The Society of Public Analysts and other Analytical Chemists

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PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

A MEETING of the Society was held at 3.45 p.m. on Wednesday, October 6th, 1943, at The Chemical Society's Rooms, Burlington House, London, W.1. The chair was taken by Dr. H. E. Cox, Vice-President, and the following papers were presented and discussed:—"The Determination of Carotene in Grass and Silage Mixtures," by T. Barton Mann; "The Rapid Determination of Arsenic in Glass," by H. N. Wilson, F.I.C. Three items of apparatus devised by M. A. Fill and J. T. Stock, B.Sc., A.I.C., were described and exhibited by them, *viz.*, (1) Reflux Apparatus for Automatic Dispersion of Froth in the Determination of Fibre, (2) An Electrical Indicator for Collecting a Constant Volume of Distillate, and (3) A Wash Bottle for Delivering Predetermined Volumes of Liquid.

NEW MEMBERS

Miss Edith Brodaty; Malcolm George Read, B.Sc. (Lond.), A.I.C.

DEATHS

WE regret to have to record the deaths of the following members:

Robert Macfarlane Clark
Leo Cooksey
John Golding
John Aitken Macnair
Walter George Messenger
Henry Llewellyn Smith

The Separation and Determination of Very Small Amounts of Aluminium and Iron in Water

BY N. STRAFFORD, M.Sc., F.I.C., AND P. F. WYATT, B.Sc.

INTRODUCTION.—The presence of residual alumina and organic matter in the feed water has caused difficulties with the operation of a new La Mont high pressure boiler plant (650 lb./sq. in.) and the associated base exchange softening plant. Colloidal alumina and organic matter, by coating the granules of carbonaceous zeolite, reduced the working exchange capacity of the softening plant to about 60% of the normal capacity, despite an increase in the amount of wash water used from 1% to 6% of the softened water output, while aluminium retained in solution, in conjunction with the silica present, caused the deposition of analcite scale, $NaAl(SiO_3)_2.H_2O$, in the boiler tube system, which resulted in two tube failures.

The water entering the softening plant contained *ca.* 0·7 p.p.m. of aluminium with *ca.* 6·0 p.p.m. of silica. The raw reservoir water is of a soft moorland type with a definitely acid reaction and contains in its natural condition up to 1·0 p.p.m. of aluminium, probably in the form of complex silicates, with a little iron. Expts. showed that virtually the whole of the aluminium, iron, organic matter and turbidity could be ppt'd. by coagulation with filter alum, provided that the *p*H was maintained within the limits 5·8–6·4. During this work need was felt for a method that would determine with accuracy the aluminium content of (*a*) raw and alum-dosed waters containing about 1 p.p.m. of Al, (*b*) final treated water containing 0·005–0·1 p.p.m. of Al.

LIMITATIONS OF EXISTING METHODS.—The most sensitive specific and reliable reagents for the colorimetric determination of such small amounts of aluminium are (*a*) ammonium aurintricarboxylate[1] and (*b*) haematoxylin.[2] Existing procedures[2,3,4,5,6,7,8] based on the use of these reagents were inadequate for our purpose in the following respects[2,3,4,5,6,7,8]:

(1) *Separation of Iron.*—Iron interferes quantitatively,[7,8,9] and the methods available for its separation are ineffective at such low concns. By the Melaven cell method[8] about

2μg of iron remain in solution, whilst the sodium hydroxide separation[7] breaks down altogether. For example, by means of the methods described later, we found 15μg of aluminium and 37μg of iron in the ppt. (*i.e.*, retained on the filter) and 38μg of aluminium and 30μg of iron in the filtrate, when the sodium hydroxide separation was applied to a solution containing 52μg of aluminium and 64μg of iron.

(2) *Aurintricarboxylate method.*—(i) Impurities present in commercially available reagents give a highly coloured "blank" (usually a deep straw colour) so that the pink colour of the alumina lake is modified and to some extent masked. (ii) Winter, Thrun and Bird[5] stabilise the lake at *p*H 7·1, while in Lampitt and Sylvester's method[7] the final *p*H is *ca.* 8·6. In the first instance, there is inadequate inhibition of interference from magnesium, etc., while at the higher *p*H the lake does not remain stable and fading is very rapid when the amount of aluminium is very small. Further, it is impossible to control the *p*H properly by the use of such unstable reagents as ammonia and ammonium carbonate.

(3) *Haematoxylin Method.*—(i) Haematoxylin does not react with aluminium in colloidal or complex form, unless the soln. is first acidified with a mineral acid before making it alkaline with ammonium carbonate. This fundamentally important fact is often ignored or overlooked, and Hatfield's procedure[2] is applied directly to the water as sampled. (ii) The *p*H range used by Hatfield, *viz.*, 8·2–8·3, is not the optimum range; the lake is best developed at a *p*H just above 7·0, to ensure maximum intensity and purity of colour and good stability and reproducibility. (iii) The intense colour of the excess of dyestuff masks the colour of the lake. On the other hand, full intensity of lake colour is obtained only if a large excess of dyestuff is used. (iv) The subsequent addition of acetic acid, whereby the final *p*H is reduced to 4·5, reduces the lake colour and leads to irregular results. (v) In addition to iron, copper and manganese interfere, although usually the amounts of these last two metals in water are too small to have much effect.

DEVELOPMENT OF MODIFIED METHODS.—(1) *Separation of Iron.*—Iron reacts with both ammonium aurintricarboxylate and haematoxylin in the same way as aluminium, giving a similarly coloured lake. Interference is quite quantitative, the colour intensity due to iron being a little less than half that due to aluminium, which suggests that the intensities are probably inversely as the atomic weights of the two metals, *viz.*, 56 : 27 or about 2 : 1. Both methods can, therefore, in absence of aluminium, be used as sensitive and accurate procedures for the determination of iron, and they can also be used to give an accurate measure of the total aluminium and iron content (expressed as aluminium) of a water sample. Smith and Cooke[10] determine very small amounts of iron by extraction as ferric thiocyanate with a mixture of amyl alcohol and ether (5 : 2). The extraction is effected in presence of nitric acid and a large excess of alkali thiocyanate, and is not carried to completion. By strictly limiting the amount of ammonium thiocyanate employed and extracting exhaustively in presence of a little hydrochloric acid, we have so modified the method that it affords an excellent means of sharply separating the minute amounts of aluminium and iron found in waters, and of determining the iron, while at the same time providing an extracted soln. in which the aluminium can be determined directly.

(2) *Aurintricarboxylate Method.*—By operating with a final *p*H of 7·5 ± 0·2, optimum conditions are obtained for preventing interference from metals such as magnesium, which form unstable lakes at the initial *p*H = 5, and at the same time avoiding appreciable instability and fading of the colour of the aluminium lake. The required precise control is obtained by substituting for ammonia and ammonium carbonate a buffer soln. containing boric acid and ammonia (in the molecular ratio of 3 : 2), which appears to have all the inhibiting properties of ammonium carbonate without its instability.

(3) *Haematoxylin Method.*—Preliminary acidification with hydrochloric acid ensures that complex or flocculated aluminium compounds are converted into ionisable form. Since "aged" alumina floc is not very readily soluble, a sufficient excess of acid must be used to ensure that solution is reasonably complete. Maximum development of the aluminium lake occurs at *p*H 7·1 ± 0·2, but is then rather slow, and it was found advisable to increase the *p*H to 7·5 to accelerate development and make the *p*H control less critical. Ammonium carbonate, on account of its instability and uncertain composition, is not an ideal reagent for obtaining the required *p*H conditions, but no satisfactory substitute was found. Sufficiently precise control is obtained by using a standardised soln. Removal of excess haematoxylin colour is achieved by adding ammonium borate, which has the effect of destroying the magenta colour of the dyestuff, so that only the pure blue colour

due to the aluminium lake itself, remains. Much greater sensitivity and accuracy are obtained by this means than are possible by Hatfield's procedure. The use of a protective colloid is essential to ensure stability and uniform purity of colour of the lake. "Starch glycerite" (see *Reagents*) gives better results than either starch or glycerin alone. Under the conditions recommended, hardness salts up to about 400 p.p.m. (calc. as $CaCO_3$) do not interfere. The effect of manganese is to catalyse the formation of a yellow oxidation product and accelerate decomposition of the aluminium lake. Up to 100μg of manganese can be present without appreciable ill effect, provided that the matching of the lake colour is done without undue delay. Copper forms an unstable purplish-blue lake and thus interferes; on addition of borate this lake is largely decomposed, so that the effect of the minute amounts of copper usually found in waters is negligible. Further, if the soln. is extracted to remove iron, the copper is also quantitatively extracted as copper thiocyanate, so that the question of interference with the aluminium determination does not arise. The presence of copper, however, in the solvent layer will, on account of the colour of its thiocyanate, lead to a high result for iron, unless the thiocyanates are decomposed and the copper and iron separated. With waters, separation is rarely necessary.

(4) *Measurement of Colour Intensity.*—In order to avoid the tedious procedure of making up a series of standards, the B.D.H. Lovibond Nessleriser can be used to measure the colour intensity. Two series of colour discs already available for use with the instrument are adaptable to the present methods. The series used for the determination of iron by the thioglycollic acid method (Discs A and B, ranges 2–18μg of Fe and 20–60μg of Fe) matches approx. the colour of the aurintricarboxylate lake, while the disc used for the determination of phosphate by Tschopp's molybdenum blue method (phosphate disc C, range 5–60μg of P_2O_5) matches reasonably closely the blue colour developed in the modified haematoxylin method. Readings throughout the investigation were therefore obtained in terms of μg of Fe or μg of P_2O_5 respectively, as measures of colour intensity by means of these discs.

(5) *Note on Houghton's Procedure.*—Since completing this investigation we have noted with interest the modification of Hatfield's method devised by Houghton,[11] and offer the following comments:—(i) The slightly acid haematoxylin reagent is much more stable than the neutral reagent we employed. We have therefore adopted it, but prefer to dissolve the reagent in the cold and omit the chloroform. (ii) The amount of hydrochloric acid used by Houghton for initial acidification of the water sample is not always sufficient to dissolve coagulated aluminium hydroxide (see p. 320). (iii) Satisfactory stabilisation of the lake under our conditions, *i.e.*, on the *alkaline* side of *p*H 7 could not be obtained with Houghton's buffer soln. (iv) The strong "background" colour due to excess of haematoxylin is still a great disadvantage in Houghton's method. Further, the colour due to the aluminium lake is not so intense on the acid side of *p*H 7 as on the alkaline side. (v) The inhibition of iron and copper by potassium cyanide, in Houghton's method, is reasonably effective, but does not give the complete freedom from interference obtained by the extraction method. Moreover, when, as in the present method, the aluminium lake is developed at *p*H 7·5, potassium cyanide does not inhibit the reaction between haematoxylin and iron. The advantages of the extraction method are particularly noticeable when determining less than 0·1 p.p.m. of aluminium.

PROCEDURE.—*Precautions.*—Owing to the very small amounts of iron and aluminium involved, special precautions must be taken to avoid contamination, *e.g.*, from atmospheric dust or from the reagents and apparatus used. All apparatus should be kept specially for the purpose and washed with hydrochloric acid followed by distilled water (quite metal-free) immediately before use. If the acidity or alkalinity of the sample exceeds the equivalent of 2 parts of $CaCO_3$ per 100,000, the sample should be neutralised with $N/10$ sodium carbonate or $N/10$ hydrochloric acid, as determined by a separate titration to methyl orange.

Reagents.—These must be of the purest quality obtainable. The factor of all standardised solns. must be 1·000 ± 0·005.' Distilled water must be used throughout.

(1) *Hydrochloric acid, 5 N.*—Prepare from conc. HCl, A.R., and standardise with N sodium carbonate to methyl orange. (2) *Ammonium carbonate, 2 N.*—Dissolve 120 g of re-sublimed ammonium carbonate (powdered) in 1 litre of cold water, filter and adjust to 2 N, standardising with N HCl to methyl orange. (3) *Ammonium borate, 0·8 N.*—Dissolve 93 g of powdered boric acid in 1 litre of ammonium hydroxide, N. Filter and

dilute to 0·8 *N*, standardising by titrating 25 ml; diluted to 150 ml, with *N* HCl to methyl red. (4) *Ammonium acetate buffer soln., approx.* 2 *N.*—Dissolve 156 g of ammonium acetate, A.R., and 108 g of ammonium chloride, A.R., in water, filter and dilute to 1 litre. (5) *Standard aluminium solutions.*—(*a*) Dissolve 1·757 g of potassium alum in water containing 50 ml of 5 *N* hydrochloric acid, and dilute to 1 litre; 1 ml ≡ 0·0001 g of Al. (*b*) Dilute 5·0 ml of (*a*) to 50 ml; 1 ml ≡ 0·00001 g (10μg) of Al. Prepare freshly as required. (*c*) Dilute 5·0 ml of (*a*) to 250 ml, after adding 1 ml of 5 *N* HCl; 1 ml ≡ 0·000002 g (2μg) of Al. Prepare freshly as required. (6) *Standard ferric iron soln.*—(*a*) Dissolve 0·7023 g of ferrous ammonium sulphate in 100 ml of water and 50 ml of hydrochloric acid, 5 *N*. Add re-distilled bromine water (reagent 7) in excess, boil off excess, cool and dilute to 1 litre; 1 ml ≡ 0·0001 g of Fe^{III}. (*b*) Dilute 10·0 ml of (*a*) to 100 ml; 1 ml ≡ 0·00001 g (10μg) of Fe^{III}. (7) *Bromine-water* (*iron-free*).—Connect a 1-litre round-bottomed flask by a ground-glass joint to a long Liebig condenser, and half fill with sat. bromine water, adding also several ml of bromine. Distil into a litre flask half filled with distilled water and well cooled in ice and water. Shake the contents of the receiver until the soln. is saturated. (8) *Ammonium thiocyanate, approx. N.*—Dissolve 80 g of ammonium thiocyanate, A.R., in 1 litre of water. To 50 ml add 1 ml of 5 *N* hydrochloric acid and extract three times with 10-ml portions of mixed solvent (reagent 9). Add 1 ml of 5 *N* ammonium hydroxide to the extracted soln. (9) *Mixed solvent.*—Mix 5 vols. of amyl alcohol, B.P., with 2 vols. of ethyl ether. (10) *Starch glycerite.*—Mix 1 g of finely ground starch with 20 ml of glycerin to a smooth paste in a small porcelain dish. Heat over a small flame until fuming occurs and stir continuously until the mass becomes quiescent and clear, taking care not to overheat. Cool, mix with 80 ml of water, stand overnight and decant or filter. (11) *Haematoxylin soln.*, 0·1%.—Crush a 0·1-g pellet of haematoxylin,* and dissolve in 100 ml of cold water containing 0·1 ml of 5 *N* hydrochloric acid. (12) *Ammonium aurintricarboxylate soln.*, 0·1%.—Dissolve 1·0 g of powdered reagent (Scherrer and Smith's formula[8])† in 1 litre of water.

METHOD.—(A) *Separation and Determination of Iron.*—(*a*) *Samples containing up to 5 p.p.m. Fe and more than 0·1 p.p.m. Al.*—Measure 10 ml of well-mixed sample (or proportionately smaller amount, if Al content exceeds 0·5 p.p.m.) into a 100-ml conical flask, and 10 ml of distilled water into a similar flask. Add to each 1·00 ml of 5 *N* hydrochloric acid and 1 ml of bromine water and boil to remove excess bromine; if the colour disappears before the soln. reaches b.p., add more bromine water, 1 ml at a time, until the yellow colour persists. When all excess of bromine has been boiled off, cool and add 1 ml of *N* ammonium thiocyanate (extracted) and 10 ml of mixed solvent to each, and transfer to 50-ml graduated cylindrical separating funnels. Shake vigorously for 15 sec., allow to separate, and confirm that the solvent layer in the blank is practically colourless. Then add standard ferric iron soln. (1 ml≡10μg of Fe) to the blank until, after vigorous shaking and separation, the colour of the solvent layer matches that of the test. Note the vol. of iron soln. used. Add to blank and test 0·5 ml of *N* ammonium thiocyanate, and continue the extraction, using successively two 5-ml portions of mixed solvent and finally extracting with 5 ml of ether alone. Wash the solvent layer with 1 ml of water after each extraction, without mixing. If the amount of iron present exceeds 20μg of Fe, give a further (4th) extraction with 5 ml of mixed solvent, after adding 0·5 ml of ammonium thiocyanate soln., before the final ether wash. Determine the iron content by comparing the colour of the combined solvent extracts from the test with that of the blank and the added iron soln. Return the aqueous solns. and washings (total vol. 15–20 ml) to their respective flasks, add to each 15 ml of water, and reserve for the determination of aluminium. (*b*) *Samples containing less than 0·1 p.p.m. Al with up to 2 p.p.m. Fe.*—Measure 25 ml of well-mixed sample, and 25 ml of distilled water for the blank, and proceed as in (*a*), but use double quantities of mixed solvent, *viz.*, 20, 10, 10 ml, and finally 10 ml of ether, with a 1-ml water wash after each extraction and the same amounts of ammonium thiocyanate soln. (1 ml + 0·5 ml) as before. The final vol. of the aqueous soln. should be 30–35 ml, and the soln. is not further diluted.

(B) *Determination of Aluminium.*—(*a*) *Haematoxylin method.*—After extraction of the iron from blank and test solns., add to each the requisite amount of 2 *N* ammonium

* Burroughs, Wellcome & Co.'s haematoxylin (microscopic stain) was used.

† We use material prepared by a slightly modified method, whereby, with a view to easier temperature control, addition of formaldehyde is carried out at 18 (± 1)° C. instead of at 3–5° C. Commercial reagent is unsatisfactory.

carbonate to give a *p*H of 7·5 ± 0·2, while swirling the contents of the flask. The amount of 2 *N* ammonium carbonate required is 5·7 ml for an unextracted soln., 4·9 ml for a soln. extracted by procedure (*a*) and 4·1 ml for one extracted according to (*b*). The lower amounts required for the extracted solns. are due to loss of acid extracted by the solvent. Next add 1·0 ml of starch glycerite soln. and 5 ml of haematoxylin soln., mix, and leave for 15 min. At this stage the colour varies from magenta in the blank through purple to almost pure blue in the test, with increasing amounts of aluminium, the intensity increasing during standing. After 15 min. standing, add 5 ml of 0·8 *N* ammonium borate soln., and leave for *ca.* 2 min., *i.e.*, until the magenta colour of the dyestuff fades out. Transfer to 50-ml Nessler cylinders, dilute to the 50-ml mark and measure the colour in the B.D.H. Lovibond Nessleriser, using phosphate disc C (range 5–60μg of P_2O_5). Then, disc reading divided by 13·5 represents μg of Al, *i.e.*, 13·5μg of P_2O_5 ≡ 1μg Al ≡ 0·10 p.p.m. Al on a 10-ml sample ≡ 0·04 p.p.m. Al on a 25-ml sample. If the aluminium present exceeds 4μg it will be necessary to take only 25 ml of the final soln., to dilute to 50 ml with water, for the comparison, and to multiply the observed reading by two.

If a Nessleriser and the appropriate colour disc are not available, prepare a series of standards in distilled water, using the standard aluminium soln. 5(*b*) for the range 0·1–0·5 p.p.m. and soln. 5 (*c*) for the range 0–0·1 p.p.m. of aluminium.

For field work, it is often unnecessary to differentiate between iron and aluminium, and a value for the iron and aluminium content (expressed as aluminium) may be obtained rapidly as follows. Measure 5–25 ml of the well-mixed sample, according to the amount of iron and aluminium expected, into a 50-ml Nessler cylinder and dilute to 30 ml. Add 1 ml of 5 *N* hydrochloric acid, mix, then add 5·7 ml of 2 *N* ammonium carbonate soln., and 1·0 ml of starch glycerite, and mix. Add 5·0 ml of 0·10% haematoxylin soln., mix again and leave for 15 min. Add 5·0 ml of 0·8 *N* ammonium borate soln., mix, dilute to the 50-ml mark and mix again. Compare as before with a blank. Then disc reading, divided by 13·5, represents μg of Al. If the amount of iron present is known, allowance can be made for it; 1μg of Fe ≡ 0·5μg of Al ≡ 7μg of P_2O_5 (disc reading).

(*b*) *Aurintricarboxylate method.*—After extraction of the iron from the blank and test solns. add to each 5 ml of ammonium acetate buffer soln. and 2 ml of 0·1% ammonium aurintricarboxylate soln. Mix, and heat in a boiling water-bath for 15 min. (transfer the solns. to boiling tubes, 6 in. × 1 in.). Cool in ice and water to 10–15° C., add 1 ml of starch glycerite, and then the requisite amount of 0·8 *N* ammonium borate to give a *p*H of 7·5 ± 0·2. The amount required is 6·5 ml for an unextracted soln., 5·4 ml for a soln. extracted by procedure (*a*) and 4·3 ml for a test soln. extracted by procedure (*b*). Mix, allow to stand for 20 min., dilute to 50 ml, and compare in the Nessleriser, using the appropriate iron (thioglycollate) disc A or B. Then, disc reading divided by 8 represents μg of Al, *i.e.*, 8·0μg of Fe (disc reading) ≡ 1μg of Al ≡ 0·10 p.p.m. of Al on a 10-ml sample ≡ 0·04 p.p.m. of Al on a 25-ml sample. If no Nessleriser is available, prepare a series of aluminium standards in distilled water.

ACCURACY OF RESULTS.—(1) *Aluminium.*—The following results were obtained by three observers on test solns. the Al content of which was known, but not to the observers. Two sets of observations were made:—A. Directly, on tests containing aluminium alone in distilled water. B. After extraction of iron, on test solns. in which aluminium was added to a hard borehole water into which had been introduced 2 p.p.m. of iron and 0·5 p.p.m. of copper.

(A) *Known amounts of aluminium added to distilled water*

Haematoxylin method				Aurintricarboxylate method			
Al added μg	Al found, μg (3 observers)			Al added μg	Al found, μg (3 observers)		
	A	B	C		A	B	C
0·5	0·45	0·5	0·4	0·9	1·0	0·9	0·9
0·9	0·75	0·85	0·85	1·3	1·1	1·25	1·25
1·4	1·4	1·45	1·5	2·3	2·4	2·4	2·4
2·3	2·3	2·1	2·5	3·8	4·0	3·8	4·2
3·7	3·8	3·5	3·6	6·2	6·2	6·4	6·0

(B) *Known amounts of aluminium added to borehole water containing 2 p.p.m. Fe and 0·5 p.p.m. Cu, of total hardness 250 p.p.m. $CaCO_3$ (Ca = 77 p.p.m., Mg = 14 p.p.m.).*

Haematoxylin method				Aurintricarboxylate method			
Al added μg	Al found, μg (3 observers)			Al added μg	Al found, μg (3 observers)		
	A	B	C		A	B	C
nil	<0·1	<0·1	—	nil	<0·1	<0·1	—
1·0	0·95	1·05	—	1·0	0·9	0·9	0·9
2·0	2·1	2·0	—	3·0	3·2	3·2	3·1
3·0	3·0	3·2	3·3	5·0	5·0	4·8	5·0
4·0	4·0	4·0	3·7	—	—	—	—

(2) *Iron.*—The following results were obtained with the above iron-free borehole water to which had been added known amounts of iron:

	1	2	3	4
Iron added (p.p.m.) ..	0·02	0·5	1·0	2·0
Iron found (p.p.m.) ..	0·025	0·55	1·0	2·0

TYPICAL RESULTS.—A few results obtained on waters by the above procedures are given in the following table:

Sample tested	Iron found p.p.m.	Aluminium found, p.p.m. Aurintricarboxylate	Aluminium found, p.p.m. Haematoxylin
Manchester Corporation water (ex Thirlmere) ..	0·015	0·01	0·01
Stockport Corporation (Lyme Park)—final treated water	none detected	—	0·005
Yorkshire raw moorland water	0·18	0·93	0·87
Yorkshire water dosed with 0·5 grain/gall. alum at *p*H 5·2 and filtered*	0·10	0·75	0·80
Yorkshire water dosed with 0·5 grain/gall. alum at *p*H 6·1 and filtered†	0·015	0·015	0·015
Scottish moorland water	0·44	—	0·60
Scottish water dosed with 0·7 grain/gall. alum at *p*H 6·3 and filtered†	0·01	—	0·01

* Poor flocculation conditions. † Good flocculation conditions.

SUMMARY.—A method is described for the complete separation and determination of iron in waters, by solvent extraction as ferric thiocyanate, in such a way that aluminium can be determined readily in the extracted soln. The aurintricarboxylate and haematoxylin methods have been modified so that it is possible to determine 0·1–0·5 p.p.m. of aluminium to an accuracy of ±0·05 p.p.m., or 0·01–0·10 p.p.m. of aluminium to an accuracy of within ±0·01 p.p.m., provided that the amount of iron originally present does not exceed about 10 times that of the aluminium content. The modified haematoxylin method is rather more convenient and slightly more sensitive than the modified aurintricarboxylate method. Both methods can be used to give an accurate colorimetric measure of the total iron and aluminium content (expressed as Al) of a water sample.

In conclusion, we desire to express our thanks to I.C.I. (Dyestuffs) Ltd. for permission to publish this communication.

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Determination of Copper Volumetrically by the Iodine-Thiocyanate Method

By C. C. OGLETHORPE, B.Sc., and C. G. SMITH, Ph.D., B.Sc., F.I.C.

(*Read at the Meeting, May* 5, 1943)

In 1918 G. Bruhns[1] suggested modifying the iodimetric method of determining copper by using a thiocyanate. He titrated the copper soln. containing potassium iodide with a mixture of sodium thiosulphate and potassium thiocyanate. As an alternative, the copper was titrated with a mixture of sodium thiosulphate, potassium thiocyanate and potassium iodide. The use of mixed solns. as titrants not being very convenient, the present investigation was restricted to the use of a single solution titrant.

Fowles[2] recommends adding to an approx. $M/10$ copper soln. 1·25–1·5 g. of solid potassium thiocyanate, followed by 0·2 g of potassium iodide, and immediate titration. Vogel[3] prefers to add the iodide first. Although the latter is the better method, both tend to give low results.

Theory of Reactions.—The well-known reaction between copper sulphate and potassium iodide, whereby iodine is liberated is not stoichimetric, and requires a considerable excess of the iodide. The reaction may be assumed to take place according to the following equation:

$$2CuSO_4 + 5KI = Cu_2I_2 + 2K_2SO_4 + KI_3. \qquad \text{i}$$

Owing to the high cost of iodides, the replacement of part of the iodide by thiocyanate has much to recommend it. Bruhns' procedure is based on the lower solubility of cuprous thiocyanate compared with the iodide, the formation of which is immediately followed by its conversion into cuprous thiocyanate, potassium iodide being re-formed

$$Cu_2I_2 + 2KCNS = Cu_2(CNS)_2 + 2KI. \qquad \text{ii}$$

The potassium iodide reacts with more cupric sulphate, so that the total reaction may be represented thus:

$$2CuSO_4 + 2KI + 2KCNS = Cu_2(CNS)_2 + 2K_2SO_4 + I_2. \qquad \text{iii}$$

If potassium thiocyanate is added first, cupric thiocyanate is formed, and, in theory, reacts with the potassium iodide as does the copper sulphate, so that the net reaction should be the same.

Unfortunately, as Bruhns[4] pointed out, it is impossible to avoid direct decomposition of the cupric thiocyanate into the cuprous salt:

$$2Cu(CNS)_2 = Cu_2(CNS)_2 + (CN)_2 + 2S. \qquad \text{iv}$$

This withdraws cupric ion from the soln., reducing the quantity of iodine liberated. By the procedure described below we aim at overcoming this disadvantage without using a mixed titrant or excess of iodide.

In 1935, Foote and Vance[5] drew attention to the inaccuracies of the ordinary method, arising from the reversibility of reaction (i), and added ammonium thiocyanate towards the end of the titration. This caused a deepening of the blue colour owing to the liberation of more iodine. The titration was completed to a sharp end-point. Foote and Vance claim that their method gives stoichiometric results. The present authors have found that excess of iodide is no longer necessary, and that the technique can be adapted to economise the iodide, without losing the accuracy Foote and Vance claim for it.

Experimental

Addition of Thiocyanate before Iodide.—Table I summarises the results of a series of titrations of a soln. of copper sulphate containing 0·6 g of the hydrated salt for each determination against 0·1012 N sodium thiosulphate The potassium thiocyanate and potassium iodide were added in this order as 10% solns.

With 3 g of potassium iodide consistent readings of 23·75 ml were obtained, which corresponded to 100% of copper recovered. Thus all titrations using potassium thiocyanate were low and inconsistent. The error increased with increase of thiocyanate, but increase

of the iodide improved the results. On addition of potassium thiocyanate to the copper soln. the original green rapidly darkened, with deposition of a considerable amount of ppt.

TABLE I

	Potassium thiocyanate g	Potassium iodide g	Thiosulphate used ml	Copper %
(*a*)	2	0·5	21·70	91·37
			22·35	94·11
			21·95	92·42
			22·65	95·37
			22·50	94·74
(*b*)	4	0·5	22·10	93·05
(*c*)	8	0·5	21·30	89·68
(*d*)	2	0·2	17·40	73·26
(*e*)	2	0·8	23·00	96·85

(2) COMPARISON OF TWO METHODS.—In a series of expts. varying quantities of potassium or ammonium thiocyanate and of potassium iodide were added in different order to the copper soln. to ascertain the most satisfactory conditions. For each determination 0·6124 g of AnalaR $CuSO_4,5H_2O$ were titrated against 0·1 *N* sodium thiosulphate. Typical results are summarised in Table II.

TABLE II

		Experiment	Thiosulphate used ml	Copper %
(*a*)	(i)	Potassium iodide alone, 3 g	24·55	100·00
	(ii)	Excess of ammonium thiocyanate followed by 0·3 g of KI..	23·40	95·41
	(iii)	KI, 0·3 g, followed by excess ammonium thiocyanate ..	23·80	97·04
	(iv)	KI, 0·3 g, titration with $Na_2S_2O_3$ soln. to end-point. Excess ammonium thiocyanate added, and titration completed	24·15	98·47
(*b*)	(i)	KCNS, 1 g, followed by 0·5 g of KI	23·70	96·63
	(ii)	KCNS, 2 g, followed by 0·5 g of KI	23·70	96·63
(*c*)		KI, 0·5 g, followed by 2 g of KCNS	24·20	98·67

Expts. (*a*, iii) and (*c*) show that even when potassium thiocyanate was added after the potassium iodide a low titre resulted. This may have been due to there being insufficient potassium iodide to convert all the cupric ion present into cuprous iodide, so that some cupric thiocyanate was formed, with consequent error due to its decomposition.

The end-point was not always easy to detect, as the ppt. was flesh-colour and, at times, almost pale chocolate-brown, especially in presence of acid. This suggested adsorption of iodine. Otherwise acid was without effect, but dilution tended to obscure the end-point still more.

(3) EFFECT OF TIME OF STANDING UPON THE TITRATION FIGURE.—If the error were due to the loss of cupric ion by way of the decomposition of cupric thiocyanate, then allowing time between the addition of potassium thiocyanate and of iodide should cause a decrease in the titre. Table III shows results obtained on 0·6 g of copper sulphate treated first with 2 g of potassium thiocyanate and, after the times stated, with 0·4 g of potassium iodide, and then titrated with 0·1012 *N* thiosulphate.

TABLE III

Time interval min.	Thiosulphate used ml	Copper %
0	22·40	94·32
1	21·20	89·26
2	20·70	87·16
3	20·30	85·48
6	19·40	81·68

Once again the green soln. rapidly became blue-black, depositing a ppt., and the odour of cyanogen was distinctly perceptible. On heating the soln. containing potassium thiocyanate just to b.p. before adding iodide, the ppt. appeared yellow, and the titre was 3·3 ml only. Further, when the soln. was boiled for a few min. before adding iodide, the cupric thiocyanate was completely decomposed, no iodine being set free from the iodide.

Three methods of avoiding the formation of cupric thiocyanate are available:—(1) Addition of a considerable quantity of sodium thiosulphate to the copper sulphate soln. before the iodide or thiocyanate. Improved results were so obtained, but only when relatively large amounts of iodide were used. Apart from undesirable side reactions, this method has nothing to recommend it in economy, accuracy or time. (2) Use of a mixture of iodide and thiocyanate. (3) Addition of the thiocyanate near the end of the titration.

(4) Use of a Mixture of Potassium Iodide and Thiocyanate.—In a later paper Bruhns[6] suggested the use of a mixture of thiocyanate and iodide, with immediate titration with thiosulphate. A repetition of this method showed that low results were not precluded thereby. The presence of acid improved the results, but made observation of the end-point difficult. The salts were dissolved in 15 ml of water in the proportions shown in Table IV. For each titration 0·624 g of AnalaR copper sulphate were used, and the thiosulphate soln. was 0·0989 *N*.

Table IV

Potassium iodide g	KCNS gms	Thiosulphate used mls	Copper %
0·2	1	23·30	92·18
0·3	1	23·70	93·76
0·4	1	24·30	96·13
0·5	1	24·90	98·50
0·6	1	24·90	98·50
0·8	1	25·00	98·90

(5) Addition of Potassium Thiocyanate Towards the End of Titration.—The potassium iodide was added to the copper soln. in the quantities indicated in Tables Va and Vb, and titrated with sodium thiosulphate, starch indicator being used. When the blue colour disappeared, potassium thiocyanate was added, and the titration was completed to a sharp end-point. The ppt. was almost white, so that the end-point was quite distinct. Results with increasing quantities of potassium iodide revealed that 0·6 g suffice for 25 ml of *M*/10 copper soln.

Table Va.

In each test 0·6 g of copper sulphate was used, and 2 g of potassium thiocyanate were added after the first end-point. The sodium thiosulphate soln. was 0·1012 *N*.

Potassium iodide g	1st titre ml	2nd titre ml	Copper %
0·2	9·3	21·80	91·79
0·3	14·2	23·00	96·84
0·4	18·3	23·65	99·58
0·5	21·3	23·70	99·79
0·6	23·2	23·75	100·00
0·7	23·4	23·75	100·00
0·8	23·5	23·75	100·00

Table Vb

In each test 0·0124 g of AnalaR copper sulphate was used, and 1 g of potassium thiocyanate was added after the first end-point. Titration with 0·1 *N* thiosulphate.

Potassium iodide g	1st titre ml	2nd titre ml	Copper %
0·2	10·0	23·60	96·22
0·3	15·2	24·30	99·08
0·4	19·6	24·35	99·28
0·5	22·6	24·55	100·00
0·6	23·9	24·55	100·00

Table Vc

Different weights of copper sulphate (99·84% purity) were used, with 0·5 g. of potassium iodide and 1 g of potassium thiocyanate. Titration with 0·09987 *N* thiosulphate.

Copper sulphate g	Final titre ml	Copper %
0·6535	26·35	99·39
0·4893	19·80	99·75
0·7410	29·90	99·46

(6) PROCEDURE RECOMMENDED.—The conc. of the copper soln. should not be much below 0·05 *M*. The most satisfactory end-points were obtained with soln. approx. *M*/10. To such a soln. add not less than 0·5 g of potassium iodide (or 5 ml of a 10% soln.). There is no need to add more than 0·6 g. Titrate with *N*/10 sodium thiosulphate until the brown colour of the iodine fades. Then add a few drops of starch soln. and continue running in thiosulphate until the blue colour first fades. Be careful not to add too much thiosulphate soln. and ignore the re-appearance of the blue colour. Add about 1 g of potassium or ammonium thiocyanate, preferably as a 10% soln. The blue colour will immediately become more intense. As quickly as possible complete the titration. The ppt. is of a pale flesh colour, almost white,[5] so that the end-point is quite distinct, and there is no tendency for the blue colour to return.

1 ml of 0·1 *N* thiosulphate = 0·02497 g of $CuSO_4,5H_2O$ or 0·006357 g of copper.

SUMMARY.—The use of the standard method for the determination of copper volumetrically by the liberation of iodine in presence of potassium thiocyanate was found to yield low (and often variable) results, especially if the thiocyanate were added before the iodide, owing to the decomposition of the cupric thiocyanate as soon as it is formed. This difficulty was overcome without the use of any considerable quantity of potassium iodide, by titrating with a small quantity of iodide present, and completing the titration after addition of a slight excess of either potassium or ammonium thiocyanate. The end-point was distinct, and the results were accurate and reproducible. The presence of small quantities of acid in the copper soln. did not affect the results adversely.

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CHEMICAL LABORATORIES
SOUTH EAST ESSEX TECHNICAL COLLEGE

February, 1943

DISCUSSION

Mr. F. L. OKELL asked if the recommended proportion of potassium iodide was sufficient to react with all the copper present. He confirmed the unsatisfactory results given by Bruhns' modifications of the classical iodide method, and enquired how the authors' method compared with that of Foote, which also required thiocyanate to be added near the end of the titration. He considered that the authors had accomplished a useful piece of work in showing how economy in iodine could be effected without loss of accuracy.

Mr. A. L. BACHARACH asked whether, in order to economise in potassium as well as iodide, it might not be possible in the method to replace potassium iodide by sodium iodide?

The Determination of Diethylaniline in Ethylaniline

BY J. HASLAM, M.SC., F.I.C., AND A. H. S. GUTHRIE

RECENTLY, we have had occasion to examine several samples of ethylaniline, with particular reference to their diethylaniline contents. Usually, the routine tests for ethylaniline involve the following determinations:—appearance; distilling range and boiling-point; water; aniline; aniline plus ethylaniline.

Water is determined by distillation with xylene. The aniline content is determined by diazotising, and then pouring the product into an excess of R-salt soln. and titrating the excess of R-salt with diazobenzene soln. In the determination of aniline plus ethylaniline, the sample is sulphonated, and a nitrite titration is carried out on the sulphonation products. After allowance has been made for the nitrite used up by the sulphonation product of the aniline, the proportion of ethylaniline is deduced by difference.

To extend the method to include the determination of diethylaniline would involve a second difference figure, anything unaccounted for in the aniline plus ethylaniline determination being assumed to be diethylaniline. There are difficulties about the application of a direct test for diethylaniline in ethylaniline because the reaction usually employed to

determine diethylaniline, *viz.*, interaction with nitrous acid to produce the yellow nitroso body, is inapplicable owing to the production and interference of the insoluble oily nitroso derivative of ethylaniline. Information on the subject in the literature is rather scanty, although Vaubel[1] put forward a method of determining aniline, ethylaniline and diethylaniline in mixtures of the three. The aniline was determined by diazotisation and titration with R-salt, and aniline and ethylaniline were then determined by measuring the temperature rise when a xylene soln. of the mixture was added to acetic anhydride. The diethylaniline was determined by difference. It is obvious that this difference method would give inaccurate results in the determination of small amounts of diethylaniline.

It seemed possible, however, that a test for diethylaniline in ethylaniline might be devised if the monoethyl compound could be converted into a derivative, and the diethylaniline subsequently separated therefrom. Such a method has been worked out. It is based on the treatment of the sample with acetic anhydride and production of the acetyl derivative of ethylaniline. The mixture is then diluted with water, the acetyl derivative remaining in solution. The soln. is rendered just alkaline and the diethylaniline is distilled off and collected in standard acid. The diethylaniline in the distillate is then determined by application of the nitrous acid reaction under standard conditions.

METHOD.—Mix 1 g of the sample and 5 ml of acetic anhydride in a dry bottle and leave overnight. Transfer the mixture to a round-bottomed 500-ml flask, dilute with water, make just alkaline to solid phenolphthalein with *N* sodium hydroxide and then add 2 drops of alkali soln. in excess. Dilute to 250 ml and distil from a flask connected *via* a splash head to a vertical condenser, the lower end of which dips beneath the surface of 10 ml of *N* hydrochloric acid in a Nessler cylinder. Collect *ca.* 75 ml of distillate in the hydrochloric acid. Pour the contents of the receiver down the vertical condenser into a 100-ml graduated flask, and rinse the receiver and condenser with 15 ml of water. Next add 2 ml of *N* sodium nitrite to the 100 ml of liquid in the graduated flask and place the flask for 2 hrs. in a thermostat at 20° C. Then measure the colour in a Spekker absorptiometer, using the 1-cm. cell and the dark blue filters, and read the weight of diethylaniline from a previously prepared graph which relates the weight with the indicator drum reading.

This graph is quite smooth and passes through the following points:

Diethylaniline, g	0	0·002	0·004	0·006	0·008	0·010
Spekker indicator drum reading	0	0·110	0·222	0·316	0·412	0·491

When the approx. amount of diethylaniline in a sample is unknown, it is advisable to make a preliminary rapid test in order that a suitable depth of colour may eventually be measured in the absorptiometer. This rapid test is as follows:—Mix 0·5 ml of the sample and 1·5 ml of acetic anhydride and, after 15 min., add 10 ml of *N* hydrochloric acid and dilute to 100 ml with water. Then add 2 ml of *N* sodium nitrite and, after 30 min., compare the resultant yellow colour with standards containing 1·5 ml of acetic anhydride, 10 ml of *N* hydrochloric acid and different amounts of diethylaniline in 100 ml of soln. Suitable standards contain 0·001, 0·002 . . . 0·010 g of diethylaniline.

If the results of the preliminary test indicate that the sample contains less than 1% of diethylaniline, follow the procedure outlined above. For amounts of *ca.* 1%, collect the distillate in 10 ml of 2 *N* hydrochloric acid, dilute finally to 200 ml and take 100 ml for the colorimetric test; for amounts of *ca.* 2% preferably, collect the distillate in 10 ml of 4 *N* hydrochloric acid, dilute finally to 200 ml, and take 50 ml for the test.

Mixtures of known composition were prepared from a specially purified sample of ethylaniline (shown by the test to contain 0·075% of diethylaniline) and diethylaniline, and examined by the method described. The results were:

Diethylaniline present, %	0·32	0·52	1·01	2·14
Diethylaniline found, %	0·33	0·54	1·01	2·09

Aniline has no material effect on the test. A mixture prepared to contain 1·99% of diethylaniline, 47·91% of ethylaniline and 50·1% of aniline, gave (i) 1·93 and (ii) 1·89% of diethylaniline.

An attempt was made to apply the principle of the method directly, *i.e.*, without distillation. One g of the prepared mixture of diethylaniline and ethylaniline was treated with 5 ml of acetic anhydride, left for 5 hrs., and then treated with 10 ml of *N* hydrochloric acid and diluted to 100 ml with water. Two ml of *N* sodium nitrite were added and, after 2 hrs. at 20° C. the colour developed was measured in a Spekker absorptiometer and the

weight of diethylaniline was read from a previously prepared calibration curve. This curve passes through the following points:

Diethylaniline, g	0	0·002	0·004	0·006	0·008	0·010
Spekker indicator drum reading	0	0·130	0·257	0·363	0·457	0·542

When more than 1% of diethylaniline was present, the acetylated products were appropriately diluted before the final colorimetric tests were applied. The following results were obtained.

Diethylaniline present, %	0·32	0·52	1·01	2·14
Diethylaniline found, %	0·41	0·67	1·16	2·27

Thus, if steam distillation is omitted, the results tend to be high.

REFERENCE

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RESEARCH DEPT., I.C.I. (ALKALI) LTD.
NORTHWICH

April, 1943

Notes

THE MICRO-DETERMINATION OF CALCIUM AND MAGNESIUM IN MILK

THE micro-determination of calcium and magnesium may be simplified and improved in accuracy by employing, suitably modified, the macro-procedure of Washburn and Shear,[1] *viz.*, hot pptn. of calcium at *p*H 3·0 by the min. excess of oxalate, and pptn. of magnesium in the filtrate with the min. excess of phosphate. Only one washing is required for each ppt., with saving of time and reduction in manipulative errors. Determinations are conveniently made on the trichloroacetic serum of Miethke and Levecke,[2] prepared as follows: To 5 ml of milk in a 25-ml graduated flask add 10 ml of water and, with gentle shaking, 2·5 ml of 20% trichloroacetic acid. Heat to boiling, cool, make up to the mark, shake and filter, rejecting the first few ml. For average milk the volume of pptd. fat and protein is *ca.* 1%.

CALCIUM.—Introduce into a pointed 15-ml centrifuge tube 5 ml of serum (≡ 1·01 ml of milk approx.) 1 drop of thymol blue indicator, and 1 ml of *M*/20 potassium oxalate (suitable for 0·8–1·5 mg of Ca). Mix the contents and place the tube on a boiling water-bath. After some minutes add *N* sodium acetate, drop by drop, until the indicator assumes a clear yellow colour (*p*H 3·0). Leave for 1 hr. at 90°–100° C., cool the tube and note the vol. (v) of its contents. Centrifuge and siphon off the supernatant liquid slowly, as completely as possible (0·05 ml of residue or less) into a second tube for the magnesium determination, and rinse the siphon with a few drops of water. Weigh the calcium tube to the nearest cg to determine the weight of residual liquid (w), wash centrifugally *once* with 5 ml of sat. calcium oxalate soln.,[3] siphon down to a residue of 0·05 ml or less and determine the calcium oxalate as usual by means of permanganate.

MAGNESIUM.—Add to the contents of the centrifuge tube containing the first siphonate from the calcium pptn. 1 ml of 2 *N* ammonium chloride and 5 drops of *M*/5 disodium hydrogen phosphate (suitable for 0·08–0·15 mg of magnesium), and mix by rotation. Then run in 1 ml of 10% ammonia and immediately scratch the tube walls for 1 min. with a fine glass rod to promote formation of $Mg(NH_4)_4P_2O_8$ (Lampitt *et al.*).[4] Allow the ppt. to stand overnight and then detach it from the walls of the tube by means of a fine rubber-tipped rod, centrifuge the tube, siphon the liquid down to a residue of 0·05 ml or less, wash *once* with 5 ml of 2% ammonia, re-centrifuge and again re-siphon. Determine the phosphorus colorimetrically by means of molybdate (Mg = 0·784 P [1 + w/v]).

ACCURACY.—Analysis of artificial trichloroacetic filtrates containing amounts of calcium, magnesium and phosphorus typical for milk yielded values within 1% of the theoretical for calcium and within 2% for magnesium. The procedure is obviously applicable, with appropriate modification, to many other milk products.

DEPARTMENT OF DAIRY CHEMISTRY
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G. T. PYNE

August, 1943

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A SIMPLE INEXPENSIVE SEPARATOR

DURING the last 2 years we have had occasion to carry out many separations of immiscible liquids, sometimes on more than 20 samples at a time. Ordinary separating funnels with taps being scarce, we have experimented with conical separators of 100–200 ml capacity in which the tap is replaced by a closed end drawn out to a point, the liquid being removed by a teat pipette with a fine tip. These have given excellent results, especially in vitamin B_1 estimations by the thiochrome method. The upper *iso*butanol layer can be drawn off quite readily, and all danger of foreign fluorescence from tap lubricant and annoyance of the tap sticking through action of alkali is avoided. The separators can be stood in tins of diameter slightly less than their maximum diameter, thus saving the use of clamps and retort stands, which are also in short supply at present. A battery of 24 of these separators has cost less than the price of 6 ordinary

separating funnels with stands, and occupies much less space. They are more easy to shake either by hand or in a shaking machine, and avoid the risk of loss of liquid through inadvertent opening of the tap of ordinary separating funnels.

FRANK WOKES
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April, 1943

METALLIC CONTAMINATION IN GUMS AND SIMILAR SUBSTANCES

SUBSEQUENT to a review of literature dealing with the presence of metals in foods (*Food*, June and July, 1943), certain raw materials used in the foodstuff industry have been analysed. In view of the increasing use of gums and similar substances, the following results are of interest. The Hamence (ANALYST, 1937, **62**, 18) procedure was followed for the determination of the metallic content, and the samples tested were commercially designated as No. 1 quality suitable for foodstuffs. The analytical work was carried out by Mr. H. W. Rawlings.

	Parts per million		
	Lead	Copper	Zinc
Agar-agar	2·9	nil	9·7
Arabic	1·8	4·0	3·0
Carob	2·0	8·0	1·0
Commercial vegetable gelatin	6·7	20	203
Ghatti	2·8	1·3	4·2
Irish moss	57	36	65
Karaya	1·4	17	2·0
Commercial sodium alginate	7·8	10	2·5
Tragacanth	4·9	23	55

CROFT HOUSE LABORATORY
DOLLIS AVENUE, FINCHLEY, N.3
R. HAROLD MORGAN

September, 1943

Analytical Methods Committee

DETERMINATION OF CRUDE FIBRE IN NATIONAL FLOUR

THE Committee regret that the following note was omitted from their Report.

In acknowledging the co-operation of the Research Association of British Flour Millers in this work it should be mentioned that the method used in the laboratories of that Association gives the same results as those obtained by the method specified in the Committee's Report (*cf.* ANALYST, 1943, **68**, 276). The Association's procedure and technique, however, are devised particularly for multiple analysis and are not so suitable for the individual analyst.

Ministry of Food

STATUTORY RULES AND ORDERS*

1943—No. 1237. The Feeding Stuffs (Regulation of Manufacture) Order, 1943, dated August 25, 1943. Price 4d.

This Order, which came into force on Sept. 1, 1943, consolidates the Feeding Stuffs (Regulation of Manufacture) Order, 1942, and its amending Orders, and revises the formulae of National compounds.

The main changes are the re-introduction of National Pig Food No. 1 (for sows and weaners), the withdrawal of National Poultry Food No. 3 (battery mash and pellets), and a reduction in the protein content of pig and poultry compounds to conform to the winter rationing scale.

— **No. 1318. Order, dated September 11, 1943, prescribing Appointed Days under the Manufactured and Pre-packed Foods (Control) Order, 1942, and granting a General Licence thereunder.** Price 1d.

The purpose of this Order is to prescribe appointed days after which the manufacture and pre-packing of baking powder and bakers' cream powder and of Christmas puddings are prohibited except under licence. *Bakers licensed to manufacture cake or to produce bread, who manufactured Christmas puddings during the year ended Sept.* 3, 1939, *may manufacture or pre-pack them without obtaining a licence under the present Order, provided that they comply with the conditions as to ingredients and price contained in the Schedule.*

THE SCHEDULE.—(1) Every Christmas pudding—(*a*) shall weigh either 1 lb. or 2 lb. net. (*b*) shall contain not less than 10% of oils and fats and not less than 36% of sugar. *These percentages shall be determined as follows :—*

(i) the % shall be determined by reference to the weight of the pudding;
(ii) the % shall be ascertained by analysis of a sample representing a fair average of the whole article;
(iii) all oils and fats and sugar contained in or added to the pudding shall be taken into account in whatsoever form they may have been introduced;
(iv) the % of sugar in the sample shall be determined by adding the % of sucrose to the % of total reducing sugars expressed as dextrose;
(v) the % of oils and fats shall be determined by ascertaining the % of the sample which is extractable with ether or other appropriate solvent after the sample has been suitably digested with diluted hydrochloric acid.

(2) *Prescribes max. prices for Christmas puddings.*

This Order also gives directions in connection with proceedings for alleged infringement of the Principal Order in respect of the weight of Christmas puddings.

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

1943—No. 1396. The Condensed Milk (Control and Maximum Prices) Order, 1943. Dated September 25, 1943. Price 2d.

This Order revokes and replaces S.R. & O., 1940, Nos. 1622, 1895 and 1788, and S.R. & O., 1942, No. 2186. It also revokes the Condensed Milk and Milk Powder (Control) Order, 1940, as amended (S.R. & O., 1940, Nos. 957 and 1621), the need for which no longer exists. *In addition to prescribed new max. prices, the Order provides that records shall be kept by traders. It also includes whey and buttermilk in the definition of condensed milk.*

"Condensed milk" means milk, skimmed or partly skimmed milk, buttermilk or whey which has been concentrated by the removal of part of its water whether with or without the addition of sugar and includes any such milk concentrate produced in the course of the manufacture of any article of food but does not include the article commonly known as dried milk or milk powder.

"Special full cream sweetened" in relation to condensed milk means full cream sweetened condensed milk which contains not less than 10% of butter fat and which is sold in a container bearing a label clearly specifying that the condensed milk in such container contains not less than 10% of butter fat.

Ministry of Health

FOOD AND DRUGS ACT, 1938

Circular 2856—Procuring Samples of Rationed and Points or Personal Points Rationed Foods.

Food and Drugs Authorities are asked to make arrangements that in every case in which samples of rationed and points or personal points rationed foods are procured by Sampling Officers for the purposes of the Act without surrender of coupons, receipts on the printed forms (supplied by the Ministry) shall be given by them. The use of these receipts does not apply to the sampling of other articles such as milk, nor affect the existing arrangements in relation to travellers' ration books or emergency cards.

September, 1943

Ministry of Supply

STATUTORY RULES AND ORDERS

1943—No. 976. The Control of Toluene (No. 3) Order, 1943, dated July 14, 1943. Price 1d.

This Order amends the Control of Toluene (No. 2) Order, 1940, mainly by substituting a new Schedule of maximum prices and by varying the descriptions of the toluene fractions in Table I of Basis Prices. The old Table III, which provided for ascertainment of "excess paraffin content" is omitted as unnecessary because of alterations in the descriptions in Table I. A test is described for determining the toluene content of any once-run toluole.

Ministry of Labour and National Service

ANNUAL REPORT OF THE CHIEF INSPECTOR OF FACTORIES FOR 1942*

THE Chief Inspector of Factories (Mr. A. W. Garrett) discusses the conditions of health and welfare and the prevention of accidents in factories, and the chief Medical Inspector, Dr. A. C. Merewether, who has succeeded Dr. J. C. Bridge, deals in fuller detail with the problems from the medical point of view. Among the questions discussed are the following.

LUMINISING (HEALTH AND SAFETY PROVISIONS) ORDER.—This Order (S.R. & O., 1942, No. 273; 1943, No. 1053) prescribes safety precautions for workers handling radioactive substances for industrial purposes. Investigation, in conjunction with the National Physical Laboratory, is in progress to ascertain if these precautions are sufficient. Work is restricted to those over 16, and initial and periodical inspections must be made. A further safeguard consists in the examination of the exhaled air of workers. So far, there is evidence of an initial stimulating effect on the blood-forming tissues and constant observation is made to see if any subsequent depressant action ensues.

A similar investigation to afford protection to those engaged in the use of X-rays in industry is in progress.

SILICOSIS.—Methods of countering the growing risk of silicosis in steel foundries are being studied by a technical committee. The report of a similar committee dealt with the dangers of silicosis in the making of dust tiles and electrical porcelain.

PNEUMOCONIOSIS AS AN INDUSTRIAL DISEASE.—The results of X-ray and clinical examination of S. Wales miners and coal-trimmers disclosed the prevalence of the condition known as dust reticulation in the lungs, and the first Report† led to the inclusion, in the Workmen's Compensation Act, 1943, of a new industrial disease, pneumoconiosis, defined as "fibrosis of the lungs due to silica dust, asbestos dust or other dust and includes the condition of the lungs known as dust reticulation." Further physical and medical studies are in progress.‡

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* Cmd. 6471. Pp. 47. H.M. Stationery Office, 1943. Price 9d. net.

† Medical Research Council. Special Report Series, 243, 1942.

‡ In the second Report, issued in 1943, it is shown that, for some unknown reason, the dust of anthracite mines is more dangerous than that of bituminous coal mines. There is no definite evidence that quartz particles contribute to the action of the dust, although this possibility cannot be entirely excluded.—EDITOR.

EXPLOSION RISKS WITH MAGNESIUM.—There are dangers of explosion in the grinding and polishing of magnesium and its alloys, as well as in the grinding of the metal to powder for pyrotechnics. There is also a risk of fire from ignition of the debris from the machines. Precautions are embodied in the Magnesium (Grinding of Castings and other Articles) Order, 1943 (S.R. & O., 1943, No. 268).

TOXIC ANAEMIA.—This condition was added in March, 1942, to the list of diseases and poisonings notifiable under Sec. 66 of the Factories Act. The term "toxic anaemia" is intended to apply to the form of anaemia occurring in a person whose work brings him into contact with X-rays, radioactive substances or any chemical compound capable of causing this effect. The list of these chemical substances is very incomplete, but it is known that T.N.T. may cause progressive anaemia, with or without the usual toxic jaundice. Of the 14 cases notified, 7 were attributed to T.N.T. and 7 to mixtures of solvents, containing low proportions of benzene, used in rubber solns.

DERMATITIS.—During the year measures for the prevention of dermatitis were defined, particularly in the application of "barrier preparations." Recommendations were also made in connection with precautions to prevent the action of synthetic glues on the skin. In explosives factories a very substantial reduction in the cases due to T.N.T., tetryl, fulminate of mercury and white spirit has been achieved by the mechanisation of many processes and the elimination of specially susceptible workers.

LEAD POISONING.—There was a slight rise in the number of cases as compared with 1941, but the total was still well below the pre-war level. Cordite fumes with lead-nickel dust produced by bullets impinging on deflection plates affected 16 of 45 workers.

METHYL BROMIDE POISONING.—The precautions required to prevent any risk of poisoning during the filling of fire extinguishers with methyl bromide were discussed with the firms concerned.

PHOSGENE POISONING.—One case was attributable to the use of a fire extinguisher containing carbon tetrachloride.

Notes from the Reports of Public Analysts

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

CITY AND COUNTY OF KINGSTON UPON HULL: REPORT FOR 2ND QUARTER, 1943

OF the 636 samples submitted by inspectors under the Act, 229 were bought formally.

TABLE VINEGAR.—The sample, an artificial vinegar, was labelled "Non-brewed Pure Table Vinegar. Described as a pure table vinegar to distinguish it from malt vinegar." In my opinion the term "Table Vinegar" should be applied only to a brewed vinegar and therefore the description on the label contains a contradiction in terms. Caution issued. The manufacturers communicated with the Ministry of Food, who informed them that the use of the term "non-brewed vinegar" to describe a product made from acetic acid is at present under discussion, and that pending a decision the label could be used.

DRESSED CRAB.—Two informal samples contained undeclared farinaceous matter (caution issued in one instance) and a later formal sample contained 18·2% thereof, calculated as wheat flour. According to the Shell Fish (Maximum Prices) Order, 1943, "Dressed Crab" means crab from which all the inedible portions have been removed (except the main shell where the same is used to hold the meat). In June, 1941, a circular letter was sent by the Town Clerk to all local fishmongers stating that an article sold as "Dressed Crab" should consist of crab meat without any foreign addition whatsoever. The vendor was prosecuted and fined £6 11s. 6d. including costs.

D. J. T. BAGNALL

Midland Agricultural College: Chemistry Department

SILAGE COMPOSITION

BY A. C. BURNS, M.Sc., F.I.C., AND JANET SMITH, B.Sc., A.I.C.

IN the earlier reports on this subject (*cf.* ANALYST, 1942, **67**, 328; 1943, **68**, 185), the compositions of different ensiled crops, in relation to the sampling of 390 silos, were contrasted in terms of "dry matter" analyses. This naturally favoured more ready comparisons of those farm crops which are not only very succulent, but also vary considerably in moisture content from the average value of 75%.

In view of the large number of samples to be examined during the Ministry of Agriculture's silage campaign, it had been expedient to overlook the fact that the normal laboratory drying of silage samples, prior to analysis, involved some loss of volatile matter other than water. In effect, a recorded dry matter content of 25% involved an under valuation by an amount "*x*," which probably varied from 2 to 5. Since this "*x*" component refers to both basic and acidic substances, nitrogenous and non-nitrogenous in character and present in very variable ratios, it follows that the contrasting of protein values in terms of the so-called dry-matter composition is subject to appreciable error.

Several investigators seem to have overlooked, or have not attempted to apply, any correction factor in relation to the "dry matter" of silage. This cannot be said of the more critical work of Watson and Ferguson (*J. Agric. Sci.*, 1937, **27**, 5). They found that *fresh* silage contained 0·5 to 2·0% of volatile acids (expressed as acetic), of which 50 to 90% (aver. 75%) was lost during the usual 4-hours' drying period at 98° C. The volatile bases, present to the extent of nil to 2%, were likewise subject to loss, in part or even wholly.

These losses are commonly considered to be insignificant in relation to those other perturbing sources of error associated with the "routine" sampling of the farm silo, as opposed to the multiple-sampling of the experimental silo. The losses can be by no means insignificant, however, and become more obvious when considered in relation to the "dry matter" component of silage.

An additional "campaign" requirement in the 1942 season, as opposed to the usual analysis of the laboratory-dried material, was a direct determination of crude protein *in the natural fresh sample*. This was mainly with a view to gauging the degree of error in the more usual "dry" analysis, and the requirement called for two sets of figures for each sample, these to be calculated back to terms of protein in dry matter.

This method of comparison almost invariably revealed the direct analysis of the fresh material to give distinctly higher protein values than were obtained in the routine analysis of oven-dried silage (see columns A and B), and our own figures were typical of the conditions noted in recent unpublished reports of other investigators. The tendency in such reports was to calculate these protein losses by a direct comparison of these two sets of "dry matter" figures, giving results indicated in column C. We considered that such direct comparison would exaggerate these losses, since the calculation involved an unknown factor, *i.e.*, the "*x*" component of the assumed "dry matter %."

It was decided, therefore, to determine the *true* nitrogen losses by recovering the actual volatile matter during the drying process. The nitrogen contents of the residual so-called dry matter and of the original fresh silage were also determined. The true nitrogen losses, as a result of oven-drying, were thereby determined in relation to the actual fresh silage sample (see column D).

The nitrogen losses, as incorrectly calculated in accordance with the campaign requirements, ranged from 0·6 to 36·6% and appeared to increase with rising *p*H of the silage, whereas the true losses showed no correlation. Furthermore, the true losses were appreciably, and sometimes considerably, lower than those obtained by the incorrect method of contrasting the two sets of "protein in dry matter" figures; *e.g.*, the true nitrogen losses, as a whole, were *ca.* 23½% lower than those calculated by other investigators. Obviously, the discrepancy was due to the fact that the dried product had lost not only nitrogenous matter (per amino-acids, etc.) but also other components, such as acetic and butyric acids, the latter often to the greater extent.

The majority of the samples examined under this heading referred to grass silage. The *p*H was re-determined on the oven-dried sample after re-wetting approximately to the original fresh condition. There was no correlation between the "volatile acid" loss figures and the change of *p*H resulting from the drying process.

METHOD.—A water-jacketed oven was used, provided with pressure-clamped door, inlet and outlet, tubes, etc. The temp. varied from 96 to 98° C., and the min. drying period was 4 hrs. The incoming air was pre-heated by passage through coils immersed in the water-jacket, after being freed from carbon dioxide and water vapour. The air-current was ultimately drawn through two (originally three) flasks containing distilled water. This was subsequently titrated for acidity, tentatively expressed in terms of acetic acid, which, in relation to the fresh silage, ranged from 0·16 to 0·76%. It is intended, when the silage-sampling season recommences, to apply at this stage an additional titration, with a view to gauging also the amino-acid component and possibly to finding some correlation with the change of *p*H previously mentioned. The neutralised volatile component from the flasks was examined quantitatively for total nitrogen by the Kjeldahl method.

It is realised that the number of samples examined for nitrogen loss is somewhat limited and that further investigation is desirable. The limitation was imposed by the other important analytical requirements of the silage campaign and by the fact that this particular investigation was postponed to almost the conclusion of the sampling season.

Crude protein in so-called dry-matter, based on analysis of		Loss of nitrogen, based on (A) (B) recovery of volatile matter		*p*H		So-called dry matter	No. of N detmns.
Fresh sample	Dried sample	Incorrect	True loss	Fresh	After drying		
%	%	%	%	%	%	%	
(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
14·21	9·01	36·6	Undetmd.	6·39	5·52	15·75	(1)
16·88	11·37	32·7	29·0	5·38	5·65	19·70	(2)
16·75	12·11	27·7	22·2	5·12	6·19	23·25	(2)
15·41	11·35	26·3	14·6	5·01	6·29	19·04	(5)
14·95	11·00	26·4	10·8	5·02	6·00	20·98	(2)
15·85	12·10	23·7	18·5	5·06	5·93	15·50	(1)
13·90	11·08	20·3	17·7	5·07	6·03	24·01	(3)
19·04	15·63	17·9	Undetmd.	5·90	4·91	23·00	(1)
15·62	13·12	16·0	17·5	5·33	6·00	24·10	(1)
18·18	15·45	15·0	17·5	4·99	5·46	22·45	(2)
22·41	19·12	14·7	4·8	5·24	6·00	22·32	(2)
14·54	12·49	14·1	Undetmd.	4·73	5·07	22·00	(1)
19·31	17·02	11·9	0·4	4·77	4·85	23·92	(2)
15·57	13·76	11·6	12·2	4·90	6·51	18·98	(2)
16·09	14·54	9·6(?)	18·5(?)	5·97	6·75	15·23	(1)
14·52	13·25	8·7	Undetmd.	5·32	5·35	23·75	(1)
13·29	12·47	6·2	Undetmd.	4·81	4·90	23·30	(1)
16·94	16·13	4·8	0·8	4·26	4·45	23·88	(2)
19·42	18·70	3·7	Undetmd.	4·40	4·49	24·40	(1)
8·80	8·68	1·4	Undetmd.	4·02	4·31	23·23	(2)
18·87	18·98	0·6 (gain)	5·2 (loss)	4·65	4·69	32·40	(1)
15·48	15·58	0·6 (gain)	0·7 (loss)	4·00	4·05	34·78	(1)

CONCLUSION.—Despite the advantages afforded by dry-matter compositions in the computing of rations for livestock, we suggest that the reporting of protein contents in terms of dry matter unduly emphasises the protein-yielding or cake-replacing power of such wet material as silage. A good grass silage, for example, yielding 16% of protein, but containing only 25% of dry matter, yields only 4% of

protein in the material as fed—a condition which is obvious to the chemist but not always to the farmer. The errors associated with the determination of dry matter and the fact that the crude protein can be accurately (if not so conveniently) determined in the original fresh material, would seem to favour the above suggestion.

SUTTON BONINGTON, LOUGHBOROUGH *August*, 1943

Department of Scientific and Industrial Research

TYROGLYPHID MITES IN STORED PRODUCTS*

THE aim of this Report, issued under the auspices of the Pest Infestation Research Committee, is to summarise accumulated information on every aspect of infestation of food, etc., by Tyroglyphid mites ("cheese mites," "flour mites," etc.). Several of the commonest species are cosmopolitan, *e.g.*, *T. farinae* L. Other common species associated with stored food are *T. dimidiatus* and the scavenging mite, *Glycyphagus cadaverum* Sch. Full references are given to the best keys for identification of species. The basic life-cycle (2–3 weeks under favourable conditions) comprises an egg and a larval stage followed by 3 (or 2) nymphal stages leading to the adult form. The second or deuteronymph stage, when present, is termed a hypopus. The optimum temp. range for the development of a number of species is *ca.* 18°–25° C. A high degree of humidity promotes rapid development; low humidity retards it or kills the mites. Thus, *G. domesticus* soon die below 60% R.H., although their encysted hypopi have survived a week at 10% r.h. The eggs of *T. farinae* can survive prolonged immersion in water.

RESISTANCE TO HEAT AND COLD.—For killing Tyroglyphids (all stages), the following exposures *inter alia* have been recorded. Mites in flour, 60 min. at 65·6° C. (Newstead), 45–60 min. at 60° C. (Sokolov), 12 hrs. at 48·9°–51·7 (Newstead); *T. farinae* isolated, 30 min. at 42° C. (Brudnaya); cheese mites (dry heat), 5–20 min. at 41·1° C.; *G. domesticus* (moist or dry heat), 24 hrs. at 40° C.

Hypopi, especially when encysted, are more resistant than other stages to cold, *e.g.*, 7° C. for 72 hrs. or 3 times as long as the adult form. Daily fluctuations between medium and high temp. had no effect on the rate of hatching of the eggs, but fluctuations between medium and low temp. reduced hatching. No eggs survived daily fluctuations between 30° and 0° C.

PREVENTIVE AND CONTROL MEASURES.—Having regard to the susceptibility of mites to desiccation, stored products should be kept in as dry a state as possible. Ventilation is of great importance when moisture is likely to accumulate. Heating is also effective, wherever possible. Only one example of the use of dehydrating dusts has been published (Aleksandrovskaya-Ivanova, 1939), but such dusts may prove effective against Tyroglyphids in grain. The possibilities of biological control appear to be limited.

Fumigation.—In addition to resisting heating, freezing and desiccation, eggs and hypopi may be resistant to fumigants. For example, Smirnov and Polezhaev (1936, 1940) found the immobile hypopi of *Glycyphagus destructor* Schr. to survive 12 days' exposure to a 5·8% concn. of hydrogen cyanide. Polezhaev therefore recommends that fumigation should be carried out under physical conditions favouring the transformation of hypopi into the third stage of development. Chernuishev (1940) found that the active stages of *T. farinae* died in 15–120 min. when chloropicrin was applied at the rate of 4–5 oz. per 1000 cb. ft., whilst recently deposited eggs survived a concn. of 8–10 oz. for 9–10 days. A second fumigation after a fortnight will overcome this difficulty. Nicotine and pyrethrum have been found ineffective against Tyroglyphids (Thomas).

BIBLIOGRAPHY.—The Report concludes with 10 pages, containing 230 references arranged in the alphabetic order of the authors' names. These bear on the following points discussed in the text:—Systematics, Morphology and Internal Anatomy, Biology, Bio-ecology, Physical Ecology, Tyroglyphids in Stored Products, and their Control.

New York: Report of the Chief Medical Examiner for 1941

BLOOD-ALCOHOL CONCENTRATION IN HIGHWAY ACCIDENTS

IN 1915 the Medical Examiner's Office was statutorily established, but it was not until 1918 that it superseded the coroner's system in New York City. Since then scientific laboratories have been established to assist by the application of physical and chemical methods the Medical Examiner in determining the cause of death in the cases reported to him by the New York City Department of Health. In the current report (for the year 1941)† the Chief Medical Examiner (Dr. T. Gonzales) deals statistically with the cases submitted to him, including *inter alia* the blood-alcohol concn. in the victims of highway accidents. In the 960 cases submitted, alcohol tests were made in 472; of the 175 positive results, 165 showed a blood-alcohol content of 0·2% or more. These accidents involved 708 pedestrians, and tests were applied in 309 cases, with the result that 95 showed the presence of alcohol, which exceeded 0·2% in 84. Blood-alcohol tests were also made on the blood of 52 of the 91 passengers who lost their lives in accidents to motor vehicles; positive results were obtained in 25 cases, and in 24 of them the alcohol concn. was 0·2% or higher. Tests on the blood of 21 of 33 drivers of non-passenger vehicles showed that alcohol was present in 5, and in 4 of them its concn. exceeded 0·3%. Drivers of passenger vehicles were involved in 49 accidents, and in 34 cases tests were made. Positive results were obtained in 20, and in every instance the concn. was 0·2% or higher. In 79 cases involving elevated, subway or railway trains 56 tests were made; there were 34 positive results, of which 33 showed a concn. of 0·2% or higher. Expts. by A. O. Gettler and T. Gonzales to ascertain whether the deceased had been drinking prior to death showed that 26·6% of 2472 pedestrians who lost their lives were under the influence of alcohol when injured. These figures support the commonly accepted view that alcoholic intoxication is one of the primary causes of motor accidents.

* By M. E. Solomon, M.Sc. (*Pest Infestation Laboratory*). Pp. 36. H.M. Stationery Office. 1943. Price 9d. net.

† By courtesy of the Superintendent, Bureau of Criminal Investigation, New York State Police. —EDITOR.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

[Determination of] Endosperm Content of Wheat. P. Halton and E. Barton-Wright. (*J. Soc. Chem. Ind.*, 1943, **62**, 123–124.)—Chemical and biological methods of determining the endosperm content of wheat were examined. The chemical method described, in which *N* lactic acid is used for softening and dispersion of the endosperm, is not absolutely reliable, as, with increased soaking, the germ and, possibly, extractable matter from the bran are gradually removed as well as the endosperm. *Biological method.*—This is based on complete destruction of the endosperm by *Calandra granaria*, the common grain weevil. After determination of moisture content, halve the grains of wheat transversely with a razor, weigh accurately *ca.* 2 g, place them in a specimen tube (12 × 2·5 cm) or a 4-oz. glass jar, and, according to the vessel used, cover them with 200 or 350 to 400 adult weevils. Place the tubes, covered with muslin, in a desiccator provided with air vent and containing saturated sodium chloride soln., which gives *ca.* 79% relative humidity. Keep at 30° C. until all, or nearly all, the weevils are dead. After removal of the weevils, dress the husks over a No. 5 silk to remove frass, dry at 120° C. for 4 hr. and weigh. The husks also contain the aleurone layer and the germ. The time is reduced from 3 weeks to 14–16 days by increasing the number of weevils from 200 to 350–400.

Normal wheat contains *ca.* 86% of endosperm. Hence, with the germ (including any appreciable removal of aleurone layer from the bran), *ca.* 88% of the wheat is available for production of bran-free National flour (85% extraction). E. B. D.

Determination of Sugar in Starch Hydrolysates by Yeast Fermentation and Chemical Means. A. S. Schultz, R. A. Fisher, L. Atkin, and C. N. Frey. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 496–498.)—*Biological method* (after Schultz and Kirby, *Cereal Chem.*, 1933, **10**, 149.)—Fleischmann enriched baker's yeast is used to ferment the common sugars (*e.g.*, dextrose, sucrose and maltose), and a special yeast (Fleischmann Hi-B_1 No. 2019) is used to ferment all these except maltose, which can then be determined by difference. The portion of the dextrin or starch subject to attack by β-amylase is determined by adding this enzyme (as soya, barley or wheat flour) to the fermentation mixture. To each of the 120-ml wide-mouthed fermentation bottles (*cf.* Schultz, Atkin and Frey, ANALYST, 1942, **67**, 170) add 0·5 ml each of a 15% soln. of magnesium sulphate ($7H_2O$) and a 10% soln. of potassium chloride, and 2·5 ml of a phosphate buffer (*p*H 6·0–6·5) containing 180 g of ammonium dihydrogen phosphate, 72 g of diammonium hydrogen phosphate and 0·2 g of nicotinic acid per litre. Use 2 of the bottles to obtain a standardisation curve by adding to them 0·5 and 1·0 g of pure dextrose, respectively, and place an amount of the sample equiv. to 0·5–1·0 g of fermentable sugars in another of the bottles; if the sample has a low sugar content, add 0·5 g of dextrose. Adjust the contents of each of the bottles to 40 ml with water, pipette 10 ml of a 10% suspension of yeast into each, and connect at once to 260-ml gas-burettes; ferment at 30° C., shaking at 110 cycles per min., and when no more carbon dioxide is evolved in a 15-min. period measure the gas vols. Use the difference between the vols. of carbon dioxide produced by the two standards to calculate the sugar content of the sample; dextrose is used as standard because under the above conditions equal amounts of it and maltose hydrate produce the same vols. of carbon dioxide. *Chemical Method* (adapted from Sichert and Bleyer's modification of Steinhoff's method, *Z. anal. Chem.*, 1936, **107**, 328). Dextrose is determined by copper acetate reduction and dextrose plus maltose by means of Fehling's soln., the cuprous oxide being in both cases added to ferric solution and titrated with permanganate. Thence the maltose can be found by means of Sichert and Bleyer's tables. These 2 methods were compared for 7 commercial starch hydrolysates and for the products obtained by adding 0–13 ml of 1% hydrochloric acid to a suspension of 5 g of maize starch in 50 ml of water, and autoclaving for 2 hr. at 20 lb. pressure. Both gave satisfactory results for dextrose, but for maltose only the biological method was reliable. The chemical method is unreliable for the determination of maltose owing to reducing dextrins in both acid and enzmatically hydrolysed starch products, but β-amylase can be used to give an indication of the amounts of such dextrins present. The work of Rolfe and Defren (*J. Amer. Chem. Soc.*, 1896, **18**, 869) on which were based curves designed to describe the composition of a starch mixture in terms of dextrose and "maltose" at any stage during acid conversion, is shown to be erroneous owing to the lack of specificity of Fehling's soln. for the determination of maltose in presence of reducing dextrins. The use of the term "maltose" to describe both maltose and reducing dextrins which reduce Fehling's soln., and also mixtures of the two, is misleading now that methods specific for maltose are available. J. G.

Mechanical Determination of the Juiciness of Meat. B. Tannor, N. G. Clark and O. G. Hankins. (*J. Agric. Res.*, 1943, **66**, 403–412.)—To determine the juiciness of meat, weighed samples, 25 to 35 g. were pressed in a special hydraulic press at 50° C. The pressure was very slowly increased and finally maintained at 9,800 lbs. (*ca.* 2,500 lbs./sq. in.) for 5 min. Loss in weight of the sample represented expressed juice. Test results showed that adjacent samples from the same, or samples from corresponding muscles of the two sides, were not significantly different. Judging-committee scores were estimated statistically from palatibility judgments; correlation coefficients between the two methods were considered encouraging. Further tests, at widely varying internal temps., on fresh pork, beef and lamb showed close correlation between the results of palatibility scores and mechanical determination,—but, for the same percentage of expressed juice, the committee rated beef as most, and pork as least juicy. Similarly, pork yielding 40% was considered only slightly more juicy than beef or lamb giving 30%, while beef giving 45% juice was judged equal to lamb giving 50%. The method is considered adaptable for use when variation in juiciness is due to animal production factors or to the internal temps. to which the meat is heated. Experimental and statistical details are given. E. B. D.

Indian Belladonna. C. E. Corfield, E. W. Kassner and E. Collins. (*Quart. J. Pharm.*, 1943, **16**, 108–118.)—The macroscopical characters of the plant from which Indian belladonna leaf is obtained differ somewhat from those of *Atropa belladonna*

and, as shown by Melville (*J. Bot.*, 1942, **80**, 54), the source is probably *A. acuminata* Royle rather than a yellow flowering variety of *A. belladonna* or *A. lutescens* Jacquemont. The volatile alkaloid in the assay residue of many samples of Indian drugs, particularly the root, is not removed by drying for 2 hr. at 100° C., and extremely high results are obtained by the U.S.P. procedure. The best method is to titrate the residue after it has been dried to constant weight at 100° C. (4 to 6 hr.). The average non-volatile alkaloid contents of both the Indian leaf and root are not appreciably lower than those of the European leaf and root; hence, the new B.P. standards for the Indian varieties (ANALYST, 1942, **67**, 230. are unnecessarily low. They could be raised to 0·25% for the leaf and to 0·35% for the root without causing inconvenience. Since it is difficult to distinguish between broken or crushed leaves of the Indian plant and of *A. belladonna*, whilst parcels of Indian root may contain mixed roots, it is suggested that the foregoing standards for leaf and for root should be the only ones applied. Stem with a width greater than 5 mm is frequentle present in parcels of Indian root; it should not by described as foreign organic matter since it contains an appreciable amount of alkaloid. The standard for stem with a width of over 5 mm should be deleted or applied only to stem with a width exceeding 10 mm, as in the U.S.P. XII. Similarly, rootstock and stem bases, frequently present in Indian root in proportions exceeding 25%, should not be regarded as foreign organic matter; the standard should be deleted or raised to not less than 50%.

Biochemical

Tentative Fabric Pest-deterrent Tests as Standardised by a Joint Association Committee. F. W. Fletcher and A. H. Goddin. (*Soap*, 1942, **18**, 117–123; *J. Soc. Dyers and Col.*, 1943, **59**, 206.)—Standard fabric for tests is obtainable from the Amer. Assoc. of Textile Chemists and Colorists (*J. Soc. Dyers and Col.*, 1943, **59**, 68). Four test specimens, each of 2 sq. in., should be used and, for yarns, 4 specimens each wound on a glass or metal slide to give a specimen of 2 sq. in. Four similar, untreated patterns should be used as controls or feeding checks. Each of these should lose more than 30 mg wt., and 15 mg of excrement should be produced in each black carpet-beetle test. Four humidity control tests should be made simultaneously with weighings before and after testing. The black carpet-beetle, *Attagenus piceus* Oliv. and the webbing clothes moth, *Tineola bisselliella* Hum., are recommended as representatives of common pests, and 10 larvae of one species should be used on each specimen. The container should be well ventilated and provide freedom of movement for the insects, and tests should be made in the dark at 80° ± 2° F. and relative humidity (R.H.) 60% ± 4%; alternatively, the test specimens are weighed after being in an open desiccator overnight, R.H. being maintained at *ca.* 70% by having sat. brine in the lower compartment. All tests and controls should be made in quadruplicate with both types of insect. In tests with the black carpet-beetle larvae, loss in wt. of fabric and wt. of excrement produced are measured, and larvae 5 months old, weighing 4·5–6·5 mg, should be kept on the patterns for 4 weeks. These insects should be reared at 80° ± 5° F. and R.H. 60% ± 10% on fish meal (70%), corn meal (25%) and brewers' yeast (5%), the whole being ground to pass a 20-mesh sieve (Heal, *J. Soc. Dyers and Col.*, 1943, **59**, 111). With moth grubs, only loss of wt. of fabric is measured, and larvae, 25–27 days old, are kept on the fabric for 2 weeks. These may be reared in wide-mouthed 2– or 4–pint glass jars, the culture medium being dried brewers' yeast (½ teaspoonsful) sprinkled on wool cloth (20 g), and the temp. and R.H. being as for the carpet beetle (Heal, *loc. cit.*). Damage of the fabric is estimated from the visual evidence, the loss of wt. of the specimen, the wt. of black carpet-beetle excrement and the % mortality of the insects. Visual damage should be classed as warp feeding (W), *i.e.*, holes in the specimen, and nap feeding (N), *i.e.*, surface feeding or shearing of the nap or pile, the damage being estimated as % of the specimen consumed. Resistance is excellent when N = 0 and W = 0, and satisfactory when W = 0 and N = 0–5. Loss of wt. of each specimen should be <8–10 mg, provided that the average loss of wt. of the feeding controls is > 30 mg. Black carpet-beetle excrement should be > 4·5 mg, provided that in the feeding control it is > 15 mg. Mortality counts are important when testing stomach-poison types of deterrent. A. O. J.

Colorimetric Estimation of Acetaldehyde in Blood. E. Stotz. (*J. Biol. Chem.*, 1943, **148**, 585–591.)—Published methods for the estimation of acetaldehyde in blood are not very specific and generally require large vols. of sample. In the present method a tungstic acid filtrate of blood or tissue is distilled and the acetaldehyde is collected in bisulphite solution. The acetaldehyde is then estimated by measuring the colour produced with *p*-hydroxydiphenyl reagent by the method of Barker and Summerson (*J. Biol. Chem.*, 1941, **138**, 535; ANALYST, 1941, **66**, 384), using an all-glass apparatus. Dilute 1 vol. of freshly-drawn blood with 7 vols. of cold water and add 1 vol. of 10% sodium tungstate soln. and 1 vol. of ⅔ *N* sulphuric acid. After mixing, stand in an ice-bath for 5–10 min. and centrifuge for 15–20 min. Put a measured vol. of filtrate (usually 8 ml) into a 50–ml flask with a quartz pebble and attach the flask to a condenser the end of which dips below the surface of 2 ml of 2% sodium bisulphite soln. contained in a 25-ml graduated cylinder resting in an ice-bath. Distil the soln. at moderate speed for about 2 min. until the cylinder contains just less than 5·0 ml. Remove the condenser and adjust the vol. to exactly 5·0 ml. After mixing, transfer 1·0 ml of distillate to a Pyrex test-tube containing 0·05 ml of 5% copper sulphate soln. Immerse in an ice-bath and add slowly and with constant shaking 8·0 ml of conc. sulphuric acid. Add 0·2 ml of *p*-hydroxydiphenyl reagent (dissolve 1 g in 25 ml of hot 2 *N* sodium hydroxide and before cooling add 75 ml of water). Stand for 1 hour at room temperature or for half-an-hour at 30° with occasional mixing and then immerse in a boiling water-bath for 1½ mins. Cool and measure the purple colour in a photoelectric colorimeter or spectrophotometer at 560$m\mu$. A blank soln., prepared in the same way as the unknown but with 1 ml of water in place of the distillate, is used in the reference cell. A 95–100% recovery was obtained by distilling amounts of acetaldehyde ranging from 1 to 60μg and recoveries of 94–99% were obtained from blood containing 1·5–20μg of acetaldehyde per ml. Alcohol, glucose, lactose, pyruvate, acetylmethyl carbinol, acetone or 2 : 3-butylene glycol do not interfere, but diacetyl gives a green colour and may lead to erroneous results if present

in sufficient concn.; 15μg yield a colour equiv. to 1μg of acetaldehyde. If necessary, it can be destroyed by preliminary treatment with periodic acid. F. A. R.

Rapid Test for Bromide in Blood and Urine. T. C. Hall. (*Lancet*, 1943, ii, 355–356.)—The usual methods of determining bromine in blood and urine are too slow for the routine testing of large numbers of specimens. The qualitative test described takes only a few min. and is of special value in the rapid diagnosis of bromism. When serum containing bromine is mixed with trichloroacetic acid and auric chloride, protein is pptd. and the auric chloride reacts with any bromide present to give a brown product which is adsorbed on the ppt. The coloured substance thus becomes concentrated in a ring instead of being diffused through the drop. Place one drop of serum on a white porcelain surface, spread it over an area of *ca.* ½ sq. in., and put in the centre of the serum one drop of a reagent made by mixing equal parts of 20% trichloroacetic acid and 0·25% auric chloride soln. In presence of bromide a circular ring of pptd. protein appears almost immediately and is coloured yellow with up to 25 mg, or reddish-brown with 50 mg or more of bromide per 100 ml. In testing urine, place 2 drops on a white porcelain surface and spread out as before, add one drop of a 10% soln. of egg-white or one drop of bromide-free serum. Mix, put 1 drop of the reagent into the centre of the urine, and note the colour of the ring that is formed. It is preferable to make the test in daylight. F. A. R.

Estimation of Flavones or Quercetin-like Substances in Certain Naturally occurring Products. L. S. Weatherby and A. L. S. Cheng. (*J. Biol. Chem.*, 1943, **148**, 707–709.)—Extract the dried sample with methyl alcohol and evaporate the extract to dryness. Remove chlorophyll and other interfering substances by extraction with chloroform and dissolve the residue in 100 ml of acetone. Make up an aliquot portion of this soln. to a definite volume with boric acid and citric acid reagent (mix 100 ml of anhydrous acetone containing 10 g of anhydrous citric acid with 100 ml of anhydrous acetone saturated with boric acid). Measure the yellow colour by means of a photoelectric colorimeter fitted with a blue filter and then measure the colour of the test soln. in a citric acid soln. alone. The difference between these two readings gives the absorption due to the colour formed by the action of the boric acid on the flavone. Calculate the quercetin equivalent by reference to a standard curve made with pure quercetin. F. A. R.

Microdetermination of Vitamin A and Carotenes. F. Urban and B. Milder. (*Biochem. J.*, 1943, **37**, 295–298.)—A method is described which simultaneously estimates vitamin A and carotene by the Carr–Price reaction. A beam of light from a 6–8 volt Mazda lamp (100 c.p.) maintained at a constant voltage by means of a rheostat is passed through a glass-stoppered cell, 1 ml in capacity and 5 cm long, containing the reaction mixture. By means of prisms the emergent light is split into two beams which pass through 620 and 589mμ filters respectively, and fall on to two recording photocells. The currents generated by these cells are stored in condensers and measured by means of a ballistic galvanometer. The estimation must be carried out at 0° C., as at room temp. the 589mμ band of β-carotene fades within a few sec. Dissolve the sample in chloroform, so that 0·5 ml contains 10–100 U.S.P. units. Put 0·5 ml of this soln. into the cell and add 0·5 ml of a sat. soln. of antimony trichloride in chloroform from a pipette. Immediately set a stop-watch going, mix the contents of the cell and, after exactly ½-min., switch on the light at a potential of 5 v. and allow this to pass through the soln. in the cell for exactly 1½ min. Measure the current stored in the two condensers by means of the galvanometer. The amounts of vitamin A and carotene present are calculated from a calibration curve prepared from standard solns. of vitamin A and β-carotene. The method can be used for the estimation of small amounts of vitamin A and β-carotene in blood. F. A. R.

Methylene Chloride in the Extraction and Determination of Vitamin A and Oil in Soupfin Shark Livers. P. C. Tompkins and R. A. Bolomey. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 437–439.)—The use of methylene chloride in place of peroxide-free ether for the extraction of oils containing vitamin A from fish livers has several advantages. The solvent containing the oil may be added directly to the chloroform soln. of antimony trichloride, so that time is saved and the risk of destruction of vitamin A during removal of the solvent is reduced. In addition, "refrigeration grade" methylene chloride may be used without further purification. The potency of mixed oils and of oils from individual soupfin shark liver samples was determined by the Carr–Price reaction, by its Rosenthal–Erdelyi modification and by ultraviolet absorption, the dilution principle advocated by Norris and Church (*J. Biol. Chem.*, 1930, **87**, 139; ANALYST, 1930, **55**, 458) being used in each method. The colour intensity of the Carr–Price reaction was measured at 620mμ with a Coleman 10–S spectrophotometer (5mμ slit), and that of the Rosenthal–Erdelyi reaction with a Klett–Summerson photoelectric colorimeter with a green (No. 54) filter, and the ultra-violet absorption was determined at 328mμ with a Beckman quartz prism spectrophotometer with *iso*propanol as solvent. In the colorimetric reactions 0·25-g samples of oil were weighed in 25-ml flasks, the experimental samples being dissolved in methylene chloride and the control samples in chloroform. Both samples, diluted as required, were treated with antimony trichloride in chloroform soln. The resulting concn. of methylene chloride in the experimental series was 10% by vol. To compare methylene chloride extraction with extraction of oil and vitamin A by ether, liver samples (previously frozen) were homogenised in a Waring Blendor and 2– to 3-g portions were extracted by the short method of Stansby and Lemon (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 341), an aliquot portion of the supernatant liquid was evaporated, and the % oil in the liver was calculated. When methylene chloride was used as the extracting agent, 1 ml of the extract was diluted with chloroform for the colorimetric procedures and with *iso*propanol for direct absorption measurement. Ether, when used as solvent, was removed in a stream of methane, the oil was dissolved in the appropriate solvent and its wt. was calculated. If V_s is the vol. of solvent, V_a the vol. of the aliquot portion, W_o the wt. of oil and D the average density of the oil, $V_s = V_a - \frac{W_o}{D}$

The oil extracted by 100 ml of solvent is $\frac{W_o \times 100}{V_s}$

and the % of oil in the original sample is

$$\frac{W_o \times 100}{V_s} \times \frac{100}{W_L}$$

where W_L is the wt. of the liver sample. Methylene chloride was found to be as effective as ether in the extraction of the oil and vitamin A, but was not suitable for extraction of the unsaponifiable portion of the oil, since persistent emulsions were formed. The use of solvents other than chloroform reduces the sensitivity of the antimony trichloride reaction (Wokes and Willimott, ANALYST, 1927, **52**, 515). Antimony trichloride is more readily soluble in methylene chloride than in chloroform, but the resulting colour intensity is reduced by 30%. Partial substitution of methylene chloride for chloroform, however, had no effect on the sensitivity of the reaction. Even though methylene chloride is less volatile than ether, care is required to prevent loss by evaporation, and owing to the toxicity of the solvent, all expts. should be made in a well-ventilated place. A. O. J.

Riboflavin and Vitamin B_1 in Nineteenth Century Buns and Ale. E. C. Barton-Wright, T. Moran and H. S. Sarson. (*Nature*, 1943, **152**, 273.)—Two currant buns, baked in 1863 and 1867, had the following analyses, respectively:—Moisture, 13·0, 13·6; protein, 11·4, 11·3; fat, 5·2, 4·4; fibre, 0·2, 0·4%; vitamin B_1, 0·15, 0·35 I.U. per g; riboflavin, 9·3, 7·3μg per g; *p*H (1 pt. bun: 2 pts. water), 4·4, 5·0. Apart from their hardness, both buns, including the currants, were in good condition. Average values for these and 2 other buns (1888 and 1890) were:—Vitamin B_1, 0·15, I.U. per g, riboflavin, 6·7μg per g. Corresponding figures for present-day buns are, 1 and 1·5–2·4, respectively. The high riboflavin value is noteworthy, and is attributed to the use of brewers' yeast in the recipe (currants contain 1μg per g). As average values found for freshly-dried, plain debittered brewers' yeasts (moisture, 12–13%) were: vitamin B_1 33, riboflavin 54, it is calculated from the assumed riboflavin contents of the constituents of the recipe believed to have been followed, that the "pint of good ale yeast" used contained about 8,000μg of riboflavin per g. The high riboflavin content of the buns cannot be explained because, taking 25 and 2μg as possible values per g and ml of yeast and ale, respectively, it would follow that each pint of ale yeast must have contained *ca.* 300 g of wet yeast (water, 75%); this is unlikely, since in bread-making 25 g of yeast per 2 lb. of flour is usually taken as the max. attainable before bitterness is apparent. The explanation may be the high values for the yeast or beer of those days, or the larger quantity of yeast that could be used. For the same reason, bread made at that time would probably have a higher riboflavin content than present National bread. The vitamin B_1 value shows, on the other hand, that considerable loss of this constituent must have occurred. The fibre figure suggests an extraction of 80% (*cf.* following abstr.). J. G.

Riboflavin and Vitamin B_1 in War-time Beers. R. H. Hopkins. (*Nature*, 1943, **152**, 274.)—War-time beers (14) contained 0·47–1·2μg per ml of riboflavin; strong ales, which were not included, probably contain more. The improved microbiological method of Barton-Wright and Booth (*Biochem. J.*, 1943, **37**, 25) was used. Aneurin contents (16 beers, including 3 strong ales) were 1–6 I.U. per ml; they were measured by a fermentation method (Schultz, Atkin and Frey, ANALYST, 1942, **67**, 170) using an appropriate strain of bakers' yeast, and were checked (when sufficient aneurin was present) by the thiochrome fluorometric method (Booth, *id.*, 1940, **65**, 610). Whilst much aneurin is lost from bright beer by removal with the yeast, almost all the riboflavin present in the original malt remains in the beer (*cf.* preceding abstr.). J. G.

Assay of Riboflavin in Cereals and Other Products. E. C. Barton-Wright and R. G. Booth. (*Biochem. J.*, 1943, **37**, 25–30.)—1. *Microbiological assay.*—With slight modifications, the method of Snell and Strong (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 346) was employed, the organism *Lactobacillus helveticus* being grown on the following medium: 50 ml of photolysed NaOH-treated peptone soln., 50 ml of cystine soln., 12·5 ml of 1% asparagine soln., 5·0 g of glucose, 0·25 g of xylose, 2·5 ml of soln. A (25 g of K_2HPO_4 and 25 g of KH_2PO_4 in 250 ml of water), 2·5 ml of soln. B (10 g of $MgSO_4.7H_2O$, 0·5 g of NaCl, 0·5 g of $FeSO_4.7H_2O$ and 0·5 g of $MnSO_4.4H_2O$ in 250 ml of water), 5 ml of yeast supplement, 12·5μg of nicotinic acid and 12·5μg of pantothenic acid, made up to 250 ml. Media and extracts were made with glass-distilled water. The medium differs from that used by Snell and Strong in the addition of asparagine, xylose, nicotinic acid and pantothenic acid. Bacterial growth is estimated both nephelometrically and by titration of the acid formed, but the latter method is preferred, as it is simpler and requires fewer tubes. Three tubes are taken for each concn. level, and the titrations are carried out in the fermentation tubes, a comparator being used to measure the colour. Prepare a buffer soln. of *p*H 6·8 by mixing 50 ml of a 0·2 *M* soln. of KH_2PO_4 with 23·65 ml of 0·2 *N* sodium hydroxide and diluting to 200 ml. To 20 ml of the soln. in a test-tube, add 20 drops of bromothymol blue indicator (tube B) and into another tube (tube A) put 20 ml of water. For the titrations take 2 of the tubes and put 10 drops of indicator in one (tube C) but not in the other (tube D). Insert the four tubes in the comparator, with A behind C and B behind D, and titrate the contents of tube C with 0·1 *N* sodium hydroxide, adding an extra drop of indicator for every ml added. Add the same vol. of alkali to tube D. The titration is complete when the colour of A+C matches that of B+D. Since starch has a markedly stimulating effect on the growth of *L. helveticus*, it must be destroyed before the estimation is made. The most convenient method of doing this is to autoclave a 5-g sample of the finely-ground material at 15 lb. pressure with 50 ml of 0·25 *N* hydrochloric acid for 15 min., or, with cooked wheaten products such as bread, for 30 min. After hydrolysis, adjust the *p*H to 6·8 with sodium hydroxide and make up to 500 ml. The amount of sample will vary with the riboflavin content and should be chosen to give an extract containing 10–12μg of riboflavin. For each assay three different levels of concn., *e.g.*, 2, 3 and 4 ml must be used. The results should not differ by more than 10%, and the mean of the values is taken as the riboflavin content. Fats also have a stimulating effect, and substances such as soya-bean, maize, wheat germ and milk should be defatted by extraction in a Soxhlet extractor with light petroleum. The following results (in μg per g) were obtained: wheat, 1·9–3·7; wheat germ, 9·7–12·85; flour, National Straight Run (75% extraction), 0·75–1·25; flour, National Wheatmeal (85% extraction),

1·7–2·1; barley, 2·3; rye, 2·65; maize, 2·3–2·7; soya bean, 3·0–4·9; baker's yeast, 23·0; brewer's yeast, 66·0. The possible destruction of riboflavin in baking was investigated, and a survey of the riboflavin contents of different milling fractions was made. 2. *Fluorometric assay.*—Two difficulties were encountered in applying the fluorometric method to the estimation of riboflavin in cereals. First, that due to the presence of colloidal or suspended particles in the extract was overcome by extracting the riboflavin with an organic solvent. The second difficulty, due to the initial low concn. of riboflavin in wheat and its products, was less easy to surmount, but was eventually solved by adsorption on "Superfiltrol" and elution with aqueous pyridine-acetic acid. Shake a sample of the finely-ground material, containing 20–50μg of riboflavin, with 100 ml of 0·25 *N* sulphuric acid and similarly treat two further samples to which have been added 10 and 20μg respectively of riboflavin. Plug the flasks with cotton-wool and autoclave at 15 lb. pressure for 15 min. or, with cooked wheaten products, for 30 min. Cool, adjust to *p*H 5 by addition of 30% sodium hydroxide soln., dilute to a suitable volume and filter through a No. 5 Whatman paper. Put 0·5 g of Superfiltrol into each of three 50-ml conical centrifuge tubes and add a 45-ml portion of each of the digests. After stirring for 5 min., centrifuge and discard the supernatant liquid. Stir for 2 min. with 20 ml of water, again centrifuge and discard the washings. Allow the tubes to drain, and add to each 8 ml of a mixture of water (9 vol.), redistilled pyridine (5 vol.) and glacial acetic acid (2 vol.). Stir for 5 min. and centrifuge at a low speed for 5 min. Decant each eluate into a glass-stoppered flask or cylinder, add 3 drops of 4% potassium permanganate soln., mix and leave for at least 1 min. to oxidise interfering substances. Then decolorise the soln. by addition of 2 drops of 10 vol. hydrogen peroxide, and add 5 g of anhydrous sodium sulphate and 20 ml of *n*-butyl alcohol. Warm the flasks to 35–40° C. and shake vigorously for 2 min. Cool, decant the supernatant layers into centrifuge tubes, and centrifuge at a low speed for 5–10 min. Transfer some of the clear butyl alcohol–pyridine layer to the cell of a Spekker fluorimeter and measure the fluorescence with blue activating light (Wratten No. 47 filter) and an orange filter (Chance's) in front of the photocell. A soln. of sodium fluorescein (1μg per ml) in weak alkali may be used as standard. Make blank estimations on each sample after destroying the riboflavin by exposure to a mercury vapour lamp or to direct sunlight for 1–2 hr. The difference between duplicate expts. did not exceed ±10%, and there was excellent agreement with the results obtained by the microbiological method. The fluorometric method is more tedious than the microbiological method. F. A. R.

Estimation of Nicotinic Acid. R. G. Martinek, E. R. Kirch and G. L. Webster. (*J. Biol. Chem.*, 1943, **149**, 245–249.)—A chemical method frequently used for the estimation of nicotinic acid comprises treatment with cyanogen bromide and an amine. Orthoform (*m*-amino-*p*-hydroxybenzoic acid methyl ester) is now recommended for this purpose; it is said to produce a more stable colour than other amines. Dilute the soln., containing 5–60μg of nicotinic acid, to 6 ml and add 6 ml of 4% cyanogen bromide soln. (made by decolorising cold saturated bromine water with 10% sodium cyanide soln. added from a burette) and 7 ml of a buffer soln. consisting of 988 ml of water, 15 ml of 15% sodium hydroxide soln., 5 ml of 85% phosphoric acid and 175 ml of 98% alcohol. Leave for 20 min. or heat on the steam-bath for 5 min. with a funnel in the neck of the flask to prevent evaporation, and then add 1 ml of 1% orthoform soln. in 95% alcohol. After 5 min., but within 15 min., measure the colour in a photometer, using a similar soln. without orthoform as a blank. Alternatively, the increase in photometric density obtained by addition of known amounts of nicotinic acid may be measured and the results calculated from a standard curve for pure nicotinic acid. To obtain 100% recovery, the *p*H of the soln. must be maintained between 6·2 and 7·05. The reaction yields no colour with pyridoxine. F. A. R.

Determination of Nicotinamide. C. F. Krewson. (*Amer. J. Pharm.*, 1943, **115**, 122–125.)—To about 0·15 g of nicotinamide previously dried over sulphuric acid for 18 hrs. and accurately weighed, add 5 ml of conc. hydrochloric acid. Boil the mixture under reflux for 15 min. and then add 15 ml of water through the condenser. Remove the condenser, add a small piece of pumice and 6 ml of a sat. aqueous soln. of sodium hydroxide, taking care to avoid loss of ammonia. Distil the soln. for about 12 min. and collect 15 ml of distillate in standard acid. Rinse the condenser and delivery tube into the receiver with 5 ml of water, add 5 drops of methyl red soln. (0·1 g in 100 ml of 95% alcohol) and titrate the excess acid with 0·1 *N* sodium hydroxide. Make a blank test with the same quantities of reagents and subtract the titre from that obtained with the test soln. Values of *ca.* 100% were obtained with samples of the pure amide, and the amount of nicotinamide in a mixture of the amide and nicotinic acid was estimated with a high degree of accuracy. The method, whilst giving just as accurate results, has certain advantages over the U.S.P. XII method. F. A. R.

Factors Influencing the A.O.A.C. Chick Method of Vitamin D Assay. I. Motzok, D. C. Hill and J. S. Slinger. (*J. Assoc. Off. Agr. Chemists*, 1943, **26**, 263–272.)—It was found that a group size of 15 chicks, as recommended by the A.O.A.C. (*J.A.O.A.C.*, 1934, **17**, 68) did not give results of high accuracy. The results obtained support the suggestion that different workers should establish their own standard of precision. The type of response to vitamin D varies with the breed of chick. Of the breeds studied, White Leghorns showed the greatest variability. The uniform response found with cross-bred chicks suggests that it may be possible to produce a hybrid the use of which would increase the accuracy and practical efficiency of the method of assay. The choice of the strain of yeast may have a pronounced effect on the degree of calcification, growth and utilisation of the ration as affected by graded doses of vitamin D. There is a suggestion that the basal diet may be deficient in a factor or group of factors necessary for growth. The apparent relationship between calcification and growth requires further investigation.

Agricultural

[Determination of Calcium in] Mineral Mixed Feeds. A. T. Perkins and J. F. Merrill. (*J. Assoc. Off. Agr. Chem.*, 1943, **26**, 212–214.)—In the official method (*Methods of Analysis, A.O.A.C.*, 1940, **48**, 365) a 2-g sample is ignited and dissolved

in hydrochloric acid (1+3), the soln. is neutralised, and the calcium is pptd. and titrated. Certain commercial mineral feeds contain the soluble orthomonocalcium phosphate, $CaH_4(PO_4)_2$, and some of them do not yield all their calcium by this method because, when ignited, they produce an insol. calcium phosphate, probably a metaphosphate: $CaH_4(PO_4)_2 \rightarrow Ca(PO_3)_2 + 2H_2O$. This calcium can be recovered either by omitting the ignition or by igniting under alkaline conditions. If the ignition is omitted, the calcium in any organic matter present will not be determined and thus the calcium pptd. will be the added mineral calcium rather than the total calcium. However, as the method is essentially for mineral foods and added mineral calcium, this differentiation is not important. If the mineral mixture is ignited with excess of sodium carbonate, the excess base prevents the formation of the insol. metaphosphate.

Nutritive Value of Cotton Seeds, Peanut and Soya Seeds. T. F. Zucker and L. Zucker. (*Ind. Eng. Chem.*, 1943, **35**, 868–872.)—Unlike cereal grain milling, the milling of oil-bearing seeds preserves the vitamin B in the same edible fraction with the protein. For food uses, the hull is the only waste product. Flours of cottonseed, peanut and soya bean are concentrated sources of protein especially suitable for supplementing white wheat flour. There appear to be moderate differences in the amounts of the three seed flours required for producing normal growth. Soya-bean flour is superior in protein quality, cottonseed flour in riboflavin content; peanut flour has shown an outstanding nicotinic acid value. Assay values (in μg per g) for vitamin B factors were as follows:

	Thiamine	Riboflavine	Nicotinic acid	Pantothenic acid	Pyridoxine
Cottonseed flour ..	10·4	10·2	85	25·5	—
Soyabean flour ..	5·4	4·1	29	15·0	6·4
Peanut flour ..	6·0	3·0	*ca.* 200	—	—
Rice bran extract ..	150·0	10	2000	275	150

The following figures for certain diet constituents were obtained:

	P %	Ca %	Mg %	Mn p.p.m.	N %	Water %	Ash %
White flour	0·13	0·014	0·039	—	2·47	9·5	—
Cottonseed flour	1·26	0·20	0·65	15	9·0	6·3	6·1
Peanut flour	0·56	0·07	0·36	45	9·7	7·6	3·6
Soyabean flour	0·58	0·24	0·25	32	6·8	8·6	4·8
Blood fibrin	0·096	0·18	0·015	3	13·7	7·1	3·4
Rice bran extract	0·54	0·03	0·16	18	1·60	37	4·9

To provide substitutes for both the protein and the vitamins of meat, a mixture of the three seed flours offers possibilities.

Organic

Identification of Organic Bases by Means of the Optical Properties of Dilituarates. E. M. Plein and B. T. Dewey. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 534–536.)—Dissolve equiv. quantities of dilituric acid (5-nitrobarbituric acid) and the sample in the min. vol. of boiling water, and allow the soln. to cool; purify the resulting dilituarates by one or more recrystallisations. Dilituric acid is prepared by direct nitration of barbituric acid (Hartman and Sheppard, *Organic Syntheses*, 1932, **12**, 58). Optical-crystallographic data (extinction angle, optical sign, α-, β- and γ-refractive indices, elongation, dispersion, crystal system and habit, and optical orientation) are tabulated for dilituric acid and 22 dilituarates of primary aliphatic amines; diagrams of crystals of these dilituarates, as they appear in the most frequently occurring orientations, are also presented. These data provide means of identifying pure amines and certain mixtures thereof. J. G.

Qualitative Test for Methoxy and other Alkoxy Groups. W. C. Tobie. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 433–434.)—The test, based on the Zeisel method (*Monatsh.*, 1885, **6**, 989), will detect lower alkoxyl groups in soluble compounds of relatively low mol. wt. The alkyl iodide produced is recognised by its pptn. of mercuric iodide from mercuric nitrate. Cut double-thickness cheese cloth into strips, 2 in. wide and 18 in. long, and fold each strip once to form a strip 2 in. by 9 in. Place the strips on a sheet of glass, thoroughly moisten each with 5 ml of impregnating soln., and allow them to dry without curling. To prepare the impregnating soln., pour a soln. of 1 g of lead acetate in 10 ml of water into 60 ml of *N* sodium hydroxide. When the heavy ppt. has redissolved add a soln. of 5 g of sodium thiosulphate in 10 ml of water and 1 ml of glycerin and dilute the mixture to 100 ml. Place *ca.* 0·1 g of the substance to be tested (finely powdered if solid) in a test-tube and cover it with 1 ml of glacial acetic acid and 1 ml of 57% hydriodic acid (sp. gr. 1·7). Roll one of the impregnated strips loosely into a cylinder and insert it into the mouth of the tube with a rotary motion, finally reversing the motion to cause the cylinder to expand and fit tightly. Push the plug down until its upper end is 1·5 in. below the mouth of the tube, and above it insert a disc of non-absorbent cotton wool, 2–3 mm. thick. Give a strip of filter-paper, 2 cm wide and 10 cm long, a slight longitudinal fold, moisten *ca.* 1/3 of its length with a saturated soln. of mercuric nitrate in 2% v/v nitric acid and rest the paper upon the cotton disc. Place the tube in a glycerin bath, *ca.* 5 cm deep, maintained at 120°–130° C. The impregnated plug will show a grey discoloration and, in presence of alkyl groups, a yellow colour spreading upward from the bottom edge of the filter-paper will change to a bright orange or vermilion. A permanent yellow colour indicates a negative or doubtful reaction. Unless the reaction has occurred, continue the heating for 10 min. The limit of sensitivity of the test is *ca.* 5 mg for vanillin and 10 mg for codeine. The method gave satisfactory results with a number of compounds of pharmaceutical importance. Sulphur often interferes, apparently by formation of mercaptans, which are not retained by the impregnated plug. The test is invariably satisfactory for alkaloids, which should be liberated from their salts before testing. The butoxy group in nupercaine is readily detected, but *n*-butyl ether gives a weak reaction and *n*-hexyl ether does not react at all. This is probably due to the high b.p. of the higher iodides and to the resistance of the simple ethers to the action of hydriodic acid. A. O. J.

Determination of Butadiene in Presence of Other Unsaturated and Saturated Gaseous Hydrocarbons. J. F. Cuneo and R. L. Switzer. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 508–509.)—The principle of the method is (*a*) absorption of the alkenes and alkadienes in mercuric nitrate soln.; (*b*) hydrogenation of these compounds to alkanes. Then, mol.-% of alkadiene = (mol.-% unsaturation by hydrogenation) — (mol.-% unsaturation by mercuric nitrate absorption). (*a*) Pass the sample through a soln. made up from 600 g of mercuric nitrate, 1250 g of sodium nitrate, 383 ml of 70% nitric acid and 2100 ml of water, until absorption is complete; 5–6 cycles are usually required with a fresh soln. Samples rich in *iso*butene produce a yellow ppt., which at first is redissolved by the reagent; when the ppt. no longer dissolves, replenish the reagent. If the sample is completely soluble, or nearly so, an inert gas (*e.g.*, air) should be added to it to serve as a carrier. Scrub the residual gas in 30% potassium hydroxide soln. to remove traces of nitric acid. (*b*) Mix a known vol. of the original sample with an excess of hydrogen, and determine the hydrogenation value. It is important that oxygen, carbon monoxide and hydrogen sulphide (which poison the nickel catalyst) and water are absent. The mixture is passed through the catalyst until a constant vol. is attained (as measured in a 3-bubbler Orsat apparatus, the gas-burette of which is so calibrated that the smallest division is not greater than 0·1 ml), and the decrease in vol. is calculated in terms of %-hydrogenation after applying a correction for the deviation of the hydrogen-hydrocarbon mixture from the ideal gas vol. (*cf.* Robey and Morrell, *id.*, 1942, **14**, 880). The method was applied to synthetic blends of *n*-butane (15·5–21·6%) *iso*butene (0·65·1%) and butadiene (15·3–81·7%), and it was compared with the usual maleic anhydride method of Tropsch and Mattox (*id.*, 1934, **6**, 104). In most instances both methods gave fairly concordant results; divergencies are shown to be due to the difficulty of obtaining reproducible results by the maleic anhydride method. The sample must be free from acetylenes; those commonly associated with butadiene and butenes produced by cracking petroleum stocks may be removed without affecting the relative proportions of the gaseous constituents (method not described). To recover the mercury, acidify the collected spent reagents with conc. nitric acid, and suspend a strip of lead in them; the lead replaces the mercury in soln., and the mercury collects on the bottom of the container. J. G.

Segregation of Component Glycerides of Linseed Oil by Chromatography II. Determination of Thiocyanogen Value. F. T. Walker and M. R. Mills. (*J. Soc. Chem. Ind.*, 1943, **62**, 106–109.)—The method previously described (ANALYST, 1942, **67**, 402) has been expanded, so that zones of constant iodine val. can be isolated by repeated fractionation, only partial separation being effected at each stage. In this way, by working in 16 preliminary columns on 70 g of linseed oil (iodine val. 180) and making 7 or 8 separations, it was possible to separate portions of sufficient purity for the determination of the thiocyanogen value. Evidence was thus obtained of the presence of trilinolenin (9 double linkings) and linoleodilinolenin (8 double linkings) in addition to glycerides with 7, 6, 5 and 4 double linkings previously separated. There was no indication of any glycerides with less than 4 double linkings. By determining the thiocyanogen val. of the mixture of highly unsaturated glycerides it is possible to calculate the thiocyanogen val. of linolenic acid. The value obtained (163·2) agrees closely with that found by recent workers who have isolated linolenic acid. It has been pointed out (Rose and Jamieson, *Oil and Soap*, 1941, **18**, 173) that differences in the technique of determining the thiocyanogen val. prevent the experimental values being applied to the calculation of the composition of oils examined by different workers. The same procedure must be followed exactly with both the parent oil and the individual fatty acids. The method here described is based on recent work, and is in accordance with the observation of Riemenschneider, Swift and Sando (*Oil and Soap*, 1941, **19**, 203), that 0·1 *N* solns. are preferable to 0·2 *N* solns. *Determination of thiocyanogen value.*—All glass ware used must be steeped in caustic soda soln., washed with soapy water, rinsed successively with distilled water, alcohol and ether and dried in an oven at 110° C. To clarify the reagent, use two No. 42 Whatman papers previously dried in the oven. *Reagent.*—Transfer 10-g portions of lead thiocyanate (prepared in the laboratory) into 300-ml glass-stoppered bottles and fill up with anhydrous acetic acid (prepared by heating glacial acetic acid under reflux with 11% of its vol. of freshly-distilled acetic anhydride) and leave in the dark for 8 days. Add 1·1 ml of bromine (dried with sulphuric acid) to the contents of a bottle and shake until colourless. Filter and determine the concn. by running 20 ml into 20 ml of 10% potassium iodide soln., diluting, and titrating with 0·1 *N* sodium thiosulphate. Finally, dilute with anhydrous acetic acid so that 30 ml are equiv. to 40 ml of 0·1 *N* sodium thiosulphate. *Determination.*—Weigh a suitable quantity of the oil to give a 150–200% excess of thiocyanogen into an iodine value flask, dissolve it in 10 ml of anhydrous carbon tetrachloride, add 30 ml of the reagent, and keep in the dark for 24 hrs. at 20° C. before adding 30 ml of 10% potassium iodide soln. and titrating in the usual way.

Rapid Determination of Fermentable Sugars. G. Menzinsky. (*Svensk. Papperestidn.*, 1942, **45**, 421–428; *Paper Ind.*, 1943, **25**, 323.)—The method (which was developed primarily for the analysis of sulphite cellulose waste liquors) depends on the fact that when a high concn. of yeast is added to a soln. containing a relatively low concn. of sugar, the latter is adsorbed selectively and rapidly by the former, whilst other reducing substances remain unadsorbed. Boil 100 ml of the sulphite waste liquor, with aeration, for 30 min., replacing the water as it evaporates, add calcium carbonate to produce *p*H 6·0, cool and filter the mixture, wash the ppt., and make the filtrate up to 100 ml. Dilute 10 ml of the filtrate to 100 ml, determine the total reducing sugars (*e.g.*, by Schoorl's method), and calculate the result as glucose per 100 ml of original sample. Agitate 50 ml of the filtrate with 2·5–5·0 g of yeast at 30° C. for 1 hr., centrifuge, and again determine the total reducing sugars in the clear liquid; the difference between the 2 figures is the value sought. Check tests with mannose, galactose, glucose and fructose, alone and in admixture, and with various types of yeast, gave satisfactory results. J. G.

Determination of Free Gossypol in Cottonseed Meal. C. M. Lyman, B. R. Holland and F. Hale. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 489–491.)—The authors have shown (*id.*, in press)

that the free gossypol content of cottonseed meal is a reliable index of the toxicity of the meal in animal feeding tests. The method of determination now described is based on the colour change which occurs when aniline reacts with gossypol in soln. in an organic solvent. Grind the sample to pass a 40-mesh sieve, wrap 2 g in a 125-mm filter paper (S. and S. No. 597, or similar grade), and then in a second filter, the top of which is left open so as to form a thimble. Extract (*e.g.*, in a Butt extractor tube) with 60 ml of peroxide-free ether, containing 2·3–2·5% of alcohol and 1·0–1·2% by wt. of water, for 72 hr., and use a piece of absorbent cotton wool in the top of the thimble to distribute the solvent, and a 250-ml conical extraction flask. The solvent should fall on the thimble at the rate of not less than 150 drops per min. After extraction add *ca.* 5 ml of *n*-butanol, remove the ether by warming under reduced pressure, transfer the residue to a 25-ml flask with *n*-butanol, and dilute to the mark with *n*-butanol. Transfer 2 aliquot portions (*vide infra*) to 2 other 25-ml flasks, add 2 ml of freshly-distilled aniline, to one of these, and dilute the contents of each to the mark with *n*-butanol. After *ca.* 20 min. measure the light transmission at wavelength 440*mμ* (the wavelength of max. absorption of dianiline gossypol) in a photoelectric colorimeter or spectrophotometer. The gossypol content is directly proportional to log I_0/I_1, where I_0 and I_1 are the intensities of the light transmitted in absence and presence of aniline, respectively. A calibration curve is prepared for each instrument with pure gossypol. The aliquot portions used should contain 0·05–0·30 mg of gossypol for spectrophotometer cells of about 1 cm thickness. When 0·024 and 0·047 mg of gossypol were added to extracts containing 0·070 mg of gossypol, the recovery of added gossypol was 102%. The presence of other coloured compounds in the extract does not affect the accuracy; 7 other samples of cottonseed meal examined contained 0·020–0·118% of gossypol. The method is of special use for very small quantities of gossypol, when the solubility of dianiline gossypol becomes a source of error in the pptn. method of Halverson and Smith (ANALYST, 1938, **63**, 55, 65). The extinction-coefficient of the colour change is a straight line function of the gossypol concn. when the latter is 0·05–0·30 mg per 25 ml of soln. The colour produced is stable for 3 hr. Absorption spectra data (cited) show that if there are substances other than gossypol in ethereal extracts of cottonseed meal which give a colour with aniline, these substances must be closely related to gossypol in chemical structure. J. G.

Amperometric Titration of Picrolonic Acid and Indirect Volumetric Determination of Calcium. G. Cohn and I. M. Kolthoff. (*J. Biol. Chem.*, 1943, **148**, 711–718.)—In a previous paper (*J. Biol. Chem.*, 1943, **147**, 705; ANALYST, 1943, **68**, 291), the polarographic behaviour of picrolonic acid was described. The polarogram of methylene blue has now been measured, and it has been shown possible to use methylene blue in the amperometric titration of picrolonic acid. Methylene blue in a buffer consisting of 0·1 *M* acetic acid, 0·0125 *M* lithium acetate and 0·1 *M* lithium chloride at 20° C., gave a wave with a well-defined diffusion current at an applied voltage of 0·3 v., and the half-wave potential at this *p*H was − 0·07 v. *versus* the saturated calomel electrode. The reduction of methylene blue involves two electrons yielding leucomethylene blue. Amperometric titration of picrolonic acid with methylene blue was carried out by adding 0·01 *M* methylene blue soln. from a micro-burette to solns. of picrolonic acid in the above-mentioned buffer soln. whilst applying 0·3 volt between the dropping mercury electrode and the mercury pool anode. This voltage is smaller than that at which the first wave of picrolonic acid starts, but is large enough to yield a diffusion current of methylene blue. Nitrogen was passed through the soln. to remove oxygen and stir the mixture. The titration was continued until the current began to increase, the end-point being the point at which the current ceased to be constant, and started to rise steeply. An attempt was made to apply this titration to the estimation of calcium by precipitation with excess picrolonic acid and back titration of the reagent. Unsatisfactory results were obtained, however, and this was traced to adsorption of picrolonic acid on filter-paper. When the calcium picrolonate was filtered through a sintered glass crucible no loss occurred and titration of the excess with methylene blue gave satisfactory results. F. A. R.

Rapid Identification of Arylamine Residues in Compounds of the Naphtol AS Series. E. J. Cross and R. W. Carlene. (*J. Soc. Dyers and Col.*, 1943, **59**, 191–192.)—A mixture containing Naphtol AS–SW, when fused with soda lime gives a distillate from which β-naphthylamine can be isolated. The possibility of using this method to replace longer methods of hydrolysis was investigated, and with a number of commercial Naphtols the arylamine residue was readily isolated, either as the free base or as the acetyl derivative. With Naphtol AS–BS (*m*-nitroanilide), the only nitro-derivative among the commercial Naphtols, attempts to isolate *m*-nitroaniline from the distillate failed. Although the alkoxyl group, when present in the arylamine residue, undergoes hydrolysis on boiling with aqueous sulphuric acid (b.p. 140°–150° C.), the group is unaffected by heating the arylamide with alkali. Although partial hydrolysis of the alkoxyl group appeared to occur on heating the alkoxy-arylamides with soda lime, satisfactory yields of alkoxy-arylamines were obtained from Naphtols AS–RL (*p*-anisidide) and AS–OL (*o*-anisidide). Naphtol AS–BR, however, gave a very low yield of dianisidine, and an attempt to isolate 5-chloro-2:4-dimethoxyaniline from Naphtol AS–ITR failed. *Method.*—Heat an intimate mixture of 2 g of the powdered Naphtol with 4–6 g of dry powdered soda lime in a hard glass tube, fitted with a bent delivery tube leading to a receiver cooled in water, until distillation is complete (5 min.). Some of the distillate condenses on the cooler part of the hard glass tube, from which it may be transferred to the receiver by means of strips of filter-paper. For a more convenient apparatus, bend the hard glass tube *ca.* 2 in. from the mouth at 120° and fit to it a short straight delivery tube. After distillation, break the tube at the bend and extract the distillate from the upper portion of the tube, the cork, the delivery tube and the receiver by means of 15 ml of hot 2% sodium hydroxide soln. followed by 15 ml of boiling dil. hydrochloric acid (1 : 20). Cool the combined extracts, make alkaline, and extract the arylamine with carbon tetrachloride or chloroform. Filter, if necessary, and evaporate the extract to dryness in a tared dish. Alternatively, add 1 ml of acetic anhydride to the carbon tetrachloride extract before evaporation and free the residue from acetic anhydride and acetic acid by

repeated evaporation with small amounts of alcohol. The following yields of arylamines (or acetylarylamines) were obtained from the Naphtols examined: —AS, 28% acetanilide; AS–BO, 59% acetyl-α-naphthylamine; AS–SW, 58% β-naphthylamine; AS–D, 32% acetyl-*o*-toluidine; AS–TR, 36% 5-chloro-*o*-toluidine; AS–RL, 36% *p*-anisidine; AS–OL, 40% *o*-anisidine. With the modified apparatus the yields were:—AS, 83% acetanilide; AS–D, 85% acetyl-*o*-toluidine; AS–RL, 49% acetyl-*p*-anisidine; AS–BR, 2% diacetyldianisidine. 1-Amino-derivatives of β-hydroxynaphthoic-arylamides, obtained by reducing the azo derivatives of the latter, also afford the corresponding arylamines when heated with soda lime. Thus, with the modified apparatus, amino-Naphtol AS, amino-Brenthol PA and amino-Naphtol AS–SW yielded respectively, acetanilide (90%), acetyl-*p*-anisidine (56%) and β-naphthylamine (88%). A. O. J.

Inorganic

Electrographic Detection of Metals. M. S. Hunter, J. R. Churchill and R. B. Mears. (*Metal Progress*, 1942, **42**, 1070–1076.)—The metals present at a metallic surface or the nature of inclusions present in it may be detected by a method consisting in (1) placing a piece of gelatin-coated paper saturated with a selected electrolyte on a suitable metallic block (the cathode), (2) pressing the specimen to be tested into close contact with the gelatin surface, (3) applying current with the specimen anodic, *e.g.*, 0·05 amp. per sq.cm. for 30 sec. or more, causing metal to be dissolved and absorbed in the paper, (4) washing the paper to remove excess electrolyte, (5) applying reagents ("developers") for the detection of metals, different reagents, if necessary, being applied to different parts of the print (see accompanying table). The following inclusions artificially embedded in metallic surfaces were readily detected: iron inclusions in copper, lead, zinc and magnesium (ferricyanide test), copper in lead, zinc and magnesium (benzoinoxime test), lead inclusions in copper, zinc and magnesium (chromate test) and nickel inclusions in copper, lead, zinc and magnesium (dimethylglyoxime test). Confirmatory results were obtained with naturally occurring inclusions. The method can be used in examination of the porosity of metallic coatings and in the identification of alloys. Thus duralumin could be distinguished from commercial aluminium by applying the test for copper, and molybdenum in 18 : 8 : 1 chromium : nickel : molybdenum steel was detectable. From tests on the sensitivity of the method, smaller proportions of alloying elements than the following could not be detected with certainty: 2% of copper in aluminium-copper alloys, 1% of iron in aluminium-iron alloys, 0·25% of chromium in aluminium-magnesium-chromium alloys, 0·5% of lead or 0·5% of bismuth in aluminium-copper-lead-bismuth alloys. S. G. C.

List of Electrographic Tests

Element sought	Electrolyte	Developer	Colour	Interfering elements
Bismuth	5% KNO_3	10% KI	Orange	Lead
Cadmium	5% KCN acidified with H_2SO_4	H_2S gas	Yellow ppt.	Those forming black sulphides
Chromium	5% K_2SO_4 or 5% KNO_3	3% H_2O_2	Yellow, changing to violet in developer	
Cobalt	5% NaF	Sat. acetonic KCNS	Blue	Copper or nickel in very large quantity
Copper	5% Rochelle salt or 5% KNO_3	5% ammoniacal benzoinoxime in alcohol	Green	
	5% KNO_3	0·5% rubeanic acid in alcohol	Black	
	5% KNO_3	NH_3 gas	Blue	
	5% KNO_3	5% $K_4Fe(CN)_6$	Red	
Iron	5% KNO_3	5% $K_4Fe(CN)_6$	Blue	
	5% K_2SO_4 or 5% KNO_3	5% $K_3Fe(CN)_6$	Blue	Chromium
	5% KNO_3	5% KCNS	Red	
Lead	5% KNO_3	1% K_2CrO_4 in *N* CH_3COOH	Yellow	Silver
	5% KNO_3	10% KI	Yellow	Bismuth
Molybdenum	5% K_2SO_4 or 5% KNO_3	Saturated soln. of potassium ethyl xanthate in 5% H_2SO_4	Purple	
Nickel	5% KNO_3	1% dimethylglyoxime in conc. NH_4OH	Scarlet	Iron, cobalt
Silver	5% K_2SO_4	K_2CrO_4	Brick red	

Detection of Gold in Plating. M. Lerner. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 416.)—The U.S.A. Tariff Act, 1930, prescribed different rates of duty for plated and unplated articles. Previous methods for the electrographic detection of gold without material injury to the surface have either failed to reveal gold in very thin "flash" plates or have not distinguished sharply between gold and other metals (*e.g.*, Yagoda's privately communicated method of electrolysing with 1% sodium chloride soln. and applying a spot test with stannous chloride). For the past 9 months the U.S. Customs Laboratory have used the following method. Use three No. 6 dry cells (approx. 4·5 volts) connected in series, and connect a small clamp with the anode and a piece of platinum wire (B. & S. gauge 18)

with the cathode. For the test soln., add *ca.* 10 g of stannous chloride to 100 ml of dil. (1 : 9) sulphuric acid, ignoring the formation of any ppt. To prevent oxidation, add a fragment of metallic tin. Attach the anode clamp to the article after removal of any lacquer. Moisten a piece of absorbent filter-paper with a drop of the test soln. and place it against the surface of the article. Press the platinum cathode against the moist paper; if there is any doubt whether a closed circuit has been obtained, a milliameter may be inserted in the circuit. In presence of gold a purple-brown stain will be formed on the paper. If the article contains silver, the test should not be made in direct sunlight or be continued too long in diffused light. Negative results were obtained with about 40 common metals and alloys, but chromium gave a light yellow, and cobalt a very light pink colour. The method gives excellent results with the usual 10-, 14-, and 18-carat jewellery.

Determination of Tetraethyllead in Gasoline. L. Schwartz. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 499–501.)—Dissolve 78 g of potassium chlorate in 550 ml of strong nitric acid by vigorous shaking in a stoppered 1000-ml measuring cylinder. When the salt has nearly dissolved, add 540 ml of water and shake until solution is complete. Evaporate a soln. of 0·1 g of copper in nitric acid to a syrup and dissolve this in the above mixture. To 100 ml of gasoline in a 500-ml separator add 15 ml of acid chlorate soln., shake gently at first with frequent pressure release, then vigorously for 3 min. until the gasoline layer is perfectly clear. Allow to settle for 1 min., draw off the lower layer into a 500-ml conical flask, and repeat the extraction twice, shaking for 1 min. Evaporate the combined extracts just to crystallisation, not to complete dryness, boil with 100 ml of hot water, cool a little, add a slight excess of ammonia, acidify with acetic acid (1 ml excess), boil and add 10 ml of 5% potassium dichromate soln. Set aside on a hot plate for 7 min., filter through a Gooch crucible, and wash the ppt. well with hot water, then with acetone (3 washes) and ether (once). Dry at 100° C., cool and weigh as $PbCrO_4$.

W. R. S.

Analysis of Cuprous Oxide Pigments. I. Baker and R. S. Gibbs. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 505–508.)—All the solns. and the water used must be saturated with carbon dioxide, and all the operations must take place in carbon dioxide under complete exclusion of air. Weigh 1 g of pigment into a separator containing 10 ml of C.P. acetone and some glass beads. Shake well for 1 min., refill with carbon dioxide, add 20 ml of hydrochloric acid (1 : 9) and 10 ml of 3% hydrazine sulphate soln., and shake gently for 1 min. Add 75 ml of 10% potassium chloride soln., refill with carbon dioxide, shake strongly for 15 sec., and filter through a 12·5 cm 41-H Whatman filter. Drain completely, wash once with 30 ml of 10%, once with 30 ml of 5% potassium chloride soln., and finally with water, keeping the liquid covered with carbon dioxide. Transfer filter and residue to a 250–ml conical flask, add 15 ml of 15% ferric chloride soln. in hydrochloric acid (1 : 3) and 15 ml of hydrochloric acid (1 : 9), warm gently to dissolve copper and cupric oxide; cool under carbon dioxide, add 2 drops of ferroin (*o*-phenanthroline ferrous complex) and titrate at once with 0·1 *N* ceric sulphate (1 ml ≡ 0·003179 g. Cu) to pale green and back to orange with 0·03 *N* ferrous ammonium sulphate. Calculate to metallic copper.

For the determination of total reducing power weigh 0·2 g into a 250-ml glass-stoppered conical flask, provided with a vent, add some glass beads and 10 ml of the ferric chloride soln., heat gently with occasional stirring for 15 min. When solution is complete, cool and titrate at once with 0·01 *N* ceric sulphate soln., as before (1 ml ≡ 0·007157 g Cu_2O). The total reducing power, less metallic copper × 2·252, gives Cu_2O. Total copper is determined by electrolysis, and cupric oxide is computed by difference. W. R. S.

Determination of Tin Coating on Tin Plate. G. H. Bendix, W. C. Stammer and A. H. Carle. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 501–504.)—A 4-sq.in. plate, forming the anode, is suspended from an electromagnet between two carbon cathodes contained in porous cylinders filled with dil. hydrochloric acid. The electrodes are immersed in a 400-ml beaker containing dil. hydrochloric acid and a known excess of iodate-iodide soln. After 2-5 min. electrolysis at 3 amp. the excess of iodine is titrated with thiosulphate. For constructional and other details consult the original. W. R. S.

Identification of Rust on Iron and Steel. R. O. Clark. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 464–465.)—Gelatin-coated paper moistened with water will remove from metallic surfaces sufficient iron rust for testing without affecting the metal itself. To prepare the gelatin paper, unexposed glossy photographic paper is fixed in 20% sodium thiosulphate soln., washed in water for 30 min., immersed in hypo-eliminator for 6 min., washed in water for 10 min. and dried. The hypo-eliminator (Kodak formula HE-1) is prepared by mixing 500 ml of water with 125 ml of 3% hydrogen peroxide soln. and 100 ml of 3% ammonium hydroxide and diluting the mixture to 1 litre. To make the test, slightly moisten the gelatin-coated surface of the paper with water and press it firmly against the surface of the specimen. After 15–30 sec. (continuous pressure is not necessary) remove the paper, avoiding the stripping of the gelatin from the paper base and moistening the back of the paper if necessary. Develop the paper in 10% hydrochloric acid containing 0·05% of potassium ferrocyanide. A Prussian blue pattern of the rusted surface is obtained. Development of impressions from freshly rusted surfaces should be short (10–15 sec.); impressions from old or worn rust require *ca.* 1 min. The pattern is usually more distinct if the paper is dried with heat. The test appears to be specific for iron oxide, and attempts to remove sulphide films from lead and copper surfaces by this method were not successful.

A. O. J.

Determination of Aluminium with Phenylhydrazine. W. C. de Moraes Bastos. (*Nat. Inst. Technology*, Rio de Janeiro, 1942, pp. 54, in Portuguese.)—Hess and Campbell's method (*J. Amer. Chem. Soc.*, 1899, **21**, 776) is applied to the determination of aluminium in manganese ores. Treat the chloride or sulphate soln. (200–300 ml) with 10 ml of strong hydrochloric acid, then with ammonia until the ppt. re-dissolves slowly, and lastly with strong ammonium bisulphite soln., drop by drop, until decolorisation occurs. Heat to boiling, cool, and add 0·5 ml of phenylhydrazine; if the soln. remains clear, add ammonia drop by drop until a ppt. forms, and then a further 0·5 ml of

reagent; otherwise simply add the additional 0·5 ml of reagent. Heat to boiling, filter at once through loose-textured paper, wash with hot neutralised 5% ammonium chloride soln., then with hot alcohol to remove excess of reagent, and again with ammonium chloride soln. Dissolve the ppt. in 20 ml of hydrochloric acid (1 : 1), neutralise as before with ammonia, add a few drops of bisulphite soln., 0·5 ml of phenylhydrazine, and ammonia dropwise until a ppt. forms. Boil, filter at once and wash as before. Ignite strongly to constant weight and weigh the Al_2O_3. The process separates aluminium from iron, manganese, calcium, magnesium, zinc, nickel, cobalt, and copper. Chromium interferes. W. R. S.

Separation of Zirconium and Hafnium. E. M. Larsen, W. C. Fernelius and L. L. Quill. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 512–515).—Cyrtolite (an altered zircon) was crushed to less than 200-mesh size and heated with an equal weight of strong sulphuric acid to 220° C. until the mixture thickened. The cooled mass was stirred into water, and settling was promoted by addition of glue soln. The residue was filtered off and washed with water; the filtrate and dilute phosphoric acid were sprayed simultaneously into 10% sulphuric acid at 75° C. to form a dense ppt. which could be filtered off and washed. The suspension of the mixed phosphates was treated with a cold soln. of sodium hydroxide and peroxide, giving the mixed acid-soluble hydroxides. The fractionation was carried out by ppting *ca.* 55% of the total oxides as phosphates. Seven fractionations raised the hafnia content of the product from 13 to 93%. Treatment of the soluble fractions by the same process gave a final zirconia fraction spectrographically free from hafnium. W. R. S.

Determination of Sodium in Presence of Molybdenum. C. H. Hale. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 516–517.)—The interference of molybdate in the pptn. of the sodium zinc uranyl triple salt, by formation of a ppt. of uranyl molybdate, is overcome by complex formation with an organic acid. Evaporate the slightly acid sulphate soln. to 10 ml or less without separation of crystals and add one drop of nitric acid, and 0·2 ml of 50% tartaric or citric acid soln. per 0·1 g of MoO_3 present. Filter a tenfold excess of zinc uranyl acetate reagent into the test soln., with vigorous stirring. Set aside for an hour at 20° C., collect the ppt. in a tared filtering crucible, wash 5–10 times with 95% ethyl alcohol saturated with the reagent and twice with ether or acetone. Dry in a desiccator for 10 min. and weigh. Na_2O factor, 0·0202. Subtract the blank result. W. R. S.

Preparation of Phosphomolybdic Acid from Phosphoric Acid and Pure Molybdic Acid. A. Linz. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 459.)—Methods given in the literature for the preparation of phosphomolybdic acid are intricate and indirect, but the reagent can be prepared directly from pure molybdic oxide and phosphoric acid. The method is applicable also to the preparation of phosphotungstic acid from tungstic oxide, and, by changing the molecular proportions, any one of the heteropoly-acids of phosphorus and molybdenum or tungsten can be prepared. To 144 g (1 mole) of pure molybdic oxide add 9·61 g (1/12 mole) of 85% phosphoric acid (U.S.P.) and enough water to make the total vol. *ca.* 1·5 litres. Boil the milk-like liquid (which soon turns yellow) for 3 hr., leave for 2 min., filter, and wash the residue of undissolved molybdic oxide with 50 ml of water. The wt. of dried residue will show that 116·4 g of molybdic oxide have been dissolved. Concentrate the deep yellow filtrate to *ca.* 100 ml (b.p. 106° C.) and allow the liquid to crystallise overnight. Collect the crystals on filter paper, without washing, and dry somewhat. The damp crystals weigh 130 g when dried at room temp. *in vacuo*, and the final wt. is 111·7 g. The mother liquor (18 ml) contains 10–15 g of phosphomolybdic acid. A. O. J.

Microchemical

Micro-diffusion Methods. Blood Glucose. E. O'Malley, E. J. Conway and O. Fitzgerald. (*Biochem. J.*, 1943, **37**, 278–281.)—The method depends on the measurement, by the micro-diffusion technique, of the carbon dioxide evolved from blood glucose through the action of yeast. Put 1·5 ml of yeast suspension (10 g in 100 ml of tap water left for one day at room temp. and then placed in the refrigerator) into the inner chambers of several micro-diffusion units (No. 1 size). Put 0·1 ml samples of the blood into the outer chambers of four No. 2 micro-duffusion units and put 0·1 ml of water into another two of these units. To all of these, except two of the four units containing blood, add 0·5 ml of 0·05 *N* hydrochloric acid containing 4% of ethyl alcohol, and to the two remaining units add 0·5 ml of 0·05 *N* hydrochloric acid containing 4% of ethyl alcohol and 0·04% of glucose. Approx. 10 min. later transfer, by means of a pipette, 0·2 ml of approx. 0·05 *N* barium hydroxide containing 5% of B.D.H. Universal indicator into the inner chamber of each small unit and immediately close each unit by a lid smeared with tragacanth fixative. Transfer 0·2 ml of the yeast suspension from the larger units to the outer chambers of the smaller units. Close the units and mix the contents of the outer chamber by rotation. After 90 min. at room temp., titrate the contents of the central chamber with 0·02 *N* hydrochloric acid from a horizontal burette to *p*H 7·5–8·0. The method gave results agreeing well with those obtained by the usual procedure, but, on the whole, slightly lower. F. A. R.

Estimation of Phosphorus by the Molybdenum Blue Method. W. I. M. Holman. (*Biochem. J.*, 1943, **37**, 256–259.)—Transfer a sample containing 1–100μg of phosphorus to a 10-ml volumetric flask, add phenolphthalein and neutralise with either 0·1 *N* sodium hydroxide or 0·1 *N* hydrochloric acid. Dilute to exactly 5 ml and add, in the following order, 1 ml of 10 *N* sulphuric acid, 1 ml of 2·5% ammonium molybdate soln. and 1 ml of 20% potassium iodide soln. containing 0·5% of sodium carbonate. Immerse in a boiling water-bath for 15 min. and then cool and add 0·5% sodium sulphite soln. from a burette, 0·1 ml at a time, mixing after each addition, until all the liberated iodine has been removed and the soln. is a pure blue. Add 0·2 ml of sulphite soln. in excess and dilute to 10 ml. Measure the colour by means of a photoelectric absorptiometer using the red filters (No. 1), or a visual colorimeter. With the former a blank should be prepared from distilled water treated in the same way as the test soln. The colour formed by reduction in this way is stable for at least 24 hrs. With a Spekker photoelectric absorptiometer results within the range of 3–100μg

of phosphorus were accurate to within 2%, and almost equally good results were obtained with a visual colorimeter when the test soln. was matched against a standard which did not differ from it by more than 30%. F. A. R.

Microscopic Identification of Ferrous Sulphate in Mixtures. G. L. Keenan and W. V. Eisenberg. (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 256–257.)—Drug and veterinary preparations of granular character frequently contain partly dried and oxidised ferrous sulphate, many of the crystals appearing under the microscope as small, brown, 8-sided forms resembling octahedra, which, in the monoclinic system, would be termed bipyramids. Normally, ferrous sulphate crystallises with $7H_2O$ in the monoclinic system, with the following refractive indices, $n_\alpha = 1{\cdot}471$, $n_\beta = 1{\cdot}478$, $n_\gamma = 1{\cdot}486$. In the mixtures mentioned above, however, the partly dried and oxidised salt may often be characterised by the indices 1·525 and 1·539, being the min. and max. values for crystal fragments showing the max. amount of double refraction with crossed nicols (parallel polarised light). These data at once suggest the presence of ferrous sulphate. For confirmation, recrystallise the partly dried material from a drop of water on a microscope slide and determine the refractive indices, which should be those of the heptahydrate.

Micro-method for the Determination of Free Sulphur Dioxide, Sulphites and Organic Compounds of Sulphur Dioxide in Presence of one another. C. F. B. Stevens. (*Paper Trade J.*, 1943, **117**, Aug. 5, *T.A.P.P.I. Sect.* 61–66.)—The method was evolved primarily to distinguish between the 3 different types of active sulphur present in pulp and paper, since the official T.A.P.P.I. method does not do so. The active sulphur content affords a measure of the extent to which a paper will develop a stain or tarnishing effects when it comes into contact with metallic objects. Disintegrate the sample (*e.g.*, 1 g of paper) with 100 ml of hot water by means of a high-speed stirrer in a flask, heat to b.p., and pass in carbon dioxide (1–2 bubbles per sec.) which is generated from acid and sodium carbonate and washed successively in sat. potassium permanganate soln. and water. The free sulphur dioxide is carried over through a nozzle into the base of a vertical column containing small aluminium helices (which have been activated by 2 ml of a soln., containing 10% each of ferrous chloride and aluminium chloride [$6H_2O$], and then covered with hot water), and to which 50% hydrochloric acid is added (from a funnel at the top). Hydrogen sulphide is thus formed by catalytic reduction, and is determined from the colour produced on a lead acetate paper through which it is carried in the stream of carbon dioxide. When the lead acetate paper no longer darkens, insert a new paper, and add 50 ml of 50% hydrochloric acid to the flask containing the sample, to liberate the sulphur dioxide from the sulphites present. When no more gas is evolved, disconnect the reducing column, stop the stirrer, add 1 g of aluminium foil to the reaction flask and fit a clamp containing a lead acetate paper to the outlet of the flask itself. In this way, organic compounds of sulphur dioxide and elemental sulphur are reduced to hydrogen sulphide and determined as above. The stains on the 3 lead acetate papers are matched against standard stains produced from known vols. of a standard soln. of calcium sulphite (≡ 0·005 mg of sulphur per ml) which has been stabilised with brucine sulphate. The stain so obtained is double the intensity of that obtained by the standard T.A.P.P.I. test from the same wt. of sulphur compound. A special all-glass apparatus is described, one feature of which is a device for ensuring reaction between the sulphur dioxide and the aluminium as soon as the acid comes into contact with the latter; 5 ml of the 50% acid should be added to the reductor during every 15 min. that it is in operation. The acid should first have been purified by placing it in the apparatus and bubbling carbon dioxide through it until no further stain is obtained on the paper. A blank test should give *ca.* 0·0005 mg of sulphur. Results found for a rejected rotogravure paper, which gave a positive T.A.P.P.I. test reaction, were:—sulphur dioxide, 0·0005; calcium sulphite, 0·0007; organic sulphur dioxide compounds plus sulphur, 0·0005%. J. G.

Physical Methods, Apparatus, etc.

Recording Low Relief in Metallic Surfaces by Cellulose Acetate Moulds. A. T. J. Dollar. (*Nature*, 1943, **152**, 248.)—The mould is produced from a colourless or dyed dispersion of cellulose acetate in a mixture of 1 vol. of tetrachloroethane and 2 vols. of "Cerric Thinner T 10" (Cellon Ltd.), as follows. Clean the surface, wet it with some of the mixed solvent used for the above dispersion and, with the surface level, flow over it a layer of the dispersion 1·0–1·5 mm deep. After the solvent has evaporated (*e.g.*, in 12–18 hrs.) strip off the cellulose acetate film. The resulting mould is strong, very flexible, transparent, 0·1–0·2 mm thick, light, and insol. in water, cold conc. hydrofluoric acid, hot Canada balsam or xylol balsam; n_D^{20}, 1·49. If it is to be kept for reference purposes, a suitable plasticiser (*e.g.*, triphenyl phosphate or dimethyl phthalate) should be included in the dispersion to prevent shrinkage and loss of flexibility. The surface tested is not affected by the treatment, except that dust, and oxide or other loose films are removed. For comparison purposes, the moulds may be superposed and examined over an illuminated tracing desk, or special portions of them may be cut out, mounted in "cooked" Canada balsam, and examined under the microscope (×500) or by optical projection. Photographic reproductions may also be made, and good results were obtained with polished etched metallic surfaces on "Kodaline Slow Paper" (exposure 15 sec., at 30 in. from a 100-watt lamp). The method has also been used for studying slags, glasses, ceramic products and refractories; for recording the crystalline structures revealed by polishing and etching serial sections of ingots, ores and alloys; for the investigation of the effects of different types of mechanical working on the structures of metals. J. G.

Determination of the Specific Gravity of Dry Paint Pigments. I. Baker and G. Martin. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 279.)—Prepare a suitable sp.gr. tube by reducing a test-tube (diam., 3·5 cm) to a length of 7 cm, and punching, on the opposite sides, near the open end, 2 small holes through which a fine platinum or steel wire can be threaded to serve as a support for hanging the tube on a balance. Clean the tube and a stirring rod (which is slightly longer than the tube), wash them with alcohol, heat them and then cool them in a desiccator. Place the stirrer in the tube, and completely submerge the latter in a 600-ml beaker

containing kerosene at 25° C.; immerse the beaker in a bath at 25° C. Wipe the kerosene from the suspending wire, support the beaker on a "bridge" over the balance pan, and weigh the tube and stirrer when they have attained 25° C. Remove the tube, and weigh into it, by difference, 1·5–25 g of the paint pigment, which has previously been dried at 105° C. for 2 hr.; for pigments of low sp.gr. (*e.g.*, carbon black), normal sp.gr. (*e.g.*, the usual white pigments except white lead), and high sp.gr. (*e.g.*, white lead and red lead take *ca.* 1·5, 12 and 25 g, respectively. Wet the pigment completely with the kerosene, and then add sufficient to cover it with a 0·25-in. clear layer. Place the tube and its contents (including stirrer) in another beaker of kerosene and heat for 30 min. at 65–70° C. on a hot-plate, stirring frequently to remove occluded air; this produces a small change in the sp.gr. of the kerosene, but a negligible change in the final wt. of the pigment in the kerosene. Remove the tube from the bath, fill it with kerosene to within 0·25 in. of the top, and centrifuge at *ca.* 2000 r.p.m. for 30 min. Fill the tube with kerosene and replace it in the original 600-ml beaker in the bath at 25° C., and, when the temp. is constant throughout the system, weigh the tube again; the increase in wt. is the wt. of the pigment in kerosene, and the wt. of pigment in air (x) minus its wt. in kerosene in the wt. of kerosene displaced (y). Determine accurately the sp.gr. of the kerosene (z) at 25° C., and calculate that of the pigment from xz/y. The variations from the average were −0·003 to +0·007 and −0·002 to +0·002 for determinations on titanium oxide (sp.gr., 3·853-3·854) and titanium-calcium (sp.gr., 3·199 and 3·207) pigments, respectively. Errors involved in the usual pycnometer methods (*e.g.*, evaporation of liquid from glass joints, incomplete removal of surface-adsorbed air and condensation of moisture on the outside of the vessel) and the prolonged vacuum treatment necessary to eliminate occluded air, are avoided.

J. G.

Reviews

MATERIA MEDICA. By SIR WILLIAM HALE-WHITE, K.B.E., M.D., LL.D. Revised by A. H. DOUTHWAITE, M.D., F.R.C.P. 25th Ed. Pp. 502 + x. London: J. & A. Churchill, Ltd. 1942. Price 14s.

This book, familiar to successive generations of medical students for half a century and now in its 125th thousand, may well defy criticism and commendation alike; it is an institution.

After an introductory section of 38 pages, mainly concerned with pharmaceutical definitions and the principles of prescribing, Part I of the book, comprising 110 pages, follows, and is devoted to the discussion of "Substances used chiefly for their Local Action." Part II, which occupies most of the remaining pages, is concerned with "Substances used chiefly for their General Action." So far as it is possible, the items are classified in accordance with their therapeutic effects, Part I being divided into thirteen groups and Part II into thirty-two. Official drugs are marked "B.P." while the names of non-official substances which have been accorded recognition in the British Pharmaceutical Codex are followed by the letters "B.P.C." The general character of all Pharmacopoeial preparations is indicated, and the doses of these and of their parent substances are always given. These useful summaries are followed by clear, concise accounts of the therapeutic application, whence the book constitutes a handy ready reference of particular value to the analyst called upon to give evidence in court on matters concerning drugs. In this connection the list of Latin phrases commonly used in the writing of prescriptions is a helpful feature.

The sections devoted to the barbiturates, sulphonamides and hormones are particularly useful, since they go far towards elucidating the complexities occasioned by the existence of multitudes of closely allied drugs. Here, as throughout the work, much help is afforded the reader by the inclusion of trade names, but one would like to have seen hexobarbitone mentioned in the table on page 220 with an appropriate cross reference under "Evipan."

Some omissions might be expected in any survey of so swiftly advancing a subject as materia medica but, in fact, very little of importance has been overlooked. Perhaps one may be permitted to mention that gentian violet, besides being a useful antiseptic for the treatment of burns, is now being administered with considerable success in the form of enteric coated pills as an anthelmintic for oxyuriasis. Although numerous printing slips suggest somewhat hurried proof reading, it may be assumed for practical purposes that significant errors are absent, but a chemist might be pardoned for doubting the remark on page 176 that charcoal "oxidises colouring matters, and consequently decolorises them."

It is explained in the Preface that the Fifth Addendum to the B.P. appeared too late for inclusion in the main body of the work but the essentials of its monographs, which are almost solely directed towards economising materials in short supply, notably alcohol, are set out on page 477. Similarly, the list of authorised alternatives embodied in the Scarce Substances Order (S.R. & O., 1942, No. 709) could not be included. This is not altogether

to be regretted, since it avoids the necessity for repeating the misleading statement that a substitute for spirit of nitrous ether can be made by diluting one part of concentrated solution of ethyl nitrite (Fifth Addendum) with seven volumes of water!

N. L. ALLPORT

ANNUAL REPORTS OF THE PROGRESS OF CHEMISTRY FOR 1942. Vol. XXXIX. Pp. 257. Published by The Chemical Society, London. 1943. Price 15s. (to Fellows 8s. 6d.).

Owing to paper shortage the Reports on Analytical Chemistry and Radioactivity are held over until next year, so that this volume comprises the Reports on General and Physical Chemistry, Inorganic Chemistry, Crystallography, Organic Chemistry and Biochemistry. Absence of the Analytical Chemistry Report should not deter the analytical chemist from perusal of this volume, in which he will find much of interest and of possible application to his own problems.

To the food analyst and the agricultural analyst the section on Nutrition in the Biochemistry Report will have special interest. The author of this section has decided that the time is ripe for a review of advances in knowledge of the inorganic "trace elements," which are of importance to animal and plant life. These comprise essential trace elements having a clearly defined function in the living organism, abnormal trace elements causing damage to the organism, and trace elements consistently occurring in the organism but for which no function has yet been discovered. The diseases of farm animals resulting from deficiency of the essential trace elements are enumerated, and the section concludes with an account of the trace elements that are toxic to farm animals. The food chemist will find the short section of this report dealing with Dehydrated Foods of considerable interest. The procedure adopted to inactivate ascorbic oxidase and thereby preserve vitamin C in the dehydration of cabbage is described, and it is shown that dried food can now be prepared with its full complement of vitamins and with its protein-value and palatability unimpaired.

In the Organic Chemistry Report reference is made to the estimation of water, alcohols, carboxylic acids and acid anhydrides by means of the Karl Fischer reagent, and this report contains a complete and interesting account of the use of boron fluoride as a catalyst in organic reactions.

Among other topics discussed in detail are the Physical Chemistry of Rubber Solutions, the Physical Chemistry of Latent-Image Formation in Photographic Emulsions, the Lignin Problem, Luminescence of Inorganic Solids and the Application of Modern Technique in Inorganic Chemistry. There is much general information in each report and such incidental matter as the chemical identity of Prussian Blue and Turnbull's Blue, the constitution of Hyperol and a description of a novel form of chromatogram.

Each report is fully documented and the style and binding of the volume are uniform with those of previous volumes.

A. O. JONES

FOOD POISONING. By ELLIOTT B. DEWBERRY, F.R.S.I. Pp. viii + 186, with 44 photographic illustrations. London: Leonard Hill, Ltd. 1943. Price 15s.

A very considerable literature has grown up around the subject of food poisoning; some of it is to be found in text books, some in monographs and much of it is scattered in scientific journals. The author has collected his material from all these sources and presented it in one handy volume which affords intensely interesting and instructive reading.

The book is divided into three parts and appendixes. Part I gives a historical sketch of the development of our knowledge of bacterial food poisoning and deals with causation, toxin production, clinical features, incubation period, symptoms and mortality, possible sources and modes of infection, and methods of prevention and control. Part II deals with contamination of food by poisonous metals, with poisonous plants, fungi, and fish, and with food allergy. Part III, to which no less than eight chapters are devoted, deals very fully with botulism, and is perhaps the most interesting section of the book. One Appendix deals with contamination (and decontamination) of food by war gases, and a second quotes the Ministry of Health, Memo 188/Med. on steps to be taken by Medical Officers of Health in suspected food-poisoning cases which includes Appendix I, Headings of Inquiry, and Appendix II, The Identification of Salmonella Types. Finally, there is an author and a general index and a bibliography.

It is evident that the author has read his subject very widely and has studied it for many years, for he displays remarkable familiarity with all its aspects. He gives numerous references to the work of Scott, Bruce White, Jordan, Tanner, Topley, Wilson, Savage (from whose writings he frequently quotes) and many other investigators, and to the Reports of the Chief Medical Officer, Ministry of Health. Many illustrative outbreaks of food poisoning are well described. He is particularly in his own element in the chapter on Prevention and Control of Food Poisoning, dealing with slaughter houses, supervision of meat foods, the importance of ante-mortem examinations, made-up foods, milk-borne infections, ice-cream, duck's eggs, rat viruses and canned foods. Here, too, are to be found the interesting results of the investigation of Leslie (1942), in which it was shown that in the six principal viruses—Liverpool, Danzig, London, Ready Rat Relief, Institut Pasteur and Ratin, the active agent is in every instance *S. enteritidis* (Gaertner).

The attractiveness of the volume is much enhanced by its photographic illustrations, which include photographs of pioneers and investigators in this work; that of Sir William Savage is particularly pleasing.

There is little to criticise, but one might suggest that the historical sketch could be a little more chronological, and attention might be called to one or two slips resulting in an inconsistent statement; one on page 95, where 1891 would appear to be later than 1926, and the other on p. 130, where a Gram-positive organism is said to "decolourise rapidly with alcohol," and it is questionable whether the word "prophylactic" on p. 142, line 36, should not be "curative." These are small matters, however, and in no way detract from the value of the volume, for this is an excellent book, abounding in scientific record and expert opinion. It will prove of great interest and very helpful to all who are concerned with food poisoning, and provides a ready means of reference to practically all the important work that has been done. The author is to be warmly congratulated, and the publisher merits a big share of praise; for the paper and binding are wonderfully good for war-time production, the type is clear and the illustrations are excellent.

D. R. WOOD

Papers for Publication in THE ANALYST

THE Editor welcomes Papers and Notes for insertion in THE ANALYST, whether from members of the Society or non-members. They are submitted to the Publication Committee, who decide on their suitability for insertion or otherwise.

Authors and prospective authors are reminded that, owing to the paper shortage, all contributions to the journal must be condensed as far as possible.

The Publication Committee have recently issued a circular containing Advice to Authors on the writing of Papers for THE ANALYST. This can be obtained on application to the Secretary, Society of Public Analysts and Other Analytical Chemists, 7–8, Idol Lane, London, E.C.3. All Papers submitted will be expected to conform to the recommendations there laid down and any that do not may be returned for amendment or rejected.

Special Notice

SPOT-TESTS FOR THE IDENTIFICATION OF CERTAIN METALLIC COATINGS AND CERTAIN METALS IN BULK

By B. S. EVANS, M.C., M.B.E., D.Sc., F.I.C., and D. G. HIGGS

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