30 minutes, the total time taken varying from 60 to 75 minutes. The light grey deposit is washed twice with water and once with alcohol during brisk agitation, dried at 80° to 90° C. for 10 minutes, and weighed. Tartaric acid, even in excess of that present in tartar emetic, was found not to interfere with the deposition. Antimony sulphide obtained by the usual methods is boiled with sulphuric acid, and the resultant solution is electrolysed; native antimony sulphide can be treated in the same manner. The results by this method were found to give an average negative error of 0·1 per cent. of the amount of metal present. W. R. S.

Determination of Arsenic, Antimony and Tin in Alloys. J. A. Scherrer. (*U.S. Bureau of Standards J. of Research*, 1938, **21**, 95–104.)—*Lead base alloys* are dissolved in nitric acid with addition of hydrofluoric acid to obtain complete solution, and the lead is precipitated as sulphate. The filtrate is freed from hydrofluoric and nitric acids by evaporation with sulphuric acid. *Tin-antimony alloys* are attacked with nitric acid, which is displaced by sulphuric acid. *Copper-base alloys* are attacked with nitric acid, the precipitate of stannic and antimonic oxides being collected and dissolved in sulphuric acid. In every instance the sulphuric acid is diluted somewhat, hydrochloric acid is added, and the solution is transferred to a special all-glass distilling apparatus provided with a thermometer well and connected with a carbon dioxide supply. Arsenic, antimony and tin are separated by fractional distillation and caught in separate receivers, the distillates being titrated. The paper is too detailed for abstraction, and should be consulted for working details. W. R. S.

Separation of Cobalt and Nickel from Manganese. E. A. Ostroumov and G. S. Maslennikova. (*Zav. Lab.*, 1938, **7**, 267–269.)—*Method.*—A neutral solution (about 200 ml.) of the chlorides of these metals is treated with pyridine hydrochloride (prepared by diluting 5 ml. of hydrochloric acid, sp.gr. 1·19, with 20 to 25 ml. of water and neutralising with pyridine, methyl red being used as indicator). The solution is heated to boiling, 5 to 10 ml. of 20 per cent. pyridine solution are added, and hydrogen sulphide is passed in for 10 to 15 minutes, with shaking. The cobalt and nickel sulphides are filtered off and washed with hydrogen

sulphide water containing a few drops of pyridine. Manganese is precipitated from the filtrate as manganese ammonium phosphate and determined as the pyrophosphate. Tests with solutions containing known amounts of manganese and either cobalt or nickel indicated that the separation was complete. In solutions containing known weights of the three metals, determination of manganese by a colorimetric method in the precipitate of mixed nickel and cobalt sulphides showed none, or only faint traces. The method can be used with very various products, *e.g.* metals, ores, and various catalysts used industrially.

Remarks.—The flask in which the sulphides are precipitated must be cleaned with chromic acid before use, to prevent adherence of the precipitate to the sides. If the solution analysed is originally acid, it is neutralised with soda until turbidity appears and this is just removed by adding a few drops of hydrochloric acid. The filtrate after the removal of the analytical sub-group IIIA from IIIB may be used for the separation (*cf.* Ostroumov, Abst., ANALYST, **1936**, **61**, **723**, **795**; **1937**, **62**, **495**; **1938**, **214**). If the volume is not too great the separation may be made after adding the pyridine salt and heating. Duplicate analyses of the mineral "asbolan" were in satisfactory agreement. The presence of pyridine in the solution of manganese chloride facilitates precipitation of the manganese ammonium phosphate. E. B. D.

Determination of Iron in the Presence of Titanium by the Jones Reductor Method. E. Truog and R. W. Pearson. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 631–632.)—In agreement with results of previous workers it was found that the interference by titanium in the oxidimetric titration method for iron involving the use of amalgamated zinc for reduction can easily be eliminated by aeration immediately after reduction in order to re-oxidise the titanium selectively. This selective oxidation by aeration after passage of the solution through the Jones reductor is now found to be better effected by adding distilled water containing dissolved air and stirring for a few minutes than by aspiration. The necessity for aeration is shown by the presence of the violet colour of tervalent titanium in the iron solution to be titrated. S. G. C.

***p*-Hydroxyphenylarsonic Acid as a Reagent for Titanium and Zirconium. C. T. Simpson and G. C. Chandlee.** (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 642–643.)—*p*-Hydroxyphenylarsonic acid has been found to separate titanium, by precipitation, from the following ions: ferric, ferrous, aluminium, zinc, cobalt, nickel, beryllium, chromic, manganous, calcium, magnesium, thallium, cerous, thorium, alkalis, phosphate, molybdate, chromate, vanadate, permanganate, uranyl and vanadyl. Interfering ions are zirconium, ceric and tin. Hydrogen peroxide interferes with the precipitation of titanium. The reagent may also be used to determine zirconium in the presence of the above-mentioned ions, and zirconium may be separated from titanium if hydrogen peroxide is present; ceric, tin, and phosphate ions, in more than very small amounts, interfere.

Titanium.—The solution (200 ml.) should contain not more than 0·06 g. of titanium oxide and the amount of acid present should be such that the solution will be approximately, but not more than, 0·6 *N* in hydrochloric acid or 1·8 *N* in sulphuric acid after the reagents have been added and precipitation is complete;

2 to 3 g. of ammonium thiocyanate are added if iron is present. The solution is heated to boiling and 100 ml. of 4 per cent. aqueous *p*-hydroxyphenylarsonic acid are added; the boiling is continued for 15 minutes to assist coagulation of the precipitate. After cooling, the precipitate is filtered off and washed first with 0·25 *N* hydrochloric or sulphuric acid containing about 0·5 g. of the reagent per 100 ml. (and about 1 per cent. of ammonium thiocyanate if iron is present), and finally with dilute (2 per cent.) ammonium nitrate solution; the precipitate is ignited and weighed as titanium dioxide. A fume-hood is required for the ignition, presumably to remove arsenic. An average deviation of 0·7 part per thousand was found in the results with pure titanium solutions. Among examples given of the applicability of the method, titanium was precipitated direct from solutions of a 2-g. sample of chrome-vanadium steel, a 5-g. sample of iron ore, 2-g. samples of an alumino-silicate refractory and a plastic clay; the results agreed well with those obtained by other processes.

Zirconium.—In the method outlined for titanium zirconium is also precipitated. The zirconium alone may be precipitated in the presence of excess of hydrogen peroxide, while in a second sample zirconium and titanium can be precipitated together (without addition of hydrogen peroxide) and determined as the mixed oxides. Alternatively, following precipitation of zirconium in the presence of hydrogen peroxide, the titanium may be determined in the filtrate after evaporation to "white fumes" with sulphuric acid in the presence of nitric acid to decompose complex titanium compounds. S. G. C.

Determination of Germanium in Minerals and Solutions. W. C. Aitkenhead and A. R. Middleton. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 633–635.)—*Minerals.*—To a 1-g. sample of the finely ground mineral contained in a platinum dish 10 ml. of nitric acid, 10 ml. of hydrofluoric acid and 2 ml. of sulphuric acid (1:1) are added, and the liquid is evaporated slowly, below the b.p. to avoid loss of germanium, until the hydrofluoric acid has been expelled (as judged by absence of white fumes when a strip of damp paper is held over the dish); the heating should not be sufficient to produce fumes of sulphuric acid. The contents of the dish are transferred to a beaker and made alkaline with sodium hydroxide; about 0·5 g. of sodium sulphide crystals are added, and the liquid is boiled for 15 minutes in order to dissolve any germanium oxide which may have separated during the slow acid-evaporation process. After cooling, the liquid is rendered just acid with sulphuric acid, and the precipitate of sulphur is filtered off after sufficient time has been allowed for it to coagulate. To the filtrate containing the germanium, as thiogermanate, 1·5 times its volume of conc. hydrochloric acid are added, together with 2 to 3 g. of finely divided precipitated copper, which serves to precipitate arsenic and antimony. If blackened within 1 hour owing to the presence of these elements, the copper must be filtered off and more added. *Distillation of Germanium.*—The liquid containing the copper is distilled in a flask fitted with a tap-funnel and a side-tube leading up to a vertical Liebig condenser; the upper end of the condenser is joined to one arm of a leading tube of inverted U-shape having a safety bulb blown in the other arm, the end of which dips into 5 ml. of water in an ice-cooled receiving tube. The distillation is con-

tinued until the water in the receiver becomes saturated with hydrogen chloride; if this fails to occur within about half-an-hour some conc. hydrochloric acid should be added to the distillation flask. *Determination by modified Marsh Test.*—This method should be used for small amounts of germanium (0·1 to 0·001 mg.). About 5 g. of pure zinc are placed in a 20-cm. test tube, to serve as generator, provided with a stopper carrying a dropping funnel and a delivery tube leading to a train consisting of a small wash bottle containing water, a drying tube loosely packed with glass wool, and a combustion tube of Pyrex glass, 12·5 cm. long × 0·6 cm. diameter, drawn out to a capillary, 5 cm. long and about 1 mm. internal diameter at the remote end. About 5 ml. of conc. hydrochloric acid are first run slowly into the generator and the combustion tube is heated, the usual precautions being observed. The germanium-containing distillate is then allowed to flow into the generator at about 1 drop per second, and finally a second 5-ml. quantity of conc. hydrochloric acid is similarly run in. The stain obtained is compared with standard stains made by operating with known amounts of germanium. The zinc used should preferably be in the form of flakes, and prepared by breaking up thin electro-deposited zinc sheet. *Gravimetric Determination.*—For amounts of germanium larger than can be dealt with by the Marsh method, the usual method of precipitation as germanium sulphide and conversion into germanium dioxide can be used. Alternatively, the distillate may be evaporated as follows:—An equal volume of 27 *N* hydrofluoric acid is added to the distillate contained in a platinum dish; 1 ml. of conc. sulphuric acid and 1 ml. of 60 per cent. perchloric acid are added, and the liquid is allowed to evaporate as far as possible on a steam-bath; the residue is then slowly evaporated to dryness by heating to a higher temperature, ignited and weighed as germanium dioxide. The application of these methods to the determination of germanium in solutions follows closely on that described above for treatment of a mineral which has been brought into solution.

S. G. C.

Determination of Traces of Rhenium in Pyrolusite. L. C. Hurd and C. F. Hiskey. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 623–626.)—The amounts of rhenium considered were of the order of 1 p.p.m. or less. The sample of pyrolusite (100 g.) is dissolved in conc. hydrochloric acid with gentle heating. Any sandy residue is filtered off and extracted with boiling hydrochloric acid, the extract after filtration being added to the main solution and the residue rejected. Sufficient stannous chloride solution is added to reduce ferric and manganic chlorides to the bivalent state; 0·6 g. of potassium thiocyanate per 100 ml. together with a further 0·5 g. of stannous chloride per 100 ml. are added. Any rhenium or molybdenum present form a coloured thiocyanate, which is extracted by shaking with several successive portions of ethyl ether. After removal of the bulk of the ether by distillation from the combined extracts, 15 ml. of hydrochloric acid (sp.gr. 1·1) are added, and the remaining ether is removed in a current of air. The solution is oxidised with hydrogen peroxide, added, drop by drop, until no colour remains; the solution should be kept at this stage for 15 minutes and any colour which develops must be discharged with hydrogen peroxide. Separation of rhenium from molybdenum is effected by distillation of the liquid, diluted to 200 ml.

with conc. sulphuric acid, at 270° to 290° C. for 2 hours, in a slow stream of a mixture of steam and carbon dioxide, the distillate containing the rhenium being collected in an ice-cooled receiver. Bromine is added, to oxidise sulphur dioxide, until a faint yellow colour is produced; 100 ml. of conc. hydrochloric acid are added, followed, after cooling, by 10 ml. of 20 per cent. potassium thiocyanate solution and 15 ml. of 20 per cent. stannous chloride solution. The rhenium thiocyanate colour is matched against standards containing similar amounts of acid and reagents to which known amounts of rhenium (as perrhenate) have been added. The results in test experiments with traces of rhenium (0·2 to 2 p.p.m.) added to rhenium-free pyrolusite samples were reasonably good. Of 80 samples of pyrolusite from different parts of the world, the majority were found to contain no rhenium. The largest proportion found, in an ore from Montana, was 0·2 p.p.m.

S. G. C.

Determination of Vanadium. A. F. Andreev. (*Zav. Lab.*, 1938, **7**, 258–262.)—This is a modification of Someya's method of oxidising bivalent vanadium, using a reduced dyestuff as indicator (*cf. Z. anorg. Chem.*, 1924, **138**, 291; 1928, **169**, 293). Berry (ANALYST, **1934**, **59**, 736) found that the oxidation was always too low (usually about 95 per cent. of theory) when phenosafranine was used as indicator and ferric alum as the oxidising agent, even when great care was taken to avoid oxidation of the vanadous salts by air. Also, the presence of molybdenum interferes with the reaction when any of the dyes mentioned by Someya are used as indicator. Acid fuchsin or trypan red, however, do not react with molybdenum. To obtain a satisfactory pink end-point with acid fuchsin the dye itself is used as the oxidising agent. For the reduction of vanadium to the bivalent state either zinc or cadmium may be used, preferably as amalgam. It was found that under the experimental conditions used chromium was reduced by zinc amalgam but not by cadmium; hence cadmium amalgam was used for further investigations. In the method of analysis worked out it is necessary to boil the reduced solution with acid fuchsin, otherwise the reaction is too slow. With trypan red, the titration can be carried out in the cold. This dye is therefore preferable, owing to the increased tendency of vanadous salts to become oxidised on heating. The reduction is effected in a conical flask provided with a ground-in stopper and having two glass tubes fused in on opposite sides; in each tube there is a glass tap. If about 50 ml. of the solution under examination are vigorously shaken with the amalgam the reduction, which must be made as usual in an air-free atmosphere, is complete in 20 minutes. The amalgam is then poured off through one tube while carbon dioxide is introduced through the other, and the titration is done immediately. The method is suitable for the determination of vanadium in steel, and the presence of titanium (as well as of chromium or molybdenum) does not interfere (except that when molybdenum is present the end-point is yellow, not pink), but tungsten must first be removed. *Determination in Steel.*—One g. of the sample is dissolved in 20 ml. of sulphuric acid (1:5) and 8 ml. of hydrofluoric acid (1:3), and oxidised by heating with a saturated solution of potassium permanganate. Excess of permanganate is removed with a few drops of hydrogen peroxide and the solution is transferred to a 250-ml. flask and made up

to the mark with 4 *N* sulphuric acid. The determination is made on 50 ml. of the solution, as described above. If tungsten is present the steel solution is oxidised with nitric acid, added drop by drop, evaporated to fuming, diluted with water, again evaporated to fuming, filtered from the tungsten and made up to 250 ml. (The solution analysed must be completely free from nitric acid.) In test determinations on three steels of known composition the percentage results were:

	Found	Present
1 (tungsten present)	1·05; 1·07; 1·05	1·10
2 (tungsten absent)	0·26; 0·27	0·26
3 (tungsten absent)	0·70; 0·72	0·70

The water for the trypan red standard solution (0·4 g. dye : 1 litre of 2 *N* sulphuric acid) must be boiled for a long time to remove dissolved oxygen. The solution is standardised against reduced vanadium. Particulars of the preparation of the amalgam are given, and also results of preliminary experimental work. E. B. D.

Volumetric Determination of Vanadium in presence of Tungsten, with Diphenylamine-sulphonic Acid as Indicator. G. A. Pevtzov. (*Zav. Lab.*, 1938, **7**, 286–289.)—For the determination of vanadium in the presence of tungsten it is essential to introduce sufficient phosphoric acid into the solution before the addition of the indicator and titration with ferrous ammonium sulphate solution. A large excess of the phosphoric acid is necessary, otherwise a complex compound with the tungstic and vanadic acids is formed; the vanadic acid complex is not decomposed on further addition of phosphoric acid and therefore not all the vanadium is titratable. Also, the yellow colour of this compound in solution reduces the sharpness of the end-point of the titration with diphenylamine sulphonic acid (with diphenylamine no definite end-point is obtained). The method used was that of Kolthoff and Sarver (*J. Amer. Chem. Soc.*, 1931, **53**, 2906), but the solutions examined experimentally were more acid. Ten ml. of approximately *N*/100 vanadic acid solution, prepared from the pentoxide, were treated with x ml. of a 1 per cent. solution of sodium tungstate ($Na_2WO_4 2H_2O$), 10 ml. of a solution (either 25 or 85 per cent.) of phosphoric acid, 10-x ml. of water, 2 ml. of sulphuric acid (sp.gr. 1·84) and, finally, the indicator as the barium salt of diphenylaminesulphonic acid (*cf.* Kolthoff, *loc. cit.*). The solution was titrated with N/100 ferrous ammonium sulphate solution. With 25 per cent. phosphoric acid the results became lower as the concentration of tungsten rose, and with the ratio V:W = 1:5 the end-point was not sharp; addition of 85 per cent. phosphoric acid gave satisfactory results even with the ratio V:W=1:10. Substitution of sodium pyrophosphate solution for the phosphoric acid was unsatisfactory. The vanadium reduced by the ferrous salt was slowly re-oxidised, and this was not prevented by working in an atmosphere of carbon dioxide. Under the usual experimental conditions the amount of re-oxidation was insignificant (approximately 1 per cent.). E. B. D.

Utilisation of Raney's Alloy as a Substitute for Devarda's Alloy in the Determination of Nitrates. E. Cattelain and P. Chabrier. (*Ann. Chim. anal.*, 1938, **20**, 285.)—Raney's alloy (nickel 30, aluminium 70 per cent.)

can be used instead of Devarda's alloy (copper 50, aluminium 45, zinc 5 per cent.) in the determination of nitrates by reduction to ammonia in an alkaline medium. The technique has been described previously (Cattelain, *J. Phys. Chim.*, 1934, **20**, 118). The results obtained in test experiments with potassium nitrate agreed closely with the theoretical values. E. M. P.

Determination of Dissolved Oxygen in Condensed Steam. J. Haslam and G. Moses. (*J. Soc. Chem. Ind.*, 1938, **57**, 344–347T.)—The method of McCrumb and Kenny (*J. Amer. Waterworks Assoc.*, 1929, **21**, 400) has been modified so as to eliminate errors arising from contamination of the reagents and permanent colour standards during preparation and storage, and from contamination of alkaline suspensions of manganous hydroxide by atmospheric oxygen. The method depends on the oxidation of manganous hydroxide by the dissolved oxygen, followed by solution of the oxidised manganese compounds in dilute hydrochloric acid, and application of the *o*-tolidine colour reaction. The (B.D.H.) *o*-tolidine was purified by heating 10 g. in a Carius tube at 160° to 180° C. for 7 hours with 50 ml. of acetic anhydride, the pressure being released on the following day, and the contents of the tube poured out in the molten state after the necessary period of immersion in a boiling water-bath. The liquid was then cooled in ice, and the tetra-acetyl derivative was filtered off on a sintered glass crucible (17G3) with suction and dissolved in the minimum amount of boiling water, and distilled water was added to the solution until a slight permanent turbidity was produced. The mixture was boiled under a reflux condenser with 2 g. of animal charcoal for 2 hours and filtered in a funnel having a hot-water jacket, and the crystals were separated from the cool filtrate by filtration and washed with dilute alcohol. Ice was added to the mother-liquor until its volume had increased 3-fold, and the precipitated crystals were again separated by filtration, washed, and finally dried at 100° C. They were then hydrolysed by boiling 2 g. for 5 to 6 hours under a reflux condenser with 50 ml. of conc. hydrochloric acid and 10 ml. of water. Water was added to the cool mixture to dissolve any precipitated crystals, and the liquid was filtered and made alkaline with 10 per cent. sodium hydroxide solution. The precipitated crystals of *o*-tolidine were finally separated by filtration, washed well with water and recrystallised from dilute alcohol; m.p. 129° C. (uncorr.). Lea's conclusion, that purified *o*-tolidine has an increased sensitiveness, was confirmed (*cf. J. Soc. Chem. Ind.*, 1933, **52**, 245T), but the product obtained by his method of purification appeared to be the diacetyl derivative. A method and apparatus for the production of water free from dissolved oxygen is described in which a stream of nitrogen is passed for 20 to 24 hours, first through 2 wash-bottles in series containing an alkaline solution of pyrogallol, then through another pair of wash-bottles containing water, and finally through a sintered glass disc in the bottom of an aspirator containing 10 litres of the water to be purified. The solutions were stored in an atmosphere of nitrogen, and an apparatus for this purpose and for treating the water is shown in a diagram. Ordinary distilled water saturated with air was used as a reference water of known oxygen-content, the dissolved oxygen being determined by a modification of Winkler's method. A special sampling bottle is also illustrated; a feature of it is the sunken stopper,

one side of which has a projecting portion which, when opposite a corresponding depression in the neck of the bottle, leaves a small space between the stopper and the neck, or when twisted so that the projecting portion is on the other (*i.e.* straight) side of the neck, effects a complete closure of the bottle. The bottle was filled with the purified water, a measured volume of the water of known dissolved oxygen-content was then added rapidly, followed by 0·25 ml. each of a 40 per cent. solution of manganous chloride ($MnCl_2,4H_2O$) and a 70 per cent. solution of potassium hydroxide in the purified water in both instances. These additions were made at the bottom of the bottle by means of special delivery burettes, so that the water near the top of the bottle, which had come into contact with the air, was ejected. The stoppered bottle was then inverted gently 3 times, and 1 ml. of conc. hydrochloric acid (which was stored in the dark) was introduced through the special stopper (see above), so that the contents of the bottle were not exposed to the air even momentarily. When the hydroxides had completely dissolved, 1 ml. of a solution of 1 g. of *o*-tolidine in 10 ml. of the hydrochloric acid, diluted to 100 ml., was added, and after exactly 5 minutes the resulting colour was matched against permanent colour standards prepared (after Yoe, *Photometric Chemical Analysis*, Vol. I, p. 157) from mixtures of solutions containing (*a*) 3·75 g. of copper sulphate and 2·5 ml. of conc. sulphuric acid in 250 ml.; (*b*) 0·625 g. of potassium dichromate and 2·5 ml. of the acid in 250 ml. The volumes (in ml.) of (*a*) and (*b*), which must be mixed and diluted to 100 ml., and the dissolved oxygen contents (in ml. per litre), to which they are then equivalent in colour, respectively, are:—0·05, 0, 0·001; 0·34, 0, 0·005; 0·69, 0·95, 0·01; 1·90, 1·89, 0·05 and 3·14, 1·92, 0·05. The method was tested with waters of known dissolved oxygen-contents (0 to 0·048 ml. per litre), and the maximum error was 0·008 ml. per litre. An apparatus for sampling condensed steam without contamination from the atmosphere is described, in which the condenser main is tapped through a valve by a sampling-tube and the steam is condensed in a block-tin cooling tube, whence the sample flows into the special sampling-bottle; the whole apparatus is flushed out well with the sample beforehand. Six determinations on each of 8 samples are recorded; the mean values varied between 0·011 and 0·016 ml. per litre, and the agreement between the duplicates was satisfactory. The absence of other substances which might affect the colour produced with the reagent should be established by measuring the effects of the addition of known quantities of water of known dissolved oxygen-content. J. G.

Microchemical

Method for the Estimation of Ultramicro-quantities of Lactic Acid. B. F. Miller and J. A. Muntz. (*J. Biol. Chem.*, 1938, **126**, 413–421.)—A method whereby as little as 0·1γ of lactic acid can be estimated was devised for use in the investigation of dental caries. The method was based on the highly sensitive colour reaction of Eegriwe (*Z. anal. Chem.*, 1933, **95**, 323). Lactic acid is oxidised to acetaldehyde by hot conc. sulphuric acid, and the acetaldehyde produces an intense bluish-violet colour with *p*-hydroxydiphenyl. Exactly 0·2 ml. of the

sample is measured into a glass-stoppered Pyrex test-tube, which is immersed in ice-water while 1·5 ml. of conc. sulphuric acid is added slowly. The tube is then stoppered, the ground-glass portion being lubricated with a drop of the acid, and the contents are gently shaken. The tube is heated in a boiling water-bath for 5 minutes and then cooled in ice-water for 10 to 15 minutes. Eight mg. ($\pm$0·2 mg.) of very finely powdered *p*-hydroxydiphenyl (purified by repeated crystallisation from cold acetone solution) are then carefully added through a funnel to avoid scattering the powder on the side of the tube. The tube is re-stoppered and the contents are gently but thoroughly mixed, care being taken to avoid splashing the walls of the tube. The maximum colour development is obtained by allowing the tube to stand for an hour at room temperature, after which it is immersed in a boiling water-bath for exactly 90 seconds and cooled immediately. The colour of the solution is measured with a Pulfrich photometer with S57 filter. The value of the extinction coefficient thus obtained is converted to γ of lactic acid per 0·2 ml. of the sample by means of a calibration chart. Teeth or carious matter are pulverised and extracted with water, and an aliquot portion of the solution is treated as described above. Blood serum is treated with an equal volume of a freshly made 7 per cent. solution of metaphosphoric acid and 8 volumes of water. After being thoroughly shaken and left for 10 minutes the solution is centrifuged and an aliquot portion of the supernatant liquid is taken for analysis. Saliva is merely diluted with an equal volume of water. The reaction is remarkably specific; pyruvic acid gives a colour under the conditions outlined above, but its interference can be eliminated by prolonging the oxidation with sulphuric acid to 15 minutes. Other acids and carbohydrates do not interfere at all. Analyses made with pure lithium lactate gave duplicate results varying by 2 to 3 per cent. with quantities of 3 to 10γ. F. A. R.

Catalytic Colour Reaction for Tungsten. E. B. Sandell. (*Ind. Eng. Chem., Anal Ed.*, **1938**, **10**, 667–668.)—Sexivalent tungsten markedly catalyses the reaction between titanous chloride and malachite green, which normally proceeds very slowly at room temperature, the tungsten becoming rapidly reduced by titanous chloride, giving reduction products that reduce malachite green to the leuco form. The reaction may be applied in detecting tungsten as follows:—To a 0·05-ml. drop of the solution (which may be neutral or 0·1 *N* in hydrochloric acid), placed on a spot plate, is added 0·01 ml. of 1 per cent. titanous chloride solution followed by 0·01 ml. of a 0·005 per cent. aqueous malachite green solution. With 10 p.p.m. of tungsten in neutral solution the blue-green colour fades in about 3 seconds; with 2 p.p.m. it is decolorised in 1 to 1·5 minutes, and with 1 p.p.m. in 3 minutes. In absence of tungsten the drop remains coloured for 4 to 5 minutes. The limit of sensitiveness is considered to be 2 p.p.m. When the test-drop is 0·1 *N* in hydrochloric acid, the reaction with tungsten is a little slower; the smallest amount detectable is 4 p.p.m., the fading occurring in 2 to 3 minutes, whilst the drop remains coloured for 3·5 to 4 minutes in absence of tungsten. The reaction fails, owing to consumption of the titanous chloride, when appreciable amounts of reducible salts are present, such as those of iron, uranium and vanadium in the higher valency state, or cations which are reduced to metal or form insoluble

chlorides. Other interfering substances are: sulphate, nitrate, tartrate, phosphate and fluoride. Molybdenum catalyses the reaction between titanous chloride and malachite green, but its effect is much less than that of tungsten. S. G. C.

Micro-determination of Magnesium in pure Solutions and in Blood Serum. M. Delaville and M. Olive. (*Ann. Chim. anal.*, 1938, **20**, 286–287.)—The authors recommend a modification of Berg's 8-hydroxyquinoline method, in which the metallic ion is determined instead of the hydroxyquinoline. In testing the method the following procedure was adopted:—A known volume of magnesium sulphate solution was neutralised with *N* sodium hydroxide solution, neutral red being used as an indicator, and 1 ml. of the sodium hydroxide solution was added in excess. The liquid was treated with 1 ml. of a saturated solution of sodium potassium tartrate and finally with 0·3 to 0·4 ml. of a 5 per cent. alcoholic solution of 8-hydroxyquinoline. The mixture was heated on a boiling water-bath for 4 to 5 minutes and centrifuged, and the supernatant liquid was decanted. The precipitate was washed with water, with centrifuging after each washing, until the washings were neutral. Two or four ml. of *N*/40 hydrochloric acid were added, the liquid was warmed on a water-bath until the precipitate had dissolved completely, and the acid was titrated hot with *N*/100 sodium hydroxide solution, in the presence of neutral red. The results obtained are shown in a table. The results obtained with quantities of magnesium sulphate ranging from 0·6 to 0·012 mg. agreed with theory within ±3 per cent.

The following procedure is used for the analysis of blood serum:—Two ml. of serum are evaporated to dryness in a platinum crucible on the water-bath, and the residue is ignited to give a white ash, which is taken up in a mixture of 2 ml. of conc. hydrochloric acid and 2 ml. of water, and then treated with 1 ml. of a solution of 6·40 g. of oxalic acid in 100 ml. of *N* hydrochloric acid made up to 1 litre with water. The crucible is covered with a watch-glass and heated for 30 minutes on the water-bath. The liquid is treated with 2 ml. of saturated ammonium oxalate solution, cooled, made alkaline to phenolphthalein (1 drop) with ammonia, and left for 2 hours. The precipitate is filtered off and washed with a little ammonium oxalate solution, the washings being combined with the filtrate. The residue on the filter-paper is calcium oxalate and can be determined if the calcium-content is required. The filtrate is evaporated to dryness and the crucible is heated carefully over a Bunsen burner to decompose the ammonium salts. The residue is taken up in 1 ml. of conc. hydrochloric acid and warmed on the water-bath until the ash has completely dissolved. The liquid is transferred to a centrifuge tube, and the determination is completed as above, care being taken to neutralise the acid completely. When 2 ml. of *N*/40 hydrochloric acid are used, the results are calculated from the formula

$$\text{magnesium, in mg.} = (5 - N) \times 0{\cdot}12,$$

where *N* is the number of ml. of *N*/100 sodium hydroxide solution used in the titration. The centrifuging can be carried out more easily by adding 1 ml. of 95 per cent. alcohol, which prevents the precipitate from creeping up the sides of the tube. E. M. P.

Reviews

(1) ORGANIC AND BIO-CHEMISTRY. By R. H. A. PLIMMER, D.Sc. 6th Edition. Pp. x + 623, with coloured plate and illustrations in text. London: Longmans, Green & Co. 1938. Price 21s.

(2) A TEXTBOOK OF BIOCHEMISTRY. By ROGER J. WILLIAMS, Ph.D., D.Sc. Pp. x + 525. London: Chapman & Hall, Ltd. 1938. Price 21s.

(3) OUTLINES OF BIOCHEMISTRY. THE ORGANIC CHEMISTRY AND THE PHYSICO-CHEMICAL REACTIONS OF BIOLOGICALLY IMPORTANT COMPOUNDS AND SYSTEMS. By ROSS AIKEN GORTNER. 2nd Edition. Pp. xx + 1017. London: Chapman & Hall, Ltd.; New York: John Wiley & Sons, Inc. 1938. Price 30s.

(1) Text-books of biochemistry must now constitute almost one of the principal exports from the United States of America to this country. "Plimmer" has the burdensome responsibility of being the senior representative of indigenous works covering the rapidly widening ground in this flourishing branch of chemical science. First published in September, 1910, as *Practical Physiological Chemistry*, it has passed through six editions or impressions; the new edition is separated by five years from the last.

Professor Plimmer's book differs from most of the others in being largely, though by no means exclusively, a practical hand-book for student and research worker in the laboratory. In the second edition (1915) the title was changed to *Practical Organic and Bio-chemistry*; in the fourth edition (1926) the theoretical part was considerably enlarged, so that it became an admirable introduction to organic chemistry for the medical student or biological worker, and the word "practical" was omitted from the title.

Nevertheless, it is as a practical guide to reactions and preparations—especially the isolation of pure substances from natural sources—that it stands in a unique position, and can well hold its own against American competitors. The new edition brings up to date many of those biochemical subjects that have been the recent object of intensive study. Thus mention is made of the anti-pellagral action of nicotinic acid; a short chapter is devoted to the composition of the nucleic acids; the modern formulation of sterols, sex hormones and anti-rachitic vitamins is clearly presented; the chapter on pigments includes descriptions of anthoxanthins, anthocyanins, haemin and the porphyrins, chlorophyll and the carotenoids or lipochromes. If one were to suggest any additions to a book in the writing of which the problem of compression must be most difficult, it might be more emphasis on the presence of *d*-ribose in many physiologically important substances, especially in association with phosphoric acid; a brief reference to one of the most important (and mysterious) properties of proteins, their "specific dynamic action"; and some slight account of the fascinating connection now established between certain water-soluble vitamins and co-enzymes. Emphasis might also be laid on the "mixed" nature of the glycerides in many fats and oils.

The volume is admirably produced, and concludes with some useful tables, a list of reagents (including indicators) and a full index. Random sampling has

failed to reveal any typographical errors. Professor Plimmer's book has achieved the classical status that results from an excellence witnessed by 28 years' existence and five re-editings. Long may he continue to be both able and willing to keep his work as up-to-date and authoritative as on this occasion.

(2) Professor Williams has written a companion to his earlier *An Introduction to Biochemistry* (1921). There the emphasis was on the vegetable kingdom; here he is concerned mainly with the animal, and especially with man. After Part I, which is called *Biochemical Materials* and discusses the chemistry of both inorganic and organic constituents of the living body, the book is mainly devoted to consideration of the physical and chemical reactions in which those substances take part. Although the amount of information to be found in these 500 pages is most extensive, it is presented in a fluent and persuasive manner. The work can almost be recommended as a "bed-book," for it can be picked up and read with profit and interest wherever it happens to be opened.

(3) Professor Gortner has set himself a task rather different from that of most writers of biochemical books. Without in any way overlooking the practice and methods of the science, he is chiefly concerned with the nature of the phenomena investigated. He is not afraid to speculate, when speculation is called for; indeed he has apparently been so much interested in this approach as to have failed to note certain rather unfortunate slips in the presentation of the facts (witness "2.2-dihydroergosterol" instead of "22-dihydroergosterol," and "irridation" for "irradiation," both on p. 895). Co-enzymes, though discussed in the text, receive no mention in the index, which is full, occupying 61 pages—23 for authors and 38 for subjects.

The scope of the book is most impressive. The author must indeed be an enthusiast for his subject, particularly for the more philosophical aspects thereof, and it can be confidently recommended to those who have perhaps a rather *recherché* taste for the interrelations of chemical substances in the living organism.

A. L. BACHARACH

AN INTRODUCTION TO INDUSTRIAL MYCOLOGY. By GEORGE SMITH, M.Sc., A.I.C. Pp. xii + 302 + 64 plates. London: Edward Arnold & Co. 1938. Price 16s. net.

This book might be described as a text-book on the mycology of the fungi with special reference to those of importance in industry. It is introductory in so far that it does not presume upon a knowledge of mycology by the reader, all terms, methods of identification, systems of classification, methods of manipulation, and so forth, being sufficiently explained; on the other hand, it is more than elementary, for a very large number of genera and species are described, those of greatest importance and most common occurrence being considered in proportionate detail.

The book opens with a foreword by Professor Raistrick of the London School of Hygiene and Tropical Medicine, at which school the author is research demonstrator, and then comes the author's preface. The first chapters are introductory. Terminology and principles of classification are dealt with and well illustrated;

the author has adopted the same system of classification as Rabenhorst in his *Kryptogamenflora*, in which the *Eumycetes* are divided into two main groups: *Phycomycetes* and *Mycomycetes*, and these into five classes: *Oomycetes*, *Lygomycetes*, *Ascomycetes*, *Basidiomycetes* and *Fungi Imperfecti*. The following six chapters are devoted to the subdivision of these classes into orders, families and genera, the distinguishing characters of which are well described and most beautifully illustrated by 256 excellent original photomicrographs, the magnifications of which are specified. Thus the order of the *Hyphomycetales* of the *Fungi Imperfecti* is divided into four families, of which the *Mucedinaceae* is one; a key of the subdivision of the *Mucedinaceae* into 11 more important genera is given and the text proceeds to the description of these genera. Here the reviewer has one slight criticism to offer: there is not quite sufficient contrast between the type of the headings to the genera and the orders. On page 86, for instance, it would help the reader if the heading of the order *Dematiaceae* stood out in rather stronger contrast with the heading of the genus *Tricothecium*. While generally a paragraph is devoted to the description of each genus, a chapter each is given to the description of the genus *Aspergillus* and to the genus and related genera *Penicillium*, 12 species of the former and 40 to 50 of the latter being described. These chapters are very well written; while easy to read, they are not in any way lacking in essential detail.

Then follows a chapter on laboratory equipment and technique, including the preparation of culture media and methods of making and examining cultures, methods of isolating moulds and making pure cultures, microscopic equipment, and methods of identification of species—a useful outline of the procedures necessary. This chapter contains many useful hints, such as the benefit to be derived from the use of the 8-mm. objective instead of the 4 mm. (or 1/6th), and of the 3-mm. oil immersion instead of the 2-mm., the loss of magnification being compensated by the use of a higher-power ocular. If by this means the author was enabled to obtain the superb photomicrographs reproduced in Figures 74 and 98, giving a magnification of 1000 diameters and an almost perfectly flat field, this suggestion does not need a stronger recommendation.

The next three chapters deal with the physiology of mould fungi: Chapter X with food requirement, respiration, reaction of medium, influence of light, temperature relationships, moisture requirements, poisons, influence of other fungi; Chapter XI with the maintenance of culture collections; Chapter XII with the control of mould growth in factory and industrial conditions.

Chapter XIII gives a brief account of the industrial uses of fungi, under the following headings:—Alcoholic Fermentation and Mould Enzymes, Mould-ripened Cheese, Oxalic and Citric Acids, Gluconic Acid, Gallic Acid, Fats, Proteins, Vitamins and Miscellaneous Products of Moulds and Fungi and the Soil. Chapter XIV, headed "Mycological Literature," gives a list of publications to which the reader is referred for a more specialised account of fungi than comes within the scope of the present work; these publications, of which a brief but very useful summary is given, include general works, monographs, books on general and systematic mycology and applied mycology, journals and periodicals.

This book should be of the greatest value to works' chemists faced with the problem of mould contamination, as for instance in margarine works, and with its

aid it should not be difficult to identify the species, or at least the genus, concerned, and to devise suitable measures for its suppression.

The book is well printed, the type is very readable, the paper is good, and there is a good index; the outstanding feature is the excellence and the very liberal number of the plates. The author, publishers and printers deserve warm praise for the production of the work, which must have involved a large amount of labour, and it can be confidently recommended not only to those who wish to acquire a first-hand and at the same time quite considerable knowledge of the mould fungi, but to all who desire a concise hand-book on the subject, suitable for ready reference.

D. R. Wood

Chemische Spektralanalyse. By W. Seith and K. Ruthardt. Pp. vi + 103, 60 illustrations and 2 plates. Berlin: Julius Springer. 1938. Price RM.7.50.

In recent years the use of spectrochemical methods for quantitative estimations of elements and certain classes of compounds has become more widespread in chemical laboratories. A striking example of its use is the detection and estimation of small proportions of strontium in a calcium salt prepared for re-determination of the atomic weight. Gerlach determined the proportions of strontium, and thus was able to supply the necessary corrections. The rapidity and convenience of the method are now appreciated, but there are few books available for the chemist who desires information as to the best methods of procedure. Messrs. A. Hilger, Ltd., have issued translations of Gerlach's and his colleagues' monographs, and also some informative booklets on the use of spectrographic and spectroscopic methods, resulting from the work of Twyman and his co-workers. These are, of course, excellent in their own field, but, apart from Swings' small work issued in 1935, little of recent date is available to the chemist who desires to consult an introductory statement on the theory and application of the methods of spectral analysis.

The small volume, now to hand, fills a gap in this respect. It is a methods book and sets out the details clearly and sufficiently fully to enable the instructions to be followed intelligently. There are many practical examples, and these will be found useful as a guide in the first instance to those contemplating the use of the method. In the small compass of the book the subject can hardly be expected to be treated exhaustively, but success should follow strict adherence to the details given.

A general introductory chapter is devoted to sources of radiation and a short description of some Continental spectrographic apparatus, and a few pages to the elementary theory of the emission of spectrum lines. Fairly full instructions for arc and spark excitation are given and a discussion of the proper method of alignment of apparatus—a most important feature in spectrographic work—is furnished (pp. 27 *et seq.*). The section on qualitative analysis considers the question of purity of substances, and identification of lines of emission.

In the discussion of quantitative methods, "homologous pairs" as developed by Gerlach and Schweitzer is one of the recommended procedures. This method depends upon the selection of pairs of lines of an element which maintain their

relative intensities on the photographic plates despite large variations in the conditions of excitation. If lines of this kind are found it will go far towards eliminating inaccuracies from small alterations in inductances and sparking potentials and photographic errors.

Visual examination of emission lines is also discussed, and examples refer to Ni, Mn and Cr in ferrous alloys, and also to cadmium in lead. The sparking of solutions of electrolytes is considered briefly, as is the production of high frequency sparks by the method of Walther Gerlach and Werner Gerlach. A few pages are devoted to absorption spectra of solutions, and there are two well-produced plates of the spectra of some of the commoner elements met with in spectrographic work. So far as this little volume goes, it is a good practical statement of the method and is free from errors. The beginner can safely follow the instructions; he will also be made to realise the need for careful calibration in special cases. Presumably, lack of space accounts for the absence of many references to the British, American, French and Belgian work on the subject and of Lundegårdh's outstanding contribution of the hot flame method.

J. J. Fox

A Treatise on Light. By R. A. Houston, M.A., D.Sc. 7th Edition. Pp. xi + 528, 2 coloured plates, 8 half-tone plates and 345 diagrams. London: Longmans, Green & Co. 1938. Price 14s.

This well-known text-book now appears in the seventh revised edition, and new matter is added. For the first time answers to the problems are given, and this is a definite advantage for the student working through the book systematically. The first quarter of the work deals with geometrical optics and includes optical methods and brief accounts of optical instruments. In the second part, dealing with physical optics, the chapters on polarisation, optical rotation and analysis of polarised light will interest chemists most. In the reviewer's opinion, these chapters contain such elements of the subject as should be known to those who employ instruments depending upon the use of polarised light. Magnetic rotation of the plane of polarisation and the Kerr effect receive rather scanty treatment.

The third part deals with spectroscopy and photometry. A good account of the simpler apparatus for use in the ultra-violet, visible and infra-red regions is furnished, together with some descriptions of gratings of various kinds. The account of X-rays and their application is extended a little and a very short statement on photoelectric cells is added. The chapter on the quantum theory is an elementary statement which does not go very far, but not much more can be expected in eighteen pages. The subjects of photometry and illumination are treated rather shortly, but the section on colour and colour vision, within its scope, is well set out, as would be expected from the author's authority on this subject.

For those who desire to obtain a fuller view of the mathematical theory of optics Part IV can be recommended. It requires some concentration to read this section, but with a little perseverance the subject matter is not too difficult to follow. The book was written for those who "are proceeding further with the study of light," and it has clearly fulfilled this objective, since it is now once again in a new edition.

The only serious criticism which can be brought is that some of the subjects, *e.g.* Raman spectra, receive very little attention. Nevertheless, the new edition, like the earlier ones, is an excellent treatise, with the advantage for chemists that the subject matter is presented so that it can, in the main, be grasped readily, with not too heavy a demand on mathematical equipment. Its form and bold print make it a pleasure to handle the book.

J. J. Fox

A TREATISE ON QUANTITATIVE INORGANIC ANALYSIS. WITH SPECIAL REFERENCE TO THE ANALYSIS OF CLAYS, SILICATES AND RELATED MINERALS. By J. W. MELLOR and H. V. THOMPSON. 2nd Edition. Pp. xxxi + 784. London: Charles Griffin & Co. 1938. Price 42s.

The first edition of this book has been out of print for the last ten years and unobtainable on loan from the principal chemical libraries or by purchase second-hand for the last five. The condition of such copies as are available in reference libraries speaks eloquently of the hard use to which they have been put. It is no exaggeration to say, therefore, that this second edition is overdue.

The reviewer is of opinion that the reason for the success of the first edition was not its special bearing on the ceramic industry, but the comprehensive nature of the contents, clarity of exposition and extreme lucidity of style combined with the critical ability and practical outlook of the author. That it should have been written by one whose life's work was closely connected with ceramics is due to the fortunate accident that the demands of that industry upon analytical chemistry cover some part of the requirements of almost all others. There can be but few problems of determination or separation of inorganic ions upon which some assistance or a new light cannot be obtained from "Mellor"; combined, in most instances, with some pleasure in the search, for he seems to have been a firm believer in gilding the philosophic pill.

It might be well if anyone handling this book for the first time would treat it as a general work on inorganic analysis, and disregarding the special emphasis on ceramics in sub-title and chapter headings, look up some troublesome separation or disputed point in a determination. He will probably be surprised at the amount of information to be obtained, either from the text itself or the very full footnotes and references that appear on every page.

Some of the old text has been revised and re-written where necessary; but much of the original writing has stood the test of time, and has every appearance of continuing to do so. Revision has consisted, for the most part, in removing the obsolete and incorporating selected methods discovered during the last twenty-five years, but only to such an extent as is, according to the author, justified by practical experience, and not with any idea of flying from the ills we have to "others that we know not of."

The printing is in the usual clear type, on the high quality paper and in the pleasing format that distinguish the productions of Messrs. Charles Griffin & Co. Another, less pleasing characteristic, is that the pages are fastened into the familiar brown cover in an inadequate fashion; the book may be expected to join ultimately the ranks of valuable broken-backed volumes on every chemist's book-shelf.

As the book has been for so long out of print, some indication of the nature of its contents would appear to be desirable. Part I (pp. 127) consists of an introductory essay on the history, scope and limitations of analytical chemistry, followed by a description of analytical procedure in general. This is written in the concise style and from the critical attitude adopted by the late Dr. Mellor in all his written work, and sets the general tone and outlook of the whole book; it is worthy of the attention of all practising and prospective analytical chemists.

The articles on sampling and preparation of the sample for analysis cover ground that is all too often unexplored, not only by chemists, but also by those in charge of the business side of operations that depend for their ultimate success on the laboratory valuation of raw materials and commercial products.

It is to be regretted that the opportunity has not been taken, while the type was being re-set, to revise the section on volumetric glassware and bring the text and correction tables for temperature into accordance with the new standard temperature for volumetric glassware (1934). The neglect of this piece of mechanical labour gives the book an out-of-date appearance that is quite at variance with the remainder of its contents. The directions for calibration of volumetric glassware also require revision to bring them into line with modern practice and N.P.L. requirements.

Part II (pp. 123) deals with the constituents of a typical silicate, including the alkalis. The respective merits and failings of the methods used for "opening up" are described in exhaustive detail, followed by articles on the separation of group precipitates and methods for the determination of the separate elements that would apply with equal force whatever their origin, and that are not specially distinctive of, or solely applicable to, silicates or ceramic materials. This is typical of the treatment throughout the whole book. Its usefulness does not cease with the disposal of the special problems created by the presence of silica. Especially noteworthy chapters are those on the ammonia precipitate and its sequelae, the determinations of iron, titanium, aluminium and beryllium.

Part III (pp. 171) treats of the separation and determination of arsenic, antimony, tin, lead, bismuth, mercury, copper, cadmium, zinc, manganese, cobalt, and nickel. Attention may be drawn to the section dealing with the behaviour of these elements in silica separations, and the essays on the theory and practice of separations by hydrogen sulphide.

Part IV (pp. 175) deals with molybdenum, tungsten, niobium, tantalum, gold, platinum, selenium, aluminium, beryllium, iron (special methods), chromium, vanadium, uranium, zirconium, thorium, part of the rare earth series, barium, strontium, calcium, magnesium, and lithium. Full use has been made of the work of Schoeller and his collaborators, whose methods have replaced the methods of Marignac and E. S. Simpson described in the first edition.

Part V (pp. 158) covers methods for the determination of free and combined carbon, water, boron, phosphorus, sulphur, and the halogens. It has been largely re-written, and contains some pertinent thoughts on the precautions necessary in weighing absorption tubes and on the properties of barium sulphate. The final chapter of this part consists of a description of methods used for the separation of mineral species in clays, the so-called "rational analysis," and a discussion on

its value and place in the appraisal of argillaceous material. It is of interest to the specialist only.

Although by page numbering, this edition contains but six pages more than its predecessor, the actual number of new pages amounts to rather more than a hundred; the extra space for text has been obtained by removing 84 pages of appendix, the name index, many old blocks and some schematic diagrams.

The reviewer owes to the late Sir Herbert Jackson his introduction to the first edition of this work, which was accompanied by words to the effect that it was one of the best books on inorganic analysis ever written. During the past twenty-five years he has had many opportunities of confirming that opinion, and considers that it still holds true for this, the second edition.

The book contains a grateful and graceful tribute from Sir Robert Robertson to the memory of Dr. Mellor and his work. F. L. OKELL

FIELD DETERMINATION OF ROCKS. By E. H. DAVISON, B.Sc. Pp. vii + 87. London: Chapman & Hall. 1938. Price 7s. 6d. net.

The aim of this book is to assist geologists in the identification of rocks in the field; the classification of rocks is therefore based on such characters as texture, mode of occurrence and mineral composition. Rock-forming minerals are listed with such of their properties as can be determined in the field, and the texture, colour, mineral composition, mode of occurrence and field relations of rocks are discussed in some detail. Rock types are illustrated by a number of plates, and three useful tables show the method of classification. Although the classification is by no means ideal, it should prove of practical value to the field geologist, and the book should form a useful companion volume to the author's publication, *Field Tests for Minerals*. A. SHAW

LABORATORY MANUAL OF PHYSIOLOGICAL CHEMISTRY. MEYER BODANSKY and MARION FAY. Fourth Edition. Pp. vii + 295. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1938. Price 10s.

The fourth edition of this excellent handbook does not differ materially from the third, which was reviewed in these pages three years ago (ANALYST, 1936, **61**, 75). Such changes as there are have been made ". . . in an attempt to clarify directions and to render them more workable for the elementary student." The book is essentially a manual for students, and its aim is declared to be ". . . to provide some experiments that were essentially of descriptive value and others which would acquaint the student with the quantitative procedures commonly employed in the analysis of urine, blood and other body fluids." It is incidentally, however, a useful book of reference for those analysts and research workers who may occasionally be required to determine the amounts of certain substances in biological material or to attempt their isolation. The book has disadvantages for this purpose, since assisting analysts and research workers is not its primary purpose, but it is nevertheless a useful little book to have available. For initiating students into the mysteries of biochemistry, and particularly of the biochemistry relating to the animal organism, it can be warmly recommended.

F. A. ROBINSON