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Obituary

SAMUEL ALLINSON WOODHEAD

DR. S. ALLINSON WOODHEAD died, in his 71st year, at his home at Barcombe, Sussex, on April 4th, 1943, following an operation and an illness lasting about six months.

Woodhead was the son of the late Mr. and Mrs. S. Woodhead of Stainton, and began his career as a pupil teacher in Stainton School, where his father was headmaster. After passing the scholarship examination he entered Durham College of Science, later Armstrong College (now King's College), Newcastle, where he obtained the B.Sc. degree. Leaving college some 45 years ago, he went to the Uckfield Agricultural College (one of the pioneer agricultural colleges of the country) as lecturer in chemistry and later became Principal. The excellence of his work during that period is proved by the high respect in which he was held by all his old students. In those days, agricultural education was most difficult. Pioneers such as Woodhead had to overcome prejudice among farmers and to gain their confidence, and it can be said of him that no one in his special line did more than he. In the County of Sussex it was regarded as a heavy loss to agricultural education when he turned his great abilities to analytical work. While still at Uckfield he proceeded to M.Sc., and a few years later, after leaving the Agricultural College, was awarded the D.Sc., conferred on him for his work on the determination of some of the constituents of milk. Woodhead was elected a member of our Society in 1899 and was a member of Council in 1911–1912. In 1900 he became a Fellow of the Institute of Chemistry.

Uckfield Agricultural College was closed owing to the 1914–1918 war, and it was at this time that he started his practice at Lewes as a consulting analyst and bacteriologist. He was Public Analyst and Official Agricultural Analyst for the Counties of East and West Sussex, the County Boroughs of Brighton and Eastbourne and the Boroughs of Hove and Worthing. He was also analyst to various water companies and a gas examiner for East Sussex County Council and Surrey County Council.

Between 1926 and 1938 he frequently acted as examiner in chemistry and bacteriology and dairy chemistry for the Royal Agricultural Society of England and for the Highland and Agricultural Society of Scotland in their examinations for the N.D.A. and N.D.D. This activity he regarded as a holiday, and he gave to it in fact the only time he would take away from his laboratory.

No description of him would be complete without stressing the love he had for the "living sciences", as he was wont to call them. He encouraged all to develop an interest in the study of plants and animals. The members of his laboratory staff and, indeed, all who knew him feel a deep sense of personal loss; they realise that a true friend has been taken from them.

He was a deeply religious man and one whose every action was governed by his Christian beliefs. His character can probably best be described in the words of a tribute paid to his memory by the Director of Agriculture for East Sussex:

> "Not only was he a most able man but he was a really 'great' man. There was nothing petty or intriguing in Dr. Woodhead's character—he was far too big a man for that. He always gave me every possible assistance when I consulted him on things which sometimes were outside the scope of his work as an analyst, but that assistance he always most ungrudgingly gave. Men such as Dr. Woodhead are very rare."

REGINALD F. WRIGHT

Determination of Fluorine in Wool treated with Fluorides

By F. F. ELSWORTH, Ph.D., A.I.C., and J. BARRITT, B.Sc., A.R.C.S., A.I.C.

(*Read at the Meeting, April 7, 1943*).

Fluorides are toxic to Clothes-moth and carpet beetle larvae, and impregnation of keratinous materials, *e.g.*, wool, hair and feathers, with solns. of organic and inorganic fluorides is a well-known method of rendering these materials indigestible to, and hence immune from attack by, pests of this type; the method is covered by numerous patents.[1] Also fluorides, particularly sodium and ammonium silicofluoride, are the active constituents of a number of proprietary moth-proofing agents at present on the market. The treatment is most successful when the materials are not required to undergo further wet-processing or household washing during the period of protection, *e.g.*, hosiery liable to prolonged storage after manufacture, stuffing materials, furnishings and dress suitings.

The method usually adopted for testing the efficiency of moth-proofing agents consists in bringing the treated material into contact with a number of vigorous young moth-larvae (Clothes-moths or Casemakers, the former being preferable), which have no other source of food, storing under suitable conditions and examining at intervals; a useful technique is that described by Stiteler.[2] The moth-proofing is assessed by (1) the damage suffered by the sample, (2) the effect on the larvae, and (3) the quantity of excrement present. This method, which gives clear-cut results for adequately proofed and unproofed materials and reasonably reproducible results for intermediate degrees of proofing, is unfortunately lengthy, 14–30 days being necessary for a satisfactory test. By examining the resistance to moth-larvae of samples of wool containing different amounts of fluorine, we in collaboration with R. S. Hartley (in the press) have shown that materials containing *ca.* 0·2% of fluorine are satisfactorily immune from attack. Thus the fluorine content of the material is a useful indication of the degree of moth-proofing, and by using the method described below for the determination of fluorine in wool it has been found possible to assess the moth-resistant properties of yarns and fabrics treated with inorganic fluorides in a comparatively short time and to eliminate much testing with moth-larvae.

Review of Methods.—For the determination of micro-quantities of fluorine in biological material it is necessary to ash the sample and then to recover the fluorine, usually as fluosilicic acid, by distillation with a non-volatile acid. In the method originally described by Willard and Winter,[3] the ashed material is distilled with perchloric acid at 135° C., and the fluorine in the distillate is estimated by titration with thorium nitrate in 50% ethanol, zirconium alizarin sulphonate being used as indicator. This method, with numerous modifications, has since been widely used for the determination of fluorine in foods, rocks and water. A study of the literature, which is too extensive to be reviewed here in detail, indicates that the principal factors which have caused difficulty in the use of the method are: (1) loss of fluorine by volatilisation during ashing, (2) interference with the fluorine estimation by the distilling acid (which cannot be completely prevented from passing into the distillate) and (3) the determination of the optimum conditions for the estimation of fluorine in the distillate.

(1) *Ashing.*—A considerable loss of fluorine was reported by Hoskins and Ferris[4] when ashing the sample at 800° C. for even a short time. Rempel,[5] ashing sodium fluoride in presence of sodium carbonate, observed a considerable loss at 500° C., and at 800° C. only a trace of fluorine remained. Calcium oxide and magnesium oxide and acetate have been used by several workers[6,7,8,9] as fixatives for fluorine during ashing, and Rempel,[5] ashing in presence of calcium oxide or wine ash (which contained calcium and magnesium oxides), showed that no loss of fluorine occurred up to 600° C. We have ashed the samples below red heat in presence of excess sodium carbonate (to neutralise any residual acid in the wool) without any addition of calcium or magnesium, and have extracted the ash with water to separate any traces of carbon remaining and other insoluble matter; the recoveries of fluorine added to wool as sodium and chromium fluorides were satisfactory. As an additional check on the ashing method, 2 mg of fluorine as sodium fluoride were heated in presence of sodium carbonate at the temp. used for ashing the wool samples; 1·94 and 2·00 mg were recovered in duplicate expts., showing that, in absence of wool, no substantial loss of fluorine occurred under the ashing conditions employed. Calcium,

derived from waters or from lime used in pulling wool from hides, is normally present as sulphate, carbonate or calcium soap in all processed wool. The calcium in the cloth used in the recovery expts. was 0·06% (on the weight of wool), and did not interfere with the recovery of the fluorine by the technique described.

(2) *Distillation.*—For the distillation of fluorine as fluosilicic acid, sulphuric and perchloric acids have been used, and the temperature in the distilling flask has varied from 125° to 150° C., leading to a wide variation in the amount of sulphuric or perchloric acid in the distillate. The majority of workers have used perchloric acid, probably because it has a less adverse effect in the fluorine titration than an equiv. amount of sulphuric acid.[4,8,10] Van der Merwe[11] by maintaining the distillation temp. at 130° C., was able to restrict the total acidity of 200 ml of distillate to 3 ml of $N/100$ acid. We have found 130° C. to be too low for complete recovery of fluorine, but at 135–140° C. adequate recovery of fluorine in amounts up to 1·5 mg was obtained in 200 ml distillate, the total acidity of which did not exceed 15 ml of $N/100$ acid. This amount of acid is of the same order as that reported by Dahle, Bonnar and Wichmann,[13] and does not interfere with the subsequent determination of fluorine.

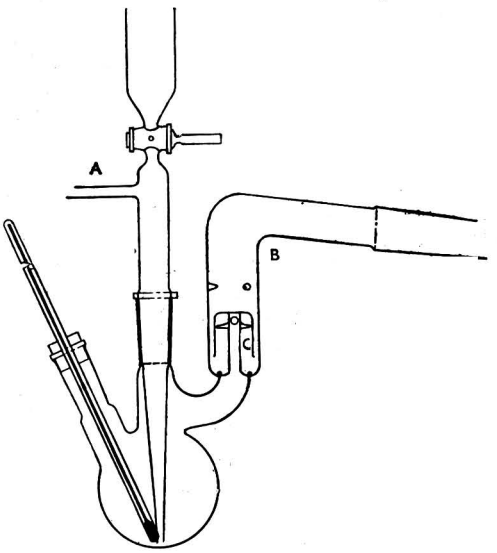

Fig. 1

(3) *Determination of fluorine in the distillate.*—The original technique of Willard and Winter[3] has been modified by many workers, the chief features that have been examined being the nature and concn. of the indicator, the nature of the medium, *i.e.*, whether aqueous or 50% ethanol, and its *p*H, and finally the influence of salts, *e.g.*, chlorides, sulphates and perchlorates. The method used by us is substantially the same as the back-titration method originally suggested by Dahle *et al.*,[12,13] and later used by Van der Merwe,[11] which depends upon the bleaching of thorium-alizarin lake through preferential formation of thorium fluoride. In this method the total acidity of the aqueous test soln. is adjusted to 2 ml of $N/20$ acid per 50 ml (*p*H 2·7), the perchloric acid present in the distillate (determined on a separate aliquot portion) being used to contribute to this acidity, thus preventing neutralisation of the distillate and avoiding the effect of sodium perchlorate.

PROCEDURE.—Completely moisten 0·5–5 g of wool (containing 0·25–5·0 mg of fluorine) with 10 ml of $N/2$ sodium carbonate in a platinum dish or crucible. Dry and ash in a muffle below red heat. Ashing is assisted if, after charring, the residue is moistened with water and dried and the ashing is continued; it is complete in *ca.* 1 hr. Extract the residue with water, filter and make up to 50 ml.

The distillation unit comprises a 50-ml distilling flask (see Fig. 1) of a modified Claisen pattern. The side-tube (A) permits the introduction of steam from a boiler. The side-neck (B), which contains an anti-splash device (C), is connected to a Liebig condenser, the distillate being collected in a 250-ml conical flask by means of an adaptor which dips below the level of the liquid in the flask. The distilling flask rests in a hole (diam. 1¾ in.) in a 6-in. square of cement-asbestos board, and is heated by means of a micro-burner; this prevents direct heating of the flask above the level of the liquid.

Introduce a suitable aliquot portion (5, or 10 ml containing 0·10–1·50 mg of fluorine) of the aqueous extract from the ash into the distilling flask and add 0·01 g of silica and 3 glass beads (diam. 0·2 in.); if a larger portion is used, preliminary boiling down is necessary. Add 10 ml of 60% perchloric acid through the tap funnel and steam-distil, maintaining the temp. at 135–140° C. by regulation of the micro-burner and the steam flow. Collect 200 ml of distillate (about 1¼ hr.) and make up to 250 ml.

Titrate 10 ml of the distillate with $N/100$ sodium hydroxide, using 0·01% sodium alizarin sulphonate in a sat. soln. of 1,2,5,8-tetrahydroxyanthraquinone[3,11] as indicator.

To a second portion of distillate (containing preferably 10–20μg of fluorine) in a Nessler tube add sufficient $N/20$ hydrochloric acid to make the total acidity equal to 2 ml of $N/20$ acid. Add 1 ml of indicator (as above) followed by $N/500$ thorium nitrate (exact strength not important) from a burette until a clear pink colour, free from yellow tone and suitable for colorimetric matching is developed (0·5–3 ml of thorium nitrate), and make up to 50 ml. Put into a second Nessler tube 2 ml of $N/20$ hydrochloric acid, 1 ml of indicator and approx. 20 ml of water, and then the same vol. of $N/500$ thorium nitrate as was used for the test. Add standard sodium fluoride* (1μg of fluorine per ml) until a colour match is obtained, final comparison being made in the same vol. Finally, make up similarly 2 more tubes, but add initially the vol. of standard sodium fluoride used in the back-titration so that final comparison with the standard is made under identical conditions. If necessary, add 0·5 ml sodium fluoride to the darker tube if matching is still imperfect. Comparison is best effected in north light by standing the tubes on a white tile and surrounding them by white card to form a box 6 in. square and at least as high as the Nessler tubes. The estimation is sensitive to 0·5 ml of standard sodium fluoride and its accuracy is thus 2·5% for 20μg of fluorine and 10% for 5μg of fluorine.

RESULTS AND DISCUSSION.—The influence of distillation temp. on the acidity of the distillate and the recovery of fluorine, added directly to the distillation flask as sodium fluoride, was determined in a series of expts. in which 1 mg of fluorine was added in each of a series of distillations at temp. ranging from 125° to 145°. The results showed that at 135°–140° C., resulting in an acidity equiv. to 0·5 ml of $N/100$ per 10 ml of distillate, the recovery was from 97·5 to 100%; this temp. was therefore used in all succeeding distillations. In further expts. in which 0·1–1·5 mg of fluorine was added to the contents of the distillation flask, the recoveries ranged from 95·0 to 100%.

Next, known quantities of fluorine were added as sodium or chromium fluoride soln. to 1 g of scoured white woollen cloth in a platinum dish, the whole was evaporated to dryness, and the fluorine was determined by the above method; the results are given in Table I.

TABLE I

RECOVERY OF FLUORINE ADDED TO WOOL

Fluorine added, mg	Acidity, ml of $N/100$ per 10 ml	Fluorine recovered mg	Recovery %
	Fluorine added as sodium fluoride		
0·5	0·56	0·44	88·0
0·5	0·42	0·44	88·0
1·0	0·50	0·94	94·0
1·0	0·42	1·00	100·0
2·0	0·50	1·88	94·0
2·0	0·30	1·88	94·0
5·0	0·48	4·88	97·6
5·0	0·52	5·00	100·0
	Fluorine added as chromium fluoride		
0·975*	0·52	0·94	96·5
0·975*	0·50	0·94	96·5
1·95*	0·54	1·94	99·5
1·95*	0·46	1·94	99·5

* Standardised against sodium fluoride by distilling chromium fluoride soln., assuming 100% recovery in distillation.

The amount of fluorine present in moth-proofed wool would not normally exceed 0·5% (on the weight of wool) and the results show that these small amounts can be satisfactorily determined on a small sample of wool with an accuracy of *ca.* 5%, which is adequate for control of the fluoride moth-proofing process. For wool with a fluorine content less than 0·1%, it is recommended that a larger sample be used.

Finally, determinations were made of 2 mg of fluorine added to wool materials that had undergone normal processing, thus containing residual substances which might

* The sodium fluoride used throughout as the standard in the colorimetric estimation was a 10- or 100-fold dilution of that used for the various recovery determinations; hence the results are not influenced by the purity of the sodium fluoride, which contained 44·7% of fluorine determined by the lead chlorofluoride method[14] (sodium fluoride requires 45·2%).

interfere with the recovery of fluorine; the results, with particulars of the samples used, are as follows:

Black worsted, chrome dyed (Cr, 0·43%).	Fluorine recovered, %	94·0; 100·0
Khaki woollen, chrome dyed (Cr, 0·30%). (Ca, 0·06%).	,, ,,	100·0; 100·0
Knitting yarn, acid dyed (sulphuric acid, 2·64%).	,, ,,	97·5; 97·5

SUMMARY.—A method for the determination of fluorine in wool moth-proofed by treatment with fluorides is described. The sample is ashed, and the fluorine is distilled from the ash as fluosilicic acid and estimated colorimetrically by its decolorising action on thorium-alizarin lake. Satisfactory recoveries of known amounts of fluorine added to wool have been obtained. The method is designed to determine up to 0·5% of fluorine (on the weight of wool) with an accuracy of the order of 5%.

We wish to thank the Director and Council of the Wool Industries Research Association for permission to publish this paper and Messrs. R. Nattrass and E. S. Holdsworth for assistance with the experimental work.

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WOOL INDUSTRIES RESEARCH ASSOCIATION
HEADINGLEY, LEEDS, 6

December, 1942

DISCUSSION

Mr. R. MILTON said that his laboratory had been working for some months on the determination of fluorine, and had encountered several difficulties. First, distillation should be prolonged so as to make certain that all fluorine came over, particularly if any pptd. silica was present, as it almost always was after fusion. Secondly, there was always a fluoride blank of about 5μg; this was not due to rubber bungs as suggested by some American writers, since it occurred with all-glass apparatus. They had also investigated dyestuffs as alternatives to alizarin, and had found Solochrome Brilliant Blue BS much superior. The lake formed with thorium was blue, giving a more definite colour change from yellow to blue on titration. The reaction with thorium, dye and fluorine was immediate, whereas the alizarin reaction was delayed. Moreover, the titration value was increased, so that about three times as much standard thorium soln. was used with a given amount of fluorine.

Mr. D. D. MOIR said that in recent months he had determined the amount of fluorine in large numbers of baking powders, egg substitute powders and similar types of food. A difficulty occurred if chloride was present in the article, since hydrochloric acid distilled over and increased considerably the acidity of the distillate. It had been suggested that silver sulphate should be added to the distilling flask, to retain the chloride as silver chloride and he had found this to be reasonably satisfactory. He asked whether the authors had had any experience with this or other methods for overcoming this difficulty. The method of determining fluorine that he had used was similar to that of the authors, which closely followed that of recent American workers.

Mr. F. L. OKELL suggested that, as fluorides were sometimes present in resistance glass, the "blank" might possibly be derived from the apparatus.

Mr. F. F. ELSWORTH, replying to the President, said that they had had no experience of the zirconium-alizarine method. The most recently published methods for determining fluorine used thorium nitrate almost exclusively and the optimum conditions had been the subject of a thorough study which had not been applied to the zirconium method. The fluorine blank on a 10- or 20-ml. aliquot portion of the distillate did not exceed 0·5μg. Almost complete recovery of fluorine had been obtained by collecting 200 ml of distillate, no appreciable amount of fluorine being found in a second portion of 200 ml of distillate. In the back-titration method, the end-point was not determined by a colour change from yellow to pink, but by matching solutions of pink colour. Loss of fluorine had been observed at temps. as low as 500° C.; they had tended towards incomplete ashing rather than risk any loss of fluorine. The white precipitate sometimes observed during titration was undoubtedly thorium fluoride, but with the amount of fluorine (10–12μg) present in the final determination in their method no turbidity had been observed. Chloride was not normally present in wool in amounts likely to cause any interference in the estimation, and hence no precautions had been taken to retain hydrochloric acid in the distilling flask.

Mastitis and the Freezing-point of Milk

By S. J. ROWLAND, B.Sc., Ph.D., A.I.C., R. ASCHAFFENBURG, Ph.D., and B. C. VEINOGLOU, B.Sc., Ph.D.

From time to time, and more frequently during the past year, we have received enquiries about the effect of udder infections on the freezing-point of milk; the enquirers wished to know whether milk with a low solids-not-fat content attributed to mastitis could be differentiated from watered milk by the determination of its f.p. depression (Δ). The available literature (1–6) deals mainly with the Δ of the markedly abnormal secretions produced in cases of clinical mastitis; it provides little information concerning the Δ of the milk of normal appearance, but of abnormal composition, which is secreted in cases of sub-clinical mastitis. Mastitis in this form is very prevalent, and its effect on the Δ is of more general importance than that of the clinical form.

During the course of a study of the effect of sub-clinical mastitis on the composition of milk, we have had the opportunity of examining the influence of this type of infection on the Δ of milk. Samples from all the individual quarters of 133 cows in full milk have been analysed. The samples consisted of half-a-pint of fore milk collected prior to the evening milking at various farms in Berkshire. They were refrigerated within 2–3 hrs. of milking and tested the following morning. For the determination of Δ an improved model of the apparatus designed by Temple,[7] which gives results in agreement with those obtained by using Hortvet's method, was used throughout the work. Determinations were also made of fat, total solids, chloride and lactose.

Table I

Cow	Δ °C.	Max. diff. between quarters °C.	Solids-not-fat %	Chloride p.p. 100,000	Lactose %
A	0·557	0·000	9·20	80	5·03
	557		9·12	69	5·15
	557		9·18	79	5·06
	557		9·18	73	5·19
B	0·556	0·006	9·17	70	5·23
	550		9·35	75	5·23
	551		9·19	74	5·19
	556		9·27	75	5·14
C	0·547	0·000	8·85	74	5·07
	547		8·73	80	5·02
	547*		6·85	200	3·16
	547		8·66	82	4·93
D	0·545	0·005	8·77	104	4·91
	549*		7·68	151	4·03
	545*		8·42	108	4·72
	544		8·94	83	5·12
E	0·546*	0·007	7·92	140	4·04
	546		8·65	78	5·01
	543		8·62	83	4·93
	550		8·54	87	4·90
F	0·546*	0·020	7·91	173	3·96
	564*		5·84	273	—
	554*		8·02	173	3·56
	544		9·03	102	5·00
G	0·551	0·060	8·73	123	4·35
	611*		7·58	249	1·53
	555		8·82	123	4·31
	556		8·70	117	4·37

* Infected quarter.

On the basis of a detailed bacteriological examination for mastitis streptococci and staphylococci applied to aseptically drawn samples of fore milk,* 39 of the animals were adjudged to be infected in one or more of their quarters, the remaining 94 cows being free from infection. For each cow a comparison was made between the Δ-values of the milk of its separate quarters, so that with infected animals the uninfected quarters served as an

* We are indebted to Dr. P. M. F. Shattock for these examinations.

exact control. In this way any difficulty of interpretation due to the natural variation of Δ from cow to cow was avoided. A representative selection of the results is given in Table I, Examples A–E.

With milk from healthy animals there was frequently no variation in Δ between the quarters (Example A); occasionally differences of a few thousands of a degree C were found (Example B). With milk from infected cows (Examples C–E) a similar picture was obtained in spite of the pronounced decrease in the solids-not-fat content of the milk of the infected quarters, the well-known complementary relationship between lactose and chlorides maintaining the relative constancy of the freezing-point. Example E shows that the maximum difference between the Δ-values of two quarters was not necessarily associated with the infected quarter.

TABLE II

	Max. diff. in Δ between quarters					
	0–1	2–3	4–5	6–7	8–9	(1/1000° C.)
No. of uninfected cows ..	66	21	5	1	1	
No. of infected cows ..	17	10	9	3	0	

The results for the 133 cows (summarised in Table II) show that there was a tendency to slightly greater variability in Δ between the quarters of the cows suffering from sub-clinical mastitis, indicating that the maintenance of the osmotic equilibrium was not quite as perfect as in the healthy cows. The magnitude of the Δ-variations, however, was still extremely small and without practical significance. This is also shown by the close agreement between the mean Δ-values of the milk of the uninfected and infected animals, which were found to be 0·547° C. and 0·548° C. respectively.

In addition to the cases of sub-clinical mastitis discussed above, a few clinical cases were examined. The results confirmed the observations reported in the literature, *viz.*, that clinical mastitis may lead to a marked increase in Δ, as shown by Examples F and G in Table I. It was observed that such an increase occurred only when the secretion was visibly abnormal and consisted of a discoloured serous fluid with or without clots. Fluids of this nature are not milk, and would not normally be included in milk for sale.

It may be concluded that an abnormally low freezing-point depression in a milk of low solids-not-fat content is indicative of the presence of added water irrespective of whether the low level of solids-not-fat is, or is not, attributable to mastitis.

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NATIONAL INSTITUTE FOR RESEARCH IN DAIRYING
SHINFIELD, NR. READING

July, 1943

Determination of the Solubility of Plasticisers in Water

BY R. N. HAWARD, PH.D.

THE work of Fordyce and Meyer[1] has emphasised the importance of plasticiser solubility and it has become increasingly common to list solubility among the published properties of these materials. For instance, a column is devoted to solubility in the table of plasticisers given in *Industrial and Engineering Chemistry*.[2] Unfortunately the data on this subject are far from satisfactory, not only because many substances are quoted as being insoluble when they are certainly not insoluble compared with other plasticisers, but also because the figures given for any particular material show a wide variation. An extreme instance is that of dibutyl phthalate whose solubility, as given by different authorities, ranges from 0·04 to 0·001%, *i.e.*, a variation of 40 : 1. Hence there was need for a simple direct

method of measuring this solubility which could be relied on to give results of the right order, even if not of the highest accuracy.

METHOD OF SCUM TITRATION.—Place a 20-cm Petri dish on a dull black material, such as black paper, and illuminate it from above and behind by means of an electric lamp. Run 100–150 ml of water into the dish so as to give a shallow fluid layer with a large surface. Then drop the plasticiser, or in general its soln. in AnalaR light petroleum (b.p. 40–60° C.), on to the surface from a pipette or burette and observe the oily scum when the solvent has evaporated. This observation is rendered easier if the atmosphere is free from dust. If there is no scum, drop more of the plasticiser soln. into the dish and continue the process until a stable scum of oily drops is obtained; often this appears as a characteristic speckling of the surface. The final end-point is reached when the quantity of scum is not notably diminished by gently agitating the dish for 5 min.

Normally a few initial expts. will be required to find very roughly the order of solubility of the material. The solubility is then calculated from the number of ml of plasticiser soln. added to a known vol. of water.

DISCUSSION.—Most plasticisers consist of esters which rapidly spread and dissolve at the air-water interface, reaching equilibrium quickly with their dil. aqueous solns. Materials which do not spread easily, such as *o*-dichlorobenzene, cannot be used. The method has the advantage of not being affected by small quantities of relatively sol. impurities, although more insoluble impurities may lead to a premature scum. However, this is presumably less common for such sparingly sol. materials. For instance, one would expect tributyl citrate to be contaminated with dibutyl citrate and perhaps a little butyl alcohol and citric acid, all of which would be more sol. impurities. In general, the accuracy of the method varies according to the quantity and visibility of the scum involved, but it is to be expected that even with the more insol. materials, *e.g.*, dibutyl phthalate, the accuracy will be within 50 per cent.; in more favourable instances the values should be within 20%.

As an example, the values obtained by four observers, using a solution of tributyl citrate, were:

	A	B	C	D
Solubility (aver. of 2 titrations) ..	0·007	0·006	0·005	0·007%

In general, the results of scum titrations agree well with those of saponification methods for measuring solubility, but with ethyl phthalyl ethyl glycollate the agreement was poor. Also, for this compound the figure does not agree with that published by Monsanto, Ltd.,[3] although in general the results agree better with theirs than with those of any other observer.

In the following table the saponification values are given only for the more soluble materials, as solutions weaker than 0·05% do not give a satisfactory acid-base titration. All the determinations were made at 13–17° C. unless otherwise stated.

SOLUBILITY OF PLASTICISERS

Plasticiser	Scum titration %	Saponification %	Published %
Dimethyl phthalate	0·40	0·43	0·41 (30° C. Monsanto)
Di-ethyl phthalate	0·06	0·07	0·058 ,, ,,
Dibutyl phthalate	0·0011	—	0·001 ,, ,,
Methyl phthalyl ethyl glycollate ..	0·11	0·11	0·09 ,, ,,
Ethyl phthalyl ethyl glycollate	0·05	0·09	0·018 ,, ,,
Methyl glycol phthalate	0·88	0·85	0·9 (25° C.), Messrs. Boake, Roberts private communication
Tributyl citrate	0·006	—	0·002 (*Ind. Eng. Chem.*, 1942, *ibid.*
Benzyl benzoate	0·0026	—	—
Butyl glycol phthalate	0·002	—	—
Butyl phthalyl butyl glycollate ..	0·001	—	0·0012 (30° C., Monsanto)
Dimethyl cyclohexanol oxalate (Barkite B)	<0·0002	—	—

SUMMARY.—A method is described for determining the solubility of plasticisers by dropping a soln. of the sample in light petroleum on to water until a stable surface scum is formed. The results obtained are compared with those already published.

I wish to thank the Directors of Messrs. Colmore Adhesives, Ltd., for permission to publish this paper.

References

1. Fordyce, C. R., and Meyer, L. W. A., *Ind. Eng. Chem.*, **1940**, **32**, 1053.
2. *Id.*, 1942, **34**, 68.
3. "*Plasticisers and Resins*," Monsanto Chemicals Co., St. Louis, U.S.A., May, 1940, 26–27.

TEAM VALLEY TRADING ESTATE
GATESHEAD ON TYNE, 11

May, 1943

Notes

COLORIMETRIC DETERMINATION OF BISMUTH IN TIN

THE following method, devised several years ago, has been found to give a fairly close approximation to the amount of bismuth in tin. Quite a small sample is required, and the determination can be made in a comparatively short time. The bismuth is separated from its soln. in hydrochloric acid by means of sodium hydroxide. Sodium stannite is formed, with reduction of the bismuth compounds as in the equations:

$$3Sn^{\cdot\cdot} + 6(OH') \longrightarrow 3Sn(OH)_2;$$
$$3Sn(OH)_2 + 6(OH') \longrightarrow 6H_2O + 3SnO_2'';$$
$$3SnO_2'' + 2Bi^{\cdot\cdot\cdot} + 6(OH') \longrightarrow 3H_2O + 3SnO_3'' + 2Bi.$$

Antimonous and lead salts form compounds that are soluble in the excess of sodium hydroxide.

METHOD.—Roll the metal into very thin foil to ensure its rapid solution in acid. Weigh accurately 0·5 g, dissolve in 10 ml of conc. hydrochloric acid, by gently warming, in a 100-ml tall-form beaker. Cool the beaker externally in a stream of cold water and at the same time add slowly cold 20% sodium hydroxide soln. until the tin hydroxide just re-dissolves; about 25 ml should suffice. When the slight permanent ppt. has settled, filter through a 9-cm No. 540 Whatman hardened filter. Wash several times, first with cold and then with hot water, and then wash the ppt. from the filter into a 100-ml wide-form beaker, using a minimum amount of water. Pass 5 ml of hot dil. hydrochloric acid (1 : 1 by vol.) and then hot water through the filter and collect these washings in the same beaker. Add 6 ml of dil. sulphuric acid (1 : 2 by vol.) and evaporate until copious white fumes are evolved. Cool, dilute to about 50 ml, again cool, add 10 ml of 2% potassium iodide soln. and then dil. sulphurous acid (10 ml of a sat. soln. diluted to 100 ml), drop by drop, to discharge any free iodine. Transfer the mixture to a Nessler glass, dilute to 100 ml and match with the standard.

Prepare the standard either by treating 0·5 g of pure tin in exactly the same way as the assay sample and then adding a known vol. of standard bismuth soln. at the final stage; or, prepare a range of standards by adding the standard bismuth soln. to each proof assay soln. immediately after dissolving the tin in acid; all the solns. are then treated alike.

To prepare the standard bismuth soln. dissolve 0·1 g of bismuth metal in the min. quantity of pure conc. sulphuric acid and dilute to 1 litre; if hydrolysis takes place during dilution, add immediately a little dil. sulphuric acid; 1 ml ≡ 0·0001 g of bismuth.

The following results were obtained when comparisons were made with the standard to which the bismuth solution was added during the final stage of the determinations.

Bismuth added, % ..	0·001	0·002	0·004	0·005	0·010
Bismuth found, % ..	0·001	0·002	0·0038	0·004	0·008

Permission to publish this note has been given by the Head of the Department.

Reference

1. Treadwell, F. P., and Hall, W. T., "*Analytical Chemistry: Qualitative*," London, 1921.

ASSAY DEPARTMENT
ROYAL MINT, LONDON, E.C.3

H. J. TABOR

July, 1943

DETERMINATION OF SULPHUR IN STEELS BY THE COMBUSTION METHOD

VITA'S method of determining sulphur in steels by combustion in oxygen at a temp. of *ca.* 1300° C. is so expeditious that for works practice it has almost superseded the tedious gravimetric method. Opinions appear to be divided as to whether or not the method is empirical, and it would seem that further research is required before this point can be decided.

STANDARDISATION.—Under the conditions commonly practised in this country the method is certainly empirical, since the titrant is standardised by combustion of a standard steel and the resultant factor is checked at frequent intervals.

ABSORPTION.—Three methods of absorbing the combustion products are in use: (*a*) Absorption in water followed by titration with a mixture of potassium iodide and iodate. (*b*) Absorption in 1% silver nitrate soln. followed by titration of the liberated nitric acid with 0·005 *N* sodium hydroxide, using methyl red as indicator. A white turbidity due to silver sulphite is produced and masks the end-point. (*c*) Absorption in hydrogen peroxide followed by titration with 0·005 *N* sodium hydroxide. This method has the advantage that a clear soln. is obtained, but does not appear to be as popular as the other two. We have used hydrogen peroxide for some time in our respective laboratories and prefer it for the reason stated. Fifty ml of 0·5% hydrogen peroxide are used in a 100-ml measuring cylinder and the titrations are carried out *in situ*. As many as 10 or 12 determinations can be made consecutively in the same absorbent.

STANDARD ALKALI.—The accurate preparation of 0·005 *N* sodium hydroxide is troublesome, and absorption of carbon dioxide causes trouble. We prefer to use sodium borate which, being a primary standard, can easily be made up to the strength required and obviously is free from liability to develop

carbonate. Its use removes any uncertainty about the exact normality, whereas with sodium hydroxide it is usual to prepare the soln. by diluting 0·1 *N* soln. and no further check is made on its strength beyond standardisation against a standard steel. Since the theoretical strength of the sodium borate is known, information as to variations in sulphur recovery can be collected.

INDICATOR.—We prefer an aqueous soln. of bromocresol purple or a mixture of methyl red and methylene blue (0·125 g of methyl red and 0·083 g of methylene blue in 100 ml of alcohol) to methyl red, the equivalence point with either of these two indicators being more easily discerned.

FILTRATION OF GASES.—In our experience it is always advisable to use a filter to remove the metallic oxides from the exit gases before absorption, otherwise with high carbon steels and irons so much oxide is carried over that titration is almost impossible. With high molybdenum steels the alkali titre is affected by molybdenum oxides if not removed, and the results are much higher than the truth. We have found ignited asbestos wool, thoroughly dried at 120° C., the most suitable filtering medium. Cotton wool is liable to ignite in the rapid stream of oxygen used in the combustion.

R. BELCHER
R. POSTLETHWAITE

DEPT. OF METALLURGY AND CHEMISTRY
THE TECHNICAL COLLEGE, ROTHERHAM; AND
GENERAL CHEMICAL LABORATORY
SAMUEL FOX & CO., LTD. (BRANCH OF UNITED STEELS, LTD.)
STOCKSBRIDGE, NR. SHEFFIELD

July, 1943

DETERMINATION OF SMALL QUANTITIES OF BORIC ACID IN ORGANIC SUBSTANCES

4 : 4′-Diamino-1 : 1′ dianthraquinonylamine, obtained by reducing 4 : 4′-dinitro-1 : 1′-dianthraquinonylamine with sodium sulphide (Eckert and Steiner, *Monatsh.*, 1914, **35**, 1129), dissolves in sulphuric acid to form a blue soln. changing to indefinite orange at 150° C. In presence of boric the colour change at 150° C. is to dull greenish-olive, with max. optical density at *ca.* 6200A. At this point (readily observed with the Hilger Visual Spectrophotometer) the change in optical density is proportional to the quantity of boric acid, provided that this does not exceed 10% of the weight of the reagent.

METHOD.—Mix 0·25 g of the substance (or proportionately less if it contains more than 0·5% of boric acid) with 0·3 g of sodium carbonate in a platinum dish and ignite until the residue is white. Dissolve the residue in 97–98% sulphuric acid and make up the soln. with the acid to 50 ml. Transfer 2 ml, 5 ml and 9 ml of this soln. to test-tubes (6″ × ¾″), treat each portion with 1 ml of a soln. of 0·1 g of the reagent in 100 ml of pure 98% sulphuric acid, make up to 10 ml with sulphuric acid and mix well. Heat the tubes in a glycerin bath for 30 min. at 150° C. and measure the optical density at 6200A in a 1-cm cell. Deduct from the result the blank obtained with the sodium carbonate and sulphuric acid. A density diff. of 1·0 ≡ 0·00467 mg of boric acid per ml. It is essential that the sulphuric acid should be free from dust, etc., which may cause the soln. to become brown at 150° C.

To purify the crude diamine, dissolve it in 10 times its weight of 98% sulphuric acid, filter, dilute the filtrate to 83% H_2SO_4, filter off the ppt. and wash it first with 83% sulphuric acid and then with water.

We wish to thank I.C.I. (Dyestuffs), Ltd. for permission to publish this note.

E. G. BECKETT
M. F. H. WEBSTER

GRANGEMOUTH, STIRLINGSHIRE

April, 1943

Errata.—July issue, p. 203. *Delete* the last line. August issue, p. 246. For "*Analyst* 1933" *read* "ANALYST 1938."

Ministry of Food

NATIONAL FLOUR AND BREAD. THIRD REPORT FROM THE SCIENTIFIC ADVISER'S DIVISION, MINISTRY OF FOOD*

ANALYSES of 379 samples of flour and 381 of bread received from Oct., 1942, to May 8, 1943, are summarised and discussed (*cf.* ANALYST, 1942, **67**, 270, 364; Anon., *Nature*, 1942, **150**, 538; Moran and Pace, *id.*, 1942, **150**, 224). During this period there has been an increase in the proportion of home-grown wheat used (present average, 43·6%); 90–95% of the flour is now fortified with 2 lb. of skim milk powder per sack and *ca.* 89% with 7 oz. of Creta Praeparata per sack; a mixture of de-hulled oats (groats) and barley is now also included in the grist.

Fibre Contents.—Average, *ca.* 0·55%; 9·8% of the samples contained less than 0·4%, and 97·8% less than 0·9%. *Vitamin* B_1.—Average, 1·00–1·05 I.U./g; 4·5% of the samples contained more than 1·20, and 98·0% more than 0·80 I.U./g.

Both figures, therefore, represent a reduction. The reduction in fibre, which is appreciable, is due to new methods of milling, and corresponds with a definite improvement in the quality and digestibility of the flour. The reduction in vitamin B_1 is very small, and is due to the higher % of home-grown wheat used and to the lower bran-content of the flour. The extractions from any added barley and groats have been fixed at 70 and 85%, respectively, and laboratory milling tests show that this dilution has no significant effect on the fibre- and vitamin B-contents of the finished National Flour.

Protein Content.—This depends on the composition of the grist; it ranged from 13·2% for a mixture of Manitoba No. 1, 50 + Manitoba No. 2, 30 + Plate, 10 + English 10 to 8·3% for all-English (red 2 + white 1 part). Random samples (22), representing mills of all sizes, contained 10·7–12·0%, the average (11·3%) corresponding with *ca.* 50% of English wheat in the grist.

Riboflavin.—The same samples of flour contained 1·4–1·9 (average, 1·5) μg per g.

* *Nature*, 1943, **151**, 629–630.

Granularity.—Both the number and size of the bran particles continued to fall. Thus, the totals over 5- and 8-silk, respectively, were (100 samples) 11·9 and 15·0% in Jan.-March, 1942, and 1·9 and 5·8% in Apr.–May, 1943. (No. 5-silk = 0·270; No. 8-silk = 0·190-mm aperture.) The data are corrected for any added Canadian G.R. flour.

Conversion Factor, Flour—Bread.—Assuming conditions of max. absorption, 1 lb. of National flour ≡ 1·36 lb. of bread, but, as most bakers use up to 1 gal. of water per sack less than the optimum, the practical conversion factor is probably *ca.* 1·34.

Bread Quality.—Both barley and groats tend to reduce the quality of the bread if present in large amounts; *e.g.*, 10% of barley gives a loaf of reduced vol. with a rather harsher crumb of duller colour. The increase in home-grown wheat content also tends to lower loaf quality, but the additions of the Creta Praeparata and skim milk are without effect. Of the loaves received, 29% were classed as "good," 26% "fair-good," 31% "fair" and 14% "poor"; corresponding figures from the previous 459 samples (*loc. cit.*) were 61, 22, 13 and 5%, respectively. There has, therefore, been a fall in loaf quality, although an improvement in its nutritional value. It is believed that this fall is partly due to the fact that in the period concerned bakers had not become accustomed to the new type of flour. J. G.

STATUTORY RULES AND ORDERS*

1943—No. 972. The Home Grown Corn (Control and Prices) (Great Britain) Order, 1943 Dated July 14, 1943. Price 2d.

This Order controls the usage and disposal of dredge corn.

"Dredge corn" means the product of a mixed crop of (i) cereal grains, (ii) pulses, (iii) cereal grains and pulses, (iv) edible seeds and cereal grains, (v) edible seeds and pulses, or (vi) edible seeds, cereal grains and pulses.

"Edible seeds" means any seeds, other than cereal grains or pulses, which are capable of being used as, or in the manufacture of forage or in the manufacture of human food or drink.

"Millable dredge corn" means dredge corn which is capable of being converted into a sound sweet flour for human consumption, having regard to the customary methods employed in the milling industry for cleaning and conditioning but does not include dredge corn containing 25% (by weight) or less of wheat, rye or barley, or any two or more of them.

"Barley dredge corn" means dredge corn, two-thirds or more of which (by weight) consists of barley.

The usage or disposal by a grower or an approved buyer (except under certain specified conditions) of dredge corn containing more than 25% by weight of wheat, rye or barley or of a combination of any two or more of them is prohibited.

— **No. 985. Order, dated July 15, 1943, prescribing an appointed day for the purposes of the Food (Restriction on Dealings) Order, 1941.** Price 1d.

On and after July 25, 1943, licences must be held to sell by wholesale "excepted products" and "specified foods" other than meat extract as defined in S.R. & O., 1942, No. 138, and 1943, No. 933.

"Excepted products" include faggots, rissoles, meat pies and puddings, etc., and "specified foods" include sausages, brawn, meat and fish pastes, and other meat products. Full lists of these products will be found in the Meat Products and Cooked Meat (Control and Maximum Prices) Order, 1942, as amended.

— **No. 1063. Order, dated July 26, 1943, amending the Meat Products and Cooked Meat (Control and Maximum Prices) Order, 1942.** Price 1d.

The Principal Order (S.R. & O., 1942, No. 1381; amended by 1943, No. 933) *is further amended by inserting in the First Schedule thereto a prescribed meat content for Meat Roll or Galantine of not less than 30% and not more than 45%.*

— **No. 1196. The Coffee (Retail Prices) Order, 1943. Dated August 16, 1943.** Price 1d.

In this Order "Coffee" includes (except where the context otherwise requires) coffee mixture, but does not include any essence or extract of coffee or of coffee and chicory, or any preparation of coffee and milk.

"Coffee mixture" means any mixture containing coffee which is commonly sold under the name of coffee, or of coffee and chicory mixture. *By Art.* 5 a person shall not manufacture or prepare by way of trade or sell by retail any coffee mixture unless that coffee mixture contains at least 66 2/3% by weight of pure coffee.

Legal Notes

The Editor would be glad to receive particulars of cases with points of special legal or chemical interest.

LIMITATION OF TIME FOR PROCEEDINGS. AIDING AND ABETTING

FULHAM BOROUGH COUNCIL *v.* LEVEN

THE SAME *v.* R. DAVIS. THE SAME *v.* SEAL PRODUCTS LTD.

ON March 18, 1943, a series of summonses, brought by the Fulham Borough Council, was heard by Sir Gervais Rentoul at the West London Police Court. In the first case Leven was summoned for describing as "concentrated peppermint" a preparation certified by the Public Analyst to contain only 0·003% of peppermint and for selling it to the prejudice of the purchaser.

Leven took out a summons under Sec. 83 of the Food and Drugs Act, 1938, against R. Kamstra (London), Ltd., as the actual offenders in the matter of the false label, and in turn Kamstra proceeded

* A summary of some Orders, italics signifiy changed wording. Obtainable from H.M. Stationery Office.

against Seal Products, Ltd. That firm was summoned by the Fulham Borough Council for giving a false warranty in writing, contrary to Sec. 85 (2) of the Act, and for giving a false label in a sale to Kamstra, and Richard Davis, Ltd., was summoned for aiding and abetting Seal Products, Ltd., in the false label offence.

Counsel for Seal Products and Davis contended that the summonses against them under Sec. 6, for giving a false label, were out of time, as the informations had not been laid within 28 days after the sample had been taken. No certificate had been issued by the Court, but even had there been one, the proceedings were invalid because more than 42 days had elapsed between the taking of the sample and the laying of information. In his view the summonses were "in respect of the article sampled" and therefore Sec. 80 (1) (*a*) applied.

For the Borough Council it was submitted that the prosecution was not "in respect of the article sampled," but in respect of a false label and that the time limit was therefore 6 months, as laid down in Sec. 11 of the Summary Jurisdiction Act, 1848. Under Sub-sec. (7) (*b*) of Sec. 80 the time limit for proceedings for the giving of a false warranty was extended to 12 months "instead of 6 months." But for that sub-section, it would have remained at 6 months for giving a false warranty, as it still remained for giving a false label.

Sir Gervais Rentoul accepted this view of counsel for the prosecution and said that his opinion was fortified by the decision in *Herman Jennings, Ltd.*, v. *Slatcher* (1942) (2K.B. 115) (*cf.* ANALYST, 1942, **67**, 292). In that case there was an appeal against a conviction for the giving of a false warranty, on the ground that in every case in which a sample had been taken the prosecution must begin within 28 days thereafter. The Court held that the mere taking of a sample did not bring the case within Sec. 80 (1) (*a*) and that the only time limit was 12 months under Sec. 80 (1) (*b*). Lord Caldecote in his judgment said: "I have come to the conclusion that par. (*a*) deals only with the case of a prosecution of the person from whom the article which was sampled and analysed was procured."

In the present case the article which was sampled and analysed was procured from Leven and not from any of the other defendants. Hence the summonses against Seal Products and Richard Davis, Ltd., for giving a false label were not prosecutions "in respect of the article sampled" so as to bring them under Sec. 80 (1) (*a*), and therefore the proceedings were within time, the informations having been laid within the 6 months allowed by Sec. 11 of the Summary Jurisdiction Act, 1848.

With regard to the summons against R. Davis, Ltd., for aiding and abetting Seal Products, Ltd., in the false label offence, counsel for the defence submitted that they could not be convicted, as they were not present, actively aiding and abetting. He relied on the case of *Bowker* v. *Premier Drug Co., Ltd.* (1928) (1 K.B. 217). Sir Gervais considered that it might have been better to have issued the summons for "counselling and procuring," but he understood that Seal Products, Ltd., were selling agents for Richard Davis, Ltd. In fact, their registered offices were at the same address and the name "Richard Davis" was on the label. Therefore, as constructively they were present assisting in the act, he held that they were "aiding and abetting."

Notes from the Reports of Public Analysts

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

CITY OF BIRMINGHAM: REPORT FOR THE 2ND QUARTER, 1943

OF the 1251 samples of food and drugs submitted by the sampling officers, 3 were taken formally.

MALT EXTRACT TABLETS.—A sample contained 19% of extraneous mineral matter (chiefly talc). Caution issued.

LABELLING OF HEALTH SALTS.—As required by the Pharmacy and Medicines Act, 1941, a sample of health salts had the analysis printed on the label. The formula included sodium bicarbonate (39·95%), tartaric acid (39·95%), magnesium sulphate (8·55%) and sodium sulphate. Analysis, however, showed that there was only 35·0% of sodium bicarbonate, 29·1% of tartaric acid and 5·6% of magnesium sulphate. There had, in fact, been partial decomposition, with formation of sodium bitartrate (14·3%). The manufacturers were cautioned.

H. H. BAGNALL

Fruit and Vegetable Preservation Research Station, Campden

ANNUAL REPORT FOR 1942

IN addition to research and ordinary advisory work the staff has given advice to the Ministry of Food on technical problems, has supervised the administration of the Fruit and Vegetable Canning Orders, and has controlled the quality of canned beans in tomato sauce for Candisco, Ltd., a company formed by the Ministry of Food for the distribution of this product. The research and experimental work (under the direction of Mr. F. Hirst, M.Sc.) has inevitably been restricted, but investigation has been continued on the following problems.

USE OF BLACKPLATE.—The results of tests on the possibility of substituting blackplate ends for tinplate ends have been reported to the Ministry of Food. The tests were planned with a view to establishing conditions that would result in the least possible corrosion of the container or deterioration of the contents, while taking into account practical canning difficulties. After these expts. had indicated the most practical type of blackplate for general use, further tests were made to show the amount of variation in corrosion with the commoner vegetables when packed in this type of can. Results cannot yet be published.

FACTORS AFFECTING THE VITAMIN C CONTENT OF CANNED FRUITS AND VEGETABLES.—The Progress Report by the Deputy Director (Mr. W. B. Adam, M.A.) gives an outline of expts. which show that there may

be a slight loss of vitamin C if gooseberries are held for periods up to 4 hrs. after snibbing. Fresh peas and dwarf or runner beans may also show an appreciable loss under similar conditions after podding or slicing. Loss of 10–30% may occur if peas or beans are held at ordinary temperatures for 4 hrs. after blanching. The temp. of closure of cans apparently has little effect on the vitamin C content of canned fruit or vegetables, at least within the range 130°–170° F. There is a slight fall in vitamin C content during the early stages of storage, but the subsequent rate of loss appears to be low.

DETERMINATION OF SMALL AMOUNTS OF BORON.—The max. concn. of boron likely to be found in normal plant material is *ca.* 50–60 p.p.m. on the dry substance. To trace small changes, of the order of 2 to 3 p.p.m., in the boron content of plum leaves a delicate colorimetric method, specific for boron and germanium, was devised by Dickinson and published in THE ANALYST (1943, **68**, 106). It is based on the fact that in conc. sulphuric acid soln. these elements combine with certain anthraquinone dyestuffs to form coloured chelate compounds. This method was used in the study of stone-gum in plums.

FRUIT GUMMING OF VICTORIA PLUMS.—Trials in 1940 showed that the magnitude and frequency of gum spots were reduced when trees were treated with boric acid either by branch injection or by spraying. This led to tests in which the soil surrounding the trees was treated with borax. Leaves were picked from each of the selected trees at several stages of growth in 1942 and the boron content was determined. The average figures for each group of trees (as p.p.m. on the dry substance) were as follows:

	June 3	July 6	Sept. 1	Oct. 2
Untreated trees ..	20	28	42	37
Treated trees ..	25	33	48	41

Whilst the boron content from the treated trees is slightly higher than from the controls, the differences are unlikely to be of biological importance. No correlation could be traced between boron content and gumming. The weight of the crop and size of the plums are also apparently without importance as factors. On the other hand, it was found that the rainfall in the latter part of the growing period (July and August) is positively correlated with the degree of gumming. Further expts. to check the conclusions from statistical evidence are in progress.

DETERMINATION OF SOLIDS AND SUGARS IN CANNED BEANS.—The introduction of official minimum standards for canned beans in tomato sauce made it necessary to study methods of determination. The procedure finally adopted is as follows.

Preparation of Sample.—Pass the contents of the can through a mincer, mix thoroughly, mince again, and continue the process until a smooth cream is obtained. Weigh the portions for analysis without delay.

Total Solids.—Weigh duplicate samples (about 10 g) into wide-mouthed weighing bottles and dry in a well-ventilated oven at 96°–98° C. for 16 to 18 hrs. Calculate the solids content as % of the original weight. Statistical treatment of the results of 50 routine samples selected at random shows that the difference between duplicates is unlikely to exceed 0·25% in more than 1 sample in 10.

Sugars.—The method of the A.O.A.C. (*Methods of Analysis*, 1935, 4th Ed., p. 341) is lengthy, has many possible sources of potential error and is lavish of alcohol. Samples were found to vary in their behaviour under such treatment, especially in the rate at which they settled after initial boiling, and after pptn. of the lead oxalate. Extraction of the sugars in a Soxhlet apparatus is shorter and requires less alcohol. It yields more consistent results than the A.O.A.C. method. Expts. showed that the treatment with lead acetate was not essential. Weigh a 10-g portion of the minced material and transfer it to a 60-ml Soxhlet tube containing a loose plug of glass wool as filter medium. Use 70% alcohol to transfer the sample and add sufficient to fill the siphon, with about 20 ml in excess (70–80 ml in all). Heat the apparatus over a hot plate and continue the extraction for 30 min. after the paste has become colourless and there is no colour in the liquid in the siphon. Then remove the Soxhlet tube, reverse the condenser, and distil off the alcohol until the vol. of the extract is reduced to *ca.* 20 ml. Filter through a No. 4 Whatman paper into a 100-ml graduated flask, wash the solids with water, and make up the filtrate to 100 ml. Acidify 50 ml of this soln. with 10 ml of conc. hydrochloric acid and heat at 70° C. for 5 min. to invert the sucrose. Cool the soln., neutralise with sodium hydroxide (methyl orange as indicator), make up to 100 ml, and determine the reducing sugars by titration with Fehling's soln., using Lane and Eynon's methylene blue method. Statistical treatment of the results of 50 routine samples selected at random shows that the difference between duplicates is unlikely to exceed 0·15% in more than 1 sample in 10.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Volume occupied by the Husk in the Analysis of Flaked Oats and of Malt. B. M. Brown. (*J. Inst. Brewing*, 1943, **49**, 195–197.)—The allowance of 15 ml for the husk, etc. adopted by the Analysis Committee of the Institute of Brewing in 1906 in their standard method, appears to have been derived from Heron's original method of malt analysis, which probably covered the wider range of two-rowed malts then available. The standard method for flaked maize prescribes a final vol. of 506 ml after mashing, thus allowing 6 ml for the insol. matter. Preliminary calculations, based on equations derived from the analytical data, gave approx. 10 ml as the vol. of insol. malt solids and 16 ml as that for flaked oats. A series of analyses was then made of malts (English and Scotch) and 3 samples of flaked oats, in which the whole of the insol. matter from the 50 g of sample was filtered off, washed, dried and weighed. The mean vol. for the malt was 10·7 ml (10·1 calculated from the equation), and for the flaked oats 16·3 ml (16·1 calculated). Hence the figure for the oats is sufficiently near 15 ml to make the use of the conventional standard flask, graduated at 515 ml, suitable for use with 50 g of this material. The effect of taking 15 ml, however, instead of 10 ml, for the insol. matter of malt is to give an unduly low value (nearly 1 lb.) to the available extract. This is not important when two-rowed British malts are being compared with one another, but it must

be borne in mind when comparing such malts with other brewing materials or when checking the mash-tun yield against the laboratory analysis.

Detection of Caramel in [Cider] Vinegar. A. M. Henry and J. W. Sanders, Jr. (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 233–237.)—Five samples of vinegar, a 4% acetic acid soln., and a 4% acetic acid soln. coloured with caramel were each tested by 19 collaborators by the following methods: (i) the paraldehyde and phenylhydrazine tests (*Methods of Analysis*, A.O.A.C., 1940, **16**(*f*), 252); (ii) the fuller's earth method (*id.*, **76**, 481); (iii) Gulick's formaldehyde modification of the Lichthardt tannin method (ANALYST, 1941, **66**, 466). In general, the results for Method (i) were very erratic; in some instances they were positive or doubtful with 4% acetic acid, and in others negative or doubtful with the acid containing caramel. The results with the fuller's earth method showed closer agreement than those for Method (i), but there was a wide variation in the % colour removed in the same sample by different samples of the earth. A few samples removed less than 50% of the caramel colour from coloured vinegar, whilst others removed more than 50% of the colour from pure cider vinegar. Possibly, if fuller's earth were standardised as to the removal of caramel from vinegar, more reliable results could be obtained (*cf.* Dubois, ANALYST, 1907, **32**, 92). The closest concordance was shown by the results with Method (iii) (*loc. cit.*), although a few discrepancies were noted. In one test a negative result was obtained with the acetic acid containing caramel, but it was found that this caramel differed from most other caramels in being basic instead of acidic; on adding a small amount of sulphuric acid to the coloured acid the modified Lichthardt method gave a positive result; however, such addition is inadvisable, for the acid concn. is somewhat critical, and on adding a large quantity positive results are obtained even when the vinegar does not contain caramel. A survey of all the tabulated results indicates that Method (iii) is, in general, reliable and has special value as a negative test.

Expressed Tropical Almond (Talisay) Oil. C. F. Asenjo and J. A. Goyco. (*J. Amer. Chem. Soc.*, 1943, **65**, 1417–1418.)—The kernels of the tropical almond tree (*Terminalia catappa* L.), are edible and on extraction yield *ca.* 55% of a fixed oil; by expression the yield is only *ca.* 35%. This oil is known in the Philippines as Talisay oil and in India as Indian almond oil; a sample expressed in the laboratory was pale yellow and of excellent odour and taste. It was found suitable for the manufacture of edible fats, cosmetics and pharmaceutical products. The constants were: sp.gr. at 25°/25° C., 0·9024; n_D^{29}, 1·4639; sap. val., 187·6; iodine val. (Hanus), 71·32; acid val., 7·39; unsap. matter, 0·65%; iodine val. of unsat. acids (Hanus), 120·7; Reichert–Meissl val., 0·08; Polenske val., 0·12; acetyl val., 4·67. The fatty acids were separated into 52·92% of unsat. acids and 40·96% of sat. acids. The unsat. acids contained 33·77% of linolic acid and 66·23% of oleic acid, and the sat. acids 1·58% of myristic acid, 89·16% of palmitic acid and 9·25% of stearic acid. E. M. P.

Component Glycerides of Safflower Oil. N. L. Vidyarthi. (*J. Indian Chem. Soc.*, 1943, **20**, 45–50.)—Indian safflower seeds (*Carthamus tinctorius*) yielded on extraction with carbon tetrachloride 30·5% of oil which had: sp.gr. at 27°/15° C., 0·9242; n_D^{27}, 1·4742; acid val., 6·3; sap. val., 192·0; iodine val. (Wijs), 136·2; acetyl val., 13·2; unsap. matter, 1·3%; hexabromide, 0·2%. To separate the component glycerides the neutral oil was dissolved in light petroleum, and the solution was chilled to −5° to +1° C. and brominated. The insol. fraction was a sticky solid and the soluble fraction a viscous liquid. Both fractions were further subdivided by treatment first with alcohol and then with methyl alcohol and acetone (1 + 1), and the nature of the fatty acids in the fractions was determined by the usual methods. The glycerides in the oil were calculated to be: oleo-myristolinolin, 3; palmito-oleolinolin, 7; oleostearo-linolin, 2; myristodilinolin, 1; palmito-dilinolin, 4; stearo-dilinolin, 1; dioleolinolin, 15; oleodilinolin, 64; trilinolin, 3%. The mixed fatty acids contained: lauric and lower acids, *ca.* 0·6; myristic, 1·3; palmitic, 2·2; stearic, 1·1; arachidic and lignoceric, 0·5; oleic, 32·6; linolic, 60·6.

Component Fatty Acids of some Vegetable Seed Phosphatides. T. P. Hilditch and Y. A. H. Zaky. (*Biochem. J.*, 1942, **36**, 815–821.)—The proportions of the fatty acids of the glycerides and phosphatides found in soya bean and rape seed oils (*Biochem. J.*, 1937, **31**, 1964; ANALYST, 1938, **63**, 123), and now determined in groundnut, cottonseed, sunflower and linseed oils are tabulated. Results indicate that (i) seed phosphatides contain characteristic, although minor, proportions (3–6% in these 6 samples) of highly unsaturated C_{20} and C_{22} acids not present in the corresponding glycerides; (ii) percentage of saturated acids (notably palmitic) in the phosphatide acids is higher than that in the corresponding glyceride acids; in cottonseed oil, however, the increase is small and palmitic acid content is decreased from 23 to 17%; (iii) all the glyceride acids also occur in the corresponding phosphatide acids; (iv) linolic acid is on the whole the most characteristic acid, forming 42–55% of the total fatty acids of the phosphatides of cotton-seed, sunflower seed, rapeseed, and soya bean (but only 23 and 20% of the groundnut and linseed phosphatides); only in rape seed oil is its proportion notably higher for the phosphatides than for the glycerides (42 and 29%), whilst in sunflower seed it is much lower (46 and 66%); Hilditch and Pedelty's previous communication (*loc. cit.*) reviews earlier work on vegetable phosphatides. The presence of appreciable amounts of highly unsaturated C_{20}, etc., acids seems characteristic of all animal and vegetable phosphatides. E. B. D.

Qualitative Colour Test for Ergot. J. W. Fairbairn. (*Pharm. J.*, 1943, **150**, 94.)—To detect ergot in admixture with other powdered vegetable drugs, shake vigorously a quantity of the sample expected to contain *ca.* 0·1 g of ergot with 5 ml of 5% sodium carbonate soln. for a few sec., then add 5 ml of chloroform and repeat the shaking. Transfer the lower layer, which may be partly emulsified, to another tube by means of a pipette and wash it once with water. Separate the clear chloroform layer and shake it with half its vol. of a reagent made by dissolving 0·1 g of *p*-dimethylamino-benzaldehyde in a mixture of 100 ml of 35% v/v sulphuric acid and 1·5 ml of 5% ferric chloride soln. After 5 min. the presence of ergot (containing ergotoxine) is indicated by formation of a blue

colour in the acid layer. The preliminary treatment with sodium carbonate soln. prevents interference from chlorophyll which may be present in a mixture of vegetable drugs. The test is also applicable in presence of aloes, cascara sagrada, cinchona and quinine.

Biochemical

Nutritional Significance of Grass. C. A. Elvehjem and H. A. Sober. (*Chronica Botanica*, 1943, **7**, 301–303.)—From the present point of view, a representative analysis of grass (dry basis) is: carotene, 45; vitamin K_1, 40; α-tocopherol, 20; xanthophyll, 60; vitamin C, 500 mg/100 g; thiamin, 12; riboflavin, 25; pyridoxine, 12; pantothenic acid, 12; niacin, 85; biotin, 0·25μg/g; protein, 25; reducing sugars, 2 (after hydrolysis, 12); ash, 11; crude fibre, 18; crude fat, 7; choline, 6%. The addition of fresh lawn clippings or of juice from pressed grass to mineralised winter milk produced a growth-rate (with rats or guinea-pigs) comparable with, or greater than, that obtained with summer milk. This is attributed to a factor differing from the known vitamins (the "grass juice factor"). When 20% of dried cereal grasses containing 35% of protein was added to a grain-mash ration, the egg-production of White Leghorn was doubled and the mortality halved as compared with the use of alfalfa meal. The short immature plant is most effective in this respect, especially when cut 18–40 days after planting (*i.e.*, just before the first joints appear); *ca.* 10,000 tons per annum are now produced for human and animal consumption. Grass protein is highly digestible and has a high biological val.; unlike most plant materials, it is relatively rich in cystine and tryptophan (over 2%), and in lysine (*ca.* 5%). Hexane extracts of grass have been used clinically to treat haemorrhagic diseases by reason of their high vitamin K activity. The relatively high folic acid content of grass is of significance in its use for poultry production, and young grass has been reported to be a good source of gonadotropic factor and of a factor required by certain acid-forming anaerobes. The nutritional value of grass will ultimately be determined by the relative availability and cost of isolation of the valuable constituents, as compared with existing methods, and on the results of future analytical studies of the grass which may reveal the presence of other factors having specific beneficial effects. J. G.

Physiologically-active Fractions of Indian Hemp. B. C. Bose and B. Mukerji. (*Nature*, **1943**, **152**, 109–110.)—The following fractions of the carbon tetrachloride extract from genuine charas were evaluated pharmacologically (Gayer, *Arch. exp. path. Pharm.*, 1928, **129**, 312), solns. of the extracts in alcohol being added by means of stomach tubes to cats (2–3 kg in weight): (1) Carbon tetrachloride extract (contains all phenols, including cannabinol, cannabidiol and cannabol; (2) the alkali-insol. residue from (1) after extraction with 0·5% sodium hydroxide soln. (contains cannabinol and possibly some of its isomers); (3) the alkali-sol. extract was acidified first with light petroleum; and finally with carbon tetrachloride (4). Care was taken to remove traces of carbon tetrachloride from all fractions before testing. In *ca.* 100 expts. the alka-sol. fractions failed to give responses for doses of 3·00 and 2·96 ml/kg after 3·18 and 3·40 hr., respectively, whereas the whole extract, 1·61 ml/kg, and the alkali-insol. fraction, 0·86 ml/kg, gave positive responses after 1·75 and 1·48 hr., respectively. This raises the question whether cannabinol can be considered as a physiologically inactive phenol, as suggested by Cahn (*J. Chem. Soc.*, 1930, 986) and by Marshall (*Lancet*, 1937, i, 235). It may, however, be the precursor of a true active ingredient having an ethenoid linkage, like the synthesised tetrahydro-cannabinols of Adams, Hunt and Clark (*J. Amer. Chem. Soc.*, 1942, **62**, 196).

Relative Suitability of Various Acids for the Extraction of Ascorbic Acid from Plant Materials. J. D. Ponting. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 389–391.)—Comparative tests were made with water and with 0·5% metaphosphoric, 0·2% oxalic, 0·07% perchloric, 1% citric, 0·5% tartaric, 0·07% nitric, 5% acetic, 0·2% maleic, 0·5% sulphosalicylic, 0·2% trichloroacetic, 1% lactic, 0·07% hydrochloric and 0·2% orthophosphoric acids alone, and in presence of a 10^{-4} *M* concn. of copper. The ascorbic acid contents were determined initially (3·23–3·32 mg per 100 g), and after 24 hr. in a stoppered flask at *ca.* 23° C. The stability of the ascorbic acid is shown to be a function of both *p*H and the nature of the acid. Thus, in absence of copper, the metaphosphoric acid (*p*H 2·1) and orthophosphoric acid (*p*H 1·87) produced average losses of 2·8 and 86·2%, respectively; in presence of copper the losses were 14·4 and 99·7%, respectively. Oxalic and metaphosphoric acids behaved similarly, and were far superior to any of the others, none of which are regarded as suitable. Oxalic acid has the advantages that it is more stable (the metaphosphoric acid should be freshly-prepared), more easily obtainable and less expensive; moreover, with some vegetable extracts (*e.g.*, of frozen broccoli) the loss of ascorbic acid in presence of copper was consistently less than in its absence, but no explanation of this is yet available. The optimum conditions for extraction are with 0·3% oxalic acid or 1% metaphosphoric acid soln., used in a ratio of at least 7 vol. of acid to 1 of plant material. Both acids prevent the enzymic oxidation of ascorbic acid, since the min. *p*H at which this occurs is 3·5–4·0. Data are tabulated showing the effects of various strengths of the acids on extracts of fresh cabbage and frozen broccoli, lima beans, peas and strawberries. There is often a difference in the degree of turbidity of extracts of fruit or vegetable tissues made with the two acids, but this turbidity does not affect the colorimetric determination, *i.e.*, measurement of the rate of reduction of 2,6-dichlorophenolindophenol in a photoelectric colorimeter (Loeffler and Ponting, *id.*, 1942, **14**, 846). Too high a concn. of any of the acids tended to bleach the dye (in absence of ascorbic acid). Almost the same rate of oxidation was found in a 0·01 *M* ammonium oxalate buffer (*p*H 5·6) as in the oxalic acid itself (*p*H 1·86); for the estimation of the activity of ascorbic acid oxidase a 0·01 *M* oxalate buffer (*p*H 6·0) is recommended, since no appreciable non-enzymic oxidation of the ascorbic acid occurs in 20 min., even in presence of up to 3 p.p.m. of copper (*cf.* Krishnamuethy, *J. Indian Chem. Soc.*, 1941, **18**, 191, 201.) J. G.

Ascorbic Acid Content of Recently-harvested Cereals and Legumes. M. N. Rudra. (*Nature*, 1943, **152**, 78.)—Guinea pigs used for the biological assay of ascorbic acid were fed on a "scorbutic" diet of casein, ground and roasted Bengal gram (*Cicer arietinum*), ground oats, cod-liver oil and salts, but it was found that they did not show depletion

or cease to grow, even after 3 weeks. This abnormality was traced to ascorbic acid in the cereals and legumes in the diet, which were harvested in March–April and used in May. Values obtained (biological assay and 2 : 6-dichlorophenolindophenol method) were, Bengal gram, 10·31; oatmeal (whole), 13·97; wheat flour (whole), 5·30 mg per g. J. G.

Microdetermination of Magnesium with the Polarograph. C. Carruthers. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 412–414.)—Low concns. of magnesium in small samples of biological tissue may be determined polarographically as the hydroxyquinolinate. Calibration is effected by pptn. of magnesium hydroxyquinolinate from a magnesium chloride soln., the ppt. then being dissolved in hydrochloric acid. With various concns. of magnesium hydroxyquinolinate in a mixture of 7 parts of 3·33 *M* phosphate buffer of *p*H 7·6 and 3 parts of 0·1 *N* hydrochloric acid, the solns. containing 0·02% of gelatin, it was found that the diffusion current was proportional to the concn. The method has been applied to the detn. of magnesium in mouse epidermis. Calcium and iron were not present in sufficient quantity in the samples under study to interfere with the pptn. of the magnesium hydroxyquinolinate. B. S. C.

Bacteriological

Disinfectant Activity of Caustic Soda. Betty C. Hobbs and G. S. Wilson. (*J. Hygiene*, 1942, **42**, 436-450.)—This paper records the first part of an investigation undertaken for the Ministry of Health into the cleaning and sterilisation of milk bottles in the course of which it was first necessary to obtain information on the bactericidal action of caustic soda under varying conditions of concn., temp. and time. The results of a series of tests with standardised suspensions of *B. coli* and spores of *B. subtilis*, both in water containing the equivalent of 0·1% of milk (prepared from full cream dried milk) and in distilled water, are recorded in tables and graphs. In working out the constants of the disinfectant at different concns. and temperatures the formulae proposed by Phelps were used, that for the reaction velocity "*k*" being

$$(1)\quad k = \frac{1}{t}\log\frac{B}{b},$$

where t = time in min., and B and b the number of viable organisms at start and finish respectively; that for the concn. coefficient "*n*" being

$$(2)\quad n = \log\frac{k_2}{k_1} \div \log\frac{C_2}{C_1}$$

where k_1 and k_2 = the reaction velocity at concns. C_1 and C_2 respectively; that for the temp. coefficient "θ" being (3) $\theta^{10°\text{C.}} = \frac{k_1}{k_2}$, where k_1 and k_2 are the reaction velocities at the higher and lower temperatures respectively, 10° C. apart.*

The outcome of the investigation is summarised as follows:

(1) With *B. coli* the concn. coefficient *n* was *ca.* 2·7, and the temp. coefficient $\theta^{10°\text{C.}}$, *ca.* 2. (2) With *B. subtilis* spores the concentration coeff. *n* was *ca.* 1·75 and the temp. coefficient $\theta^{10°\text{C.}}$, *ca.* 1·5. (3) With *B. coli* the values for the reaction velocity constant *k* tended to be irregular at 40° C. and with *B. subtilis* spores at 70° C., suggesting that at these temperatures some additional factor, presumably heat coagulation of the protein, was beginning to affect the results. (4) With both organisms the value of the reaction velocity constant *k* was relatively low at the start and tended to increase progressively during the course of disinfection. Whether it diminished again as sterility was approached could not be ascertained for technical reasons. (5) With both organisms the presence of 1/1000 milk did not seem to affect the rate of disinfection as compared with distilled water. (6) One expt. with *B. coli* suggested that the rate of disinfection was affected appreciably by the number of organisms present. Increasing the number of organisms in the suspension 100-fold diminished the value of *k* by about one-third. (7) The value of *k* was about 3,000,000 times greater with *B. coli* than with *B. subtilis* spores. (8) If the mean value of *n* is taken as 2·2, it follows that doubling the concn. of caustic soda increases the reaction velocity by 4·6-fold. If, *e.g.*, with a given concn. of caustic soda sterility was reached in 9 min., then doubling the concn. would reduce this time to 2 min., while halving the concn. would increase it to about 40 min. (9) If the mean value of $\theta^{10°\text{C.}}$ is taken as 1·75, it follows that a rise of 10° C. increases the reaction velocity 1·75-fold. If, for example, with a given temp. sterility was reached in 9 min., raising the temp. 10° C. (18° F.) would reduce this time to about 5 min., while lowering the temperature 10° C. would increase it to about 15 min. Above 40° C. (104° F.), however, the rate of destruction of vegetative organisms, and above 70° C. (158° F.) the rate of destruction of sporing organisms in presence of caustic soda is probably increased by the effect of the heat itself. (10) A comparison of the figures for caustic soda with those of Chick for phenol shows that a 0·05% soln. of caustic soda at 20° C. destroyed *B. coli* about five times as rapidly as a 0·5% soln. of phenol at 20° C. destroyed *B. paratyphosum B*, and that a 5% soln. of caustic soda at 20° C. destroyed *B. subtilis* spores nearly three times as rapidly as a 5% soln. of phenol at 33·3° C. destroyed anthrax spores. The superiority of caustic soda over phenol, particularly at concns. likely to be used in practice, is manifest. (11) Regarding the standardisation of disinfectants, it is concluded that the value of *k* taken in the middle stage of the reaction, or from the beginning of disinfection to about the end of the middle stage, affords the most suitable measure of comparison. This is essentially the same conclusion as that reached by Withell (1942), who uses as his index the time necessary to destroy 50% of the organisms. D. R. W.

Cleaning and Sterilisation of Milk Bottles, Betty C. Hobbs and G. S. Wilson. (*J. Hygiene*, 1943, **43**, 96–120.)—After the preliminary investigation (*cf.* preceding abstract) a routine survey of 105 milk-washing plants, representative of 26 different types, was carried out in Greater London. For convenience, these are grouped into (*a*) large plants of straight-through and come-back type; (*b*) small rotary plants; (*c*) plants employing steam sterilisation in a cabinet after washing by hand or mechanical means; (*d*) plants using hand washing alone. The mean counts per bottle expressed as pints were:

* *Abstractor's Note.*—As one would expect in such biological reactions, the constants are approximate; for instance, the reaction velocity constant for a 0·1% NaOH soln. with *B. coli* at 20° C. has a range from 0·46 to 0·33 with an arithmetic mean of 0·37, but they are sufficiently constant for working out optimum conditions.

Group	(*a*)	(*b*)	(*c*)	(*d*)
At 22° C. ..	2008	7982	23,671	96,065
At 37° C. ..	2324	7389	9704	37,818

and the numbers of bottles giving counts less than 600 at 22° or 37° C. and more than 25,000 were:

	(*a*)	(*b*)	(*c*)	(*d*)
Less than 600 ..	55·5%	49%	50%	0%
More than 25,000	1·1%	6·4%	23·5%	83%

From experimental observations in the laboratory on the reaction velocity, the concn. coefficient and the temp. coefficient for solns. of caustic soda, the following table was worked out to show the concns. % required for the destruction of 25% of *B. subtilis* spores:*

Temperature	Minutes				
° F.	1	2	4	8	16
120	2·44	1·64	1·10	0·74	0·50
130	2·15	1·44	0·97	0·65	0·44
140	1·90	1·20	0·86	0·58	0·39
150	1·66	1·12	0·75	0·51	0·34
160	1·46	0·98	0·66	0·45	0·30

These values are worked out on the basis of the following figures: K=0·00735 at 120° F. and with 16 min. exposure (derived from the mean value observed with a 0·5% soln. by equation (2) of previous paper); $n=1·75$ (hence rate of destruction is increased 3·4-fold when concn. is doubled); $\theta^{10°F.} = 1·25$ and $\theta^{10°C.} = 1·5$.

Provided that (*a*) large particles of milk clot and other gross material are removed in the pre-rinse section, (*b*) the detergent soln. is properly filtered to remove suspended matter, (*c*) the soln. is kept up to strength, (*d*) the tanks are cleaned out every few days, and (*c*) due allowance is made for the intermittent exposure of bottles to the detergent in spraying machines, the concns. given in the table are recommended. The use of supplementary loosening substances, *e.g.*, basic phosphates and hexametaphosphates, is recommended, not as substitutes but in addition to the given concns. of caustic soda. Bottles emerging from the detergent section are practically sterile, but tend to be re-contaminated in the rinsing operations. It is shown that in 11 hrs. at 42° C. the bacteria in rinse water may increase from 3,500 to 11,000,000. The employment of hot re-circulated rinse water at a temp. too high for bacterial growth is recommended for removal of detergent, and for the cooling of the bottles external rinses of re-circulated water progressively decreasing in temp. followed by cold spray internally and externally from the main supply. The temp. of bottles in discharge should not exceed 68° F. if they are to be filled at once. The ordinary wide-mouthed bottle with a press-in disc is regarded as peculiarly susceptible to contamination and should not be allowed unless fitted with a hooded cap; a narrow-necked bottle, closed with a deep press-over aluminium cap covering the rim, is recommended. Review of the literature has disclosed the occurrence of numerous outbreaks of infectious diseases attributed to bottles coming from infected houses and used again without adequate sterilisation. The method of carrying out the bottle count is described in detail; briefly, it consists in rinsing the bottles (1 pint and under) with 20 ml of 1/4 Ringer solution and plating out 5 ml with 10 ml of milk agar. In reporting the count it is suggested that the 22° and 37° C. counts for each bottle should be averaged and the mean counts for each of 12 bottles recorded separately. The average of the 12 bottle counts should then be taken. If this final mean, which is based on 24 plate counts, does not exceed 600 per bottle, reckoned as pints, the bottles shall be regarded as conforming to a satisfactory standard of cleanliness.

D. R. W.

* [*Note.*—Doubling these values will result in a destruction of about 60%, and halving them in the destruction about 7% of *B. subtilis* spores.]

Water

Breakdown of Paraffin Wax by Bacteria; a Source of Error in Corrosion Tests. T. H. Rogers. (*Nature*, 1943, **152**, 105–106.)—Tests on the corrosion of metals by waters from glass sampling-vessels which had been coated with paraffin wax to prevent solution of alkali metal silicates, and tests made in such vessels, gave inconsistent and non-reproducible results. It was noted that some of the coatings were attacked and disintegrating, and inoculation of the water from such vessels into a sterile nutrient soln. containing no source of carbon other than flakes of the wax, and incubation at 30° C., resulted in a few days in a growth of bacteria, possibly a strain of *Micrococcus paraffinae*, which, according to Söhngen (*Centr. Bakt.*, 1933, **37**, 595), is aerobic, of soil origin, and commonly found in surface waters. Determinations made on tap waters stored in waxed and unwaxed stoppered Winchester bottles, showed that if cultures of the above organism were added, the apparent free carbon dioxide content increased by *ca.* 20-fold in 40 days, whilst that of uninoculated water in unwaxed bottles or of inoculated water that had been sterilised by heat or disinfectants did not alter. The determination was made by titration with 0·05 *N* sodium carbonate, to phenolphthalein; organic acids formed by the bacteria are thus included as free carbon dioxide. These differences were reflected in the results of corrosion tests on a domestic water in metal pipes closed at both ends with wax; the corrosion rates were:—Untreated, bacteria-free water, 0·9; water inoculated with wax bacteria, 4·1; sterilised water, 0·7; sterilised water after re-inoculation, 4·0. It is pointed out that many other microbiological processes normally occurring in natural waters may increase the carbon dioxide content, that a correct assessment of the corrosive properties of a water cannot be made unless the biological state is taken into account, and that it is seldom safe to assume that a natural water which has been stored for any length of time is still representative of the supply originally sampled.

J. G.

Agricultural

Concentration Methods in Spectroscopic Analysis. R. O. Scott and R. L. Mitchell. (*J. Soc. Chem. Ind.*, 1943, **62**, 4–8.)—Preliminary concn. increases the accuracy of spectrographic determination of certain trace element contents of plant materials and soil extracts. The use of 8-hydroxyquinoline gives a quantitative separation of traces of cobalt, nickel and molybdenum and of somewhat larger amounts of copper and zinc from the alkalis and alkaline earths. Iron and aluminium are pptd. at the same time and serve as carriers. *Procedure for pasture samples.*—Ignite 20 g of well-ground oven-dry material in a platinum basin at 400°–450° C. overnight in an electric muffle furnace, transfer to a platinum crucible, mix with 4 g of sodium carbonate and fuse for 15 min. Extract the melt with hydrochloric acid, dry on the water-bath and take up in 50 ml of 1 : 2 hydrochloric

acid. Filter off the silica on a Whatman No. 41 paper and wash with boiling water. Cool, dilute to 150 ml, and add 10 ml of 5% 8-hydroxyquinoline in 2 *N* acetic acid. Then add 1 : 1 ammonia, drop by drop, until the colour of the soln. just becomes emerald-green at *p*H 1·8–1·9. Add 50 ml of 2 *N* ammonium acetate, resulting in *p*H 5·1–5·2. Prepare the ammonium acetate soln. from ammonia neutralised to *p*H 7 with acetic acid, this avoids the molybdenum contamination likely to occur when using AnalaR ammonium acetate. Stir the soln. vigorously, set aside overnight, then filter through Whatman No. 540 paper and wash with cold water. After drying, ash the ppt. (with the paper) at 450° C. Make up this ash to a total wt. of 40 mg with pure powdered quartz. *Procedure for soil extracts.*—The total content of any soil constituent seldom gives reliable information on the availability of that element to the plant. The following extraction procedure, which gives reasonable correlation with field results, is suggested:—Shake 20 g of air-dry soil (passing 2 mm screen) overnight with 800 ml of 1 : 40 acetic acid. Filter through a Whatman No. 30 paper, dry and treat with hydrogen peroxide to remove organic matter. Dissolve the residue in 1 : 2 hydrochloric acid and filter. Add 10 ml of an iron soln. (free from nickel and cobalt) equiv. to *ca.* 3 mg of Fe_2O_3 and dilute to 150 ml. Then ppt. with 8-hydroxyquinoline as described above for the pasture samples. The spectrographic procedure is that of Davidson and Mitchell (*J. Soc. Chem. Ind.*, 1940, **59**, 213). This necessitates an iron content of 3% to 15% Fe_2O_3 in the material being examined, iron being the internal standard, together with a knowledge of the actual iron content. The presence of iron is ensured by the method of preparing the sample and the amount is determined colorimetrically by the method of Scott (ANALYST, 1941, **66**, 142). The spectrographic data and concentration ranges are as follows:

Element	Analysis line	Fe comparison line	Concn. range
Cobalt	3453·46A	3451·92A	15 to 3000 p.p.m.
Nickel	3414·77	3413·13	15 to 3000 ,,
,,	3101·55	3099·90	300 to 10,000 ,,
Molybdenum	3170·34	3196·93	15 to 3000 ,,
Copper	3273·96	3305·97	10 to 1000 ,,
,,	2961·17	2970·11	0·3% to 10%
Zinc	3345·02	3305·97	0·3% to 10%

Results obtained by this method for synthetic samples resembling ashed plant material seldom differed from the true value by more than ±10%, except with zinc, whose spectrographic behaviour is generally less satisfactory. B. S. C.

Determination of Magnesium in Plants and Soils. M. E. Weeks and J. R. Todd. (*Ind. Eng. Chem., Anal. Ed.*, 1945, **15**, 297–299.)—Plant material (2 g), ground to pass a No. 20 A.S.T.M. sieve, is oxidised by the method of Gieseking *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 185). For ordinary plant material it is not necessary to heat with nitric acid before adding the mixture of nitric and perchloric acids. For oily seeds the following procedure is safe.—Extract 20 g of dried material several times with anhydrous ether. Heat the residue with 20 ml of conc. nitric acid, stirring vigorously until frothing ceases, evaporate the liquid slowly in a covered beaker to a thick yellow paste, add 30–40 ml of nitric acid and maintain the temp. at *ca.* 100° C. for several hrs. Heat the residue carefully with a mixture of nitric and perchloric acids (2 : 1) at 140°–160° C. until the liquid is clear, adding more nitric acid if necessary. Allow most of the perchloric acid to evaporate in an open beaker, dissolve the residue in 10 ml of dil. hydrochloric acid (1 + 1), heat at 100° C. for 20 min. and filter. Wash the filter 6 times with hot 10% hydrochloric acid and 3 or 4 times with water. Dilute the filtrate to 50 ml and take aliquot portions for analysis. For soil, use any of the methods commonly employed for obtaining solns. of total and replaceable bases. Treat the residue with 10 ml of dil. hydrochloric acid (1 + 1), as described for plant material, and dilute the filtrate to 50 ml.

To the soln. to be analysed (≡ 0·1–0·7 mg of magnesium) in a 15-ml conical centrifuge tube, add 5 drops of glacial acetic acid, 1 drop of methyl red and dil. ammonia (1 + 1) from a burette until the colour changes from red to a very faint red or pink (not yellow) corresponding with *p*H 6, and finally add 2 or 3 drops of dil. acetic acid (1 + 4) to give a more distinct red. The *p*H of the soln. should now be 5·0–5·3. Add 3 drops of a soln. of 1 g of 8-hydroxyquinoline in 50 ml of 95% alcohol (prepared fresh every 2 or 3 days) and heat the tube in hot water for 10 to 15 min. to ppt. iron and aluminium. Centrifuge the hot liquid and pour the supernatant liquid into a similar centrifuge tube. Wash the sides of the first tube carefully with a thin stream of warm water from a 2-ml pipette, stir, centrifuge and transfer the washings to the second tube. To ppt. calcium, add 1 ml of a sat. soln. of ammonium oxalate to the contents of the second tube, place the tube upright in hot water, maintain the temp. at *ca.* 100° C. for 30 min. and allow the ppt. to settle for 2 to 4 hrs. Add 5 or 6 drops of alcohol to break the surface layer of calcium oxalate and centrifuge for 10 min. Transfer the supernatant liquid to a third tube, wash the ppt. twice with 2-ml portions of a mixture of equal parts of alcohol and 10% ammonium hydroxide, adding the washings to the third tube. To the contents of the third tube add 0·5 ml of the hydroxyquinoline reagent (1 ml in presence of more than 0·7 mg of magnesium) and 2 ml of conc. ammonia. Stir thoroughly, remove the stirring rod, washing it with a fine stream of water, and, when pptn. starts, cover the liquid with a 1-cm layer of alcohol. Heat the tube in hot water for 20 min. and, after replenishing the alcohol layer (if necessary) to prevent formation of a surface film of ppt., set the stoppered tube aside at room temp. for at least 2 hrs. Centrifuge for 10 min., remove the supernatant liquid by gentle suction through a tube with an upturned capillary end and wash the ppt. twice with 2-ml portions of the alcohol and ammonia mixture, covering the suspension each time with alcohol before centrifuging. Dry the ppt. carefully for a few min. in hot water, avoiding formation of a hard mass. Remove the tube from the bath, add 10 ml of a soln. of 10 g of ferric chloride hexahydrate in 2 litres of water containing 10 ml of glacial acetic acid and break up the ppt. by stirring or shaking. The full green colour of ferric hydroxyquinolinate develops in *ca.* 30 min. Dilute an aliquot portion (2 ml) with 10 ml of the ferric chloride soln. and determine the light transmission in a photoelectric colorimeter or spectrophotometer, and from the transmission value determine the magnesium content by means of a standard curve prepared by pptng. 1 to 10-ml portions of 0·01 *N* magnesium sulphate soln. by the method described. The extinction

curve for magnesium hydroxyquinolinate shows max. absorption at 660$m\mu$ with a secondary maximum at 460$m\mu$. Beer's law was found to hold for concns. of 1 to 10 mg per ml. The phosphate ion has little, if any, effect on the pptn. of magnesium hydroxyquinolinate. A. O. J.

Determination of Small Quantities of Sodium in Soil Solutions and Soil Extracts. M. Y. Shawarbi and A. G. Pollard. (*J. Soc. Chem. Ind.*, 1943, **62**, 71–73.)—The following modification of Leva's method (*J. Biol. Chem.*, 1940, **132**, 487) is recommended. *Reagents.*—(1) *Manganous uranyl acetate stock soln.*—To 160 g of $UO_2(OAc)_2.2H_2O$, 490 g of $Mn(OAc)_2.4H_2O$ and 138 ml of 30% acetic acid add 1500 ml of water and make the soln. up to 2 litres. After 24 hrs., filter, and store in a dark bottle. (2) *Dilute alcoholic manganous uranyl acetate soln.*—Mix 180 ml of reagent (1) with 60 ml of 95% alcohol and filter, after 4 hrs., through a No. 42 Whatman paper. Stored in a dark bottle; the soln. keeps for 3 weeks. (3) *Zinc uranyl acetate stock soln.*—Dissolve 160 g of $UO_2(OAc)_2.2H_2O$, 440 g of $Zn(OAc)_2.4H_2O$ and 138 ml of 30% acetic acid in 1500 ml of water and dilute to 2 litres. After 24 hrs. filter and store in a dark bottle. (4) *Dilute alcoholic zinc acetate wash soln.*—Mix 120 ml of reagent (3) with 40 ml of 95% alcohol, stand in an ice-bath for 1 hr., saturate with 32 mg of solid manganous triple salt (see below) and filter, after at least 1 hr., through a No. 4 sintered glass crucible, using suction. Store in a dark bottle, when the soln. keeps for 3 weeks. (5) *Sodium manganous uranyl acetate.*—Treat 125 ml of reagent (1) with 2 ml of 5% sodium chloride soln. Centrifuge after 30 minutes. Remove the supernatant liquid, wash the ppt. 3 times with 95% alcohol and twice with ether and dry at normal temp. (6) *Oxidising soln.*—Dissolve 0·75 g of potassium periodate in 150 ml of water, add 25 ml of syrupy phosphoric acid, and dilute to 200 ml. This soln. keeps for a month in a cool place. *Procedure.*—Place the test soln., containing 50–500μg of sodium in 1 ml, in a 30-ml beaker, add 10 ml of reagent (2) and mix by shaking. Stand for at least 4 hrs. at room temp., then collect the ppt. on a No. 4 sintered glass crucible, using suction. Wash the beaker and the ppt. 5 times with 5 ml of ice-cold wash liquid. Rinse the outside of the crucible with water. Dissolve the triple acetate salt by adding 3 portions of 5 ml of warm 2 *N* sulphuric acid, using slight suction. Wash the crucible twice with water, collecting the filtrate and washings in a 100-ml beaker. Boil the liquid over a low flame for 5–7 min. to remove the last traces of alcohol. Add 25 ml of potassium periodate reagent. The max. colour intensity is reached after boiling for 5–7 min. Cool the coloured soln., make up to 50 ml, and match the colour in a Lovibond–Schofield Tintometer, using a 1-cm cell. With solns. containing less than 50μg, 10 ml of the test soln. is reduced to 1 ml in a 30-ml beaker and the above procedure followed. The straight-line relationship between the quantity of sodium and the violet colour (red-blue) is indicated in a table and a graph. Phosphate and the common soil bases do not interfere. Potassium, when present in 3–4 times the quantity of the sodium, causes the results to be high. E. M. P.

Anhydrous Copper Sulphate in the Kjeldahl Nitrogen Determination. C. Beatty. III. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 476.)—Replacement of the copper sulphate pentahydrate catalyst used for Kjeldahl nitrogen determinations (Assoc. Off. *Agric.* Chem., *Official and Tentative Methods of Analysis*, 4th Edn., II, 1935, p. 25) by the anhyd. salt has the following advantages.—Since the salt does not dissolve completely in sulphuric acid, the fine residual crystals serve to eliminate bumping during boiling; for the same reason a larger flame can be used; the salt is useful as an internal indicator at the distillation stage. For semimicro work add 8 ml of conc. sulphuric acid, 2 g of a finely-ground mixture of the anhyd. copper sulphate with potassium sulphate (1 : 2) and 20 mg of powdered selenium to 20–35 mg of sample; digest the mixture for 15–25 min. J. G.

Organic

Determination of Water in Alcohol with Aid of Dicyclohexyl. G. R. Robertson. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 451–452.)—The Crismer method for the determination of the water content of alcohol from the critical soln. temp. of a mixture with kerosene (Osborne, McKelvy and Bearce, *Bur. Standards, Bull.*, 1913, **9**, 344) suffers from the disadvantage that each batch of kerosene must be calibrated by a laborious process. The dicyclohexyl dodecahydrodiphenyl ("Dicyclohexyl") now available on the commercial scale (from the hydrogenation of diphenyl) is suggested in place of kerosene, and since it is a single substance, it need be calibrated only once and for all. The system ethanol-dicyclohexyl has the convenient critical soln. temp. of 23·4° C., with an increase of 18° C. for the first 1% of water added to the alcohol. To 2·0 ml of the sample in a dry 15-mm test-tube add 4·0 ml of dicyclohexyl, stir with a dry thermometer, heat the mixture until clear, and allow it to cool slowly, with stirring. As the critical soln. temp. is reached the liquid becomes opalescent (resembling a very dil. soap soln.), but the thermometer column is still readable. Suddenly (within a temp. range of 0·2 C.), the liquid becomes so turbid that the height of the thermometer thread cannot be read through 5 mm of liquid. This temp. is recorded, and the % of alcohol is obtained from it by means of the calibration graph (given in the original paper). The graph is almost linear, and can be constructed with a reasonable degree of accuracy from the following alcohol contents (%) and their corresponding temperatures (°C.), respectively:—100, 23·4°; 99·1, 39·8°; 98·8, 44·2°; 98·0, 54·2°. Data are given in the original paper for other ratios of vols. of alcohol and dicyclohexyl. Sources of error are as follows. The shift of the peak of the miscibility curve towards the dicyclohexyl axis with increase in water content calls for care in measuring vols., and the probable error is an increasing one; determinations made on samples containing less than 99% of alcohol are, therefore, only approx. The development of opalescence just above the max. temp. of true turbidity (*cf. supra*) also lowers the precision as compared with Crismer's method, but with a good thermometer 99·90 and 99·91% alcohol can be distinguished (99·900 and 99·903% by Crismer's method). On the other hand, the purity of commercial dicyclohexyl is adequate, and standardisations of the Eastman Kodak (m.p., 3·5° C.) and Dow Chemical Co. (m.p., 3·4° C.) products, and of the latter after fractionation and recrystallisation (m.p. 3·63° C.) against 99·9 + % alcohol showed no significant differences. The reagent should, however, be filtered through a dry paper to remove all the suspended and some of the dissolved water; there

is no necessity to dry it further or to protect it from the atmosphere. The standardisations were carried out against a specially calibrated paraffin oil and highly purified alcohol. J. G.

Use of Xanthydrol as a Reagent for the Characterisation of Primary Amides. R. F. Phillips and B. M. Pitt. (*J. Amer. Chem. Soc.*, 1943, **65**, 1355–1357.)—Primary amides can be characterised directly, without preliminary hydrolysis, by condensation with xanthydrol and determination of the m.p. of the resulting xanthyl amides. Two procedures are suggested. (1) Dissolve 0·5 g of xanthydrol in a mixture of 5 ml of ethyl alcohol, 2 ml of glacial acetic acid and 3 ml of water. If an oil separates, decant the supernatant soln. Add 0·5 g of amide and heat at 85° C. on the water-bath in a loosely corked test-tube until the product appears, or at any rate for not longer than 40 min. If no product appears in the hot soln., it will crystallise out on cooling. (2) Dissolve 0·5 g of xanthydrol in 7 ml of glacial acetic acid. Decant the clear soln. if an oil separates. Add 0·5 g of amide and allow to stand, or, if more rapid condensation is required, heat for not more than 40 min. on the water-bath. The acetic acid technique is to be preferred, but when the amide is not sufficiently soluble the first procedure is preferable. The products can be crystallised from 65% dioxane and water, using a higher proportion of dioxane for the more insol. derivatives. Pyridine and water, and acetic acid and water can also be used. Dry the products at 80° C. for about 15 min. The m.p. and nitrogen contents of the products from 22 primary amides and 2 imides are tabulated. E. M. P.

Microchemistry of Pulp Fibres. Significance of the Fibre-ballooning Test. W. M. Harlow. (*Paper Trade J.*, 1943, **117**, July 8; *T.A.P.P.I. Sect.*, 15–17.)—Fibre ballooning, or the production of alternating bead-like swellings and ring-like constrictions in chemically-treated fibres by certain reagents, is probably due to the difference in the natures of the primary (outer cambial) and secondary fibre walls. The former strongly resists enlargement by chemical or mechanical methods while the latter is more spongy, and can be stretched or swollen considerably before rupturing. These properties of the primary wall are due partly to its spiral structure, in which the fibres are aligned substantially at right angles to the fibre axis, and probably also to the fact that it is not a continuous sheet of cellulose, but consists of laterally wrapped bands cemented together with a non-cellulosic material. The best swelling reagent for these studies is a soln. of ruthenium red in trimethylbenzyl ammonium hydroxide (*cf.* ANALYST, 1943, **68**, 292) since it is less drastic and more selective than other suggested reagents, and the swollen fibres are stained so that the fine details of the fibre may readily be photographed through a green filter (illustrations in the original paper). Tests with white pine groundwood which had been cooked for varying periods by the kraft process showed that ballooning was most conspicuous for the pulp showing the max. average sheet strength; this corresponded with a lignin content of *ca.* 6%. It was also possible by the ballooning test to identify the 7 kraft pulps and to arrange them in order of lignin contents between 3 and 23·7% of lignin, although with some uncertainty for the 2 pulps of highest lignin contents in the series. J. G.

Inorganic

Determination of Zinc and Cadmium with Anthranilic Acid. P. Wenger. (*Helv. Chim. Acta*, 1942, **25**, 1499–1500.)—The metals may be pptd. at the ordinary temperature (Cimerman and Wenger, *Mikrochem.*, 1935, **18**, 53) and also at 100° C., as pointed out by Funk (*Z. anal. chem.*, 1942, **123**, 241). S. G. C.

Turbidimetric Determination of Small Amounts of Chlorides. E. N. Luce, E. C. Denice and F. E. Akerlund. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 365–366.)—Adjust the *p*H of the sample in a 50-ml calibrated flask (with 1·0 *N* nitric acid or sodium hydroxide) to phenolphthalein neutrality, dilute to 20 ± 1 ml, add 20 ml of abs. ethanol, a drop at a time from a pipette, and then, while swirling the flask, 5 ml of a soln. containing 12·5 ml of conc. nitric acid and 1·70 g of silver nitrate per litre. Dilute to the mark, shake, place the flask in a bath at 40° C. for 30 min., cool it rapidly to room temp., pour the contents into the 20-mm optical cell of the Hellige turbidimeter (*infra*), stir-in 10 ml of abs. ethanol and, when bubbles no longer form and before 30 min. have elapsed since attaining room temp., match the turbidity. Allow for the reading obtained with the reagents alone, and reject any samples which are turbid before the addition of the nitric acid and silver nitrate reagent. No preparation of standards is required with the Hellige turbidimeter, in which a beam of light is compared with the Tyndall effect produced by lateral illumination of the soln. by the same light source. The beam appears as a circular spot in the centre of the Tyndall effect, and this can be made lighter or darker by manipulating a precision slit (*cf.* Sheen, Kahler and Ross, *id.*, 1935, **7**, 262). By matching the brightness of the 2 fields the apparatus may be calibrated for a range of chloride concns., using a standard soln. equiv., after pptn., to 0·5 p.p.m. of chloride ion. Typical calibration curves are given for 0 to 5·0 p.p.m. of chloride; they may also be constructed to cover the use of 95% in place of abs. ethanol. Turbidities equiv. to more than 250μg of chloride cannot be determined accurately; for concns. of 1–2 and less than 1 p.p.m. the milk-glass and grey-glass filters supplied with the apparatus should be used, respectively, but the apparatus must be calibrated with the appropriate filter in position. The error of setting the dials (±1 unit for the same or for different operators) limits the accuracy of the method, but the max. deviation of less than 3% for the whole range of concns. is comparable with that of an ordinary nephelometer; the main advantage of the method, however, is the rapidity of determination (less than 15 min.). The presence of interfering electrolytes may often be offset for routine purposes by adding them in the appropriate proportions to the standard soln. used for calibration; when, however, chloride concns. of 0·005% or less are required to within one significant figure, a special reference curve is unnecessary. The other principal interfering factors are the effects of temp., time of standing, mixing conditions and relative concns. (*cf.* Lamb, Carleton and Meldrum, ANALYST, 1926, **45**, 150). Good results were obtained for the routine determination of chlorides in wash liquors and, in conjunction with the lamp combustion method, in organic matter. Acetic acid may be used with substances insol. in the alcohol soln., provided that a special calibration curve is prepared. J. G.

Physical Methods, Apparatus, etc.

Colour Index for Petroleum Products. I. M. Diller, J. C. Dean, R. J. DeGray and J. W. Wilson. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 367–373.)—A proposed method for the evaluation of the colour of petroleum products, tentatively known as "photoelectric colour," enables both lubricating oils and the light-coloured oils to be included in the one system. The colour is expressed in terms of the readings given by a special photoelectric absorptiometer. For dark oils, two parameters are sufficient to designate the colour; these are obtained from readings made with optical filters giving "North Sky" and "Red" illuminations respectively. It is pointed out that colour values expressed on this system indicate at a glance both the optical density and the degree of green or red tint of the oil. For the light oils, all of which have negligible absorption at wavelengths greater than 550$m\mu$, it is sufficient to measure the absorption, using a special violet filter. The value so obtained is then converted to the North Sky value by a numerical factor, thus relating it to the colour values for the darker oils. The advantage of the violet filter method for the light oils is that the same cell depth may then be used for both dark and light oils. The relations between the proposed system and existing systems are discussed, and a method of obtaining C. I. E. colorimetric data from the "photoelectric colour" is given. B. S. C.

Applications of Near Infra-red Spectrophotometry. E. I. Stearns. (*J. Opt. Soc. America*, 1943, **33**, 27–30.)—An automatically recording visual range spectrophotometer can be modified to cover the extended wavelength range 375 to 1200$m\mu$. The extension to the near ultra-violet enables the absorption maxima of dyes such as Direct Fast Yellow B to be measured. In the near infra-red region, measurements at 960$m\mu$ enable the amount of ethyl alcohol in water to be determined within 0·2%; this determination can be made in 5 min. Another infra-red application is the differentiation of the three dyes Indanthrene Blue RS, GCD and GCS. These differ only in their chlorine content, which increases in the ratio 0, 2, 3 atoms per mol. respectively. Determination of the absorption curves over the range 750 to 850 $m\mu$ reveals the most significant differences in the spectra of the three dyes. One important source of error peculiar to the infra-red instrument is discussed. For example, the dye Naphthalin Green V is fluorescent; on absorption of visible radiation of wavelength 640$m\mu$ it emits infra-red fluorescent radiation. This may be overlooked because it is not visible. A photoelectric cell which is sensitive to near infra-red radiation in addition to visible light will therefore respond to both the transmitted and the fluorescent radiation, leading to a false absorption value when making measurements at 640$m\mu$. Where this effect is suspected, it may be verified by the use of a photoelectric cell of a type not sensitive in the infra-red. B. S. C.

Applications of the Spectrograph to Steelworks Analysis. H. T. Shirley and E. Elliott. (*J. Iron and Steel Inst.*, 1943, advance proofs.)—Using a standard spark method of excitation, a carbon rod as one electrode and samples in the form of small chill ingots, 3 in. long by 1¼ in. sq., routine analysis of high-alloy steels can be carried out satisfactorily by means of the spectrograph. All line intensities are measured with a non-recording photoelectric microphotometer, iron lines serving as internal standards. The necessary strict control of the spectrographic and photographic processes is discussed in detail. The method has been applied to the analysis of many thousands of casts of two high-alloy steels having the following nominal composition:—

	Steel A %	Steel B %	Max. routine spectrographic errors normally encountered
Silicon	0·9	1·2	±0·1%
Manganese	5·5	0·5	±0·2% in A, ±0·03% in B
Chromium	5·0	14·5	±0·2% in A, ±0·3% in B
Nickel	12·5	12·5	±0·25%
Vanadium	0·3	—	±0·01%
Tungsten	—	3·0	±0·15%

B. S. C.

Pressed Pellet Electrode Method for the Spectrographic Analysis of Nickel Alloys. C. J. Neuhaus. (*J. Opt. Soc. America*, 1943, **33**, 167–174.)—The pressed pellet technique enables electrodes of uniform size and shape to be obtained from samples having a variety of forms. Millings, filings and small cuttings are all suitable for pressing into pellets, 1/4 in. diam., 5/32 in. long, containing approx. 1 g of material. Using a Carboloy die and a carbon steel punch, an applied pressure of 16,000 lbs. for 30 sec. is suitable. If less than 1 g of sample is available, the pellets may be made to standard size by using some other available nickel or copper millings as a fill-up material at the bottom of the die. Care must be taken that this does not penetrate too far into the sample proper. The sparking face of each sample pellet is finished by grinding to a face angle of 8°. The spectrum of the sample, which is held in a silver-faced copper grip, is then excited in a normal spark circuit, a graphite rod, pointed down to 2 mm diam., being used as the second electrode. For the determination of iron, manganese and magnesium in nickel, analytical curves are prepared, using chemically analysed standards; these cover the following concn. ranges when using the specified line pairs.

Element	Concn. range	Line	Nickel comparison line
Iron	0·03 to 0·50%	2599·4A	2670·3A
Manganese	0·04 to 0·30%	2701·7A	2670·3A
Magnesium	0·05 to 0·90%	2790·8A	2825·2A

B. S. C.

Use of Powders in Spectrochemical Analysis. A. E. Ruehle and E. K. Jaycox. (*J. Opt. Soc. America*, 1943, **33**, 109–112.)—It is sometimes advantageous when using solution methods of spectrochemical analysis to take the soln. to dryness before loading the electrode. This permits additional operations, such as the admixture of a buffer, which result in improved reproducibility in arcing. The method can be applied to the analysis of tin lead solders for the following impurities:—aluminium, arsenic, bismuth, copper, iron, nickel, antimony and zinc. *Procedure.*—Weigh approx. 3 g of the granulated sample (*e.g.*, sawings from the bar) and dissolve in 10 ml of 15% nitric acid. Evaporate the soln. to dryness, bake, grind and mix thoroughly with an equal weight of purified carbon dust containing 20% by wt. of pure ammonium

nitrate. Place the sample in a hole (3/16 in. diam. by 1/8 in. deep) in a 1/4 in. graphite rod electrode, and arc at 250 v., 9 amp. Control the exposure to obtain lines suitable for densitometric measurements. Photograph the spectra of standards under exactly similar conditions. *Standards.*—Dissolve spectrochemically pure tin in conc. nitric acid. To the cloudy soln. resulting, add a soln. of pure lead nitrate so as to obtain the desired tin/lead ratio. Add measured amounts of nitrate solns. of the desired impurities to make a suitable series of standards. Impurity concns. of 0·001%, 0·003%, 0·01%, etc., up to 0·3% are suitable. Take to dryness and mix with carbon dust and ammonium nitrate as for the unknown sample. Determine the various impurities in the sample by the usual methods. The advantage of adding the ammonium salt is that its rapid decomposition provides gases that assist in carrying the powdered sample into the arc stream. B. S. C.

Testing and Rating Air Filters. O. C. Eliason. (*Bell Lab. Record,* April, 1943, 243–247).—The apparatus comprises a wind tunnel (with a variable-speed blower, pitot tubes and gauges to control the vol. of air) and a device for feeding dust into the air-stream at a constant rate; the standard dust is a mixture of lamp black, powdered charcoal, iron oxide and wood flour. The amount of dust in the air before and after it has been passed through the air-filter under test (*i.e.*, without and with this air-filter in the air current) is determined by collecting the dust from known vols. of air on filter-papers weighed under conditions of constant temperature and humidity; the results provide a measure of the effectiveness of the air-filter.

Review

STARCH AND ITS DERIVATIVES. By J. A. RADLEY, M.Sc., F.I.C. Second Edition. Pp. xii + 558, with 61 micrographs and 60 figures. London: Chapman & Hall, Ltd. 1943. Price 36s. net.

Since the publication of the first edition three years ago (see ANALYST, 1940, **65**, 481) this work has undergone enlargement to nearly twice its original length. Incorporation of new matter has extended almost all the chapters and has burst the bounds of the chapter on physical properties, which has now been divided into five; several entirely new chapters have been added, including one on the relation of starch to the foodstuff industry and a lengthy one by Professor F. F. Farley on the oxidation of starch, and there is a new section (Part V, pp. 87) on amylases. The work is now a very comprehensive and well documented text-book on starch and dextrins. The attention given to recent work is one of its most valuable features. The reviewer of the first edition commented on its wealth of references; in the new edition there are about 1200 more,—an indication of the vastness of the subject and the labour that must have gone to the preparation of the book.

The analytical part (Part IV), which includes chapters on the General Examination of Starches (pp. 25), the Determination of Starch (pp. 23) and the Analysis of Dextrin (pp. 15), has not been greatly enlarged, but a useful new feature is a 4-page table showing the types of methods for starch determination that have been applied to various materials, and there is also a 4-page table of data on the composition of various starch-bearing materials.

A work of this kind gives abundant opportunities for minor errors, but remarkably few have been noted. One slip may be mentioned here, as it concerns analysis. V. Jahn's method for determining starch in sausages (p. 400) is wrongly placed among the hydrolytic methods and described as one in the table on p. 407. It is in fact Ewers' method applied to the residue from extraction with alcoholic potash. The mistake no doubt arose from Jahn's misuse of the verb "invert" to describe the action of the acid on the starch,—a misuse that has now been transmitted to p. 400 of this book.

All chemists whose work requires an up-to-date knowledge of starch, and particularly those concerned in its study and technical applications, will be grateful to the author for this valuable survey of a complex subject and guide to what is perhaps a still more complex literature. J. HY. LANE

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