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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting was held at 5 p.m. on Wednesday, April 7th, at Burlington House, with the President, S. Ernest Melling, in the chair. The following papers were read and discussed:—"The Determination of Cantharadin in Beetles and Native Medicines," by J. C. Bodenstein (read by Dr. J. R. Nicholls on behalf of the author); "The Determination of Fluorine in Wool treated with Fluorides," by F. F. Elsworth, B.Sc., Ph.D., and J. Barritt, B.Sc., A.R.C.S., A.I.C.; "Polarographic Studies: III. The Determination of Vanadium," by J. E. Page, B.Sc., Ph.D., F.I.C., and F. A. Robinson, M.Sc., F.I.C.

NEW MEMBERS

THE following have been elected members of this Society:—Arthur Duncan Burman*; Alfred Eden, M.A., Ph.D., Dip.Agric. (Cantab.), F.I.C.; Henry Elder, A.H-W.C., A.I.C.; Eric French Gregg, B.Sc. (Glas.), A.I.C.*; Edwin Charles Jessop, A.I.C.; Norman Ralph Jones, B.Sc. (Lond.), A.I.C.; James Ernest Page, B.Sc., Ph.D. (Lond.), F.I.C.; Douglas Cornish Sievers, B.S. (Georgia School of Techn., Atlanta); Arthur Willie Trash.

DEATHS

Frederick William Jackson — Herbert Stanley Redgrove
Adolf Jaffé — Kenneth Wallis
Samuel Allinson Woodhead.

The Determination of Magnesium in Aluminium Alloys

BY F. PITTS, M.A., A.I.C.

THE analysis of most aluminium alloys entails the determination of magnesium. Methods based on the pptn. of magnesium ammonium phosphate are accurate but tedious,[1] as they involve the preliminary separation of most other metals present in alloying quantities. The more promising and rapid alternative methods are based on pptn. of the magnesium with 8-hydroxyquinoline (oxine), but in our hands the published procedures did not yield sufficiently accurate results to justify adoption in the routine laboratory. The need, particularly under war-time conditions, for a rapid process for the determination of magnesium led us to the methods described below.

The major problem in the determination of magnesium in aluminium alloys is its complete separation from the aluminium remaining in the insol. residue after a caustic soda attack on the alloy. Various rapid methods have been devised in which this remaining aluminium is separated by pptn. as hydroxide or by means of oxine in acetic acid soln. prior to the pptn. of magnesium with this reagent in ammoniacal soln., but in our experience these invariably involve errors through adsorption or co-pptn. of the magnesium.

According to Berg,[2] magnesium can be determined gravimetrically by pptn. with oxine from a soln. containing sodium hydroxide and sodium tartrate, in presence of aluminium, the only interfering elements being zinc, copper, cadmium and ferrous iron. There is little published work on this use of oxine, and an investigation was therefore carried out on the application of Berg's method to the analysis of aluminium alloys. Preliminary expts. were made on pure magnesium solns., prepared from magnesium sulphate or from pure magnesium (99·9% purity), and standardised by the pyrophosphate method. Results by Berg's method showed a positive error of 2–4% in the determination of 0·01–0·02 g of magnesium, when the oxinate was dried at 105° C. (*Cf.* Chirnside, Pritchard and Rooksby, ANALYST, 1941, **66**, 399.) This error was increased when the complex was ignited to oxide. To eliminate it, recourse was had to re-pptn. as follows.

* Through the Scottish Section.

Magnesium was pptd. from a soln. containing 5 g of neutral sodium tartrate and 15 ml of 2 *N* sodium hydroxide in 100 ml by addition of a slight excess of a 2% alcoholic soln. of oxine. After heating to 60° C. and cooling, the ppt. was filtered off, washed with cold, dil. sodium hydroxide soln. containing 1% of sodium tartrate, and re-dissolved in dil. hydrochloric acid. One ml of 2% oxine soln. was added, and the magnesium oxinate was re-pptd. from the hot soln. by addition of excess of ammonia (30 ml, 0·880 sp.gr.). The ppt. was collected on a Jena 1G4 sintered glass crucible, washed with hot, weakly ammoniacal water, dried at 105° C. and weighed as $(C_9H_6ON)_2Mg.2H_2O$. This method gave results accurate to 0·5%.

To ascertain the effect of other metals on the determination of magnesium by this method a series of expts. was made in which the magnesium in a standard soln. was determined in presence of aluminium, ferric iron, manganese and nickel. It was found that considerable co-pptn. of manganese with magnesium occurred under the conditions specified by Berg, but that it was considerably reduced by pptng. in a soln. of higher alkalinity. Consequently, the amount of 2 *N* sodium hydroxide was increased to 35 ml. Under these conditions the determination of magnesium was only very slightly affected by the presence of 0·1 g of aluminium and 0·05 g of ferric iron, but small amounts of manganese (and nickel) still interfered (see Table I).

TABLE I

	Additional metals in soln.			Magnesium, g	
				Taken	Found
(i)	Al,	0·1 g	.. ..	0·0061	0·0062
(ii)	Fe,	0·05 g	.. ..	0·0061	0·0061
(iii)	Mn,	0·01 g	.. ..	0·0121	0·0136
(iv)	Ni,	0·01 g	.. ..	0·0076	0·0086

This difficulty was overcome by re-pptng. the magnesium from alkaline tartrate soln. prior to the final pptn. from ammoniacal soln. In this way satisfactory results were obtained in presence of 0·01 g each of manganese and nickel, and, provided that copper and cadmium were first removed as sulphides and iron was oxidised to the tervalent state, magnesium could be determined in aluminium alloys in presence of any alloying constituents except zinc. The details of the method are as follows.

METHOD FOR ALUMINIUM ALLOYS FREE FROM ZINC.—Attack 0·25–1 g of millings with 20 ml of 20% sodium hydroxide soln. (together with 4–5 g of sodium peroxide if chromium is present), dilute to 250 ml and boil. Filter on a pulp pad and wash with hot water containing a little sodium hydroxide. Extract the residue with hot dil. (1 : 1) aqua regia, wash with hot water, add 20 ml of 10% sulphuric acid and "fume" for 5 min. Dilute to 200 ml with hot water, add a few drops of sulphurous acid (if manganese is present) and boil off the excess. Add 5 ml of 15% sodium sulphide soln., filter off the copper sulphide on a No. 4 Whatman paper, and wash with hot slightly acidified water saturated with hydrogen sulphide.

Boil off the hydrogen sulphide, oxidise with 5 ml of bromine water, and evaporate to 50 ml. Add 25 ml of 20% sodium tartrate soln., dilute to 100 ml, cool and add 60 ml of 2 *N* sodium hydroxide and 15–30 ml of a 2% alcoholic soln. of 8-hydroxyquinoline. Leave, with occasional stirring, until pptn. is complete (30 min.), heat to 60° C. to coagulate the ppt. and cool. Filter off the ppt. on a pulp pad, wash with a cold 1% aqueous soln. of sodium tartrate containing 0·1% of sodium hydroxide, and extract with 25 ml of hot 1 : 4 hydrochloric acid. Add 15 ml of 20% sodium tartrate soln. and 5 ml of 2% oxine soln. and cool. Re-ppt. the magnesium oxinate by pouring into 60 ml of 2 *N* sodium hydroxide, while stirring. Leave, with occasional stirring, until pptn. is complete (30 min.), heat to 60° C., cool, filter off on a pulp pad, wash with cold 1% aqueous sodium tartrate soln. containing a little sodium hydroxide, and extract with 35 ml of hot 1 : 2 hydrochloric acid. Add 2 ml of 2% oxine soln., dilute to 200 ml, heat to b.p. and ppt. with 30 ml of ammonia, while stirring. Leave for 15 min., filter off the ppt. on a 1G4 sintered glass crucible and wash with hot weakly ammoniacal water (1–2 ml of conc. ammonia per litre). Dry at 100–105° C. for 2 hrs., cool and weigh as $(C_9H_6ON)_2Mg.2H_2O$ (Factor, 0·0698).

This method was found satisfactory for all normal aluminium alloys except those containing zinc in amounts greater than 0·05%. The results of a series of 86 determinations on various types of alloys showed a standard deviation of ±0·012% of magnesium for Mg

contents up to 1·5% and ±0·027% for Mg contents of 1·5–2·5%. Table II gives typical results.

TABLE II

Type of alloy	Magnesium, %	
	Oxine method	Pyrophosphate method
0·5% Si; 0·5% Mg; 0·4% Fe	0·56, 0·57	0·56
	0·64, 0·65	0·64
1% Si; 1% Mg; 0·4% Fe	1·06, 1·04	1·05
	0·93, 0·93	0·93
4% Cu; 0·6% Mn; 0·6% Mg; 0·4% Si; 0·4% Fe ..	0·67, 0·68	0·68
	0·74, 0·72	0·72
3% Cu; 0·5% Sb; 0·2% Sn; 0·6% Mg; 0·3% Si; 0·4% Fe	0·56, 0·55	0·56
	0·56, 0·56	0·57
4% Cu; 2% Ni; 1·5% Mg; 0·5% Si; 0·5% Fe ..	1·55, 1·54	1·53
	1·51, 1·53	1·51
2·5% Mg; 0·2% Cr; 0·1% Si; 0·2% Fe	2·33, 2·31	2·34
	2·36, 2·37	2·33
5% Mg	4·79, 4·87	4·83
	4·91, 5·02	4·94

Each horizontal row of figures represents a different sample.

In all these expts. a "blank" was obtained by making a concurrent determination on a standard soln. of known magnesium content.

DETERMINATION OF MAGNESIUM IN ALUMINIUM ALLOYS CONTAINING ZINC

When the content of zinc exceeds 0·05% the zinc is not completely removed during the preparation of the caustic soda soln. of the alloy, and zinc remaining in the insol. residue is subsequently pptd. quantitatively with the magnesium. Preliminary expts. showed that, with a pure zinc soln., no pptn. of zinc oxinate occurred from an alkaline tartrate soln. containing potassium cyanide.

To ascertain if zinc could thus be retained in soln. while magnesium was pptd. quantitatively as oxinate, a series of solns. was prepared to contain known amounts of magnesium and zinc and 5 g of sodium tartrate in a vol. of 125 ml. The solns. were made alkaline with 35 ml of 2 *N* sodium hydroxide, varying amounts of a 30% soln. of potassium cyanide (30 g per 100 ml of water) were added to each, and the magnesium was pptd. with 15 ml of a 2% alcoholic soln. of oxine. The soln. was stirred to induce pptn. and left with occasional stirring until pptn. was complete, then heated to 60° C. and cooled. The magnesium oxinate was filtered off, washed, re-dissolved in 35 ml of 1:2 hydrochloric acid, and re-pptd. with ammonia as in the oxine process described above. The complex was dried at 105° C. and weighed as $(C_9H_6ON)_2Mg.2H_2O$. From the difference between the weight of the ppt. and the weight of that obtained similarly from a soln. containing the same amount of magnesium but no zinc, the amount of zinc pptd. was calculated. In one expt. the results were checked by dissolving the residue in hydrochloric acid, destroying the oxine by wet oxidation with sulphuric acid and ammonium nitrate and pptng. the zinc with mercuric potassium thiocyanate. Results are given in Table III.

TABLE III

Expt.	KCN used ml	Zn taken g	Mg taken g	Wt. of ppt. (W_1) g	Wt. of Zn oxinate (W_1–W_2) g	Zn in ppt. g
1	3	0·050	0·0060	0·2033	0·1161	0·0216 [0·0219 by $ZnHg(CNS)_4$]
2	7	0·050	0·0060	0·1146	0·0274	0·0051
3	10	0·050	0·0060	0·0991	0·0119	0·0022
4	—	—	0·0060	0·0872(W_2)	—	—

Next, a series of expts. was made, as described above, on a soln. containing 0·0060 g of magnesium and varying amounts of zinc, 10 ml of 30% potassium cyanide soln. being used in each instance. The results (in g) are given in Table IV.

The results in Table III show that, with 10 ml of 30% potassium cyanide soln. and an initial zinc content of 0·05 g, the amount of zinc remaining after a single pptn. from

alkaline-tartrate-cyanide soln. is 0·002 g (approx.), which, after a second pptn., is reduced to a negligible amount (Table IV). Consequently, the use of this amount of cyanide (during each of the alkaline tartrate pptns.) is sufficient to prevent the interference of zinc in any quantity likely to be met with in the determination of magnesium in aluminium alloys.

TABLE IV

Expt.	Zn taken	Mg taken	Mg found
1	0·001	0·0060	0·0061
2	0·005	0·0060	0·0060
3	0·010	0·0060	0·0061
4	0·020	0·0060	0·0065

In the expts. described above the liquid was stirred to induce pptn. of the magnesium oxinate and at intervals during the pptn. It was observed, however, that if the soln. was only stirred initially in order to mix the reactants and was then allowed to stand without further stirring until the ppt. had settled out, the magnesium was not completely pptd. This does not occur in absence of cyanide. To investigate this, a series of expts. was made as described above, on pure magnesium solns. and varying amounts of 30% potassium cyanide soln. and 2% oxine soln. without stirring during pptn. In a large number of expts., in each of which 0·0060 g magnesium was used, the results ranged from 0·0047 to 0·0058 g of magnesium found and did not depend upon the amount of cyanide or oxine employed. In numerous other expts. 15 ml of 2% oxine soln. and 10 ml of 30% potassium cyanide solution were used, with solns. containing 0·0060 g of magnesium,- the solns. being stirred to induce pptn. and then at intervals until the ppt. began to coagulate (20–30 min.). All the results were satisfactory (0·0059–0·0061 g of magnesium found).

A series of expts. was then made on solns. containing known amounts of magnesium, zinc, copper, ferrous iron, manganese, cadmium and aluminium. The results are given in Table V.

TABLE V

Expt.	Additional metals in soln.	Mg taken, g	Mg found, g
1	0·05 g Zn	0·0060	0·0061*
	,, ...	,,	0·0060*
2	0·01 g Zn, 0·005 g Fe^{II}	0·0060	0·0060
3	0·01 g Zn, 0·006 g Mn	0·0060	0·0060
4	0·01 g Zn, 0·01 g Al	0·0060	0·0059
5	0·08 g Cu	0·0060	0·0060†
	,, ...	,,	0·0059
6	0·01 g Zn, 0·02 g Cd	0·0060	0·0059

* Residue contained 0·0001 g Zn. † Residue contained 0·00002 g Cu.

Equally satisfactory results were obtained in presence of 0·006 g of antimony, 0·002 g of tin and 0·01 g of bismuth. From the results it is apparent that magnesium may be determined by pptn. as oxinate from alkaline tartrate soln. containing potassium cyanide, in presence of zinc, copper, cadmium, and ferrous iron. 8-Hydroxyquinoline is therefore a specific reagent for the determination of magnesium under these conditions. The details of the method for the determination of magnesium in aluminium alloys containing zinc, copper and cadmium are as follows.*

METHOD FOR ALUMINIUM ALLOYS CONTAINING ZINC, COPPER AND CADMIUM.—Attack 0·25–2·0 g of millings with 20–40 ml of 20% sodium hydroxide soln., dilute to about 250 ml and boil. Filter on a pulp pad and wash with hot water containing a little sodium hydroxide. Extract the residue with hot dil. (1:1) aqua regia, wash with hot water, add 10 ml of 10% sulphuric acid and "fume" for 5 min. Dilute to about 50 ml, add, if necessary, 5–6 drops of sulphurous acid (if manganese is present) and boil for *ca.* 2 min. to expel excess SO_2. Add 12–15 drops of bromine water and boil for 5 min. to drive off excess bromine, filter through a No. 4 Whatman paper, to remove silica, and wash with hot water.

Cool, add 25 ml of 20% sodium tartrate soln. and dilute to 100 ml. Make alkaline with 60 ml of 2 *N* sodium hydroxide, add 10 ml of 30% potassium cyanide soln., and ppt. the magnesium with 15–30 ml of a 2% alcoholic soln. of 8-hydroxyquinoline. Stir vigorously to induce pptn., then intermittently until the ppt. begins to coagulate (20–30

* Details of this method have already been given in the Company's handbook No. 399 (*"Analysis of Aluminium and its Alloys"*).

min.), heat to 60° C., cool, filter off the ppt. on a pulp pad, wash with a cold 1% soln. of sodium tartrate containing about 0·1% of sodium hydroxide, extract with 25 ml of hot 1:4 hydrochloric acid, and wash with hot water. To the extract, add 15 ml of 20% sodium tartrate soln. and 5 ml of 2% oxine soln. and cool. Re-ppt. the magnesium by pouring into a mixture of 60 ml of 2 *N* sodium hydroxide soln., and 10 ml of 30% potassium cyanide soln., with continuous agitation. As before, stir vigorously to induce pptn. and then intermittently until the ppt. begins to coagulate. Heat to 60° C., cool, filter on a pulp pad and wash, as before, with 1% sodium tartrate soln. containing sodium hydroxide. Extract the ppt. with 35 ml of hot 1 : 2 hydrochloric acid and wash with hot water. Add to the extract 1–2 ml of 2% oxine soln., dilute to 200 ml., heat to boiling, and ppt. the magnesium oxinate by addition of 30 ml of ammonium hydroxide (sp.gr. 0·880). Leave for 15 mins., filter off the ppt. on a 1G4 sintered glass crucible, and wash with hot weakly ammoniacal water. Dry at 105° C. for 2 hrs., cool and weigh as $(C_9H_6ON)_2Mg.2H_2O$. (Factor, 0·0698.)

This method proved satisfactory for all types of aluminium alloys. Table VI contains the results of a series of determinations carried out on various types of alloys. In each expt. a "blank" was obtained by making a concurrent determination on a standard soln. of known magnesium content. A series of 40 determinations showed a standard error of ±0·013% magnesium.

TABLE VI

Type of alloy	Zn, %	Magnesium, %	
		Oxine	Pyrophosphate
1% Zn; 0·3% Bi; 1% Mg; 0·2% Si; 0·3% Fe ..	0·91	1·00	0·97
	1·00	1·11	1·10
4% Cu; 0·6% Mn; 0·6% Mg; 0·4% Si; 0·4% Fe ..	0·17	0·45	0·46
	0·26	0·69	0·70
10% Zn alloy	10·8	0·25	0·24
11% Zn; 0·7% Sn; 0·1% Sb; 0·4% Mg; 0·1% Cu; 0·2% Si; 0·4% Fe	11·3	0·36	0·38
D.T.D.424	0·2	0·01	0·01
	0·2	0·07	0·07
D.T.D.428	3·0	0·03	0·03

Whilst the use of this modified process is essential for alloys containing zinc, in absence of zinc it may be desirable to retain the use of the method originally described, as it is more easily carried out and avoids the use of cyanide.

RAPID SEMI-MICRO METHOD FOR THE DETERMINATION OF MAGNESIUM IN ALUMINIUM ALLOYS.—The rapid semi-micro method described in the Company's handbook No. 399 (*"Analysis of Aluminium and its Alloys,"* pp. 79–81) was developed primarily for use with duralumin, and, whilst it is satisfactory for this alloy, experience has shown that it is not of sufficiently general applicability, particularly in presence of zinc. An investigation was therefore undertaken to devise a rapid semi-micro method suitable for all types of aluminium alloys and, as a basis for this, the oxine process just described seemed to be most suitable, for in this method no separations are necessary prior to that of magnesium. Expts. were first made to determine whether the final (ammoniacal) pptn. of magnesium oxinate could be avoided by carrying out the process on a semi-micro scale. For this purpose various amounts of a standard magnesium soln. (1 ml ≡ 0·00030 g of Mg) were pipetted out and diluted to 100 ml in standard flasks, from which 10-ml portions were pipetted into a series of 150-ml beakers. Ten ml of water were added to each, and then 5 ml of 20% sodium tartrate soln. and 1 drop of 1% phenolphthalein soln. The solns. were neutralised with, and given 2 ml excess of, 2 *N* sodium hydroxide, and then treated with 2 ml of 30% potassium cyanide soln., and 2 ml of 2% alcoholic oxine soln. The solns. were stirred mechanically to induce pptn. and then for a further period of 1 min., left for 10 min. and again stirred for 1 min., heated to 60° C. and cooled. The ppts. were filtered off on Jena 3G3 sintered glass funnels cut down to a height of 17 mm above the disc and provided with asbestos pads, washed with *ca.* 120 ml of a cold 1% soln. of sodium tartrate containing about 0·1% of sodium hydroxide, in 10 portions, and then redissolved in 20 ml of hot 1 : 1 hydrochloric acid and 30 ml of hot water. The solns. were cooled, excess standard potassium bromate soln. (1 ml ≡ 0·05 mg of Mg) was added with shaking, 10 ml of 10% potassium iodide soln. were added to each, and the excess bromate was

determined by titration with sodium thiosulphate soln. (starch as indicator). The standard solutions were as specified on p. 139. The results were approx. 10% high.

The expts. were repeated, but instead of 1% sodium tartrate as wash soln. a soln. composed of 500 ml of rectified spirit, 430 ml of water, 50 ml of 20% sodium tartrate soln. and 20 ml of 2 *N* sodium hydroxide soln. was used, since oxine is more sol. in aqueous alcohol than in water, whilst magnesium oxinate is insol. even in abs. alcohol. Satisfactory results were obtained in a series of 24 expts.; *e.g.*, for 4 expts., in which the quantities of magnesium taken were respectively 0·15, 0·30, 0·60 and 1·20% on 1 g, the pairs of duplicate results were 0·17, 0·17; 0·30, 0·33; 0·59, 0·63; 1·18, 1·20.

To ascertain the effectiveness, on this semi-micro scale, of a single pptn. of magnesium as oxinate from alkaline tartrate-cyanide soln. for the complete separation of magnesium from other metals, a series of determinations was made in which 20-ml portions of the standard magnesium soln. and various amounts of standard solns. of other metals were diluted to 100 ml in standard flasks. Ten-ml portions were pipetted out, 10 ml of water and 5 ml of sodium tartrate soln. were added, and so on as described above. The results, given in Table VII, indicate that it is sufficient, on a semi-micro scale, to separate the magnesium by a single pptn. as oxinate from alkaline tartrate-cyanide soln.

TABLE VII

Expt.	Other metals, etc., present, % on 1 g.	Magnesium, % Taken	Found
1	Mn, 1·0	0·60	0·56, 0·61
2	Cu, 8·0	0·60	0·61, 0·58
3	Zn, 2·0	0·60	0·59, 0·62
4	Al, 5·0	0·60	0·59, 0·60
5	Ni, 0·75	0·60	0·60, 0·61
6	Fe, 2·0	0·60	0·62, 0·61
7	Si, 1·0	0·60	0·60, 0·61

On these results a rapid semi-micro method for the determination of magnesium in aluminium alloys has been based, and in a series of 80 determinations there was a standard deviation of ±0·019% of magnesium for Mg contents 0–1·0% and of ±0·037% for Mg contents 1·0–2·5%. Table VIII gives some typical results.

TABLE VIII

Type of alloy	Sample weight, g	Magnesium, % Semi-micro Oxine	Pyro-phosphate
4% Cu; 0·6% Mn; 0·6% Mg; 0·4% Si; 0·4% Fe ..	1	0·46, 0·48	0·46
,, ,, ...	1	0·72, 0·71	0·70
10% Zn alloy	1	0·25, 0·28	0·24
,, ...	0·5	1·18, 1·16	1·18
D.T.D.424	2	0·05	0·07
D.T.D.428	2	0·01	0·03
3% Cu; 0·5% Sb; 0·2% Sn; 0·6% Mg; 0·3% Si; 0·4% Fe	1	0·51, 0·51	0·51
,, ,, ,,	1	0·48, 0·48	0·49
1% Zn; 0·3% Bi; 1% Mg; 0·4% Si; 0·4% Fe ..	1	0·71	0·73
	0·5	1·09	1·10
4% Cu; 2% Ni; 1·5% Mg; 0·5% Si; 0·5% Fe ..	0·5	1·43	1·46
	0·5	1·47	1·46
2·5% Mg; 0·2% Cr; 0·1% Si; 0·2% Fe	0·5	2·37	2·34
	0·5	2·32	2·34
	0·5	2·37	2·33

Semi-micro Method.—Attack 0·5–2·0 g of millings with 20–40 ml of 20% sodium hydroxide soln., dilute to 150 ml and boil. Filter off the residue on a pulp pad, and wash with hot water containing about 0·2% of sodium hydroxide. Extract with 15 ml hot dil. (1:1) aqua regia and wash with hot water. Boil the extract for *ca.* 1 min., cool and make up to 100 ml in a standard flask. Pipette 10 ml into a 150-beaker, add 5 ml of water, 5 ml of 20% sodium tartrate soln. and 1 drop of phenolphthalein (1%). Neutralise with 2 *N* sodium hydroxide and add 2 ml excess. Add 2 ml of 30% potassium cyanide soln. and 2 ml of 2% alcoholic oxine soln. (3 ml for Mg contents >2·0%. Stir to induce pptn.

and then for a further period of 1 min., allow to stand for 10 min. and again stir for 1 min. Heat to 60° C. and cool. All reagents are to be added from pipettes or burettes.

Filter off the precipitate under suction on a short 3G3 funnel with an asbestos pad and wash with about 120 ml of a solution composed of 500 ml of alcohol, 430 ml of water, 50 ml of 20% sodium tartrate soln. and 20 ml of 2 *N* sodium hydroxide, in 10 portions. Extract the ppt. with 20 ml of hot 1:1 hydrochloric acid and 30 ml of hot water. Cool and add 20 ml of standard potassium bromate soln. (40 ml for Mg >20%), with shaking and at once add 10 ml of 10% potassium iodide soln. Titrate with standard sodium thiosulphate soln., adding a little starch towards the end of the titration. Make a simultaneous determination on a soln. of known magnesium content and obtain the "blank" by difference.

Reagents.—Potassium bromate: 0·458 g of $KBrO_3$, 4 g of KBr and 0·1 g of KOH per litre (1 ml ≡ 0·05 mg Mg); sodium thiosulphate: 4·10 g of $Na_2S_2O_3.5H_2O$ per litre; 20% sodium tartrate soln.; 30% potassium cyanide soln.

This method is very rapid; a single determination takes about 1 hr. and a series of 10 determinations 4 hrs. as compared with 8–9 hrs. for 10 determinations by the macro-oxine process described on p. 136, and with 36–40 hrs. for the same number of determinations by the pyrophosphate process.

SUMMARY.—An investigation has shown that magnesium may be determined in aluminium alloys by means of 8-hydroxyquinoline (oxine) more quickly than by the standard phosphate process. Details are given of a full-scale gravimetric method suitable for alloys not containing zinc, and of a modification enabling alloying quantities of zinc to be dealt with. A rapid, semi-micro volumetric method based on this modified procedure is also described.

In absence of zinc, the bulk of the aluminium is removed by a caustic soda attack, copper and cadmium are pptd. as sulphides, and iron is oxidised to the tervalent state before pptn. of the magnesium by means of oxine from alkaline tartrate soln. A re-pptn. from the same medium and a final pptn. from ammoniacal soln. with the same reagent effects complete separation from all other elements. In presence of zinc, the magnesium is pptd. from alkaline tartrate soln. containing cyanide. Under these conditions, copper, cadmium, zinc and ferrous iron do not interfere and pptn. of sulphides is unnecessary. This is more rapid than the first method. The presence of cyanide retards the pptn. of magnesium, and vigorous stirring is necessary to make the pptn. quantitative. Re-pptn. is carried out as before, and then a final pptn. from ammoniacal soln.

This latter method forms the basis of a very rapid semi-micro method suitable for all normal alloys and involving only a single pptn. from alkaline-tartrate-cyanide medium, the smaller quantities of interfering elements and smaller excess of oxine rendering further pptns. unnecessary. The pptd. magnesium oxinate is redissolved and determined by the standard volumetric method with bromate. The accuracy is somewhat less than in the two previous methods, although it is sufficient for all control purposes. In all the methods a control determination is made simultaneously on a soln. of known magnesium content.

This work was carried out in the Laboratories of the British Aluminium Co., Ltd., under the general direction of Dr. A. C. G. Gwyer, Scientific Manager. I am indebted to the Company for permission to publish. I also wish to thank Mr. J. H. Dickin, Laboratory Manager at Warrington, for helpful advice and criticism, and Miss L. Fairbrother, who did much of the experimental work; also my colleagues at the Company's Kinlochleven Laboratory, particularly Mr. A. C. Coates and Mr. G. H. Stott, for the assistance I received from a study of the alternative rapid modification of the oxine process developed by them and published in the Company's handbook, "*Analysis of Aluminium and its Alloys*" (No. 399).

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RESEARCH LABORATORIES, BRITISH ALUMINIUM CO., LTD.
WARRINGTON, LANCS.

September, 1942

The Determination of Sulphur Dioxide in Citrus Juices

By A. H. BENNETT, B.Sc., and F. K. DONOVAN, B.Sc.

(*Read at the Meeting, November* 4, 1942)

Sulphur dioxide is universally used for the preservation of citrus juices, and its rapid determination is of importance, since the amount present may vary indefinitely from cask to cask (or in concentrated juices even in different parts of the same cask) and the results found on an average sample of a large consignment give no guarantee for the individual casks which may have to be stored for a considerable time before use.

Any process of determination involving distillation is tedious and requires special apparatus, and the easiest and most rapid method is direct titration of the juice with iodine soln. This could most conveniently be used by the manufacturers of citrus juices in order to assure themselves that each lot of the freshly squeezed juice has been given the amount of preservative required, but its application to juice which has been for some time in storage is complicated by two factors. First, the presence in the juice of natural reducing substances (principally ascorbic acid) which react with iodine and, secondly, the "fixation" of part of the added sulphur dioxide by the sugars of the juice, compounds being formed which do not react immediately with iodine. The proportion thus fixed increases with time and may amount to 20–60% of the total sulphur dioxide present. The compounds formed are extremely labile and, if the free sulphur dioxide is removed by oxidation with iodine and the liquid is allowed to stand, a portion of the combined sulphur dioxide is liberated and becomes titratable; by repeating this process at intervals practically the whole of the sulphur dioxide present, free or combined, can be determined.

Jensen[1] called attention to this fixation of sulphur dioxide in glucose syrups and proposed the following method for its rapid determination: Dilute 50 g of the syrup with an equal quantity of water, cool to 15° C. and treat the soln. with 20 ml of 5% sodium hydroxide soln. After 15 min. add 30 ml of 20% sulphuric acid and 100 ml of water together with a little starch soln. and immediately titrate with $N/20$ iodine soln. until a blue colour, permanent for 1 min., is obtained.

Sulphur Dioxide in presence of other Reducing Substances.—The following expts. show that similar effects are produced in more dilute solns. approaching the composition of orange juice.

A soln. containing 11% of invert sugar and 1·3% of citric acid, which immediately after addition of potassium metabisulphite gave by direct titration 1195 p.p.m. of sulphur dioxide, after 30 min. showed 1075. The colour faded after a few min. and by repeated further additions of iodine at intervals during 48 hrs. the final result was again 1195. After 2½ hrs. standing, direct titration gave 985 p.p.m. and after 48 hrs. 704. At this point the liquid was treated with excess of soda and after 10 min. standing acidified and immediately titrated, the result being 1200 p.p.m.

In a more conc. soln., containing 39% of invert sugar and 4% of citric acid, corresponding to orange juice conc. to ⅓ vol. or less, the fixation of sulphur dioxide was more rapid. A mixture containing 1000 p.p.m. of sulphur dioxide gave by direct titration, after 2 hrs. standing, 467 p.p.m. and, after 20 hrs., 240. Then after treatment with soda, and acidification as above, 998 p.p.m. were found.

This process has been applied to citrus juices, with satisfactory results. All operations are carried out in stoppered bottles, and it has been found that the alkaline treatment for a time not exceeding 10 min. has little effect on the natural reducing substances present. These, as is well known from the results of many workers on the ascorbic acid content of juices, are not constant in freshly prepared juices; they diminish in storage, even in presence of sulphur dioxide, and may eventually disappear almost entirely. It is necessary, therefore, to determine in each instance the amount of iodine corresponding to these substances and deduct it from the total titration figure. This can be done in two ways:

(1) By diluting the juice with 2 or 3 vols. of water, boiling to expel the sulphur dioxide, cooling rapidly and titrating. The natural reducing substances of the sulphited juice are not appreciably affected by this procedure, and the figure obtained, subtracted from the total iodine required after the treatment with soda as described, gives the amount corresponding to the sulphur dioxide present.

(2) By the method suggested by Mapson[2] for the determination of ascorbic acid. To 20 ml of juice add 8–10 ml of acetone and leave for 10 min. before titration. The compound of sulphur dioxide and acetone thus formed does not react with iodine, and the figure found on titration represents the natural reducing substances only. This process can be applied to the liquid after treatment with excess of alkali, but it is then necessary to add sulphuric acid just equiv. to the alkali employed and not a large excess as described above, for the acetone sulphur dioxide compound is not stable in presence of strong acid. The results have shown that the natural reducing substances are not appreciably affected by the alkaline treatment in the short time employed.

In this way, by 3 titrations, which can be carried out in a few min., the amount of preservative and of the natural reducing substances can readily be ascertained.

EXAMPLES.—*Orange juice.*—A sample, slightly diluted to allow for the vol. of metabisulphite soln. to be added, gave by direct titration natural reducing substances equiv. to 152 p.p.m. of sulphur dioxide. Metabisulphite was added in such quantity as to give 1070 p.p.m. of sulphur dioxide in the mixture. After standing 24 hr. it gave the following results:

Direct titration required iodine equiv. to 872 p.p.m. of sulphur dioxide.
Titration after treatment with alkali, etc. ≡ 1203 p.p.m. of sulphur dioxide.
Natural reducing substances after boiling ≡ 150 p.p.m. of sulphur dioxide.
Titration in presence of acetone ≡ 146 p.p.m. of sulphur dioxide.
Subtracting the mean of the last two figures from the previous ones we have: Free sulphur dioxide 724 and total sulphur dioxide 1055 p.p.m.
Determined by distillation and pptn. as barium sulphate the amount was 1045 p.p.m.

Grape fruit juice, freshly pressed in the laboratory, gave on direct titration reducing substances equivalent to 190 p.p.m. of sulphur dioxide. Sulphur dioxide was added in the form of a strong soln. of sulphite and the liquid was titrated at intervals.

	Time after mixing			
	3 hrs.	7 days	14 days	29 days
Direct titration (*a*)	791	680	684	620
After treatment with soda, etc. (*b*)	834	805	810	760
After boiling off SO_2 (*c*)	188	180	175	175
Free SO_2 (*a*—*c*)	603	500	509	445
Total SO_2 (*b*—*c*)	646	625	635	585
Total SO_2 by distillation and pptn. as $BaSO_4$ ..	631	626	626	567

The proportion of free to total sulphur dioxide diminished on standing, notably during the first 7 days, but afterwards changed very slowly. The juice was kept in corked bottles throughout the experiment and portions were withdrawn from time to time for analysis, and in the last 14 days there was some loss of sulphur dioxide without, however, any appreciable change in the reducing substances.

COMMERCIAL SAMPLES.—The following results were obtained:

	1	2		3		4	5	6
	Orange juice (probably 5–6 months in store) p.p.m.	W. Indian grape fruit juice		W. Indian grape fruit juice		S. African grape fruit juice p.p.m.	Concntd. orange juice (×5) p.p.m.	Concntd. orange juice (×7) p.p.m.
		As received p.p.m.	After 3 months p.p.m.	As received p.p.m.	After 3 months p.p.m.			
Direct titration (*a*) ..	536*	2067	1484	334	140	260	1623	1360
After treatment with soda, etc. (*b*) ..	795	2963	2356	579	352	590	4127	1520
Natural reducing substances after boiling (*c*) .. ≡	125	128	32	—	24	15	—	—
Natural reducing substances by titration in presence of acetone (*d*) ≡	132	128	32	77	—	—	625	1290
Free SO_2, ...	404	1939	1452	—	116	245	598	70
Total ,, ...	663	2855	2324	—	328	575	3502	230
Total SO_2, gravimetric	—	—	2303	—	327	552	3511	230

* Increasing on further additions of iodine during 18 hrs. to 789 p.p.m.

It will be seen that some of these samples contain very large amounts of sulphur dioxide, but that does not prevent a continuous diminution in the natural reducing substances on keeping. On the other hand, we have kept in the laboratory a concntd. orange juice of the type of No. 6, containing only a small amount of preservative, in partly filled wide-mouthed jars, for 4 years without any fermentation or growth of mould. The material darkened considerably and the ascorbic acid content diminished, but after 2 years was still more than half the original value. We do not think that such large amounts of sulphur dioxide as are here shown are in any way necessary if the juice is carefully prepared in the first instance.

The question whether combined sulphur dioxide is efficient as a preservative cannot at present be certainly answered. Since it has been shown that when the free sulphur dioxide is oxidised the combined sulphur dioxide is gradually set free, it appears probable that the compounds constitute a reserve, but since the liberation is slow and produces only a low concn. in the soln., this might not be effective against any fresh contamination with yeasts. It is hoped to make some further expts. on this point.

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87–89, Aldgate High Street, London, E.C.3 *December*, 1942

Discussion

Mr. Norman Evers said that the authors' method was of value because it distinguished between free and combined sulphur dioxide. It would be interesting to know whether the combined sulphur dioxide was effective as a preservative. In his experience yeasts would grow even in presence of 800 p.p.m. of sulphur dioxide and the explanation might be found in this combination of the sulphur dioxide with sugars.

A Method for Estimating the Added Prepared Chalk B.P. (Creta) in National Flours

By A. W. Hartley, A.I.C., and Albert Green, M.C., M.Sc., Ph.D., F.I.C.

The method here described has been used for some time as a routine procedure in estimating the added calcium carbonate content of the National flours produced in a number of flour mills. The Ministry of Food requires 7 ozs. of Prepared Chalk to be incorporated in each sack (280 lbs.) of National flour. In essentials, the following procedure is that described by Hutchinson and MacLennan[1] for assessing the carbonate content of soils, but it differs from theirs in some details and in manipulation. The apparatus is shown in Fig. **1**. The decomposition section consists of a 300-ml Pyrex bolt-head, round-bottomed flask D, fitted with a tap tube C, a 50-ml glass-stoppered cylindrical funnel, and an exit tube which is packed just above the cork with a glass-wool plug. Decomposition of the calcium carbonate is carried out in this flask. The liberated carbon dioxide is absorbed in a second Pyrex bolt-head, round-bottomed flask, E, of 1,500 ml capacity connected to the decomposition flask by a short length of semi-pressure tubing and also fitted with a 50-ml stoppered cylindrical funnel. The glass tube C and that between the flasks are of 8 mm internal diam.

Provision is also made for a supply of CO_2-free air, and we have found convenient a combination of a soda-lime packed tower (8 in. high) connected to tube C and preceded by a gas-washing bottle of 180 ml capacity with a sintered glass bubbler of porosity I (Gas Wash Bottle 180 ml, B.40, S.G.J.) containing 50 ml of potassium hydroxide soln. These two are not connected to the decomposition flask until the later stages of the estimation.

Method.—Weigh the flour (25 g) into the dry 300-ml flask and connect as shown in the figure, tubes C and F being in the raised positions. Into the funnel B (larger flask) run from a burette 25 ml of 0·1 *N* barium hydroxide, and place 50 ml of approx. 2% hydrochloric acid (6 ml of conc. HCl, sp.gr. 1·16, in 100 ml) in the other (decomposition) funnel, A.

Reduce pressure in the apparatus through tap C to about 5 cm of mercury. After closing C, run the bulk of the baryta into flask E, and push the lead-in tube F (lubricated with a

little glycerin) almost to the bottom of the flask. Retain a small quantity of baryta in the stoppered funnel to avoid loss of vacuum. Run two 50-ml portions of 2% hydrochloric acid on to the flour in flask D without allowing air to enter. (The end of the funnel should be so cut as to allow the acid to run on to the flour in a steady stream, for a spray of acid leads to excessive frothing.) Shake the mixture gently until the flour is evenly wetted. We find that a smooth suspension is rapidly produced without the aid of glass beads or similar disintegrating agents. Next push tube C to the bottom of the small flask and connect it to the soda-lime tower, which is joined to the potash wash bottle. By carefully opening tap C allow a gentle stream of CO_2-free air to pass through the flour suspension, and by suitable adjustment, continue aspiration so that in 15 min. the pressures are completely equalised. A tendency to excessive frothing at any stage is effectively counteracted by gentle agitation of the flour flask. When no more air passes close the screw clip on the rubber connection between the two flasks and disconnect the large absorption flask. Swirl the baryta round this flask for *ca.* 1 min. to absorb any traces of free carbon dioxide and then wash the remaining alkali into the flask from the funnel B with distilled water. Rinse down the tubes (inside and outside) and sides of the flask, using a total vol. of 150 ml of water. Finally, titrate the excess barium hydroxide with a 0·1 *N* soln. of an organic acid, using one drop of phenolphthalein as indicator.

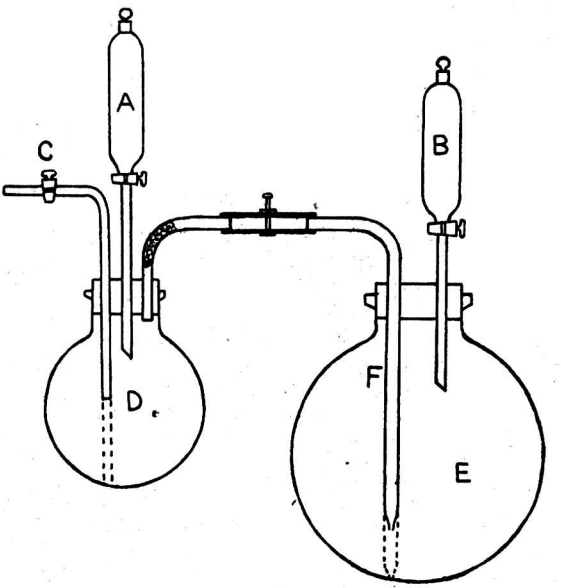

Fig. 1

The distilled water for rinsing down is stored in a large aspirator bottle protected from atmospheric carbon dioxide and is applied through a fine jet at the end of rubber tubing. A mouth wash-bottle is not used.

RESULTS.—The theoretical content of pure calcium carbonate in a flour containing 7 ozs. of prepared chalk per 280-lbs. of flour is 153 mg per 100 g of flour, assuming the chalk to be of 98% purity by the B.P. method of assay. Blanks for the carbon dioxide content of 25 g of unsupplemented flour, 100 ml of 2% hydrochloric acid and 150 ml of wash water are carried out when required. The average figure for this blank for a number of our determinations is 5·5 mg of $CaCO_3$ per 100 g of flour.

In a large number of routine determinations duplication has been very good, and the recovery of carbon dioxide from laboratory-prepared samples is invariably close to theoretical. Furthermore, decomposition of both calcium carbonate (A.R.) and Prepared Chalk (B.P.) in the apparatus, not in admixture with flour, gives yields of carbon dioxide in very close agreement with the results of the B.P. method of assay.

The foregoing method differs from the soil carbonate method of Hutchinson and MacLennan[1] in the use of larger flasks; the use of baryta instead of sodium hydroxide; a shorter aspiration time, which we have found to be adequate; the dipping of the jetted tube below the surface of the alkali. We prefer this method to gravimetric methods[2] mainly because of its relative rapidity and the fact that while the carbon dioxide evolved from 25 g of flour utilises approx. 7·6 ml of 0·1 *N* barium hydroxide, its weight is very small relative to that of the gravimetric absorption train.

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CENTRAL LABORATORIES, SPILLERS LIMITED, BIRKENHEAD *October 20th, 1942*

Two New Colour Reactions for Stilboestrol

By T. TUSTING COCKING, F.I.C.

Several years ago, in an attempt to assay stilboestrol by means of its bromine absorption, the formation of a bright green colour was observed in some expts. As esterification with acetic anhydride offered a simpler method of assay, no further work on the bromine absorption was carried out at that time. Recently this bromination has been studied further, to ascertain if a delicate identity test and possibly also a means of estimating small quantities colorimetrically could be based on the colour reaction. Attempts were made to produce the green colour by warming an acetic acid soln. of stilboestrol with slightly more than 12 equivs. of bromine. No green colour was formed but a clear orange soln. was obtained which, when evaporated to dryness on a water-bath in a current of air, left a pale orange residue. After one such expt. the reaction flask was washed out twice with glacial acetic acid, several times with water and then with a little acetone. The acetone was immediately coloured violet; this was found to be due to the action of water on a soln. of brominated stilboestrol containing free bromine in a water-miscible solvent.

Violet Colour Reaction.—In the early experiments, bromination under the following conditions yielded a soln. from which the violet colour could be readily developed:—equal volumes of a 1% soln. of stilboestrol and a 5% v/v solution of bromine, both in glacial acetic acid, were mixed in a small test-tube and warmed in a water-bath for 1 min. One drop of the resulting orange soln., with 5 drops of acetone followed immediately, by 2 ml. of water, produced a deep violet colour. If the water was not added immediately, the acetone soln. slowly became colourless owing to absorption of the free bromine, and then no colour was produced on addition of water. Addition of a trace of bromine to the decolorised acetone soln. restored the power of colour production.

With absolute alcohol instead of acetone, absorption of free bromine did not appear to take place and on the subsequent addition of water a purple colour, becoming bluer on dilution, was produced. In further expts. alcohol was found to be a more suitable solvent than acetone.

These coloured aqueous solns. are colloidal in nature and the colours vary from purple to violet according to the dispersion of the colloidal particles. The colouring matter is readily extracted from its aqueous dispersion by many organic solvents; it dissolves readily in ether, chloroform, amyl alcohol, amyl acetate, light petroleum and benzene, producing clear red solns. Of these, the soln. in chloroform appears the most suitable for colour comparisons.

Although the orange soln. will give a violet colour with water alone, the colouring matter rapidly coagulates, leaving the soln. only slightly coloured. Hence, to secure a good dispersion on dilution with water the presence of a small quantity of a miscible solvent is necessary. Additional glacial acetic acid would appear to be the obvious solvent, but more uniform colours are obtained when alcohol is used.

If the orange soln. is diluted with a water-insol. solvent, *e.g.*, chloroform, and then shaken with water, little or no colour develops; it is essential to form first the colloidal substance which may then be extracted by chloroform.

If the free bromine is removed completely from the orange soln., by contact with acetone for a few mins. or by evaporating in a current of air and dissolving the residue in abs. alcohol, the resulting soln. gives no colour with water but produces the violet colour with water containing a trace of bromine or chlorine (but not iodine).

The violet colour of the colloidal dispersion fades gradually. The orange solution appears to be stable as long as the free bromine persists and, even after standing in an open test-tube for several days, immediately produces the colour on being mixed with alcohol and water.

The reaction appears to be quantitative, and 1μg of stilboestrol dissolved in 0·1 ml of glacial acetic acid may be detected. The presence of any oily substance or anything that prevents the dispersion of the colloidal particles lessens or entirely prevents the formation of colour.

Chloroform Extract of the Colouring Matter.—If the aqueous dispersion is shaken with chloroform the whole of the colouring matter dissolves in this, forming an orange red soln. which fades only slowly so long as it is covered by the aqueous layer. When separated and dried by means of anhydrous sodium sulphate, however, the chloroform soln. fades

rapidly, and consequently cannot be used for accurate colorimetric determinations. All attempts to prevent fading have been unsuccessful. Removal, by means of sodium thiosulphate, hydroxylamine, or acetone, of the last trace of free bromine left *after* the colour has been formed, hastened the fading as also did addition of more bromine, acetic acid, hydrobromic acid or sodium acetate. Numerous solvents were tried, including strong alcohol and mixed alcohol and chloroform, but, invariably, as soon as the soln. became clear the rate of fading increased. It is possible, however, to use the colour for a rough estimation by carrying out tests under the same conditions with known quantities of stilboestrol and comparing the colours in test-tubes without preliminary separation of the chloroform layer.

Colorimetric Standard.—A suitable standard for this purpose may be made by dissolving 1 mg of stilboestrol in 4 ml of glacial acetic acid by warming gently, then adding 1 ml of a 1% v/v soln. of bromine in the same solvent and warming in a water-bath for a few minutes. The resulting orange soln. may be kept as a standard. To produce the colour, mix 0·1 ml of this soln. (≡ to 0·02 mg of stilboestrol) in a small test-tube with 0·1 ml of abs. alcohol and then with 1 ml of water. The resulting violet colour may be used for comparison directly or it may be transferred to chloroform by shaking vigorously with 1 ml of the solvent and allowing to separate. The vol. of chloroform used may be varied to aid matching, but the extract should not be separated from the aqueous layer and diluted. The colour given by 0·04 mg of stilboestrol, extracted by 5 ml of chloroform, which was separated rapidly, dried, and measured in a 1 cm cell 5 red + 1 yellow Lovibond units.

GREEN COLOUR REACTION.—It was later discovered that the green colour already mentioned may be produced by warming an acetic acid solution of stilboestrol with a smaller proportion of bromine. The minimum quantity of bromine that will produce a green colour is approx. $\frac{1}{8}$ atom per mol. of stilboestrol, but with more bromine the colour increases to a max. at about 4 atoms per mol., while with still more bromine it decreases rapidly until no colour is produced. In this reaction the bromine is absorbed by the stilboestrol, forming a colourless soln. which on warming in a water-bath slowly becomes first yellow and then brilliant emerald green. This colour is relatively permanent, but as its intensity is dependent on the proportion of bromine used, it is not suitable for use in colorimetry. As an identity test, however, it may be useful.

The green colour reaction may be used as a rapid colorimetric test for stilboestrol in compressed tablets made up with lactose, but it is not satisfactory for sugar-coated tablets. In presence of sucrose, the colour produced is not green but a deep blue changing to dull purple and orange red. On adding a trace of sucrose to a normally produced green soln., and continuing to heat this on the water bath, the green colour rapidly turns blue, then purple, and finally reddish. This reaction does not appear to be given by other sugars. Dextrose, galactose, mannose and maltose did not affect the colour of the green soln., but a slight reaction was given by laevulose, probably owing to the presence of a trace of sucrose, and a very slight change of colour was observed with sorbose. A drop of acetone causes the green colour to change to a deep blue black, which appears to be relatively permanent. Many aldehydes and ketones cause change of colour, the majority eventually producing dull straw, reddish or grey colours. A few, however, produce blue colours, which are relatively permanent. Thus furfural, vanillin, camphor, benzaldehyde and salicylaldehyde form bright blues which very slowly fade and become duller.

The green colour given by 1 mg of stilboestrol in a total volume of 5 ml, measured in a 1 cm cell in the Lovibond–Schofield tintometer, was 15 blue + 22 yellow with a scale reading of −1·1. Its absorption spectrum had one maximum in the visible range at $680m\mu = 1{\cdot}9$ (1 cm.). The blue produced with acetone was 7·2 blue with scale reading + 0·64 and absorption at $680m\mu = 2{\cdot}0$ and at $540m\mu = 1{\cdot}7$ and the blue with salicylaldehyde was 21 blue + 13 yellow with scale reading −0·7 and absorption at $655m\mu = 2{\cdot}0$.

BEHAVIOUR OF OTHER OESTROLS.—Neither reaction is given by stilboestrol dipropionate, stilboestrol diacetate or hexoestrol. Dienoestrol gives both reactions; the colloidal colour and that of its solution in chloroform have about half the intensity of those given by stilboestrol, whilst the green colour requires for its maximum production only about one-half of the amount of bromine required by stilboestrol and the colour is slightly weaker. The latter reaction may be used to distinguish dienoestrol from stilboestrol. Thus 2 equivs. of bromine will give green colours with both substances, whilst 4 equivs. will produce the colour with stilboestrol but not with dienoestrol.

ψ-Stilboestrol, for a sample of which I am indebted to the courtesy of Dr. E. Walton, of the Wellcome Chemical Works, gives the violet reaction described above. In the other test, however, when treated with 2–4 atoms of bromine per mol., it gives only a pale green colour, which on long continued heating in a water-bath slowly changes to a dull pink. Stilboestrol under the same conditions remains green but becomes duller and darker in shade.

This research has been carried out in the laboratories of The British Drug Houses, Ltd., to the Directors of which I am indebted for permission to publish these results.

GRAHAM STREET, CITY ROAD, LONDON, N.1 *March*, 1943

Notes

ABNORMAL AND WATERED MILK

DURING the past fifty years numerous researches have been made on the chemical and physical properties of milk. The knowledge gained has been applied by public analysts to discriminate between genuine milks of abnormal composition and those which are adulterated. Many papers on the composition of "abnormal" milk have been published in THE ANALYST; one of the earliest was read at a meeting of our Society in 1893 (ANALYST, **18**, 1).

The proportion of "abnormal" milk in a public supply is by no means large, but there is ample evidence that on certain occasions a cow may give milk containing considerably less than 8·50% of solids-not-fat, and the analyst may then be confronted with the problem of whether the milk is "abnormal" or watered.

PHYSIOLOGICAL ASPECT.—If a deficiency in one constituent of the blood tends to lower the osmotic pressure, some other constituent is increased by the processes of metabolism, which readjusts the osmotic pressure. Exactly the same happens with milk. If for some reason there is a deficiency in milk sugar, the metabolic processes cause the production of an equivalent increase of electrolytes, mainly sodium chloride, which raises the osmotic pressure. Usually it has been proved that a low solids-not-fat from natural causes is due to a deficiency in milk sugar. In these milks it is invariably found that the ash is high owing to an increased secretion of chlorides and other salts. Thus it has been founp that a milk low in solids-not-fat has a freezing-point depression of at least 0·530° C. (Hortvet). This is due to metabolic processes having stabilised the osmotic equilibrium of both blood and milk by a readjustment of constituents.

ASH.—According to Droop Richmond (ANALYST, 1893, **18**, 271) the most constant figure in normal milk is the percentage of the ash in solids-not-fat; it averages 8·3% and is invariably within the limits of 8·0 and 8·5%. There has been ample corroboration of this. Milk naturally poor in solids-not-fat usually has a high ash; this rarely falls below 0·70%. Analytical data given by many analysts have shown that abnormal milks give a percentage of ash in the solids-not-fat of 8·5 to 15·0% or more. The chlorides (as sodium chloride) in these milks ranged from 0·174 to 0·471%.

The determination of the ash requires the greatest care. In a series of expts. carried out by one of us (A. S. D.) it was found that there was very little loss of chlorides if the temperature of ignition were kept below 700° C. An Argand burner may be used, or a carefully regulated muffle furnace, but when an exact determination of ash is required it is advisable to employ the more tedious process described by Droop Richmond. He charred, lixiviated and ignited the soluble and insoluble portions of the ash separately.

The saline constituents of normal milk were investigated by Söldner, Droop Richmond, and others. According to these investigators the salts—chlorides, citrates and phosphates—lose *ca.* 1/6 of their weight on ignition, which converts the sol. phosphates and citrates into insol. phosphates and carbonates of sodium, potassium, calcium and magnesium. Since the saline osmotic pressure in the milk depends on the quantities and ionic dissociations of the salts as they exist in solution in the milk, and the salts remaining in the ash (other than chlorides) are of a different nature, these changes on ignition in the composition of the mixed salts in milk explain the apparent irregularities and lack of correlation between the quantity of ash and the f.pt. Although the increase of chlorides is a noticeable feature in abnormal milk samples, it would appear highly probable that the other salts will also, to a certain extent, vary in amount. The relationships between the soluble salts in milk are not without interest, and are to a certain extent explanatory of the peculiarities observed in the f.pt. depression. The weight of sol. citrates and phosphates in normal milk is about 4 times that of the chlorides present; *i.e.*, if the chlorides amounted to 0·18%, then the citrates and phosphates amounted to 0·72%. Now, according to Fiehe and Kordatzki (*B.C.A.*, 1928, 687B) these citrates and phosphates in normal milk account for about 25% of the depression of f.pt. There is no evidence that the ratio of citrates and phosphates to chlorides is the same in abnormal milks. Nevertheless an increase in any of the salts in milk will have the effect of raising the ash as well as the saline osmotic pressure, and an abnormal milk with a high ash and a normal osmotic pressure (freezing pt. depression) must be associated with a salt of lower osmotic pressure than sodium chloride, *e.g.*, potassium phosphate.

ABNORMALITY DETECTION.—The detection of some extraneous chemical substance which has obtained access to the milk, either through watering or through being added to hide watering, may help to determine adulteration by means of water. These include nitrates, borax, cane sugar, salt, etc. Vieth gave the average proportion between milk sugar, proteins and ash in normal milk as 13 : 9 : 2. Many other analysts, including ourselves, have found this ratio to be exact to the nearest whole figure. The relationship between solids-not-fat and the ash has already been referred to; in most instances it affords sufficient proof of normality.

The freezing-point test has been applied as a means of detecting added water for nearly 50 years and it has been tested by innumerable investigators. The standard technique of Hortvet was approved by the Association of Official Agricultural Chemists of America several years ago and by the S.P.A. in 1933 (ANALYST, **58**, 318). The consensus of opinion is that cow's milk never gives a f.pt. depression (Hortvet) appreciably lower than 0·530° C. (ANALYST, 1930, **55**, 423; 1932, **57**, 653; 1934, **59**, 146, 691).

Mathieu and Ferré in 1914 (*Ann. Falsif.*, **7**, 12) endeavoured to obtain a constant, which was based on the amounts of chlorides and lactose in milk. This was subjected to analytical criticism by Monier-Williams in his Report to the L.G.B., 1914, p. 27. He found, on the basis of his own results, that the variation was not large. Mathieu and Ferré called the figure a "simplified molecular concentration constant." This was obtained by the formula A + (B × 11·9), where A represents the number of grams of hydrated lactose, and B the number of grams of chloride (as NaCl) per litre of milk. According to these authors the constant rarely fell below 74, but Monier-Williams found that it may fall as low as 70. Nevertheless this constant may be of some use as a corroborative indicator of gross adulteration.

P. Post (*B.C.A.*, 1926, 846B) introduced a constant, which was called the "Cryolac" Number. It was obtained by calculating the f.pt. depression due to lactose and chlorides (as NaCl). It has a range of 393–435 with a mean of 413. It has been recommended as a substitute for the f.p. when this cannot be determined for sour milks. Fiehe and Kordatzki (*B.C.A.*, 1928, 687B), found that in normal milk the Cryolac Number accounted for 75% of the total f.pt. depression.

An elaboration of these ideas in the light of practical experimenting might prove a solution to the problem of interpreting sour milk analysis (ANALYST, 1932, **57**, 456; 1907, **22**, 172, and Letter from Board of Agriculture to Local Authorities, August 17th, 1903, on Sour Milk).

ABNORMAL HERDS.—Mastitis has become increasingly prevalent in the past thirty years, and it is well known that this disease has a deleterious effect on the cow's health, and that this effect is reflected in the quantity and quality of the milk. A sample of mixed evening and morning milk yielded by an infected herd of seventeen cows gave the following results:

Total solids, %	11·39	Freezing-point depression (Hortvet)	0·537° C.
Fat, %	3·48	Chlorides (NaCl), %	0·16
Non-fatty-solids, % ..	7·91	Acidity (as lactic acid), %	0·108
Ash, %	0·69		

Both the evening and morning milk taken from the above herd contained a somewhat low proportion of solids-not-fat, but they yielded 0·74% of ash and the f.pt. (Hortvet) was −0·537° C. and −0·543° C., respectively. These samples were examined while quite fresh. Separate samples were then taken from each cow, and it was found that the ash in every instance was at least 0·73%, and that the minimum salt content was 0·136%. The f.pt. (Hortvet) of these samples varied between −0·532 and −0·557. Every cow, with the exception of two, was yielding milk with a solids-not-fat of less than 8·50%, the lowest being 6·22%; in that milk the ash content was 1·01%.

In conclusion, our investigations have shown the danger, when a milk analysis is being judged, of drawing a conclusion on the evidence afforded by the solids-not-fat determination or, indeed, on any result alone. Also, that the "Appeal-to-cow" test, if carried out properly and thoroughly, may prove invaluable to the prosecution and at the same time a safeguard to the farmer.

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December, 1942

GROWTH OF COLIFORM BACTERIA IN WATER

THE communication by Bigger and Nelson on the growth of coliform bacilli in distilled water (*cf.* p. 124) forms an interesting supplement to results that I published in the *J. Inst. Water Engineers* (June, 1919). My work dealt mainly with the differentiation of *B. coli* into the now well-recognised excretal and non-excretal types and their comparative viability. The majority of the non-excretal types examined were found to show capsule formation, and these capsulated organisms displayed remarkable viability in boiled (or steamed) hard water. In one expt. the organism added to such water, containing no measurable trace of saline or organic ammonia, was isolated from 1 ml after 2 years, and in another expt. after 3½ years, after which times the expts. were discontinued. Only in boiled (or steamed) hard water was such viability observed, and the phenomenon seems to be dependent upon the slow deposition, by supersaturation, of calcium carbonate or magnesium hydroxide on the capsulated organism; non-capsulated excretal *B. coli* treated in the same way died out in 5 weeks. In the first 5 to 11 weeks, multiplication of the capsulated organisms from 50 to 100-fold was recorded.

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COUNTY LABORATORY, COUNTY HALL, TAUNTON

March, 1943

SUGAR TITRATION END-POINT IN THE LANE AND EYNON METHOD

UNLESS one is highly experienced in sugar analysis, it is absolutely essential, with the Lane and Eynon method, to run blanks and do repeated titrations to obtain 100% accuracy when viewing the soln. with its internal indicator of methylene blue by reflected light. If, however, transmitted light is used, even inexperienced workers find no difficulty in assessing an absolute end-point. The method adopted in my laboratory is to place the Fehling's soln. in a flat-bottomed conical flask on an open-mesh wire gauze resting on a tripod, stand the tripod on a white tile, lay on this a 40-watt opal bulb, switch on and titrate. In this way it is quite possible to assess the end-point without adding methylene blue soln., but if this is added, the titration is more speedy, as a progressive colour change is noted and the end-point is particularly sharp. This method has been tested by several workers and the reports have all been favourable.

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January, 1943

A DISTILLATION RECEIVER FOR USE WITH THE TATE AND WARREN APPARATUS

THE adjunct to the Tate and Warren apparatus (ANALYST, 1936, **61**, 367) shown in Fig. 2, was designed to avoid the necessity for a separate distillation unit for recovery of the liquid entrainer. It is made with standard interchangeable ground-glass joints and fits in the apparatus as shown in Fig. 3. The usual Tate and Warren assembly is shown in Fig. 1.

The adjunct is used when the moisture determination is complete. Heating is temporarily stopped, and the graduated tube is replaced by the receiver, into which the remaining liquid entrainer is distilled. In practice the receiver has proved quite successful. Its dimensions are such as to allow ample clearance from other parts of the equipment, and its capacity provides for a considerable excess over the quantity of liquid normally used.

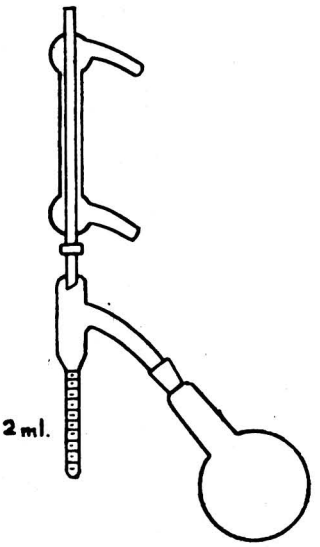

Fig. 1

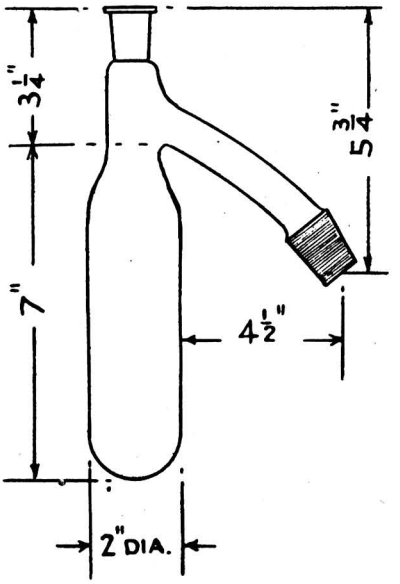

Fig. 2

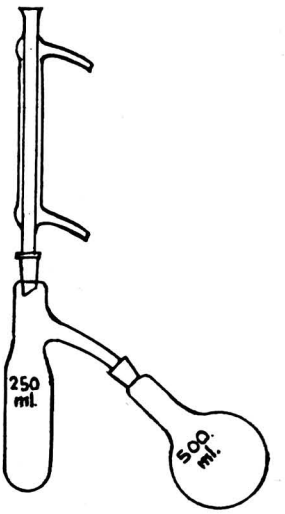

Fig. 3

Acknowledgments are made to Mr. L. V. D. Scorah, M.Sc., who was responsible for its manufacture, and to the Engineer and Directors of the Dudley, Brierley Hill and District Gas Company for permission to publish this note.

NORMAN B. BIGGS

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October, 1942

GOAT'S MILK

IN view of the comparative scarcity of information regarding the composition of goat's milk the following analyses of two samples recently received may be of interest. Both were the produce of a single goat, the first being afternoon milk and the second morning milk; the interval between the two milkings was twelve hours.

	Quantity pints	Total solids %	Fat %	Solids-not-fat %	Hydrated lactose %	Protein %	Ash %	F.p. depression °C.
Afternoon milking	2·1	14·6	5·3	9·3	4·20	4·06	0·99	·578
Morning ,,	2·3	13·6	4·5	9·1	4·14	3·92	0·96	·559

CITY ANALYST'S LABORATORY

BIRMINGHAM, 3

H. H. BAGNALL

March, 1943

Ministry of Agriculture and Fisheries and Department of the Secretary of State for Scotland

STATUTORY RULES AND ORDERS

portant to icultural naiysts

1942—No. 2495. The Fertilisers and Feeding Stuffs Regulations Amendment Order, 1942. Dated December 4, 1942.*

This Order is made jointly by the Minister of Agriculture and the Secretary of State for Scotland.

1. *It makes the following variations in the Schedules to the Fertilisers and Feeding Stuffs Act*, 1926.

SCHEDULE I—*Part II.*—In the sentence beginning "Compound cakes or meals" there shall be inserted before the words "produced by grinding, crushing or otherwise treating together" the words "(other than millers' offals and meal produced from a mixture of brewery grains and potato)."

After "Maize meal; Indian meal—None" there shall be inserted "Meal produced from a mixture of brewery grains and potato—None. Millers' offals—None."

The words "wheat offals or millers' offals" shall be omitted, and the words "wheat offals" inserted.

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* H.M. Stationery Office, 1942. Price 1d. net. (Italics signify changed wording.)

SCHEDULE IV—*Part II.*—Before the words "Molasses feeds" and the definition thereof, there shall be inserted—"Millers' offals—The by-product obtained from milling together in the permitted proportions, for the production of flour in accordance with an approved specification, wheat and any authorised ingredients of flour. Such by-product shall not contain more than 4% of other vegetable substances, and all such substances shall be substances extracted by the producer of the offals from the wheat and other ingredients in the process of cleaning. In this definition "permitted," "approved," and "authorised" mean respectively "permitted, approved and authorised for the time being by the Minister of Food."

The words "wheat offals; millers' offals" shall be omitted and the words "wheat offals" inserted.

2. The Fertilisers and Feeding Stuffs Regulations, 1932 (S.R. & O., 1932 (No. 658) p. 478), shall be varied as follows:—In Article 2. Limits of variation for Feeding Stuffs, the figures and words "31. Wheat offals or millers' offals" shall be omitted, and the figures and words "31. Wheat offals . . . . Fibre: if the actual amount exceeds that stated, one eighth of the amount stated, if the actual amount is less than the amount stated, no limit" shall be inserted.

3. *The Order came into force on December* 14, 1942.

Ministry of Food

STATUTORY RULES AND ORDERS*

1943—No. 68. Order, dated Jan. 14, 1943, prescribing an Appointed Day under the Manufactured and Pre-packed Foods (Control) Order, 1942, and giving Directions supplementary thereto. Price 1d.

By this Order, Article 3 *of the Principal Order* (*S.R. & O.*, 1942, *Nos.* 1863 *and* 2073) *came into force in respect of flour mixtures on Jan.* 17, 1943. *Flour mixture does not include* (i) *custard powder or blancmange powder manufactured by licence under The Starch Food Powders* (*Control*) *Order*, 1941 (*S.R. & O.*, 1941, *No.* 1742) *;* (ii) *any cooked manufactured product ; or* (iii) *flour as defined in S.R. & O.*, 1943, *No.* 11 (ANALYST, 1943, **68**, 113) *; but subject thereto means any article of food containing not less than* 25% *of flour.*

— **No. 79. The Food (Inspection of Undertakings) Order, 1943. Dated Jan. 15, 1943.** Price 1d.

Under this Order the Minister may authorise any specified person or persons to enter and inspect any specified premises used for any food undertaking, to carry out any test or investigation, or to take samples of any material or product on the premises. Every person carrying on a food undertaking must keep such records as the Ministry may require. "Food" includes (*a*) any livestock or living creature used for human food and any feeding stuffs for such livestock or living creature; and (*b*) any article used as food or drink for human consumption other than water, including any article which ordinarily enters into or is used in the composition or preparation of human food, tea, coffee, cocoa and any flavouring matter or condiment.

— **No. 143. The Flavouring Essences (Current Prices) Order, 1943. Dated Jan. 29, 1943.** Price 1d.

This Order regulates the prices at which flavouring essences may be sold. "Flavouring essence" means any essence, emulsion, syrup or concentrate which is suitable for use as a flavouring for human food or drink and which contains essential oils or their derivatives or chemicals having flavouring property, and/or is a preparation of natural gums, gum resins or any substance of vegetable origin, but does not include any preparation containing yeast, coffee, chicory or any substance prepared by the hydrolysis of protein-containing materials, any substance in respect of which a maximum price or a fixed price is prescribed on any sale thereof by any Order of the Minister for the time being in force, or any substance recommended as a medicine.

— **No. 144. The Fruit (Canning, Bottling and Freezing) (Control and Maximum Prices) Order, 1943. Dated Jan. 29, 1943.** Price 2d.

This Order, which includes specifications for the sizes of cans of various designations, gives the following definitions :

"Degrees Brix" in relation to any syrup means the percent. by weight of cane or beet sugar contained in such syrup.

"Dried" in relation to any fruit includes fruit dried whether by natural or artificial means or both.

"Fruit" includes rhubarb, and any fruit (*a*) whether or not mixed with any other article; and (*b*) whether fresh or dried, wholly or partly cooked, or otherwise processed or prepared; and includes fruit juices and fruit pulps or purees, but does not include tomatoes or jam, marmalade, mincemeat or similar products.

Except under licence, no fruit may be canned other than apples, apples and blackberries, blackberries, cherries, gooseberries, loganberries, plums (including damsons and greengages) and rhubarb. Previously canned or dried fruit may not be canned or bottled. The bottling or freezing of any fruit for sale, in excess of 20 *cwts. in* 12 *months, except cyder, is prohibited except under licence.*

Schedule I gives the min. weights of the different kinds of fruit which cans of specified designations must contain. The weights are to be exclusive of the weight of any covering liquid. The liquid shall be drained off for at least 1 *min. before the weight of the fruit is ascertained. The weight*

* A summary of some Orders. Obtainable from H.M. Stationery Office. Italics signify changed wording.

of any fruit is its weight immediately after being placed in the can ; if the weight is taken subsequently, an appropriate adjustment shall be made in respect of estimated gain or loss in weight. All fruit other than apples or other than fruit packed in an A10 can shall be packed in syrup of density 29 to 31 degrees Brix. Any fruit (other than apples) packed in an A10 can shall be packed (a) in syrup of 14 to 16 degrees Brix and labelled "Packed in light syrup"; or (b) in water, in cans labelled "water pack." Apples (other than solid pack apples) shall be packed in syrup of 14 to 16 degrees Brix and labelled "Packed in light syrup." Except where otherwise expressly provided, any fruit in the above list shall not be mixed with any other fruit, whether mentioned or not in the list.

— **No. 211. The Cod Liver Oil and Veterinary Oil (Control) Order, 1943. Dated Feb. 10, 1943.** Price 1d.

Except under licence, no person shall, by way of trade or business, (a) manufacture, produce or refine cod liver oil or any other fish liver oil ; (b) manufacture, produce, refine, alter the composition of or pack any veterinary oil. "Veterinary oil" means any mixture of oils or dilute oils which has as an ingredient cod liver oil or other fish liver oil, but does not include any such mixture suitable for human consumption and prepared solely for that purpose.

— **No. 327. Order, dated March 4, 1943, amending the Meat (Maximum Retail Prices) Order, 1942.** Price 1d.

In effect the First Schedule to this Order defines "Edible offal," and is thus important in connection with the analysis of sausages. Edible offal includes the liver, heart, tongue and kidneys of calves, sheep and lambs, oxen and pigs ; brains ; sweetbreads of calves, sheep and lambs and oxen ; fries of sheeps and lambs (skinned) ; head—ox (excluding tongue and brain), sheep and lambs (including tongue and brain but excluding skin and eyes), calves (scalded, including tongue and brain) ; feet—calves (scalded) and pigs ; tail—ox and calves ; skirt—ox (thick and thin) ; melt and lights ; tripe (dressed ready for cooking) ; pig's fry (liver and fat) ; ox-cheek (boneless) ; udder—cows' (uncooked).

Ministry of Supply

THE RAW MATERIAL GUIDE*

THIS pamphlet gives particulars of the nature and land of origin of raw materials, the procedure for obtaining supplies, and the measure of control exercised over dealings, as shown by summaries in chronological order of the Statutory Rules and Orders. Monthly addenda will be published to notify changes in Control and Procedure.

The Guide opens with a Summary of the Statutory Rules and Orders defining the powers of the Minister. Next comes an alphabetical list of raw materials showing control and the branch department which handles each, arranged under key numbers, *e.g.*, for abrasives, cotton, derris, iron, fertilisers, leather, non-ferrous metals, paper, sulphuric acid, timber, wool.

The commodities are dealt with in detail in 62 pages on the lines indicated above. The chemical substances include arsenic, bromine and bromides, camphor, diatomaceous earth, graphite, gums, industrial gases, miscellaneous chemicals, molasses and industrial alcohol (including formaldehyde, acetic acid, ethers, etc.), pesticides, shellac, sulphuric acid.

The Fertiliser Control, working under the Ministry, controls all fertilisers other than nitrogenous fertilisers and works in conjunction with the Sulphuric Acid and Industrial Ammonia Control. Prices are stabilised at the levels of the 1940–1 seasons, and raw materials and imported fertilisers are now sold at a loss. The Guide summarises the contents of the 22 Statutory Orders issued since November 7, 1939.

Notes from the Reports of Public Analysts

The Editor would be glad to receive Reports containing matter of special interest

COUNTY OF KENT: QUARTERLY REPORTS FOR 1942

LEAD IN CURRY POWDER AND CURRY SAUCE.—Two samples of curry powder contained 40 and 98 p.p.m. of lead. Prosecutions were instituted. A sample of curry sauce contained 500 p.p.m., but several further samples contained only small amounts of lead.

ORANGE FLAVOUR CORDIAL.—One sample had a red oily layer on the surface. This proved to be lemon or lemon grass oil coloured with an aniline dye.

MUSTARD.—A sample was labelled in large letters "Mustard of the finest quality," but also bore a small notice that it was sold as a mixture. It contained 40% of added starch, and therefore the label, that it was of finest quality, was misleading.

SOAP.—One sample contained only 15% of fatty acids, with an excessive amount of water, common salt and mineral matter. Now that soap is rationed, its composition should be regulated, if not standardised. It may be difficult to take such action as would lead to the suppression of sales of very inferior soap. Possibly, at least, suitable indication of the composition of such soaps is advisable. The country was flooded with food substitutes before the action of Public Analysts brought offenders into the Police Court, and then the Ministry concerned took action.

FLUE DUSTS.—Dust from the flues of blast furnaces may contain at least 10% of potash, but it varies widely in composition, and is usually sold at "unit value." Warranties up to 20% of potash were given on the sale of some of these dusts. Analyses of some samples gave results for potash ranging from 5·2 to 20·8%;

* H.M. Stationery Office, York House, Kingsway, London, W.C.2. Pp. 75. Price 1s. net.

in 44 other samples the range was from 5·1 to 30·6%, the majority containing 9–11%. In the medium grade flue dusts approx. 80% of the potash is soluble in water and the remainder should become available. The flue dusts from ordinary factories are invariably not rich in potash and several contained only 0·2–0·7%. These results show the necessity for analytical control of these products. Occasionally the dusts contain substances toxic to plants, but, provided that they are used early in the winter, no harm should result.

COCOA SHELL AS A FEEDING STUFF.—Cocoa shell, which is often found in compound cakes, has been advocated and used as a cattle food, but it has been known to kill horses, and is an unsafe food to give to non-ruminants. Ground cocoa shells have been offered as a fertiliser, and they form a good organic dressing. They contain *ca.*, nitrogen, 2·6; phosphoric acid, 1·0; potash, 3%.

WOOD ASHES.—The value of wood ashes as a fertiliser depends largely on the wood from which they were derived. Hard wood and old wood yield ashes containing little or no potash, but young and green woods yield ashes with *ca.* 5%. The phosphoric acid in these ashes averages *ca.* 5%. It is important that they should not be exposed to rain before application, as the potash is immediately washed out.

POULTRY FOOD SUBSTITUTES.—Different products are being sold as "poultry food substitutes." Some samples examined consisted of more or less impure "blitzed" grain; one contained nearly half its weight of mortar, and another *ca.* 33% of mortar and grit. Inert material was therefore present in large proportion, although the price was high.

Presence of Lead.—Another impurity sometimes occurring in "blitzed" grain is lead, volatilised by the heat and well distributed throughout the material. It is difficult to suggest a limit for lead in poultry food, but the amount found in one sample (150 p.p.m.) was undoubtedly excessive.

CHICKEN FOOD.—This "food" consisted of a mixture of calcium carbonate and salt. Most of the chickens fed with it died. Investigation showed that the food had been exposed for sale as a mineral mixture; doubtless the purchaser was unaware of its use, and fed it as ordinary chicken food, with disastrous consequences.

F. W. F. ARNAUD

CITY AND COUNTY OF KINGSTON UPON HULL: REPORT FOR 4TH QUARTER, 1942

OF the 614 samples received from inspectors, 436 were taken informally.

FISH CAKES.—Some of the fish cakes sold in Hull contained only 10% of fish. In my opinion they should normally contain at least 50%, but in view of war-time conditions, the Ministry of Food was asked for an opinion as to a minimum standard, and, on the information received, a local minimum standard of 25% was adopted in September, after an unsuccessful effort had been made to come to an agreement with the local manufacturers. So far as is known, that was the first occasion upon which a standard for fish cakes had been set up by a local authority. It is interesting to note, therefore, that on December 28 the Fish Cakes (Maximum Prices) Order, 1942, came into force, prohibiting the sale of fish cakes containing less than 25% of fish; also, the sale of fish cakes weighing less than 2½ oz.

POTTED MEAT.—Samples (from 2 vendors) contained the following percentages of wheat flour and excess water: (*a*) 13·2 and 24·6; (*b*) 9·0 and 20·4; (*c*) 11·5 and 19·4; (*d*) 11·3 and 24·3. One sample also contained 0·01% of boric acid. Cautions were issued. The sale of potted meat, as distinct from meat paste, is prohibited by the Meat Products and Cooked Meats Order, 1942.

BRAWN.—Three samples contained 4·5, 7·1 and 11·6% of wheat flour. In my opinion wheat flour is not a normal constituent of brawn, and its presence should be declared. Cautions were issued.

GROUND CLOVES.—A sample contained 5·5% of volatile ether extract and 17·3% of crude fibre, instead of not less than 10% of extract and not more than 10% of fibre. Excess of clove stalks was present. A caution was issued.

TINCTURE OF MYRRH.—Two samples (one source of supply) contained only 2·1 and 2·2% of total solids and 81·1% v/v of alcohol. Tincture of Myrrh prepared from Myrrh of B.P. quality normally contains 5–7% of total solids and 82–87% v/v of alcohol. Caution issued.

LEMON CHEESE.—Only 0·2% of fat was present. In my opinion the purchaser should be notified of this deficiency. Caution issued.

D. J. T. BAGNALL

Legal Notes

The Editor would be glad to receive particulars of cases of legal or scientific interest

DATE OF "INSTITUTION OF A PROSECUTION"

ROBERTSON *v.* PAGE

ON August 7, 1942, the defendant was charged at the Central Police Court, Glasgow, with an offence under the Food and Drugs (Adulteration) Act, 1928, alleged to have been committed on June 17, 1942. On July 11, the Procurator Fiscal (Mr. J. Robertson) had tendered a complaint to the clerk of court, who had formally fixed August 7 for the hearing of the case. The complaint was served on July 18.

When the case was called it was submitted on behalf of the defendant that the complaint had not been served in time, since under Sec. 27 of the Act, where, as in this case, a sample had been purchased for test purposes "any prosecution under this Act in respect of the sale thereof shall not be instituted after the expiration of 28 days from the date of purchase." Although the date of hearing had been fixed by the clerk of court within the 28-day period, the complaint had not been served until after its expiry. No good cause for the delay, which was undue, had been shown. The police court judge accepted the view that the prosecution had not been "instituted" until the complaint had been served and dismissed the case.

The Procurator Fiscal appealed to the High Court of Justiciary, basing the appeal upon Sec. 26 of the Summary Jurisdiction (Scotland) Act, 1908, which reads:—"All proceedings under this Act in respect of the contravention of any Statute or Order shall, unless the Statute or Order under which the prosecution is raised fix any other period, be commenced within six months after the contravention occurred. . . . Proceedings shall be held as being commenced within the meaning of this section as of the date when a

warrant to apprehend or cite the accused is granted, provided that such warrant is executed without undue delay." It was contended that the words "within the meaning of this section" did not exclude from the rule of the final sentence proceedings under some other Act which prescribed its own particular timetable.

On November 6, 1942, the High Court upheld this view and allowed the appeal. Lord Carmont said: "It is worthy of note that the Food and Drugs (Adulteration) Act is a statute which applies not only to Scotland but also to England, and they have to face the same difficulty as to the meaning of "institution of prosecution" under Sec. 27. It is satisfactory to know that it was long ago settled in regard to a previous Food and Drugs Act in England, where that previous Act had said that a prosecution shall not be instituted after the expiration of 28 days from the time of purchase—the same language that is used in the Act which is current to-day—it was decided that the laying of the information and not the service of the summons was the institution of the prosecution.* Interpreting that, as one must do with a view to its application in Scotland, it appears that the tabling of the case and the dieting of the case, to use the terminology in Scotland, was the institution of the prosecution and not the service of the complaint. That authority is not binding on this Court, but it is satisfactory to know that a similar interpretation to the one which I propose to your Lordship has been followed in regard to a similar matter by a Court of such high authority."

Lord Fleming and the Lord Justice-General (the Rt. Hon. Lord Normand) concurred.

British Standards Institution

WAR EMERGENCY BRITISH STANDARDS†

CAMOUFLAGE PAINTS. No. 987—1942. CAMOUFLAGE COLOURS. No. 987c—1942

CAMOUFLAGE PAINTS.—This Specification, issued under the authority of the Ministry of Works and Buildings, embodies the requirements previously incorporated in the Civil Defence Camouflage Establishment Specifications Nos. 1 and 2. It is based essentially on "performance requirements" determined as here described. No restrictions are placed on the composition of the paints, except as regards the use of chromium oxide and other controlled materials and the composition of bituminous emulsion paint.

The specified tests are for consistency, opacity, colour and finish, drying time (16 hrs. at *ca.* 60° F.), reflection value, water resistance, cement test (for paint to be used on alkaline surfaces), accelerated weathering test (measurement of brightness), hardness, and special tests for paint for asphalt or bituminous surfaces (absence of drying oils and/or aromatic petroleum residues).

The reflection value is measured by applying the paint to a smooth metal sheet and leaving it to dry for 24 hrs. at *ca.* 60° F. This panel is placed horizontally in the apparatus 2 in. below a 60-watt lamp. A pad of matt white paper is fixed vertically 3 in. from the lamp, and to it is attached a metal graining comb level with the middle of the bulb of the lamp. On the other side of the lamp, also at a distance of 3 in., is a vertical metal screen, the bottom of which approaches to within 1/8 in. of the surface of the painted panel. At a distance of 3 in. from this metal screen there are 4 peep-hole sights into the apparatus, so arranged as to restrict the sighting to near grazing observations, *i.e.*, to angles of 5°, 10°, 15° and 20° to the surface, respectively. The reflection value is the max. angle at which a reflected image of the graining comb can be seen.

Change in Brightness after Accelerated Weathering.—The brightness of the exposed panel is measured at the same time as that of an unexposed duplicate panel in light and in coloured light. In the apparatus described the measurements are made by means of a light-sensitive cell and a galvanometer. A white magnesium oxide screen is used as the standard, and light reflected by the painted surface is expressed as a percentage of that reflected by the magnesium oxide, as calculated from the relative galvanometer readings. The max. permitted increase of brightness in white light and the max. permitted difference in brightness change under coloured light (specified filters) and under white light are tabulated for each of the 11 camouflage colour numbers.

CAMOUFLAGE COLOURS.—The 11 official colours, designated by number, are issued under the authority of the Directorate of Camouflage after verification at the Paint Research Station. The shades shown on the colour cards range from a yellow-buff to terra cottas, dull sage greens, slate, browns and black.

Union of South Africa: Department of Agriculture and Forestry

CHEMICAL COMPOSITION OF SOME S. AFRICAN CEREALS AND THEIR MILLING PRODUCTS‡

THIS is the first of a series of contributions on the chemical composition of S. African food substances, about which there has hitherto been little information. In studying the composition of the cereals grown in the Union special attention has been given to maize and wheat. The analytical methods used were in general those of the 1935 issue of the A.O.A.C. Calcium, magnesium and phosphorus were determined as described by Malan and van der Lingen (*Rept. of Dir. of Vet. Serv. and Animal Ind.*, Part II, pp. 443–452, Pretoria) and iron by the method of Elvehjem and Kennedy (described in "*Practical Physiol. Chem.*," Hawk and Bergeim, London, 1931).

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* In the case of *Beardsley* (1904, 1 K.B. 847).—EDITOR.

† Obtainable from the Publications Dept., 28, Victoria Street, London, S.W.1. Price No. 987, 2/-, post free 2/3; No. 987c, 1/6, post free 1/9.

‡ Science Bull. No. 20. Chemistry Series No. 171. By D. C. Crawford, M.A., B.Sc., P. J. Hamersma, D.Sc., and B. W. Marloth, B.A., Ph.D., Div. of Chemical Services, Pretoria. Pp. 100. 1942.

MAIZE.—Of the numerous tables of results, the following aver. figures will be useful for reference:

Average Percentage Composition of S. African Maize Meals.

	Moisture	Protein (N × 6·25)	Fat	Fibre	Carbohydrates (diff.)	Ash	No. of analyses	mg per 100 g Ca	Mg	P	Fe
Maize	12·15	9·34	4·05	2·02	71·37	1·07	65	17·6	103	204	3·7
Straight run meal	12·08	9·55	4·30	2·21	70·70	1·16	52	19·7	108	212	4·5
No. 1 Maize meal	12·26	9·18	2·98	0·82	73·90	0·86	45	16·4	74	171	2·9
Meal with bran removed	12·00	9·67	3·85	1·21	72·26	1·01	44	18·5	92	194	3·9
Meal with bran and seconds removed	12·09	9·28	3·36	0·89	73·47	0·91	42	20·5	87	187	3·4
Meal with bran and germ removed	12·60	9·01	2·77	0·79	74·03	0·80	12	11·6	72	142	2·1
Meal with bran, germ and seconds removed	11·87	8·64	0·87	0·43	77·83	0·36	6	13·2	25	52	1·9

Maize Products.	Moisture	Protein	Fat	Fibre	Carbohydrates (diff.)	Ash	mg per 100 g Ca	Mg	P	Fe
Polenta (mean of 2), %	11·72	9·49	2·28	1·23	74·50	0·78	11·5	—	113	2·8
Samp (mean of 3), %	11·52	8·46	0·57	0·43	78·72	0·30	11·0	19	33	3·9
Maize rice (mean of 9), %	12·08	8·88	1·52	0·82	76·19	0·51	12·5	27	98	1·8
Maize flour (mean of 7), %	12·56	5·81	2·06	0·55	78·37	0·65	15·1	57	103	3·0
Maize starch (mean of 2), %	13·15	4·49	0·79	0·57	80·62	0·39	10·1	24	58	4·0
Maize bran (mean of 70), %	11·04	7·36	5·80	13·32	60·50	1·98	34·3	213	342	5·5

The analyses show that S. African maize is as rich in nutrients, especially protein, as that grown in U.S.A. The investigation also showed the desirability of standardising and grading individual maize-milling products. Many, quite different, products are sold under the same trade name, and the food value of individual products ranges from nil to that of a high-grade foodstuff.

WHEAT.—More than 150 analyses of wheat and its milling products from the Transvaal and Orange Free State were made. For the former province the protein range was 11·69 to 18·38% and for the latter 11·25 to 15·44%. On the moisture-free basis, the protein content is lower than for American wheat, but the fat, fibre and ash contents are very similar. Flours from the two provinces were similar in composition, but the brans showed a wide range of variation, *e.g.*, for 28 samples the figures were: protein, 13·24–18·12; fat, 1·0–3·75; fibre, 7·17–15·13%.

Average Percentage Composition of S. African Wheat and its Milling Products.

	Moisture	Protein (N × 6·25)	Fat	Fibre	Carbohydrates	Ash	No. of analyses	mg per 100 g Ca	Mg	P	Fe
Wheat	12·00	11·95	1·79	2·48	70·24	1·54	71	60·0	121	314	7·5
Unsifted meal	11·96	13·44	1·84	2·20	69·11	1·45	22	54·3	128	279	5·9
Sifted meal	12·09	11·99	1·31	0·53	73·43	0·65	35	29·9	46	121	4·3
Flour	12·11	11·29	1·00	0·21	74·59	0·44	12	26·8	17	76	2·3
Bran	11·34	15·95	2·96	10·06	55·48	4·21	28	135·0	409	933	12·6
Pollard	11·35	15·65	3·29	4·17	63·14	2·40	21	74·0	181	507	8·9
Germ meal	10·51	24·96	6·83	2·72	51·40	3·58	3	38·1	—	824	10·2

KAFFIRCORN.—The principal types of grain sorghum grown in S. Africa are the Blackhull and Whitehull Kaffircorn (both white seeded) and Red Kaffircorn, which contains tannin in the outer husk. Their nutritive value is only slightly less than that of maize. The red variety contains rather more protein than the white, but is otherwise of similar composition. Both varieties are similar to American Kaffircorn.

Average Percentage Composition of S. African Kaffircorn and its Milling Products.

	Moisture	Protein (N × 6·25)	Fat	Fibre	Carbohydrates (diff.)	Ash	No. of analyses	mg per 100 g Ca	Mg	P	Fe
Whole grain	11·98	10·36	3·42	1·96	70·93	1·35	8	32·2	122	232	6·6
White grain	12·80	10·85	3·40	1·30	70·03	1·62	1	—	—	—	—
Red grain	13·50	12·17	3·70	1·40	67·73	1·50	1	—	—	—	—
Straightrun meal	11·90	9·59	2·74	2·28	72·18	1·31	3	33·8	—	238	24·9
Household meal	11·91	9·52	2·72	1·48	73·27	1·10	15	38·4	115	225	8·7
Malt	11·60	10·88	2·39	3·52	69·75	1·86	6	70·5	—	209	10·8
Sprouts	11·79	10·69	1·55	2·75	71·91	1·31	2	67·0	—	211	6·9

The malt and sprouts were residues from the germination and fermentation of Kaffircorn in the making of beer

RYE.—The two analyses made gave results similar to those recorded for American rye.

Percentage Composition of S. African Rye and its Milling Products.

	Moisture	Protein (N × 6·25)	Fat	Fibre	Carbohydrates (diff.)	Ash	No. of analyses	mg per 100 g P	Fe
White grain	11·14	11·29	1·80	2·00	72·19	1·58	2	312	4·2
Meal	12·20	12·17	1·73	1·86	70·65	1·39	1	—	—
Flour	12·08	9·25	1·25	0·83	75·91	0·68	1	—	—

OATS.—Apart from a lower protein content (9·44% mean of 52 analyses, as againt 12·00% mean of 960 analyses) the composition of S. African oats is very similar to that of American oats.

Average Percentage Composition of S. African Oats and their Milling Products.

	Moisture	Protein	Fat	Fibre	Carbohydrates (diff.)	Ash	No. of analyses	mg per 100 g			
								Ca	Mg	P	Fe
Whole grain, Transvaal ..	9·31	11·24	5·74	11·66	60·35	1·70	1	—	—	320	6·6
Whole grain, Cape	9·85	9·44	6·03	10·20	60·86	3·62	52	102	—	560	—
Hull-less grain ..	10·20	15·68	6·34	1·66	64·37	1·75	1	—	—	—	—
Husks	7·78	2·42	0·66	38·72	43·74	6·68	1	—	—	—	—
Meal	8·13	14·86	7·21	1·82	66·04	1·94	1	—	—	—	—
Rolled oats ..	10·03	8·69	3·99	13·88	61·5	1·85	2	—	—	—	—

Errata.—May, 1942, p. 179, *l.* 26–28. *For* "Europium as lanthanide . . . other metals." *read* "Hence europium can be separated from the other lanthanides (*i.e.*, rare-earth metals) by the following procedure."

March, 1943, p. 81, *l.* 11 from bottom, *for* "ANALYST, 1938, **63**, 542" *read* "ANALYST, 1933, **58**, 542."

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Food Tables: Their Scope and Limitations. E. M. Widdowson and R. A. McCance. (*Lancet*, 1943, i, 230–232.)—Many workers, mainly using the 1926 or 1937 tables of Sherman, have shown that under certain conditions the composition of a diet may be calculated from food tables. There is general agreement that the analytical figures for nitrogen agree closely with the calculated values, whilst the calcium figures from the tables tend to be higher than those found by analysis (Gutman and Low, *J. Nutrition*, 1939, **18**, 257; Hummel *et al.*, *id.*, 1942, **24**, 41). The agreement for phosphorus is usually better than for calcium, but the values for calcium have agreed much better when the results for a number of persons over a week, or for a single person over a period of several weeks, have been averaged. Agreement between the iron results has been poor, probably owing to heavy contamination of the food. Numerous metabolism expts. have been made in the Biochemical Dept. of King's College Hospital and at Cambridge, and the authors have used the analyses made to test the value of their own food tables (*Spec. Rep. Ser. Med. Res. Council*, No. 235, 1942). Their analytical technique was as previously described (*J. Physiol.*, 1942, **101**, 44), special precautions being taken to avoid contamination of the food. The averages for (1) the analytical and (2) the calculated values (g per week; Fe mg per week) for the food intake of 6 persons over a period of 7 days were as follows: protein, 469, 462; fat, 810, 827; potassium, 28·2, 28·8; calcium, 4·68, 4·11; magnesium, 2·09, 2·03; iron, 65·0, 61·6; phosphorus, 7·40, 7·26. The iron discrepancy is attributed to the curried fish, which formed a main item in the week's menu (curry powder contains a large and variable amount of iron). Stress is laid on the difficulty of avoiding iron contamination in metabolism expts. Fresh apples, cut up with a stainless steel knife and boiled in distilled water in a beaker, contained 0·31 mg of iron per 100 g; when cut up with an ordinary kitchen knife and boiled in the same way, they contained 2·30 mg and, when boiled in a chipped enamel saucepan, 6·00 mg per 100 g. Thus 100 g of stewed apple, prepared in this way, would be as good a source of iron as the best roast beef, and would provide half the daily requirement. Raw beefsteak, as purchased, contained 2·73 mg of iron per 100 g; after mincing it contained 4·79 mg. The calculated calcium values were too low; this is attributed to the fact that, although the subjects of the expts. drank distilled water, the food was prepared with London tap water. The calcium contents (mg per 100 g) of potatoes (1) boiled in distilled water, (2) boiled in Cambridge tap water, and (3) boiled in tap water with added kitchen salt, were as follows: (1), 4·71; (2) 6·69; (3) 9·28. Analogous results were obtained with peas: (1) 22·4; (2) 38·9; (3) 44·9. Taking Widdowson's (1936) and Widdowson and McCance's (1940) values for the average potato intakes of men and women (38 oz. and 21 oz. per week respectively) the foregoing amounts would provide men with 7 mg and women with 4 mg more calcium per day than they would be reckoned to have according to the food tables. These amounts are small in comparison with the 60 mg per day that people in Cambridge must be getting from their drinking water. In districts where the water is very hard, up to 200 mg of calcium may be obtained from the drinking water, *i.e.*, as much as is in the adult milk ration in winter. The general conclusion drawn from all the expts. is that the calculated and analytical results are sufficiently close to warrant the use of food tables in dietary surveys.

Determination of Soya Flour in Sausages and other Meat Products. J. Bailey. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 776–781.)—The method is based upon the separation of a definite fraction of the glycinin of the soya flour from the proteins of the meats, vegetables and binders occurring in meat products. The procedure is conveniently divided into steps, and interruptions of the analysis (*e.g.*, overnight) should occur only after steps (1), (2*b*), (3), (4) and (6). Samples should be submitted to the first step as soon as possible, after which they may be stored. Filtrations are accelerated if the paper is supported in a wire triangle of suitable size placed on the funnel. (1) Remove skin or hard outer portions and grind the product finely. Treat 50 g with 75 ml of acetone for 3–4 hr. with occasional stirring, decant

and filter the liquid, and replace any residue on the filter-paper in the main bulk. Reject the liquid, boil the residue with 75 ml of carbon tetrachloride in a water-bath, leave for 3–4 hr., and decant and filter as before through the same paper. Reject the liquid and free the residue from solvent on the water-bath. (2) Add 250 ml of cold water, mark the level of the mixture, make faintly alkaline to phenolphthalein, noting the vol. of *N* sodium hydroxide required, and just remove the colour with *N* hydrochloric acid. Heat cautiously and finally boil for 5 min., dilute the cooled mixture to its original vol., and add *N* hydrochloric acid equiv. to the sodium hydroxide previously added. In absence of starch omit step (2*a*). (2*a*) Add 5 ml of fresh diastase soln. (2 g of U.S.P. IX malt diastase powder, digested with 100 ml of water for 1–2 hr. and filtered) and maintain at 40°–50° C. until the starch has disappeared. (2*b*) Add 1–5 ml of *N* hydrochloric acid until the liquid is orange or pink to ethyl orange indicator (0·015 g of ethyl orange in 30 ml of 50% alcohol), stirring the liquid and allowing the sediment to settle after each addition of acid. Filter and reject the filtrate. (3) Wash the residue on the paper back into the main bulk with 200 ml of 10% sodium chloride soln., mark the level of the liquid and leave at room temp. for 30 min., maintaining alkalinity by additions (*ca.* 1 ml) of *N* sodium hydroxide. Heat in the water-bath so that the temp. reaches 85°–90° C. in 15–20 min. and maintain this temp. for 30 min. with occasional stirring and addition of alkali if necessary. Cool, replace the water lost, filter and reject the residue. (For leaving overnight at this stage, make the liquid just acid to phenolphthalein and alkaline again when work is resumed.) (4) Make just acid to phenolphthalein and measure the vol. Add 30 g of magnesium sulphate ($7H_2O$) per 100 ml in *ca.* 3-g portions, raise the temp. to 50° C. in exactly 30 min., filter without cooling and reject the residue. (5) To the soln. at 35°–40° C. add 11 g of anhydrous sodium sulphate per 100 ml of the sodium chloride soln. added in (3), maintain the temp. for 75 min. longer, but do not stir after the ppt. begins to agglomerate. Filter the warm liquid, dividing it between two papers if necessary, reject the filtrate and proceed immediately to (6). (6) Dissolve the ppt. in *ca.* 200 ml of warm water made alkaline to phenolphthalein. (Interruption at this stage must be under the conditions noted after (3)). (7) Make the soln. just acid to phenolphthalein, measure its vol., add 22 g of ammonium sulphate per 100 ml in *ca.* 2-g portions and keep at 40° C. for 15 min. with only gentle stirring. Filter without cooling and reject the filtrate. (8) Immediately repeat step (6), then cool to room temp. and make the liquid just yellow to phenol red with *N* hydrochloric acid. (If desired, leave overnight at this stage.) Measure the vol., add 10 g of magnesium sulphate per 100 ml in 3-g portions, add methyl red indicator and, if necessary, *N* sodium hydroxide until the liquid is yellow to both indicators, and filter. (9) Add 20 ml of a filtered 10% soln. of crystalline copper sulphate and maintain at 40°–45° C. for 1 hr. with slow stirring, which must be discontinued when the ppt. begins to agglomerate. (An interval of 2 hr. is permissible here.) Filter through a tared paper, using water not above 45° C. while the ppt. is in contact with glass, and water at 60°–70° C. to loosen it from the paper if clogging occurs. Wash the ppt. two or three times with hot water, and dry and weigh the paper. Each 0·035 g of ppt. ≡ 1·0% of soya flour. All the indicators mentioned are used internally. In the original paper the theoretical basis of each step is discussed.

A. O. J.

Characteristics and Composition of Guanabana Seed Oil. C. F. Asenjo and J. A. Goyco. (*J. Amer. Chem. Soc.*, 1943, **65**, 208–209.)—The Puerto Rican guanabana (*Annona muricata* L.) has a heart-shaped fruit, 15 to 20 cm long and 9 to 12 cm broad with green skin with isolated curved fleshy spinules. The pulp, used in the preparation of a local fruit drink, is white, juicy and sub-acid. The seeds embedded in the pulp yielded 23·86% of a yellowish-brown odourless oil on extraction with acetone and somewhat less on hot expression (110° C.). It had: sp.gr. at 25°/25° C., 0·9178; n_D^{20}, 1·4709; iodine val. (Hanus), 87·79; sap. val., 197·0; acid val., 2·29; acetyl val., 12·56; Reichert–Meissl val., 0·81; Polenske val., 0·56; unsap., 1·02; sol. acids, 0·37; insol. acids, 91·90; sat. acids (corr.), 22·02; unsat. acids (corr.), 70·02%; iodine val. of unsat. acids, 105·1; sap. val. of unsat. acids, 202·1. The unsaturated acids yielded tetrabromostearic acid, m.p. 114° C.; linolenic acid was absent. The proportions of fatty acids (calc. on the oil) estimated from the iodine val. and by distillation as methyl esters and formation of anilide derivatives, were: linolic, 11·64; oleic, 58·58; myristic, 0·32; palmitic, 16·20; stearic, 5·51%.

E. B. D.

Assay of Iron and Ammonium Citro-Arsenite for Arsenic Trioxide. C. R. J. Ruthven. (*Quart. J. Pharm.*, 1942, **15**, 368–369.)—In the assay in the Fourth Supplement to the B.P. Codex 1934, replacement of the sodium bicarbonate by sodium hydrogen tartrate, in the titration of excess of iodine with sodium thiosulphate (*cf.* ANALYST, 1911, **36**, 132) leads to more accurate results. It is suggested that the assay should be modified to read: "Dissolve 5 g of iron ammonium citro-arsenite, accurately weighed, in 50 ml of water in a stoppered flask. Add 1 g of sodium hydrogen tartrate and 20 ml of *N*/10 iodine, stopper the flask and allow to stand in the dark for 5–10 min. Titrate the excess of iodine with *N*/10 sodium thiosulphate, using 2 ml of starch soln. as indicator; each ml of *N*/10 iodine ≡ 0·004949 g of As_2O_3."

E. M. P.

Assay of Mercury in certain Organic Compounds. J. S. Pierce. (*Quart. J. Pharm.*, 1942, **15**, 367–368.)—The following method is recommended for the determination of mercury in phenylmercuric nitrate, mersalyl and neptal; it may be of more general application. Weigh 0·3–0·5 g of the sample into a 100-ml flask, add 5 ml of 85% formic acid, 15 ml of water and 1 g of zinc dust, and heat under reflux for 30 min. Filter off the amalgam, wash until the washings are not acid to litmus, and dissolve in a mixture of 20 ml of nitric acid and 20 ml of water. Leave on the water-bath for 3 min. and then add 0·5 g of urea and sufficient *N*/10 potassium permanganate to give a permanent pink colour. Cool, decolorise with a few drops of hydrogen peroxide, and titrate with *N*/10 ammonium thiocyanate, using ferric alum as indicator; 1 ml of *N*/10 ammonium thiocyanate ≡ 0·01003 g of mercury.

E. M. P.

Biochemical

Estimation of Chlorides in Biological Fluids by the use of Adsorption Indicators. Determination of Plasma Volume of Blood. A. Saifer,

J. Hughes and E. Weiss. (*J. Biol. Chem.*, 1942, **146**, 527–535.)—When whole blood is dropped slowly into a mixture of abs. alcohol and anhydrous ether (3 : 1) in such a way that the cell walls are not ruptured, transport of the chloride ions is prevented, so that when the supernatant extract is titrated with silver nitrate the titre (A) is a measure of the chloride ion in the plasma of the whole blood sample. If this value is divided by the titre (P) for an equal volume of plasma, the ratio represents the relative volume of plasma in the blood and the volume of cells in the blood = (P–A)/P. To determine the whole blood plasma value (A), pipette 1·0 ml of oxalated blood into a 50-ml Pyrex centrifuge tube containing 35 ml of alcohol-ether mixture. Stopper the tube and stir up the red cells from the bottom by gently tapping the tube with the finger, centrifuge at 200 r.p.m. for about 5 min. and pour off the supernatant liquid. Wash the ppt. twice with 5-ml portions of alcohol-ether, stirring the ppt. with a rod, re-centrifuge and titrate the combined centrifugate and washings with 0·02 *N* silver nitrate, using 8–10 drops of dichlorofluorescein indicator (0·05% soln. in 75% alcohol). The end-point is reached when a pink colour appears. To determine the plasma value, pipette 0·5 ml of oxalated plasma into a 50-ml Pyrex centrifuge tube containing 25 ml of alcohol-ether, stopper and shake, and titrate as before. The accuracy of the method was determined by testing artificial mixtures of cells and plasma. The observed value differed from the theoretical by not more than ±2·5%. A procedure was also developed for which less than 2 ml of oxalated blood were required to determine the plasma vol. in duplicate. A special micro-burette of the horizontal type was used and the results were almost identical with those obtained by the macro method. F. A. R.

Estimation of Urea in Blood and Urine. A. A. Ormsby. (*J. Biol. Chem.*, 1942, **146**, 595–604.)—The reaction described by Fearon (*Biochem. J.*, 1939, **33**, 902) is made the basis of a new method of estimating urea. When urea is heated with diacetyl monoxime in acid soln. a yellow colour develops which deepens on subsequent oxidation with potassium persulphate. Many substituted ureas give a red colour, only urea itself giving a yellow colour. Put 1–2 ml of the sample, containing 0·1–0·2 mg of urea, into a test-tube (generally 0·01 ml of urine or 3 ml of a Folin–Wu blood filtrate are sufficient), 1 and 2 ml of a standard urea soln. (0·1 mg per ml) into similar tubes, and 3 ml of water to serve as a blank into a fourth. Make up the solutions to 3 ml with water, and add to each exactly 5 ml of conc. hydrochloric acid, and then 0·5 ml of 3% diacetyl monoxime soln. After mixing, immerse the tubes in boiling water for exactly 10 min., reducing evaporation by covering the tubes with a small funnel or glass marble. Cool the tubes for 2 min. in running water, and add slowly 0·25 ml of 1% potassium persulphate soln. so that a separate layer is formed. Stopper all the tubes and mix simultaneously by inverting a few times, measure the colour in each tube at intervals in a Klett photoelectric colorimeter with a No. 42 filter, and note the max. intensity. The amount of urea in the unknown may be calculated either directly from the colours given by the two standard solns. or, better, from a calibration curve. The method gives results agreeing well with the Van Slyke–Cullen method, although less satisfactory agreement was obtained with blood than with urine. The recovery of urea added to urine was between 97·5 and 102·4% of the theoretical, whilst the recovery of urea added to blood was 99·5 to 102·3% of the theoretical. F. A. R.

A Lactobacillus Assay Method for *p*-Aminobenzoic Acid. J. C. Lewis. (*J. Biol. Chem.*, 1942, **146**, 441–450.)—For assaying *p*-aminobenzoic acid, *Lactobacillus arabinosus* 17–5 can be used, the basal medium consisting of glucose 1·0, Norit-treated acid-hydrolysed casein (vitamin-free) 0·5, *l*-cystine 0·1, *l*-tryptophan 0·01, sodium acetate 0·6, $K_2HPO_4 3H_2O$ 0·05, KH_2PO_4 0·05, magnesium sulphate ($7H_2O$) 0·02, sodium chloride 0·001, ferrous sulphate 0·001, manganese sulphate 0·001%; adenine 10, guanine 10, uracil 10, aneurine 0·1, riboflavin 0·2, pantothenic acid 0·1, nicotinic acid 0·4, pyridoxine 0·1, and biotin 0·0004 p.p.m. Transfer 5-ml aliquot portions of the basal medium to Pyrex test-tubes, and add a series of dilutions of standard *p*-aminobenzoic acid soln. to one set of tubes, and the test solns. to another. Dilute the contents of each tube to 10 ml, plug with cotton-wool and autoclave at 15 lbs. for 10–15 min. Cool, inoculate, and incubate at 30° C. for 3 days, and then titrate the acid produced with 0·1 *N* sodium hydroxide, using brom-thymol blue as indicator. All glassware should be carefully cleaned and washed before use. Maintain stock cultures of the test organism on yeast extract glucose agar, sub-culturing monthly. To prepare sub-cultures for inoculating test solns., dilute the basal medium with an equal vol. of water containing 1μg of *p*-aminobenzoic acid per 10 ml and, after incubating for 24 hrs. at 30° C., centrifuge the cells and re-suspend in the original vol. of sterile saline. Inoculate the assay tubes from this suspension. A standard curve is prepared and, from this, the concn. of the unknowns can be calculated. Methods for liberating *p*-aminobenzoic acid from inactive complexes have not yet been worked out, but *p*-aminobenzoic acid is not destroyed by autoclaving with 0·1 *N* sodium hydroxide for 30 min. Treatment with *N* and 10 *N* sodium hydroxide, however, destroys 10 and 50% of the activity respectively. Sulphuric or hydrochloric acid in concns. from 0·1 to 10 *N* cause 30% inactivation. The recovery of added *p*-aminobenzoic acid was within the limits of the exptl. error (5–15%). The method is specific. The following values (in p.p.m.) were obtained for the *p*-aminobenzoic acid content of certain foodstuffs by simple water-extraction:—brewer's yeast 6·6–61, dried whole egg 0·2–0·36, dried egg yolk 0·8, dried egg albumen 0·055, dried carrots 0·18, dried cabbage 9·7, skim milk 0·004. The results obtained with extracts treated with sodium hydroxide indicated the presence of combined *p*-aminobenzoic acid in certain materials. F. A. R.

Inactivation of Biotin by Rancid Fats. P. L. Pavcek and G. M. Shull. (*J. Biol. Chem.*, 1942, **146**, 351–355.)—An emulsion of biotin soln. and the rancid oil to be tested was made with gum ghatti, and incubated at 37° C. After a certain time the entire contents of the flask were diluted, and the amount of biotin was estimated microbiologically by the method of Shull, Hutchings and Peterson (*J. Biol. Chem.*, 1942, **142**, 913). The degree of inactivation was approx. proportional to the peroxide val. of the oil, and up to 96% inactivation resulted when biotin was incubated for 12 hrs. with ethyl linolate of high peroxide value. In presence of α-tocopherol inactivation was less, only 40% being destroyed by 48 hrs. incubation. The

inactivated product still had 50% of its original activity when tested by the yeast-growth method, a result similar to that obtained when biotin is inactivated with dil. hydrogen peroxide. This suggests that a sulphoxide is formed by both hydrogen peroxide and organic peroxides, and that this can be reduced to biotin by yeast, but not by *Lactobacillus helveticus*. F. A. R.

Estimation of Urinary Aneurine by the Prebluda-McCollum reaction. B. Alexander and J. E. Levi. (*J. Biol. Chem.*, 1942, **146**, 399–406.)—The thiochrome method for aneurine is not specific and the original diazo method of Prebluda and McCollum has been criticised adversely. Various modifications have been suggested, such as the use of other diazo reagents, and preliminary adsorption to remove interfering substances, but even these modified methods do not give good results in the estimation of aneurine in urine. The substances in urine which interfere with the selective adsorption of aneurine and its reaction with diazotised *p*-aminoacetophenone have now been shown to be uric acid and ascorbic acid respectively. Uric acid can be removed by pptn. with zinc acetate and sodium carbonate, and ascorbic acid by treatment with basic lead acetate. *Method.*—To the urine, preserved with toluene, add enough 10% sulphuric acid to give *p*H 3 or less, leave for at least 24 hrs. for the urate to ppt., and then add 5 ml of 20% zinc acetate soln. to 100 ml of the filtered urine, redissolving any pptd. zinc phosphate by adding a few drops of 10% hydrochloric acid. Add sat. sodium carbonate soln. to *p*H 7·4 and then a further 5 ml of zinc acetate, followed by 10 ml of lead acetate reagent (made by dissolving 100 g of neutral lead acetate in 200 ml of water and adjusting the *p*H to 7·5 with 2 *N* sodium hydroxide). Add more sodium carbonate to adjust to *p*H 7·2, centrifuge and filter the supernatant liquid into 12 ml of 10% hydrochloric acid. Wash the ppt. twice with 15 ml of water containing a few drops of sodium carbonate soln., and acidify the combined filtrate and washings to *p*H 4·5. Adsorb with 600 mg of Superfiltrol for 1 hour (Emmett, Peacock and Brown, *J. Biol. Chem.*, 1940, **135**, 131; ANALYST, 1940, **65**, 661), centrifuge and decant the supernatant liquid. Re-adsorb with another 600 mg of Superfiltrol for 1 hr., again centrifuge and discard the supernatant liquid. To each adsorbate add 5·0 ml of water, 5·0 ml of 95% alcohol containing 5·0 mg of phenol per ml, and a few drops of thymol blue. Adjust the mixture to *p*H 7–8 and add the diazotised *p*-aminoacetophenone reagent. After 2 hrs. filter and wash the ppt. and flask 3 times with 5·0 ml of water in all. Transfer the adsorbate and filter-paper to a dry centrifuge tube, add 4 ml of 95% alcohol through the filter, shake and centrifuge. Measure the intensity of the colour in an Evelyn photoelectric colorimeter, using the 540$m\mu$ filter. The average recovery of added aneurine was 86% and the average discrepancy between duplicates was 3%. The incomplete recovery is not regarded as a disadvantage for ordinary clinical work, where great accuracy is not required, but for accurate analyses a simultaneous recovery determination should be carried out to determine the % loss. Better recovery is obtained if less urine is taken for analysis, whilst the lowest yields were obtained with very concentrated urines. F. A. R.

Distribution of Nicotinic Acid in Feeds. E. B. Hale, G. K. Davis and H. R. Baldwin. (*J. Biol. Chem.*, 1942, **146**, 565–570.)—The method outlined in the preceding paper and in some instances the microbiological method also was applied to the estimation of nicotinic acid in feedingstuffs and other substances, with the following results (in mg per 100 g): barley 6·0–8·1, maize 1·7–2·8, maize germ 3·1, hegari 6·8, milo 8·6, kafir 4·0, oats 1·8–2·1, polished rice 1·2, rye 1·7–2·2, spelt 4·9–5·7, wheat 6·0–9·6, wheat bran 24·2–40·9, wheat germ 5·2, cottonseed meal 4·1–5·0, linseed meal 5·5, palm kernel meal 4·4, soya beans 4·0, soya bean meal 3·6–4·0, beet pulp 2·6, chicory root 2·3, beet molasses 4·7–5·0, cane molasses 4·4–5·0, meat and bone scraps 4·6–8·2, fish meal 6·9–9·0, beef muscle 4·4, beef liver 21·2, bakers' yeast 28·9–54·3, skim milk powder 1·4–1·6, buttermilk powder 1·3–2·1, alfalfa hay, brome hay, clover hay, timothy hay, alfalfa leaf meal 3·5–5·3, silage 1·0–1·5. These results indicate that several cereals are highly deficient in nicotinic acid. Wheat bran, however, is an excellent source, and the amount of nicotinic acid present in various wheat runnings appear to depend upon the proportion of bran present. Rice-bran was also rich in nicotinic acid. F. A. R.

Vitamins in Rose Hips. F. Wokes, E. H. Johnson, J. G. Organ and F. C. Jacoby. (*Nature*, 1943, **151**, 279.)—The prominence given to rose hips as a source of vitamin C (*cf.* Pyke and Melville, ANALYST, 1942, **67**, 336.) has tended to obscure their value as a source of other vitamins. Dried extracts of ripe hips, mainly from *R. canina* and *R. dumetorum*, collected in the autumn of 1942, were found to have carotene contents equiv. to 6,000 I.U. of vitamin A per 100 g, *i.e.*, of the order of those of carrots. The vitamin C contents were 1300–1500 mg per 100 g, the loss in 6 months at normal temp. being negligible, although there is evidence (*cf. Quart. J. Pharm.*, 1942, **15**, 314) that under similar conditions rose hip syrup loses *ca.* 50%. The vitamin P content of one of the dried extracts was 520 G.L. units per g (*cf.* Bacharach and Coates, ANALYST, 1942, **67**, 313); this high value as compared with those previously recorded (Bacharach and Coates, *loc. cit.*) may be due to a 10-fold greater vitamin P content of the original hips, or to the minimisation of loss of vitamin between collecting and testing by reason of the special precautions taken to avoid loss of vitamin C by the action of the oxidising enzymes in the fresh hips. If the former reason is correct, there must be as wide a variation in the vitamin P content of the hips as in the vitamin C content, but not necessarily any parallelism. Rose hips contain no significant quantities of vitamin B_1 (*cf.* Pyke, *id.*, 1940, **65**, 470). J. G.

Spectrographic Analysis of Rat Tissues for Ingested Vanadium. E. P. Daniel, E. M. Hewston and M. W. Kies. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 921.)—Vanadium in small samples of ash from biological material has been determined spectrographically, with chromium as an internal standard. The samples, as prepared for excitation on the arc, consisted of 2 mg of the ash plus 0·03 ml of a chromium oxide soln. containing 0·1% of chromium. The sample was placed in a shallow cavity drilled in a pure graphite electrode, kerosene being placed in the electrode before introduction of the sample to prevent creeping of the arc and penetration of the salts during arcing. Trials showed that the sample was completely volatilised in 20 secs. with an arc current of 10 amps.

and a 50-volt drop across the 4-mm arc gap. The measured density of the vanadium line 3185.4A was compared with that of the chromium line 3188.0A. Standardisation was effected by using vanadium-free biological ash impregnated with sodium metavanadate soln. of known concn. The method proved suitable for vanadium contents of 30 to 80 p.p.m. (*Abstractor's note.*—The polarity of the arc electrode holding the sample is not specified, all other experimental details are given.) B. S. C.

Polarographic Microdetermination of Sodium in Biological Material. C. Carruthers. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 70.)—With prepared standard solns. of sodium zinc uranyl acetate in 0·5 *N* hydrochloric acid, the diffusion current was found to be proportional to the concn. over the range 0·1625 to 0·975 millimolar. The 0·1625 millimolar soln. (≡ 3·47μg of sodium per ml) has a diffusion current in excess of one microamp. In biological materials, interfering substances other than phosphate and organic compounds are rarely found. To determine sodium in 100 to 400 mg of epidermal tissue, remove the organic material by ashing and any phosphate by the method of Butler and Tuthill (*J. Biol. Chem.*, 1931, **93**, 171). Then from the residue and standard zinc uranyl acetate soln., prepare the sodium zinc uranyl acetate, dissolve in 0·5 *N* hydrochloric acid and polarograph this soln. Run "blanks" on the hydrochloric acid, water and the calcium hydroxide used in the phosphate removal. B. S. C.

Agricultural

Rotenone and Related Substances in Berebera Seeds. Chromatographic Separation of Deguelin and Tephrosin. E. P. Clark. (*J. Amer. Chem. Soc.*, 1943, **65**, 27–29.)—Rotenone, dehydrorotenone, tephrosin and two new compounds, one $C_{21}H_{20}O_6$, m.p. 164–5° C., and the second, $C_{23}H_{20}O_6$, m.p. 189–90° C., have been isolated from the seeds of the African berebera tree (*Millettia ferruginea* Hochst.). Procedures were as follows. *Rotenone.*—Extract 3500 g of ground berebera seeds with light petroleum to remove fat and oil, exhaustively percolate the dried marc with ether, free the extract from solvent and dissolve the residue in 3500 ml of methanol. Pass the solution through a thin layer of Norit, evaporate to 300 ml, and allow to crystallise. A yield of 36 g of rotenone, m.p. 163° C. after crystallisation from ethanol, was obtained. *Dehydrorotenone.*—Dilute the rotenone mother liquors to 600 ml, add 5 ml of 50% aq. potassium hydroxide, and leave overnight; a little over 6 g of crystals separate. On standing another day, *ca.* 2·5 g of dehydrorotenone, m.p. 218° C. after recrystallisation from chloroform-methanol, separates. *Tephrosin.*—Dissolve 2-g lots of the mixture (the 6 g obtained above) in 20 ml of chloroform, and pass through 150 × 12-mm aluminium oxide columns. Collect the percolates in small fractions, evaporate to a syrupy consistency, dissolve in methanol, boil to remove all chloroform, and leave the solns. to crystallise. The material is thus divided into 4 fractions of increasing m.p. ranges. Repeat the process until 3 materials of sharp m.p. are obtained. One fraction (*ca.* 3 g) is tephrosin, m.p. 201° C.; the second fraction, $C_{21}H_{20}O_6$, has m.p. 164–5° C., and the third, with m.p. 189–90° C., corresponds with $C_{23}H_{20}O_6$. The high m.p. (201° C.) found for "tephrosin," led to the investigation of so-called pure tephrosin, m.p. 189° C. On subjecting this to the fractional recrystallisation described above it was separated into tephrosin, m.p. 201° C., and *iso*tephrosin, m.p. 260° C. Chromatographic treatment of recrystallised "*iso*-tephrosin," m.p. 252° C., separated this also into *iso*tephrosin and tephrosin. The following chromatographic method of separating tephrosin and deguelin was devised:—Dissolve, *e.g.*, 1 g of deguelin and 0·5 g of tephrosin in 20 ml of chloroform, pass the soln. through a 150 × 12-mm aluminium oxide column and elute with chloroform. In one expt. the first 50 ml of percolate yielded 0·6 g of deguelin, m.p. 170–1° C.; the second fraction yielded 85 mg of a mixture, m.p. 165–72° C., the third 180 mg of tephrosin, m.p. 198–200° C., and the fourth 40 g of tephrosin, m.p. 199–201° C. The recovered deguelin is somewhat yellow, but passing a chloroform soln. through a bed of Norit removes all colour and gives a pure product, m.p. 171° C. Repetition of the process upon the tephrosin fraction is necessary for complete purification. E. M. P.

Ash "Free from Carbon." J. L. St. John. (*J. Assoc. Off. Agr. Chem.*, 1942, **25**, 969–973.) Methods for ashing feeding stuffs and plant material frequently specify that heating shall continue until the sample is free from carbon. This criterion is indefinite and should not be used as a measure of complete ashing (St. John, *J. Assoc. Off. Agr. Chem.*, 1940, **23**, 635). A number of feeding stuff ingredients of plant and animal origin were ashed at 500°, 550°, 600° and 700° C., the other conditions being those of the official method of the A.O.A.C. The ashed material was examined macroscopically, microscopically and by photomicrography. In general, a variation was found in the relative amount of carbon in ash prepared at different temp. and also in the different types of material ignited at the same temp., and in many instances a notable amount of carbon remained in the ash at 700° C. Differences in the ash of a dairy feed and a poultry feed of known composition could not be attributed to any one ingredient, and there were pronounced variations in the amount of carbon remaining at 700° C. in these samples. At 500° and 600° C. the residual carbon was somewhat larger, although the proportion of carbon to total ash was not great. Ash from alfalfa and from meat meal appeared to contain little carbon even at 500° C. Soya bean ash at 600° and 700° C. appeared quite free from carbon, but more was visible in ash prepared at 500° C. Herring meal ash contained progressively less carbon as the temp. of ignition was raised. At 650° C. the ash from soya bean, cottonseed, pea, and bone meals appeared almost free from carbon; that from herring meal, coconut meal and the poultry feed appeared to contain somewhat more carbon. Macroscopical examination of the various types of ash showed that a judgment of the completeness of ashing cannot be based upon such examination, although the colour of the ash of any one sample showed, in general, a progressive change towards a lighter colour with rising temp. This is not of marked significance, since alfalfa had a grey ash at each temp. and the ash of meat meal became lighter with rising temp., although both materials yielded ash containing little carbon, even at 500° C. It is concluded that neither a macroscopical observation nor a judgment by the analyst as to whether the ash is free from carbon or not can be used to determine the optimum degree of ashing or the temp. or duration of ignition necessary for complete ashing. Ashing should be done under definitely

specified conditions such as those of the A.O.A.C. ("*Methods of Analysis*," 1940), in which the specified temp. is 650° C. The results of these expts., together with those of earlier work (*J. Assoc. Off. Agr. Chem.*, 1940, **23**, 620; 1941, **24**, 848), suggest that a temp. of 600° C. might well be specified.

A. O. J.

Gas Analysis

Determination of Olefines in Gaseous Hydrocarbons. B. R. Stanerson and H. Levin (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 782–784.)—The apparatus consists essentially of a 50-ml Erlenmeyer flask suitably connected with a water-jacketed mercury gas burette (Shepherd burette), a manometer, a vacuum pump and, through drying tubes, to the sample of gas. The degree of unsaturation of the gaseous mixture is determined by means of 1% v/v bromine soln. in glacial acetic acid, which is standardised daily against 0·1 *N* sodium thiosulphate after addition of potassium iodide soln. Place 5 ml of chloroform in the flask and surround it with a mixture of "dry ice" and kerosene at −48° C. or lower. Evacuate first the flask and then the burette (1 mm of mercury or less) and collect 100 ml of the gas in the burette. After recording the temp. of the water jacket and the manometric pressure, transfer the sample to the flask by mercury displacement, and agitate the flask to promote condensation of the gas and soln. in the chloroform. Admit air into the flask by means of a tap so situated that the gas in the tube connecting the flask with the burette is drawn into the flask. After this residual portion of gas has dissolved, disconnect the flask and immediately titrate the contents with the bromine soln. until a colour equal to that of a 100-fold dilution of sat. bromine water persists for 60 sec. This method of titration is applicable to gaseous mixtures containing less than 10% of ethylene, which is not included in the analysis. If the gas contains no ethylene, titrate by the following more accurate method. Titrate rapidly with the bromine soln. and add an excess of 0·5–1·0 ml. Allow the flask to stand for at least 30 sec. and not more than 30 min., add 10 ml of 10% potassium iodide soln. and titrate the liberated iodine with 0·1 *N* sodium thiosulphate. If A is the number of ml of bromine soln. reacting with the olefines, B the strength of the soln. (mg of bromine per ml) and C the vol. of gas condensed (ml) the % unsaturation on the gas volume basis is $\frac{100AB}{7{\cdot}14C}$. Each ml of gaseous olefine at N.T.P. is equiv. to 7·14 mg of bromine on the assumption that 1 mol. of bromine reacts with 1 mol. of olefine. Hydrogen sulphide, mercaptans and 1,3-butadiene interfere with the method and must be removed before the analysis. The method gave accurate results with samples containing *iso*butene, 1-butene and 2-butene in admixture with *iso*butane and *n*-butane.

A. O. J.

Organic

Production of Furfural from *d*-Lyxose and *d*-Ribose. R. C. Hockett, A. Guttag and M. E. Smith. (*J. Amer. Chem. Soc.*, 1943, **65**, 1–3.)—The standard procedure for determining pentoses by conversion into furfural and weighing the latter as its phloroglucide (Wheeler and Tollens, *Ann.*, 1889, **254**, 329; "*Methods of Analysis of the A.O.A.C.*, 1940," p. 361) has been applied to *d*-lyxose and *d*-ribose. With quantities of *d*-lyxose of 0·01–0·30 g, the standard equation was found to be:—*d*-lyxose = $(a + 0{\cdot}0052) \times 1{\cdot}0977$, where a is the weight of phloroglucide; the average deviation of the weights of phloroglucide from the quantities calc. by this equation was 0·0046 g. By simply evaluating the constants in the equation:—Sugar = $a + bp$, where p = weight of phloroglucide, one obtains:—*d*-lyxose = $0{\cdot}0051 + 1{\cdot}118\,p$; the average deviation of individual values from those calc. by this formula is only 0·0031 g. For *d*-ribose the standard equation is:—*d*-ribose = $(a + 0{\cdot}0052) \times 0{\cdot}9664$, average deviation 0·0014 g and the equation of the second type is *d*-ribose = $0{\cdot}0036 + 1{\cdot}027\,p$; average deviation 0·0035 g. Hence *d*-lyxose and *d*-ribose will not introduce into total pentose determinations errors much larger than those caused by the difference between arabinose and xylose.

E. M. P.

Alkaline Degradation of Phenylglycosides. New Method for Determining the Configuration of Glycosides and Sugars. E. M. Montgomery, N. K. Richtmyer and C. S. Hudson. (*J. Amer. Chem. Soc.*, 1943, **65**, 3–7.)—The configuration of phenylglycosides is determined by their ease of conversion into sugar anhydrides on boiling with alkali. Glycosides which readily form anhydrides may be assumed to have the glycosidic OC_6H_5 and the terminal CH_2OH groups in the *cis* positions in relation to the pyranoid ring. β-Phenyl-*d*-glucoside and β-phenyl-*d*-galactoside are readily degraded by hot aqueous potassium hydroxide to *d*-glucosan $<1,5>\beta<1,6>$ and *d*-galactosan $<1,5>\beta<1,6>$ respectively. α-Phenyl-*d*-glucoside is unaffected and α-phenyl-*d*-galactoside attacked only very slowly. The configurations of other anomeric glycosides and sugars which can be correlated with these can therefore also be deduced.

E. M. P.

Determination of Small Amounts of Combined Sulphur in Cellulose Derivatives. C. J. Malm and L. J. Tanghe. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 940–942.)—Sulphuric acid is widely used as a catalyst in the commercial production of cellulose esters, and the small amounts remaining in them have an important effect on their stability and physical properties after ageing. Existing methods for the determination of this residue in terms of the sulphur content are unreliable because of the small amounts involved, and of the presence of large quantities of organic matter. In the following modification of the method of Zahnd and Clarke (*J. Amer. Chem. Soc.*, 1930, **52**, 3275) and of Klingstedt (ANALYST, 1938, **63**, 365), the sulphur is oxidised and the organic matter destroyed simultaneously by nitric acid, and the residue is fused with potassium nitrate:—Heat overnight in a 500-ml. round-bottomed flask with a ground-glass joint under a reflux condenser, 13·7 g of sample, 0·5 g of potassium nitrate, a small crystal of carborundum (to prevent bumping), and 60 ml of conc. nitric acid. The sample dissolves and nitrogen dioxide is liberated copiously in the initial stages. Distil off the residual nitric acid, with continuous shaking (*vide infra*) until 2–3 ml remain, add 5 g of potassium nitrate and 10 ml of conc. nitric acid, and again heat under reflux for 4 hr. Evaporate the mixture to dryness, and just fuse the potassium nitrate; if blackening occurs the wet oxidation is incomplete, and therefore boil the residue for 1 hr. more with a further 10 ml of conc. nitric acid. The final fused residue should be light coloured, with only local dark areas (important, *vide infra*). As the molten nitrate cools, shake the flask gently to distribute the crystals, add 20 ml of

conc. hydrochloric acid, evaporate to dryness, and heat the residual potassium chloride strongly (without fusing it) to drive off all the nitric acid. Cool, dissolve the residue in 100 ml of water, filter the soln., acidify the filtrate (total vol., with washings, 200–250 ml) with 0·5 ml of conc. hydrochloric acid and heat on a steam-bath. Then ppt. the sulphate by adding 5 ml of 5% barium chloride soln., leave overnight on a water-bath, and filter off the ppt. (*ca.* 10–30 mg) in a porous crucible and allow for a blank expt. (1–2 mg of barium sulphate). The procedure specified avoids explosion hazard during the first evaporation, but it is important to keep the flask in motion; for the same reason the completion of the wet oxidation is essential before the fusion takes place. The initial addition of some of the potassium nitrate prevents loss of sulphate due to local overheating. The propionate and butyrate of cellulose acetate are less readily decomposed than is cellulose acetate itself, although the conditions specified are suitable. Cellulose esters containing large amounts of higher acyl (*e.g.*, stearyl) groups, and aromatic cellulose sulphonic esters resist complete oxidation by this method; if with cellulose itself evaporation to 3 ml cannot be carried out without the deposition of sludge, more nitric acid must be added and boiling under reflux continued for another 2 hr. before evaporation. Expts. with cellulose acetate containing large amounts of salt (*i.e.*, non-combined) sulphates and combined sulphates, showed that the former may be removed from the finely-ground sample by means of two successive 30-min. rinses in a Buchner funnel with 20 parts of 0·1% hydrochloric acid, followed by rinsing with distilled water until the filtrate is neutral. The residue then contains only combined sulphur, which is determined as described above. The propionates and butyrates of cellulose acetate are, however, more water-resistant and almost fully esterified, and with these a better method therefore is pptn. from a soln. in dil. acetone by means of the 0·1% acid. When a commercial grade of acetone-sol. cellulose acetate was pptd., washed until neutral, filtered off, dried for 48 hr. in a current of air at 70° C., and washed with the dil. acid and finally with water until neutral, the sulphur content was reduced; if the drying stage was omitted, no such reduction occurred. Some of the combined sulphur, therefore, is split off during drying. J. G.

Fastness to Perspiration Test for Coloured Fabrics. Amer. Assoc. Text. Chemists and Colorists. (*Amer. Dyes Rept.*, 1942, **31**, 362–363; *J. Text. Inst.*, 1942, **33**, 520A.)—The following standard test for fastness to perspiration is recommended. The artificial test solns. are: (1) *Acid*—sodium chloride, 10 g; 85% lactic acid, 1 g; disodium hydrogen phosphate 1 g in 1 litre. (2) *Alkaline*—sodium chloride, 10 g; ammonium carbonate, 4 g; disodium hydrogen phosphate, 1 g in 1 litre. *Test.*—Steep samples (*ca.* 2 in. wide) of the fabric under test and of a "composite test cloth" (a light worsted fabric containing wool, cotton, silk, viscose rayon and acetate rayon yarns as floats on one face) in solns. (1) and (2) until they have taken up twice their weight of liquid, and roll them up, with the test fabric inside. Place 4 acid and 4 alkaline rolls in test tubes (15 × 75 mm for light fabrics and 22 × 120 mm for heavy fabrics), so that the bottom two-thirds are protected from evaporation and the tops project. Maintain the tubes at 100° ± 2° F. for periods of 40 min., 2 hrs., 6 hrs. and 18 hrs. respectively, and examine for marking off on the "composite test cloth" and for change of colour in the sample. Four classes of fastness are recognised: No. 1, "poor"; No. 2, "fair"; No. 3, "good"; No. 4, "fast." The criteria for these are (1) appreciable marking off and change of shade in 40 min.; (2) appreciable marking off but no change in shade in 2 hrs.; (3) appreciable marking off but no change in shade in 6 hrs.; (4) no marking off or change in shade. "Appreciable marking off" is defined as giving a stain equiv. to the Munsell neutral stain No. 8.

Detection of Acid or Basic Substances in Damaged Fabrics. C. Whitworth and D. W. Poxon. (*Nature*, 1943, **151**, 198–199.)—The application to a cotton or woollen fabric which has been damaged by alkali, of a soln. of a nickel salt which has been completely pptd. with dimethyl glyoxime and filtered, produces a pink colour. Fabrics damaged by acid acquire a dark red-brown colour when spotted with a satd. soln. of silver chromate in 6 *N* ammonia. Poor results are obtained with cotton damaged by hydrochloric acid, and wool so damaged gives a white spot inside a dark ring. These reactions are all plainly visible under the microscope when the fabric is coloured, even with a colour resembling that produced by the reaction used (*cf.* Feigl and Da Silva, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 317). J. G.

Extraction of Metallic Constituents from Oils. E. P. Rittershausen and R. J. DeGray. (*Ind. Eng. Chem. Anal. Ed.*, 1942, **14**, 806–807.)—The oil is extracted under reflux by means of the lead tetra-ethyl extraction apparatus (*Amer. Soc. Testing Materials*, D–526–41T) with a suitable aqueous solvent, 6 *N* hydrochloric acid being the most widely applicable. Place the extraction medium (50 ml) in the extractor with a convenient amount of the sample (*ca.* 20 g of heavy oil and up to 200 ml of light products such as petrol), rinsing the sample in, if necessary, with enough petroleum naphtha of distillation range 200°–250° F. (Sovasol No. 3) to give a total organic layer of *ca.* 100 ml. If the sample is not easily soluble in naphtha, use toluene. Greases may require a preliminary dispersion with some of the toluene. Add 5 ml of butyl alcohol to prevent emulsion and boil the mixture until extraction is complete. The time varies with the nature of the sample but does not usually exceed 30 min. Allow the layers to separate, adding more butyl alcohol and warming gently if an emulsion has formed. Separate the aq. layer, repeat the extraction or wash the organic liquid with water, if necessary, and analyse the aq. extract for its metallic content by any desired method. Generally, as in the determination of lead tetra-ethyl, the hydrochloric acid is removed by evaporation, and the small amount of organic matter may be removed by means of sulphuric, nitric or perchloric acid. The organic layer is available for certain tests, *e.g.*, the determination of fatty acids from soaps. The method has been applied successfully to oils containing tin, copper, cadmium, aluminium, lead and iron, to paint driers, greases and compounded lubricating oils and to used oils containing metals in suspension as well as in soln. No work was done with paints containing titanium oxide and lithopone, but the proper choice of extraction agent and time of refluxing should give complete extraction though not solution. Expts. showed that the method is as rapid as, and requires less attention than, ashing methods and, with oils containing metals volatile at ashing temp., is more precise. A. O. J.

Inorganic

Volumetric Determination of Lead in Brass. P. M. Fisk and F. F. Pollak. (*J. Chem. Soc.*, 1943, 41–42.)—Direct pptn. of lead as chromate is employed followed by titration of the ppt. Dissolve a 1·5-g sample (1 to 4% of lead) in 15 ml of 1 : 1 nitric acid. Heat to expel nitrous fumes, dilute to 100 ml, and neutralise with sodium carbonate. Acidify with glacial acetic acid and add 10 ml in excess. Add 30 ml of one-third saturated potassium dichromate soln. Boil for 3 min., filter off the lead chromate on a 11-cm No. 41 Whatman filter-paper, and wash with hot 5% acetic acid and finally with hot water. Dissolve the ppt. by stirring the filter in the original beaker with 25 ml of acid mixture (100 ml of 75% phosphoric acid and 180 ml of conc. sulphuric acid per litre) and 5 g of solid ammonium chloride. Dilute to 120 ml, add 25 ml of ferrous ammonium sulphate soln. (20 g in 50 ml of 20% sulphuric acid diluted to 1 litre) and back-titrate with $N/20$ potassium dichromate with 3 drops of sodium diphenylamine sulphonate soln. as indicator (0·5 g of sodium sulphate in 10 ml of water added to 0·32 g of barium diphenylamine sulphonate in 90 ml of water, and filtered). For standardisation, titrate a separate 25 ml of ferrous ammonium sulphate soln. under similar conditions of acidity; 1 ml of $N/20$ dichromate = 0·003453 g of lead. The dichromate soln. is standardised against pure lead treated as described above. Copper, cadmium, zinc, manganese, iron, aluminium, nickel and cobalt do not interfere. With up to 1% of tin present, it is unnecessary to filter off metastannic acid. Arsenic up to 0·1%, phosphorus up to 1% and bismuth up to 0·1% are without effect. S. G. C.

Determination of Copper with 8-Quinolinecarboxylic Acid. G. R. Gilbreath and H. M. Haendler. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 866–867.)—Add a slight excess of ammonia to the soln. (100 ml; 0·05 g of Cu), decolorise the blue liquid with 3 *N* acetic acid and add 5 drops in excess. Heat to boiling and, while stirring slowly, add 60 ml of reagent (a saturated aqueous soln., 60 ml containing about 0·4 g of the acid). Set aside in the cold for 2 hrs., collect in a fine sintered-glass crucible, wash with a little water containing 1% of reagent, and then a few ml of water, and dry to constant weight at 110°–120° C. Copper factor, 0·15585. The process effects quantitative separation of copper from cadmium and zinc at *p*H 3·5–4·0 (addition of 0·1 *N* acetic acid until litmus paper is just reddened). Silver and gold interfere; lead, nickel, cobalt and mercury are without effect.
W. R. S.

Testing of Continuity of Thin Tin Coatings on Steel. R. Kerr. (*J. Soc. Chem. Ind.*, 1942, **61**, 181–183.)—The hot-water porosity test and the ferricyanide paper test, designed for hot-dipped tinplate, have been modified so as to be applicable to electro-tinplate carrying a much thinner tin coating (2 to 8 oz. per basis box). A new test has been evolved based on colorimetric determination of the amount of iron dissolved from pores in the tin coating by acid. *Modified Hot-water Test.*—Degrease the specimen cathodically in cold 1% sodium carbonate soln., rinse and pre-film it by immersion in 10% chromic acid soln. for 5 min. at 90° C. Rinse in tap water, then in distilled water and immerse in distilled water (*p*H 4·5–5·5) in a beaker or tinned-copper tank and maintain at 95° C. for 40 min. The number of pores (rust-spots) may be assessed visually, without counting, by comparison with reference specimens, preferably under low magnification (*e.g.*, ×4). *Paper Test.*—Degrease the specimen cathodically in 1% sodium carbonate soln., rinse and leave it to dry. Soak a piece of suitable smooth paper in a soln. of 10 g of potassium ferricyanide, 5 g of sodium chloride and 5 g of "Tergitol 08" per litre, drain for 5 sec. and lay it on the specimen, dislodging air bubbles with the fingers. Absorb excess soln. with blotting paper and squeegee, remove the blotting paper and brush on the ferricyanide soln. to moisten the paper uniformly. Leave the paper in contact for 10 min.; brushing on fresh reagent, if necessary, to keep it moist. Remove the paper, wash and dry. As it is impracticable to count the blue spots, compare the paper with that from a reference specimen. *Thiocyanate Test.*—Degrease the specimen (8 × 6 cm) and coat the edges by dipping them in melted wax. Immerse in 250 ml of a soln. of 20 g of ammonium thiocyanate, 10 g of glacial acetic acid and 10 g of hydrogen peroxide (20 vol.) per litre. Remove the specimen after 10 min. and determine the amount of iron colorimetrically by means of the Tintometer or by comparison with standards in Nessler cylinders. The result, expressed as mg of iron per sq. dm. of surface, is assessed in relation to that given by reference specimens. This test does not reveal the distribution of discontinuities, but by combining the results of the thiocyanate and hot water tests a more complete assessment of quality may be obtained. S. G. C.

Determination of Thickness of Tin Coatings. (*Publication No.* 115, *The Tin Research Institute*, 6 pp., 1943.)—Various methods used in practice are collected together and concisely described with working instructions. They comprise (*a*) Clarke's hydrochloric acid—antimony chloride loss-in-weight method (ANALYST, 1934, **59**, 525) applicable to tin on steel, copper and brass; (*b*) a cuprous chloride loss-in-weight method for tin on copper, which is perhaps slightly more accurate for this purpose than Clarke's method (Nachtsheim and Hoeckstra, *Chem. Weekblad*, 1937, **34**, 541); (*c*) a sodium plumbite loss-in-weight method for the free tin part of the coating, leaving the tin-iron or tin-copper alloy unattacked (Hothersall and Bradshaw, *J. Iron and Steel Inst.*, 1936, **133**, 225); (*d*) a nitric-hydrochloric loss-in-weight method, which may be useful for approx. tests on large steel articles where the use of solutions as in the above methods might be inconvenient (J. C. Jones, *J. Iron and Steel Inst.*, 1931, **124**, 13); (*e*) the dropping test for determining local thickness in which the time taken for a stream of drops of 10% trichloroacetic acid to perforate the coating gives a measure of the thickness, an American application to tin of Clarke's dropping test for cadmium (*E.I. du Pont Tech. Service Manual*, 1940); (*f*) the iodine titration analytical method; (*g*) direct weighing before and after tinning. Inter-conversion tables of weight per unit area, thickness in inches and mm, and "pounds per basis box" units, are appended. S. G. C.

Rapid Tests for Nickel Steels. Anon. (*Nickel Bull.*, 1943, **16**, 23–24.)—The following dimethylglyoxime qualitative tests are stated to be capable of distinguishing between steels of moderate, low, and nil nickel content: (*a*) Clean a small area by filing and apply a drop of acid mixture (100 ml of

conc. nitric acid, 25 ml of 85% phosphoric acid, 125 ml of water). After 10 sec. add a drop of reagent (soln. of 1 g of dimethylglyoxime in 60 ml of glacial acetic acid mixed with soln. of 10 g of ammonium acetate in 30 ml of ammonia, sp.gr. 0·9). (*b*) Moisten a ½-inch square piece of filter-paper with 10% nitric acid and place it in close contact with the steel for 2 min. Transfer it to a dish, add 5 ml of 15% ammonium persulphate soln. and a few drops of 10% nitric acid, and mix with 10 drops of 5% tartaric acid soln, 5 drops of 1% alcoholic dimethyl glyoxime and 1 ml of ammonia; sp.gr. 0·9. In both methods a comparative estimate is based on the intensity of the red colour. S. G. C.

Separation of Iron as Phosphate from Cobalt. V. North and R. C. Wells. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 859–860.)—In slightly acid acetate soln. iron is pptd. as ferric phosphate, which does not adsorb cobalt. Treat the acid soln. with hydrogen sulphide, filter off any ppt., oxidise soln. or filtrate with nitric acid, dilute to 400 ml, heat to boiling, and add methyl orange and 25 ml of reagent (40 g of disodium phosphate crystals per litre) per 0·1 g of iron present. Neutralise with ammonia while stirring, add 1 ml of glacial acetic acid (which should produce a pink colour), stir in filter pulp and keep on the water-bath for a few min. When the ppt. has settled, filter through Whatman No. 40 paper, wash with 0·4% sodium phosphate soln. slightly acidified to methyl orange with acetic acid. Ppt. the cobalt in the filtrate with nitroso-β-naphthol as usual, ignite and weigh as Co_3O_4. If the quantity is very small, dissolve it in the crucible in aqua regia, evaporate to dryness, and repeat the evaporation with a little hydrochloric acid. Dissolve the residue in 1–5 ml of water, add the liquid to 0·5 g of ammonium thiocyanate in a 30-ml beaker. If traces of iron colour the soln. add 1 ml of phosphate reagent. Dilute the soln. with an equal vol. of acetone and match the blue tint with that of a blank containing the same amounts of reagents, to which is added a standard cobalt soln. Nickel and the alkaline earth metals are also separated from iron in the above procedure. W. R. S.

Colorimetric Determination of Cobalt. R. J. De Gray and E. P. Rittershausen. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 858–859.)—Treat the soln. (0·5 to 4 mg of Co), free from other metals, with 6 ml of 9 *N* sulphuric acid and evaporate until white fumes appear. Cool, dilute, transfer to a graduated 100-ml flask, neutralise to litmus paper with sodium hydroxide, and slightly acidify with sulphuric acid. Dilute to 60 ml, add 10 ml of 1% potassium ferricyanide soln. and 20 ml of 15 *N* ammonia, and make up to vol. Set the colorimeter to 100% transmission with a blank, free from cobalt, containing ferricyanide. Standardise the colorimeter with a soln. containing 1 g of Co per litre, measured vols. of which (1, 2, 3, and 4 mg) are treated as described above, so as to obtain a linear curve. The authors use a photoelectric colorimeter measuring in the region of 5200A or a Diller colorimeter with a Hellige filter No. 469–40. W. R. S.

Detection of Perchlorate and Chloride after Ignition with Manganous Nitrate. M. J. Preising and J. H. Reedy. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 875–877.)—*Perchlorate.*—The procedure detects 0·0001 g of perchlorate in presence of 0·1 g of chlorate, chloride, or both. Acidify the soln. with nitric acid, ppt. chloride with silver nitrate and filter. Reduce the chlorate in the filtrate with zinc and dilute sulphuric acid by 30 min. heating on the water-bath, and add silver nitrate to ppt. chlorate chlorine. Filter, ppt. zinc with sodium carbonate, avoiding excess, again filter, add a little manganous nitrate soln. free from chlorine, evaporate to dryness in porcelain, and heat the residue to incipient redness, which reduces the perchlorate to chloride by means of the finely divided manganese peroxide. Extract with dil. ammonia, filter, acidify the filtrate with nitric acid and add silver nitrate. A chloride ppt. indicates presence of perchlorate.

Chloride in presence of thiocyanate.—To the test soln. add a slight excess of sodium carbonate, and filter off any ppt. Evaporate the soln. almost to dryness in a small crucible, moisten the residue with manganous nitrate soln., evaporate and heat the residue to incipient redness. The residue should be black, otherwise insufficient manganous nitrate has been added. Extract the residue with dil. nitric acid, filter, boil the filtrate with dilute nitric acid to expel any hydrogen cyanide, and test with silver nitrate. Bromides are not completely destroyed by the procedure. Chlorate and perchlorate interfere in the test; if present, the halide group should be pptd. as silver salts, and the ppt. decomposed by warming with zinc and dil. sulphuric acid. The soln. is then treated as described above. The test detects 0·0355 mg of chloride in presence of 100 times as much thiocyanate; hence it is much more delicate than other tests. W. R. S.

Colorimetric Determination of Phosphate in Presence of Fluoride. L. T. Kurtz. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 855.)—Even minute amounts of fluoride cause negative errors in the molybdenum blue reaction. They may be eliminated by evaporation with perchloric acid, but this has certain disadvantages. The following procedure is rapid and accurate. Transfer a portion of test soln. containing less than 0·015 mole of fluorine (≡ 0·3 mole per litre in the final vol.) to a test-tube, and add 15 ml of 0·8 *M* boric acid. Make up to 25 ml with water and to 50 ml with the reagents for the colorimetric determination (ANALYST, 1941, **66**, 82). The full development of the colour is retarded somewhat by the fluoborate, and photometer readings should be made 10 min. after preparation of the soln. Within the above fluorine concn. the calibration curve for phosphate solns. is applicable; at higher concns. a special curve may have to be constructed with phosphate solns. containing a uniform amount of boric acid. W. R. S.

Photometric Determination of Silica in Presence of Phosphates. M. C. Schwartz. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 893.)—The ammonium molybdate method for the determination of silica may be used when phosphorus is also present, provided that the phosphomolybdic acid complex is destroyed; this may be done with oxalic acid. The method described refers particularly to the determination of silica in phosphate-treated boiler waters and the like. *Procedure.*—Filter the sample, if necessary, and dilute with distilled water to suit the range of the photometric instrument to be used. Add and mix 4 ml of ammonium molybdate soln. and 2 ml of hydrochloric acid (1:1) in rapid succession to a 100-ml sample. Wait 5 to 10 min. for the colour to

develop, and then add and mix-in 3 ml of oxalic acid soln. Determine the silica colour intensity on a suitable absorptiometer. Make a blank test on the reagents and water. Both the ammonium molybdate and oxalic acid solns. are prepared to a strength of 10 g per 100 ml of water. For standardisation, sodium silicate soln. was found to be quite stable if stored in a hard-rubber bottle. This soln. is prepared by fusing 3 g of sodium carbonate with 0·2 g of pure dry silica and dissolving in 200 ml of water. B. S. C.

Physical Methods, Apparatus, etc.

Determination of Potassium by its Natural Radioactivity. R. B. Barnes and D. J. Salley. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 4.)—Apart from the uranium-radium, uranium-actinium and thorium series, the only elements showing appreciable natural radioactivity are potassium, rubidium and samarium. A simple method for the determination of potassium by measuring its radioactivity is of value, since the determination of potassium in presence of other alkalis and certain anions is difficult and lengthy. The investigations described have established that such a method is practicable for routine analysis. The apparatus used consisted of a Geiger counter tube with an outer jacket, the potassium soln. being introduced into the annular space between the counter tube and the jacket. A conventional amplifier enabled the count to be made for any desired length of time. After making allowance for the background count (when the annular space was filled with distilled water) it was found that the net count was directly proportional to the potassium concn. With the exception of the other radioactive elements already mentioned, the nature of any accompanying anion or added salt had no appreciable effect on the counting rate. Once the apparatus had been set up, a determination required from 10 min. to 2 or 3 hrs., depending on the sensitivity of the counter, the potassium concn. and the accuracy desired. B. S. C.

Spectrophotometric Determination of Iron with o-Phenanthroline. J. P. Mehlig and H. R. Hulett. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 869.)—The extinction coefficients, at wavelengths 490$m\mu$ and 505$m\mu$, of the orange complex formed by the combination of three mols. of *o*-phenanthroline with one ion of ferrous iron have been determined; similar data have been obtained for the cherry-red nitro-*o*-phenanthroline-ferrous complex. The values of the "specific extinction coefficients" (defined as the extinction coefficients for a 1 cm length of soln. of strength 1 g/litre) are as follows:

o-phenanthroline-iron system:
490$m\mu$ 10,590. 505$m\mu$ 11,080.

nitro-*o*-phenanthroline-iron system:
490$m\mu$ 11,130. 505$m\mu$ 11,410.

Procedure for iron in ores.—Dissolve approx. 0·5 g of ore in 25 ml of conc. hydrochloric acid, filter off siliceous residue if necessary, transfer to a 1000-ml volumetric flask, dilute to the mark and shake. Transfer an aliquot portion (10 ml) to a 100-ml flask, dilute to the mark and shake. Transfer 10 ml of this soln. to a second 100-ml flask and add 1 ml of 10% w/v hydroxylamine hydrochloride soln. and about 65 ml of water. Add 10 ml. of *o*-phenanthroline soln. (0·1% soln. of the monohydrate, made by dissolving in water warmed to 80° C.) or nitro-*o*-phenanthroline soln. (0·1% in 95% alcohol) and dilute to the mark. Measure the transmission of this soln. in a 1-cm. cell at 490$m\mu$ or 505$m\mu$ by means of a suitable spectrophotometer. Correct the value by measuring the transmission of a blank soln. at the same wavelength. Calculate the percentage of iron present, using the appropriate value of the "specific extinction coefficient" given above. The *o*-phenanthroline reagent is recommended, since the colour is developed much more rapidly than with the nitro reagent. The method is claimed to have the following advantages: it is not necessary to make up a standard iron soln., the *p*H need not be regulated closely, the colour formation occurs in acid soln. and very few other ions interfere with the colour. B. S. C.

Preparation of Purified Inorganic Compounds for Use in Spectrographic Standards. R. C. Hughes. (*J. Opt. Soc. America*, 1943, **33**, 49.)—Methods are described for preparing inorganic compounds of high purity for use as components of synthetic standards for the spectrographic analysis of agricultural samples. Substances whose preparation and purification are described in detail include silica, calcium chloride, magnesium sulphate, potassium chloride and sodium chloride. The study of the impurities present at various stages in the purification processes was principally spectrographic, since it is only those impurities thus detected that are of interest in the preparation of spectrographic standards. B. S. C.

Separation of Salts by Flotation. A. Guyer and R. Perren. (*Helv. Chim. Acta*, 1942, **25**, 1179–1187.)—The process was investigated on a laboratory scale for technical rather than analytical purposes. The mixture of finely ground salts to be separated is suspended, with mechanical agitation, in a saturated soln. of the salts containing an addition agent to depress the surface tension, *e.g.*, sodium oleate or the sodium salt of a sulphated fatty alcohol. The mixture is delivered into one limb of a vessel in the form of a U-tube having an additional channel connecting the limbs of the U. This limb contains a rapidly rotating stirrer, and a stream of finely divided air is injected into it. The liquid on passage into the other limb becomes enriched in one of the salts. By adjustment of the rate of stirring and of the size of an orifice in the bottom of the U-tube together with a suitable proportion of addition agent present, a separation of up to about 98% could be effected with pairs of salts, such as ammonium chloride and potassium chloride. Varying degrees of separation were obtained with mixtures of chlorides, sulphates and nitrates of sodium, potassium and ammonium. S. G. C.

Reviews

RICHMOND'S DAIRY CHEMISTRY. 4th Ed. By G. D. ELSDON, D.Sc., F.I.C., and G. H. WALKER, Ph.D., F.I.C. Pp. vi + 472. London: Charles Griffin & Co., Ltd. 1942. Price 30s.

The nutritional significance of milk and dairy products is receiving a wider and wider appreciation as the war goes on, and this appreciation will not cease with the conclusion of hostilities. Not merely quantity and hygienic quality, but also the varying nutritive, *i.e.*, compositional, quality of milk will inevitably receive more consideration both from a public steadily becoming better informed and from a Government taking more effective interest in national health. The time may not be far distant when all milk will be purchased on a basis which will require an assessment of *both* hygienic *and* compositional quality. Analytical methods for determining quality and the practical factors controlling it are bound to assume greater importance both for the milk to be consumed in the household and for that going to manufacture.

In this respect the appearance of the new edition of "Richmond," completely rewritten by Elsdon and Walker, is opportune. A comparison with the 1920 edition, which was revised by Richmond himself, shows in a notable way the great extension during the past twenty-two years of chemical and physico-chemical technique to the analysis and control of milk and milk products. The new edition, with indexes, extends to 472 pages, against 490 in the old. Despite this slightly smaller compass, considerably more material —at least 25% more—is compressed into it. The net increase is actually greater than 25%, since a good deal of irrelevant matter in the 1920 edition has been entirely omitted from the new. All this has been done, even under war-time conditions, with an improvement in legibility and clarity. The lay-out of the new volume is pleasing, and the fact that references to the original literature are now immediately available at the foot of each page makes for good temper when the reader is hurried.

The division of matter into two almost equal parts, clearly separable, is also a betterment of the rather uneasy division, into three parts, of the 1920 edition. Part I, "General considerations," reviews the composition of milk and milk products from different angles. Precision, ease of reference and compression of published facts into small space are afforded by over 200 tables. Part II, "Detailed methods and determinations," gives a clear account of almost all the common methods, both chemical and physico-chemical, used for the analysis of milk and milk products. A number of the less common ones are also carefully described. Part II is, in fact, an indispensable laboratory manual. Further useful tables are in the text of this part, and more follow in an appendix.

Excellent though the present edition is, there appear to be a few points where improvement might perhaps be made. Appraisal of the analytical methods which are described is not always sufficiently critical. The references given might with advantage include more from journals published outside this country, and might also in certain sections be brought closer to date. Thus, to take casein alone: (i) there are amino-acid analyses of this protein later than those of Foreman in 1919 (there is room for another useful table here); (ii) there is no mention of the work of Linderstrøm-Lang on caseins of different chemical composition that he separated from cows' milk; (iii) no reference is made to modern work on the mode of combination of the phosphorus in the casein molecule, although earlier speculations are mentioned; (iv) the "casein number" of Rowland might have been discussed. In another field, no reference is made to the resazurin test, which has received some prominence in milk control literature for three or four years and is now an official test under the National Milk Testing and Advisory Scheme. Perhaps, too, since milk is first and foremost a foodstuff, some statement might have been expected in an up-to-date manual of Dairy Chemistry as to chemical and physico-chemical methods for the determination of certain of the vitamins in milk and milk products. More also might perhaps have been said about the effect of mastitis—from which at least 40% of our dairy cows suffer to a greater or lesser degree—on the chemical composition of milk.

These criticisms are, nevertheless, minor, and possibly niggling. The book has so many outstanding excellences, brings together—and that in a convenient form—such a large amount of valuable but otherwise scattered information on all aspects of dairy chemistry, and is such stimulating reading for anyone interested in the science fundamental

to dairy technology that far more delinquencies than the few that careful reading will disclose would be freely forgiven. That this volume is an essential part of the furniture of the working bench of every dairy chemist and public analyst is a plain statement of fact.

H. D. KAY

FUEL TESTING: LABORATORY METHODS IN FUEL TECHNOLOGY. By GODFREY W. HIMUS, Ph.D. 2nd Ed. Pp. xvi + 288. London: Leonard Hill, Ltd. 1942. Price 21s.

In this second, revised and much enlarged edition of his book first published in 1932, Dr. Himus gives an account of the numerous methods and specifications of the British Standards Institution issued and re-issued during the last decade for sampling, testing and valuing coal. He also describes the current laboratory methods for the scientific examination of solid, liquid and gaseous fuel in general; shows how laboratory tests are translated into terms of works practice and commercial economics; and enriches the whole with a record of observations made and opinions formed during his own extensive experience in this field of work. More than half the book deals with the important subject of coal; but gas and oil receive adequate treatment.

The weak spot in coal technology would appear to lie in the gross or first sample fraction, which must, perforce, in many instances violate the first principles of the sampler's art. The B.S.I. specifications, with a calculated precision of plus or minus 1% for 99 samples out of 100, represents, in general, the least that is acceptable to science and the most that business will stand. But when all is said and done, it is just that hundredth sample that causes so much trouble. Fortunately, for many samplers the conditions are more favourable than those that can be envisaged in standardised specifications; the more scientifically minded are not slow to profit by the opportunity.

The author draws special attention to the contamination to which coal and coke samples are liable by abrasion of pulverising apparatus. The effect of cast-iron bucking plates and some disc grinders is not always appreciated. It can usually be rendered insignificant by impact crushing in hardened steel mortars combined with frequent sieving to remove "fines."

The book is well documented by references to collateral literature; a select bibliography follows each chapter. The few misprints are of a self-evident nature. There is an adequate index. A section on the analysis of coal ash is contributed by Mr. W. C. Hancock.

Somewhat surprisingly, in a book of this nature, there is a short section on the art of technical exposition that may well be read with profit by those who have devoted more time to acquiring scientific erudition than to attaining literary skill. To the short list of standard works for writers with which it closes, might be added A. Rickard's "*Technical Writing.*"

The author makes out a strong case for purchasing industrial fuel by contract against assay and calorific value. An equally strong case might be argued for selling domestic coal at a price regulated by its ash and moisture contents. It should not be beyond the wit of man to devise some system whereby the grosser forms of inequity at present practised upon the domestic consumer might be prevented.

Those interested in fuels, either in the laboratory or in the practical application of laboratory data, will find in this volume both lucid instruction and hard-headed common sense.

F. L. OKELL

X-RAY CRYSTAL ANALYSIS IN WORKS CONTROL. Pp. 8. London: Adam Hilger, Ltd. 1943.

The title of this brochure might more justifiably be "An X-ray aid to the recognition of structural differences in metals," since the subject discussed is the utilitarian employment of X-ray diffraction technique for the routine inspection of metals during manufacturing processes. Three interesting examples of actual applications are described, in all of which the essential feature is the recognition of differences between the back-reflection X-ray diffraction photographs of "satisfactory" and "unsatisfactory" material. It is suggested that, after some experience of the method, the metallurgist without a training in physics is able to derive information about metals, not obtainable by other means. Whilst it may be true that "the simplicity of the technique involved is such that the examination may be left to the charge of an intelligent assistant," one cannot help but feel that there should

be available for consultation some member of the laboratory staff with more than the average metallurgist's knowledge of X-ray crystallography.

The booklet is of interest to all analysts connected with metallurgy, although it does not deal with X-ray crystal analysis in the full sense of the term. A useful summary is included of the more important characteristic types of diffraction pattern that may be met with when applying the method. B. S. COOPER

WAR-TIME INFORMATION FOR PHARMACISTS. Compiled by The Pharmaceutical Journal (with the assistance of J. A. STEWART, B.Sc., Ph.C., Barrister-at-law). 2nd Ed. Pp. 63. London: The Pharmaceutical Press, 1943. Price 1s.

The new edition of this little booklet provides pharmacists with a fund of information that will not only help them to comply with the never-ending output of new regulations, but will also enable them to answer the unexpected questions of their customers. At the same time it will also serve as a useful work of reference on many subjects that concern all analysts whose work is connected with drugs.

The more specialised sections (all arranged in alphabetical order) deal with such questions as Advertising, Calling-up Regulations, Central Pharmaceutical War Committee, Treatment of Burns, Control of Cod-liver Oil, Confectionery, Prices of Goods, Purchase Tax, and so forth. A concise Summary is given of Acts of Parliament, Defence Regulations, and Statutory Rules and Orders from the outbreak of war to February, 1943, in so far as they have a direct or indirect pharmaceutical bearing. Among the subjects of wider interest are (to select a few at random) such items as Alternatives for Alcohol in B.P. Preparations, Fertilisers, Fire Watching, Income Tax, The Pharmacy and Medicines Act, Labelling, Composition of Proprietaries, Tonic Wines, and Water Sterilisation. The pamphlet concludes with 4 pages of useful addresses, such as those of Government Departments, Ministries (including the numerous branches of the Ministry of Food and the Ministry of Supply), medical, scientific and professional societies, and various trade associations. The work of compilation has been carefully done, and the booklet is well worth the modest price at which it is sold. EDITOR

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The following Reports may be obtained direct from the Editor of THE ANALYST, 16, Blomfield Road, London, W.9 (not through Trade Agents), at the price of 1s. 6d. each to Members of the Society, 2s. each to non-Members. Remittance must accompany the order, and be made payable to "The Society of Public Analysts."

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