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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at 5 p.m. on Wednesday, May 5th, at The Chemical Society's Rooms, Burlington House, London, W.1. The President, S. Ernest Melling, occupied the chair, and the following papers were presented and discussed:—"The Separation of Vitamin A from Xanthophylls in Presence of Egg Yolk Sterols," by T. Barton Mann; "Two New Colour Reactions of Stilboestrol," by T. Tusting Cocking, F.I.C. "The Determination of Copper Volumetrically by the Iodine-Thiocyanate Method," by C. C. Oglethorpe, B.Sc., and C. G. Smith, B.Sc., Ph.D., F.I.C.

NEW MEMBERS

Vernon Harbord, A.R.S.M., A.I.C.; John Harold High, B.A. (Oxon.), B.Sc. (Glas.), Stanley Cecil Mitchell, B.Sc. (Lond.), A.I.C., Frank George Young, Ph.D., D.Sc. (Lond.).

ANALYTICAL METHODS COMMITTEE

THE Council regrets to announce that Mr. Hinks, who has been Chairman of this Committee since it was formed in 1924 (as the Standing Committee on Uniformity of Methods of Analysis) has, for reasons of health, resigned from that office, though he will continue to serve as a member of the Committee.

The members of the Analytical Methods Committee and the President recently entertained Mr. Hinks to lunch, to mark their appreciation of his long and valuable service and particularly of his personal influence on the successful working of the Committee—and also to have an opportunity of jointly expressing their esteem.

Photometric Estimation of Potassium by a Modification of the Jacobs-Hoffman Method*

BY A. EDEN, M.A., PH.D., F.I.C.

(*Read at the Meeting, February* 3, 1943)

THE Kramer–Tisdall method[1] for the determination of potassium by cobaltinitrite pptn. in blood serum and in solns. of ashed biological material has, almost since its introduction, been subjected to various criticisms and modifications. The principal objections have been the empirical composition of the ppt., and the difficulty in obtaining consistent results even with the same material. The washed ppt. is finally oxidised by standard permanganate soln., but the factor relating quantity of permanganate used to potassium present appears to vary considerably amongst different analysts even when standard solns. of potassium are employed.

The variability of the factor may be attributed to two causes: (1) variations in the composition of the ppt., usually stated to be $K_2NaCo(NO_2)_6,H_2O$ and (2) variations in the washing technique. The composition of the ppt. is usually stated to vary with the Na : K ratio of the fluid under examination, although with blood serum this is approximately constant except in certain pathological conditions. In any event the variation of the Na : K ratio is hardly sufficient to account for the type of variation found in the $KMnO_4$: K factor. It is to the second cause that insufficient attention has been paid. The ppt. of potassium sodium cobaltinitrite is appreciably sol. in water, the solubility increasing rapidly with rise of temp. The Kramer–Tisdall procedure of washing four times with water, "avoiding disturbances of the precipitate," aims at striking an equilibrium between min. solution of the ppt. and max. removal of the pptg. cobaltinitrite. It is evident that such a procedure is at best a compromise, and under identical conditions of pptn. the

* Since this paper was read my attention has been drawn to a paper by Lewis and Marmoy (*J. Soc. Chem. Ind.*, 1933, **52**, 177T), in which several methods of determining potassium as cobaltinitrite (including that of Jacobs and Hoffman) in agricultural analysis are described. The value of 70% ethyl alcohol as a washing fluid is also stressed.

variability of the permanganate factor is attributable to imperfections in reaching the correct equilibrium. Water is therefore not a suitable washing fluid.

Recently I had occasion to analyse a series of biological fluids, which were either pptd. directly or first ashed and dissolved in dil. hydrochloric acid, and previous experience with potassium determinations on cattle sera had shown a need for improved technique. Search of the literature revealed a paper by Jacobs and Hoffman,[2] who not only described a new colour reaction for the estimation of cobalt in the ppt. but also considered the problem of washing. They drew attention to the inadequacy of washing by water and suggested the use of 70% ethyl alcohol as a washing fluid. The colour reaction for cobalt, based on the formation of an emerald-green complex by cobaltous salts, choline hydrochloride and sodium ferrocyanide, was essentially simple, and lent itself readily to colorimetric and photometric estimation.

It was thought that this reaction should be more widely known to analysts, particularly those concerned with the estimation of small amounts of potassium of the order of 0·1 mg absolute weight, or 0·02 mg per ml, and the present paper therefore records the technique now adopted in this laboratory. Minor alterations in the conditions of pptn. and washing are employed, and a photometric finish is recommended, although visual comparison of the final colour can be used. Besides being directly applicable to serum the method can be readily applied to solns. of ashed tissues or inorganic solutions free from ammonium ions and should prove of value to agricultural analysts for the estimation of total and available potassium in soils and of the potassium content of feeding stuffs.

METHOD.—*Reagents.*—(1) *Sodium cobaltinitrite* (formula of Kramer and Tisdall). Dissolve 120 g of $NaNO_2$ A.R. in 180 ml of water, and pour 210 ml of the soln. into 50 ml of water in which have been dissolved 25 g of $Co(NO_3)_2,6H_2O$ A.R. and 12·5 ml of glacial acetic added. Draw air through the liquid until all nitrous fumes have disappeared, and after leaving the solution in the refrigerator overnight filter through a Whatman No. 40 paper. Preserve in the cold, and filter before use each time. (2) *Sodium nitrite A.R. (K-free).* A 50% w/v soln. (3) *Choline hydrochloride.* A 10% soln. stored in the cold. Dilute to 1% just before use. (4) *Potassium ferrocyanide.* A freshly prepared 2% soln. (5) *Standard potassium soln.* 0·4457 g of dried K_2SO_4 A.R. to 1 litre: 1 ml≡0·20 mg K. (6) *Standard cobalt soln. A.R.* Cobalt sulphate is dried in an oven at about 160° C. for 6 hours. Water is lost and the residue consists of $CoSO_4,H_2O$. Dissolve 0·485 g of this product in a litre of water containing 5 ml of *N* H_2SO_4. One ml contains 0·165 mg of cobalt, which corresponds approx. to the amount in the ppt. from 1 ml of standard potassium soln. Each analyst, however, should standardise his cobalt soln. against the standard potassium soln. (7) *Normal washing fluid.* Ethyl alcohol, 70% v/v. (8) *Washing fluid for serum.* Precipitate sufficient sodium potassium cobaltinitrite, wash centrifugally with water, and form a sat. soln. by shaking with water. Leave overnight, centrifuge down the excess ppt. and use the supernatant fluid for washing. This avoids any possible pptn. of protein by high concn. of alcohol when serum is analysed directly. For the second and third washings use the normal washing fluid.*

Procedure.—To a suitable aliquot portion of the fluid, containing between 0·1 and 0·3 mg of potassium, or to 1 ml of serum, in a graduated 15-ml centrifuge tube add 0·5 ml of 50% sodium nitrite soln. Mix, dilute to 4 ml, mix again and add 2 ml of sodium cobaltinitrite reagent from a burette, drop by drop. Mix, leave for 1 hr., and centrifuge for 10 min. at *ca.* 2,500 r.p.m. When serum is used remove the supernatant fluid with a hand siphon having a fine, slightly upturned tip, and then add 2 ml of the serum washing fluid and re-centrifuge for 5 min. Remove the supernatant fluid as completely as possible with the siphon, wipe the mouth and upper portion of the tube with a clean cloth damped with 70% alcohol, and then disintegrate the ppt. with 5 ml of 70% alcohol. Centrifuge for 5 min., remove the supernatant liquid as before, repeat the washing with 5 ml of 70% alcohol, disintegrating the ppt. and rinsing down the sides. Again completely remove the supernatant fluid, suspend the ppt. in 3·0–3·5 ml of water, and immerse the tube in a beaker of boiling water, whereupon, with the aid of a stirring rod if necessary, the ppt. should all dissolve in about 5 min. Cool, add 1 ml of 1% choline hydrochloride soln. and then 1 ml of potassium ferrocyanide soln., dilute to 6 ml and mix. Prepare a standard from 1 ml of

* Hoffman[3] has recommended a sat. soln. of potassium sodium cobaltinitrite in 10% ethyl alcohol as a washing fluid for the first washing of a ppt. direct from serum.

standard cobalt solution, dilute to 4 ml and add 1 ml of choline soln. and 1 ml of ferrocyanide soln. as above. Check the cobalt soln. against 1-ml portions of the standard potassium soln., treated as above. The unknowns can then be compared visually with the standard cobalt or in a Pulfrich photometer employing 1-cm. cells against a blank containing 1 ml each of the choline and ferrocyanide solns. diluted to 6 ml. Filter S57 is most suitable, although filters S47 and S61 may also be employed. Over the range 0·05 to 0·35 mg of potassium in the aliquot portion the relationship between extinction coeff. and potassium is linear, the straight line passing through the origin. Each analyst should prepare his own factor or chart but the following are the results obtained in this laboratory.

My factors, for 0·20 mg of potassium in the aliquot portion taken, are E = 0·265 with S47, E = 0·345 with S57 and E = 0·545 with S61. For serum, when 1 ml is taken, E × 57·97 = mg K per 100 ml, with filter S57.

Under the conditions described, quantities of potassium exceeding 0·35 mg give colours too intense for accurate spectrophotometric reading and a smaller aliquot portion of the fluid should then be taken. Within the range 0·1–0·3 mg, constant and reproducible results are obtained. Recoveries of added potassium are quantitative, as the following table shows.

TABLE I.—RECOVERIES OF ADDED POTASSIUM

A. Pure K_2SO_4 soln.		B. 0·5-ml portions of ashed ascaris body fluid re-dissolved in dil. HCl			C. Blood serum of sheep (direct)
K added mg	K found mg	K added mg	K found mg	K added recovered mg	mg K per ml
0·050	0·045	nil	0·094	—	0·188
0·100	0·098	0·045	0·145	0·051	0·192
0·150	0·159	0·072	0·168	0·074	0·195
0·200	0·207	0·090	0·188	0·094	0·192
0·250	0·257	0·135	0·229	0·135	
0·300	0·300	0·180	0·282	0·188	
0·350	0·343				
0·400	0·394				

The data on serum agree with the usually accepted figures; Jacobs and Hoffman showed that there was practically no difference between the figures obtained for potassium on serum direct and on the serum ashed and redissolved in dilute acid.

Procedure for Feeding-stuffs and Soils.—Standard methods for total and available constituents in soils are employed up to the point of obtaining the potassium in inorganic form in slightly acid soln. Suitable aliquot portions are then taken to obtain a quantity of potassium between 0·1 and 0·3 mg, and the above procedure is applied.

For feeding-stuffs dry ashing is carried out as usual, the ash is taken up with hydrochloric acid and evaporated to dryness on the water-bath and about 2 ml of *N* hydrochloric acid in sufficient water are added. The insol. siliceous matter is filtered off, and the filtrate is made up to known vol. Potassium is then determined in a suitable aliquot portion by the method outlined.

DISCUSSION.—Jacobs and Hoffman recommended a standard soln. of cobalt containing 0·6469 g of $CoSO_2,7H_2O$ per litre, of which 1 ml, theoretically containing 0·136 mg of cobalt, is equal to the cobalt equiv. of 0·18 mg of potassium in the cobaltinitrite pptn. under the conditions they recommend for pptn.; 0·18 mg was probably selected as an average potassium value of normal serum.

This assumes that the composition of the ppt. is $K_2NaCo(NO_2)_6,H_2O$. Under the conditions of pptn. in presence of excess sodium now described, 0·136 mg of cobalt corresponds only to about 0·165 mg of potassium, a result which is about 9% too low. Consequently the strength of the cobalt solution has been increased so that each ml of standard cobalt soln. contains 0·165 mg of cobalt, corresponding to 0·20 mg of potassium. It seems, therefore, that with the present method the atomic ratio of potassium to cobalt is slightly less than 2 : 1, and this may imply that the ppt. of constant composition is one represented by no simple formula. Tentatively we may assume that a fraction of the ppt. may consist of $KNa_2Co(NO_2)_6,xH_2O$. The excess of sodium over the potassium is more than 450 times (0·5 ml of 50% $NaNO_2$ contains approx. 83 mg of Na).

In the initial stages of pptn. this addition of 0·5 ml of 50% sodium nitrite serves to ensure not only that the ppt. does not adhere to the sides of the tube (Peters and Van

Slyke[4]) but also that it subsides clearly and quickly on centrifuging; it also has the advantage of "swamping" the sodium normally present in the fluid under examination by such an excess that pptn. occurs virtually under the influence of a constant Na : K ratio and hence the ppt. is of constant composition. In spite of the arbitrary composition of the ppt., a common feature of all potassium analyses involving the use of cobaltinitrite, theoretical results are shown by the straight line relationship, and satisfactory recoveries of added potassium are readily obtained under the conditions outlined for pptn., washing and development of colour. Photometric estimation of the cobalt-choline-ferrocyanide complex is simpler and less prone to error than the permanganate oxidation procedure, which involves three measured additions from micro-burettes, apart from the washing and re-solution errors mentioned above.

SUMMARY.—Attention is drawn to the method of Jacobs and Hoffman for the determination of potassium in small quantities by the cobaltinitrite method. Minor improvements of the conditions of pptn. and washing are suggested, and the potassium is estimated photometrically on the basis of the cobalt of the ppt. by the formation of a green complex with choline hydrochloride and potassium ferrocyanide. Consistent results are obtained, and the method is directly applicable to the micro-estimation of potassium in blood serum and solns. of ashed biological fluids. It should be of service in the analysis of feeding stuffs and soils when the potassium is ultimately obtained in solution free from ammonium ions and organic matter.

My thanks are due to Dr. H. H. Green for his interest and advice in the preparation of this paper.

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1. Kramer, B., and Tisdall, F. F., *J. Biol. Chem.*, 1921, **46**, 339.
2. Jacobs, H. R. D., and Hoffman, W. S., *id.*, 1931, **93**, 685.
3. Hoffman, W. S., *id.*, 1937, **120**, 57.
4. Peters, J. P., and Van Slyke, D. D., "*Quantitative Clinical Chemistry*," Vol. II (*Methods*), p. 748.

MINISTRY OF AGRICULTURE AND FISHERIES
VETERINARY LABORATORY, NEW HAW, WEYBRIDGE, SURREY

October, 1942

DISCUSSION

Mr. N. L. ALLPORT asked whether Dr. Eden had had any experience with the method proposed by C. P. Sideris (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 145), which was based upon the colorimetric determination of cobalt, using nitroso-R salt. He thought that this reaction was more sensitive than the one recommended by Dr. Eden and he had obtained satisfactory results with it. He also asked if Dr. Eden had tried the proposal to determine the cobalt by the use of cysteine hydrochloride and hydrogen peroxide (A. E. Sobel and B. Kramer, *J. Biol. Chem.*, 1933, **100**, 561), or whether he had considered the suggestion, made by a number of investigators, to measure the blue colour produced in 70% acetone on addition of ammonium thiocyanate. Another procedure for the indirect determination of potassium depended upon assessing the amount of nitrite present by measuring the intensity of the green colour formed on addition of antipyrine (M. Mousseron, *Bull. Soc. Chim. biol.*, 1931, **13**, 831).

Dr. J. R. NICHOLLS said that all would agree that the best procedure was to determine the potassium in the ppt. rather than the cobalt. But, as no process was known for the small quantities of potassium involved, it was legitimate to base the analysis on the cobalt content of the ppt., provided that it could be ensured that the ppt. was of constant composition. This was not difficult when uniform conditions of pptn. could be maintained, but when other substances were present it was general experience that the composition of the ppt. varied. This meant that the method proposed might be suitable for blood, but should not be used for other materials, *e.g.*, fertilisers, without proof that it really was applicable.

Mr. R. W. SUTTON agreed with Dr. Nicholls that the indirect determination of the potassium by evaluation of the Co or NO_2 portion of the ppt. was a weakness, since the ppt. was stated to be somewhat variable in composition. There was a need of a reaction based on the potassium part of the cobaltinitrite precipitate. He referred to a method published by C. S. Piper (*J. Soc. Chem. Ind.*, 1934, 392T), which he had used recently, with reasonably satisfactory results, for the determination of small amounts of potassium. The procedure depended on a permanganate titration of the separated cobaltinitrite, and the author also used a relatively large excess of sodium salts in an attempt to secure a ppt. of more constant composition. It was found that the permanganate titration figures were not directly proportional to the K_2O, but, when plotted, gave a smooth curve which fitted an equation of the second degree. Dil. (35%) alcohol was used as a washing liquid followed by a very small portion of water. The author also recommended the use of separate sols. of sodium nitrite and cobalt nitrate rather than sodium cobaltinitrite, which slowly decomposed on keeping. Mr. Sutton also asked if it was essential to siphon off the supernatant liquid, and suggested that the ppt. ought to become sufficiently compact to allow the soln. to be poured off.

Mr. F. L. OKELL, in expressing appreciation of the paper, considered that by defining the conditions for more exact pptn. of potassium by cobaltinitrite the author had rendered a distinct service to general analytical chemistry; also that the investigation of the colorimetric determination was welcome in that, although indirect, it covered a concn. range over which existing chemical methods were often inadequate.

Mr. G. TAYLOR referred to Dr. Eden's use of the micro method for the determination of available potash in soils. He thought it more probable that this particular determination was generally made by a macro method; it was only with such that the speaker had had any experience, and for this purpose he had found the perchlorate method for determining the potash sufficiently accurate. But the principle which might be said to underlie the difference between the two methods, and which frequently determined which method should be used, was that whereas with the cobaltinitrite method the potash was taken out from the "impurities," with the perchlorate method the "impurities" were removed from the potash.

The colour test for cobalt which Dr. Eden used was new to the speaker, but it suggested another possible valuable use in agricultural chemistry, namely, a method for substantiating and possibly approximately determining small quantities of cobalt in soils and animal feeding stuffs in connection with which the question of a disease due to deficiency of cobalt in the diet had arisen.

Dr. EDEN, replying, said that whilst the perchlorate method was reliable for determining large amounts of potassium, it had the disadvantage that sulphate ions must not be present. Similarly, the platinic chloride method was reliable only when the potassium was present as chloride. The choline hydrochloride—potassium ferrocyanide reaction for cobalt was not as sensitive as the nitroso-R colour reaction for cobalt. He had had no experience of the use of antipyrine for the determination of the nitrite ion. He was very interested to know that other workers had found the permanganate oxidation procedure not so reliable as the text books suggested. The siphon method for removal of the supernatant fluid in the centrifuge tube was preferred to the pouring off technique in that greater control was possible. He was aware that some authors produced the sodium cobaltinitrite for pptn. *in situ*, but for large scale work, where a number of determinations had to be simultaneously carried out, it was preferable to make up enough sodium cobaltinitrite in advance. The soln. could be stored in the refrigerator and filtered each time before use.

The Determination of the Original Freezing-Point of Milk Preserved with Formalin:

DETERMINATION OF FORMALDEHYDE IN MILK

BY F. J. MACDONALD

FOR some time past a reasonably rapid method has been needed in these laboratories for arriving at the original f.pt. of milk samples containing unknown proportions of formaldehyde. Removal of the preservative by boiling is neither elegant nor complete, and it was found preferable to estimate its concn. and make a suitable correction.

EFFECT OF FORMALDEHYDE ON THE FREEZING-POINT.—Several sets of samples were prepared from milks of known original f.pt., by adding previously standardised formalin (38% H.CHO), so that each set contained amounts of formaldehyde of the order of 100, 200, 300, 400, 500, 1000, 2000 and 3000 p.p.m. Both genuine and watered milks were used. As a check on the accuracy of these additions, the formaldehyde content of several of these sets was determined by the method described below, and in the other sets the same vols. of formalin were delivered into water and determined by means of alkaline iodine solution.

The f.pt. (Hortvet) of each sample was determined, and for each separate set of samples a graph was plotted of the increase in depression against the concn. of formaldehyde. From each of these graphs a factor was deduced which gave the increase in depression per 100 p.p.m. of formaldehyde. Not all the figures involved are quoted, but only the original f.pt. and observed factor for each of the sets of samples are given.

Original $\triangle$° C. ..	0·541	0·547	0·534	0·551	0·498
Factor	0·0089	0·0095	0·0088	0·0092	0·0088
Original $\triangle$° C. ..	0·514	0·535	0·542	0·472	0·484
Factor	0·0090	0·0095	0·0088	0·0088	0·0090

Each of these graphs showed a straight-line relationship between the formaldehyde concn. and the resultant increase in depression, and the above results indicate that it is independent of the original f.pt. of the milk. The factor finally adopted for purposes of correction was taken as the average of the above results, *i.e.*, for every 100 p.p.m. of formaldehyde present 0·009° C. is subtracted from the observed depression.

Three similar series of results were obtained on salt solutions.

Original $\triangle$° C.	0·524	0·603	0·488
Factor	0·0095	0·0096	0·0094

An interesting point, arising from a comparison of the factors for milk and saline, is that there appears to be no immediate combination of formaldehyde and casein within

the concns. studied. With a milk containing *ca.* 3000 p.p.m., no formaldehyde could be detected in the protein ppt. resulting from treatment with acetic and phosphotungstic acids, after the adherent filtrate had been removed by successive washings (with an aldehyde-free milk filtrate) and centrifuging. On the other hand, the slight increase in titratable acidity at concns. of 2000 p.p.m. and over does indicate some slight combination.

EFFECT OF STORAGE ON FORMALDEHYDE CONTENT AND FREEZING-POINT.—The effects of storage for 7 days at temp. of 48–50° F. and 70–72° F. on two sets of preserved samples were compared, the f.pt., formaldehyde content and titratable acidity being determined at the beginning and end of the period. Similar results were obtained with both sets, and figures for one only are quoted:

Original sample			Stored at 48–50° F.			Stored at 70–72° F.		
Δ° C.	H.CHO/10^6	Acidity	Δ° C.	H.CHO/10^6	Acidity	Δ° C.	H.CHO/10^6	Acidity
0·542	Nil	16·0	—	Nil	Sour	—	Nil	Sour
0·550	120	16·0	0·548	100	17·0	0·554	90	18·0
0·557	160	16·0	0·556	150	16·0	0·559	130	18·0
0·564	260	16·0	0·562	250	16·0	0·562	180	18·0
0·578	400	16·0	0·576	400	16·0	0·569	270	18·0
0·582	460	16·0	0·579	450	16·0	0·574	320	18·5
0·620	880	16·5	0·621	860	16·5	0·608	680	20·0
0·716	1920	18·5	0·718	1910	18·5	0·674	1440	21·0
0·775	2600	21·5	0·779	2600	21·5	0·750	2340	25·0

The titratable acidity is expressed in ml of $N/10$ sodium hydroxide per 100 ml of milk. No marked changes in the 3 quantities measured could be observed during storage at 48–50° F. for 7 days. During the week's storage at 70–72° F. there was apparently some combination between formaldehyde and casein, as shown by the parallel decrease in free formaldehyde and depression, together with some increase in titratable acidity.

The relationship between free formaldehyde and increase in depression is unaltered by the changes produced during storage.

DETERMINATION OF FORMALDEHYDE.—Apart from colorimetric methods, which are applicable only to low concns., previously published methods have the disadvantage that the aldehyde must be separated from the milk by distillation before it can be estimated. Successful distillation of milk is tedious, and, unless it is carried to dryness and beyond, all the formaldehyde is not recovered[1]; assumptions have therefore to be made concerning the proportion distilling under some standard set of conditions.[2] Hence it was decided to attempt the determination on a fat-and-protein-free filtrate. The more usual oxidation methods using iodine or hydrogen peroxide in alkaline soln. and the reaction with cyanide were not applicable to such solns., so the possibilities of the sulphite method[3] were investigated. Erratic results were obtained when the interaction of sulphite and aldehyde took place in acid soln., but reproducible figures were obtained in presence of free alkali.

The method finally evolved was as follows: Fifty ml of milk were pipetted into a 100-ml graduated flask, and followed by 30 ml of water, 4 ml of 2 *N* acetic acid and 2 ml of 15% phosphotungstic acid soln. The mixture was made up to volume, mixed, left for 10 min. and filtered, the first few ml being rejected. Of the filtrate, 25-ml portions were pipetted into glass-stoppered bottles, 5 ml of *N* sodium hydroxide and 20 ml of $N/5$ sodium sulphite were added and the bottles were allowed to stand for 15 min. After acidification of the mixtures with 2 ml of 2 *N* acetic acid, 3 drops of 10% potassium iodide soln. and 1 ml of 1% starch soln. were added as indicators, and the excess of sulphite was titrated with $N/10$ chloramine-T. The sulphite soln. was standardised against the chloramine-T in presence of a 25-ml aliquot portion of an unpreserved milk filtrate, the same procedure being used throughout. From the diff. in titre of this blank and the test mixture the formaldehyde was calculated (1 ml of $N/10$ chloramine-T ≡ 1·5 mg of H.CHO).

Notes.—(1) The end-point of the titration, although it faded off after about 30 sec., was quite definite. (2) A correction for the vol. of ppt. can be calculated from the fat and solids-not-fat of the milk according to the formula:

$$\text{Vol. of ppt. for 50 ml of milk} = 0{\cdot}56 \times \text{fat \%} + 0{\cdot}15 \times \text{S.N.F. \%}.$$

As the fat and S.N.F. would be determined as a matter of course, this does not entail any extra work, and has been found to be sufficiently accurate for the purpose.

The following results were obtained on preserved samples whose original f.pt. were, at the time, unknown to me.

Sample	Observed △° C.	Formaldehyde parts/10^6	Correction in ° C.	Calculated original △° C.	Original △° C.	Error ° C.
A	0·553	227	−0·020	0·533	0·530	+0·003
B	0·570	200	−0·018	0·552	0·547	+0·005
C	0·790	2664	−0·240	0·550	0·545	+0·005
D	0·578	479	−0·043	0·535	0·534	+0·001
E	0·552	Nil	Nil	0·552	0·552	Nil
F	0·592	875	−0·079	0·513	0·514	−0·001
G	0·766	2478	−0·223	0·543	0·538	+0·005
H	0·545	522	−0·047	0·498	0·501	−0·003
I	0·664	1380	−0·124	0·540	0·543	−0·003
J	0·672	1471	−0·132	0·540	0·545	−0·005
K	0·537	210	−0·019	0·518	0·519	−0·001
L	0·540	745	−0·067	0·473	0·470	+0·003
M	0·596	539	−0·049	0·547	0·552	−0·005
N	0·602	655	−0·059	0·543	0·545	−0·002

The above results indicate that the original f.pt. can be determined within ±0·005° C. by this method, which would thus appear to be applicable to the determination of added water in churn milks.

REMOVAL OF FORMALDEHYDE BY BOILING.—One of the methods proposed by the Government Analyst for Madras[4] was to take 100 g of the preserved milk in a weighed beaker, dilute with 100 ml of water and boil down to 50 ml. After cooling, the original weight was restored by addition of water, and the f.pt. was determined, the assumption being made that all the formaldehyde had been removed.

A number of unpreserved milks were treated according to this method, and it was found that a decrease in depression resulted, which was in every instance of the order of 0·020° C. With preserved milk the following results were thus obtained.

Original	Preserved sample		Boiled sample	
△° C.	△° C.	H.CHO/10^6	△° C.	H.CHO/10^6
0·551	0·572	250	0·545	60
0·530	0·571	455	0·528	136
0·542	0·710	1870	0·570	540
0·548	0·809	2900	0·594	900

In none of these expts. was the formaldehyde completely removed, *ca.* 30% of the amount originally added remaining. With an original concn. of *ca.* 600 p.p.m., the residual 180 p.p.m. after boiling would cause an increase in depression approx. equal to the decrease in depression due to this boiling, thus yielding a final result comparable with the original value for the untreated milk. This would appear to be the reason for the satisfactory results obtained by Venkatachalam. With original concns. much exceeding 600 p.p.m. the retention of formaldehyde would render this method unsatisfactory.

SUMMARY.—(1) The relation of formaldehyde concn. to increased depression of f.pt. in milk was determined.

(2) A method for the estimation of formaldehyde in milk is described, whereby the original freezing-point can be derived from (1).

(3) The removal of formaldehyde from milk by boiling was investigated.

I wish to thank Mr. B. Crowhurst for his assistance in this work, and the Governing Director of the Express Dairy Co., Ltd., for permission to publish.

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Visual Method for Vitamin B_1 Assay in Flour

By C. W. HERD, B.Sc., Ph.D., F.I.C., L. M. MUNDY F.I.C., Ph.C., and H. N. RIDYARD, B.Sc., A.I.C.

In the estimation of vitamin B_1 by oxidation to thiochrome,[1,2,3,4,5,6,7] it has usually been considered essential to keep the volumes of all reagents constant for both standard and unknown solns., because there is an appreciable partition of thiochrome between the aqueous and *iso*butyl alcohol layers. We have attempted to determine this partition, using independent methods.

Method of Repeated Extraction.—In one laboratory (C. W. H. and L. M. M.) different amounts of water were added to 0·5 ml of standard aneurine soln., 30 mg/litre, followed by 2 ml of methyl alcohol, 2 ml of 30% sodium hydroxide soln. and 2 drops of 0·95% potassium ferricyanide soln. The vol. of the aqueous layer was read, 10 ml of *iso*butyl alcohol were added, the whole was well shaken and the aqueous layer was removed. Further extractions with *iso*butyl alcohol were carried out, in some instances, and the whole vol. was made up to 30 ml.[4,7] The fluorescences were compared visually. The following results were obtained with 0·015 mg of aneurine present in each instance.

No. of extractions	No water added (aq. vol. 4·5 ml)	2 ml water added (aq. vol. 6·8 ml)	4 ml water added (aq. vol. 8·4 ml)	6 ml water added (aq. vol. 10·6 ml)
1	0·0138 mg	0·0120 mg	0·0115 mg	0·0115 mg
2	0·0150 ,,	0·0143 ,,	0·0136 ,,	0·0125 ,,
3	—	0·0152 ,,	0·0148 ,,	0·0138 ,,
4	—	—	0·0154 ,,	0·0154 ,,

The partition co-efficients corresponding to the figures in the top line are: 5·6, 2·7, 2·8 and 3·5.

A flour extract, and another similar extract saturated with sodium chloride, were also treated with several portions of *iso*butyl alcohol, with the following results:

No. of extractions	Flour extract Aneurine, μg per g	Flour extract Sat. sodium chloride Aneurine, μg per g
1	1·67	1·87
2	1·87	2·12
3	2·00	2·08
4	2·02	2·10

This indicates that at least 3 extractions with *iso*butyl alcohol are required with flour extracts, or 2 if sodium chloride is used. As the salt caused manipulative difficulties if bubbling was used for mixing the solns. it was found advisable to filter the *iso*butyl alcohol extract to obtain a clear soln. for matching.

The difficulties of the saturation procedure can be overcome by using 1·5 g of sodium chloride, instead of the 1·9 g required for saturation of the 10 ml of aqueous layer. On the same flour as above and using 1·5 g of sodium chloride, a figure of 2·12μg per g was obtained after the 2 extractions with *iso*butyl alcohol. If more than one extraction with *iso*butyl alcohol is made, it is desirable that the contents of the unoxidised tube be extracted the same number of times, as each shaking may extract further fluorescent material. Vigorous shaking was a satisfactory method of extracting the aqueous layer with *iso*butyl alcohol, and concordant results could be obtained by different workers. Bubbling with air gave no improvement in extraction; in fact, in every instance less complete extraction was effected by bubbling than by vigorous shaking.

Method of Extraction of Residues.—In the other laboratory (H. N. R.) the absolute amount of thiochrome in the two layers was estimated by the photoelectric method.[7] Instead of extracting the aqueous layer with 25 ml of water-saturated *iso*butyl alcohol in one operation, the same quantity was used in 3 successive portions. The mixed extracts were compared on the "Spekker" fluorimeter with standards prepared in the usual manner. Three results gave a value of 0·15μg left in the residue when 2μg of vitamin B_1 had been added to the contents of the tube, *i.e.*, 7·5%.

To confirm this result the residues from 3 or 4 standard tubes were then added together and extracted with 25 ml of wet *iso*butyl alcohol, and the extracts were examined on the fluorimeter. The figures were corrected for the 7·5% left unextracted in the standard

tubes and for approx. 7% for each aqueous layer added to the mixture for the second extraction. The values on 4 different days were 0·45μg, 0·45μg (three layers), 0·61μg, 0·57μg (four layers)—in good agreement with the earlier figure of 0·15μg per layer.

The method was extended to examine the layers obtained in the various stages of the visual method. Both water-saturated and quick-lime-dried *iso*butyl alcohol were used; each of the results below is a mean of several determinations made at the same time.

Method	*Iso*-butyl alcohol	Vol. alcoholic layers ml	Vol. aqueous layers ml	NaOH concn. g/ml	B_1 in extract μg	B_1 in residues μg	B_1 added μg	B_1 concn. in alc. layer / B_1 concn. in aq. layer
Photo-electric ..	Water-saturated	26·6	4·4	0·068	1·85	0·15	2·0	2·0
Visual standard ..	,,	10·7	4·3	0·14	28·4	1·65	30·0	6·9
	,,	10·7	4·3	0·14	30·3	1·90	30·0	6·4
,, extract ..	,,	12·2	10·5	0·057	2·19	0·60	3·0	3·1
	,,	12·2	10·5	0·057	2·19	0·78	3·0	2·4
,, standard ..	Dry	12·5	2·5	0·24	30·4	0·33	30·0	18·4
	,,	12·5	2·5	0·24	—	0·27	30·0	—
,, extract ..	,,	15·5	7·5	0·08	2·3	0·20	3·0	5·6
	,,	15·5	7·5	0·08	2·3	0·29	3·0	3·8

The influence of the components of the mixture is shown by the wide variation in the partition coefficient. Particularly will it be noted that this changes in a fairly regular manner with the sodium hydroxide concn. This effect is similar to that of sodium chloride mentioned earlier.

CONCLUSIONS.—The extent of the partition of thiochrome between aqueous and *iso*-butyl alcohol layers used in various methods has been determined and has been found to be generally of the order of 5, with wide variations mainly occasioned by the concn. of salts in the aqueous layer. It will be seen, therefore, that it is most important to treat all standard and unknown solns. in precisely the same manner or, alternatively, to ensure complete extraction of thiochrome in every instance. Neglect of this could lead to an error as great as 25%.

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The Separation of Metals by means of the Mercury Cathode: Chromium*

BY R. C. CHIRNSIDE, F.I.C., L. A. DAUNCEY, B.Sc., AND P. M. C. PROFFITT

INTRODUCTION.—In a previous communication[1] we have described a simple form of electrolytic apparatus employing a mercury cathode. Eight sets of apparatus have been in use in these Laboratories for some years and the principal applications have been those described in the earlier paper, *viz.*, in the separation of nickel from nickel-aluminium, nickel-magnesium alloys and the like, but large quantities of other metals, *e.g.*, copper, iron and chromium, have also been separated. In the main, the remaining electrolytes have been analysed for aluminium content, but phosphorus, titanium, and alkaline earth and alkali metals have also been determined.

In our view this is the most effective method for the separation of aluminium from alloys of which it is a constituent. This view was also put forward by Etheridge in a

* Communication (No. 309) from the staff of the Research Laboratories of The General Electric Company Limited, England.

recent paper,[2] but the virtues of the method do not appear to be sufficiently emphasised in his communication. He claims, for example, that amounts of metal up to 2 g can be removed over mercury, whereas we have frequently removed 10 g of copper, 10 g of nickel, or 5 g of iron. In particular, in discussing the removal of chromium he states that the method "is so slow that a weight of 0·5 g requires 4 or 5 hrs. at 4 amps. current," and he suggests that this is due to the presence of ammonium sulphate resulting from the neutralisation of sulphuric acid.

Our experience does not support his views as to the degree of limitation of the method relating to the separation of chromium, nor do we agree with his explanation of the causes of such limitations as there are. In the following section are given the results of some expts. on the separation of chromium under different conditions. Subsequently, tentative explanations are put forward to account for the difference between our results and those of Etheridge.

EXPERIMENTAL.—(1) *Apparatus.*—The apparatus used was similar to that we have previously described,[1] save for a slight alteration in the method of making a connection to the cathode. Some trouble was experienced owing to cracking of the platinum-glass seal at the higher current values used, and this has now been obviated by the construction shown in Fig. 1.

DIAGRAM OF PLATINUM-GLASS SEAL

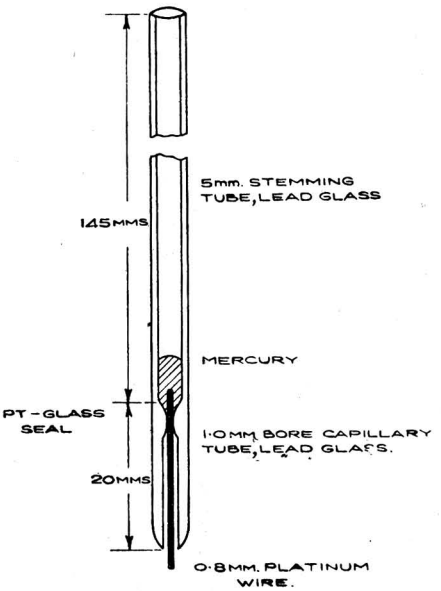

Fig. 1

(2) *Effect of ammonium sulphate on rate of chromium deposition.*—(*a*) *In N/8 sulphuric acid.*—The effect of increasing quantities of ammonium sulphate was first investigated. The solution was initially of the acidity normally used in our method, *viz.*, 1 ml of sulphuric acid (1:1) in 150 ml of soln. (*ca. N/8*). The results are given in Table I, Expts. 1–5. For the purpose of the expts. the current was restricted to 4 amps. and the quantity of chromium to 0·5 g, so as to give conditions comparable with those mentioned by Etheridge.

It will be noted that at this relatively higher acidity 0·5 g of chromium was deposited in presence of up to 5 g of ammonium sulphate in 65–75 min., whereas in Etheridge's method 4–5 hrs. were required. With 10 g and 20 g of ammonium sulphate respectively not only was the deposition incomplete but a black layer, found by X-ray analysis to consist of metallic chromium, was formed on the surface of the mercury and on the walls of the beaker.

(*b*) *In N/80 sulphuric acid.*—On reducing the acidity of the solution to 0·1 ml of sulphuric acid (1:1) in 150 ml of soln. it was found that 0·5 g of chromium could be completely removed in presence of up to 30 g ammonium sulphate in 75 min. (Table I, Expts. 6–10). By increasing the current to 6·5 and 8 amps. the chromium was removed in presence of 10 g of ammonium sulphate in 50 and 40 min. respectively (60 min. at 4 amps.).

We are therefore in agreement with Etheridge in finding it an advantage to keep the amount of excess sulphuric acid to a minimum.

(3) *Effect of alkali sulphate.*—We normally neutralise the excess sulphuric acid with sodium hydroxide, a method which, by implication, Etheridge has found to be unsatisfactory. The expts. described were carried out on solns. prepared from chrome alum, *i.e.*, containing potassium in amount equivalent to the chromium. The results of expts. on a soln. containing chromium sulphate only, and on another containing chrome alum to which a further 10 g of potassium sulphate, were added, show that potassium has no influence (Table I, Expts. 11 and 12).

(4) *Removal of excess sulphuric acid by evaporation.*—Etheridge stated that "elimination (of sulphuric acid) by evaporation is not permissible, as it would produce an insoluble

form of chromium sulphate." We have found in the past, when preparing solns. for electrolysis for the determination of the aluminium content of nickel-chromium alloys, that addition of potassium sulphate in substantial amount during the evaporation of the sulphuric acid prevents the formation of basic chromium sulphate. We were satisfied that the addition of alkali sulphate did not affect the rate of deposition of the chromium (see (3) above).

It is true that chromium is by no means as readily separated as some other metals, but the absence of ammonium salts and the use of the min. amount of sulphuric acid greatly increase the rate of deposition, and in some instances allow deposition to take place when it would otherwise have been impossible. These conditions are sometimes, as Etheridge indicates, difficult or impossible to attain in practice. We have therefore devised a simple method by the use of which it should be possible to separate chromium rapidly and completely in presence of considerable quantities of ammonium salts.

(5) *Effect of addition of nickel.*—In view of the ease with which nickel is removed, it was decided to investigate the effect of addition of small quantities to the soln. containing the chromium. The results of the expts. are shown in Table I, Expts. 13–15. The conditions chosen, *viz.*, $N/8$ acidity and addition of 10 g of ammonium sulphate, were such that in the normal way separation of chromium is incomplete and a black layer is formed on the mercury surface (Expt. 4). It will be noted that the addition of as little as 0·05 g of nickel (0·25 g of $NiSO_4.7H_2O$) to 0·5 g of chromium resulted in complete separation of the chromium (and nickel) in 90 mins., the mercury remaining bright and clean. It was shown too that a further reduction in time to 60 min. could be effected by reducing the acidity to $N/80$ (Expts. 16 and 17).

In our view this is a simple way of effecting rapid and complete separation of chromium when the various inhibiting influences are present. Nickel can be obtained in a very "pure" form and, as it is subsequently removed, there is no objection to the addition. It may well be that even smaller additions would be effective, but this has not been tried.

Alloys containing chromium frequently also contain nickel, so that no addition will in fact be necessary in these circumstances.

(6) *Effect of iron and copper.*—Ferro-chrome and chrome copper represent two other types of alloy that may be encountered. The effect of addition of iron or copper to the chromium solns. is shown in Table I, Expts. 18, 19 and 20. Iron alone allows complete removal of the chromium possible, but only after 4 hrs. Both copper and nickel, in the form of pre-deposited amalgams, *i.e.*, by a preliminary electrolysis of a soln. containing copper or nickel, are effective in assisting the removal of chromium. It will be seen from Table I, Expts. 19 and 20, that in presence of 0·15 g of copper and 20 g of ammonium sulphate 0·5 g of chromium can be removed in 65 min. in $N/80$ acid or 105 min. in $N/8$ acid. At the lower acidity this represents a slight gain in time, and at the higher acidity the removal of chromium was not otherwise possible. The separation of chromium from chrome-copper should therefore present no difficulty.

The result of an expt. on a sample of ferrochrome (67·5% Cr) is also given in the Table, Expt. 21: 0·5 g of chromium was removed in 95 min. in presence of considerable amounts of ammonium sulphate. It is probable that addition of nickel would have increased the rate of deposition of chromium.

(7) *Effect of addition of silver.*—In the course of further expts., carried out in the main with the object of checking the results obtained in $N/8$ sulphuric acid and in presence of considerable quantities of ammonium sulphate, it was found that 0·5 g of chromium could be readily removed by electrolysis in presence of as much as 20 g of ammonium sulphate (Expt. 27); it had previously been possible in presence of 5 g, but not of 10 g of this salt (Expts. 3 and 4). On examination this effect was found due to the presence, in the mercury, of a spectrographic trace of silver. On repeating the expt., using spectroscopically pure mercury, results similar to those at first noted were obtained (Expt. 28).

Seventy ml of a soln. of silver sulphate, equiv. to 10 mg of silver, were electrolysed over a pure mercury cathode, and Expt. 28 was then repeated over the preformed silver-mercury amalgam. It was now found possible again to separate the chromium completely in presence of 20 g of ammonium sulphate (Expt. 29). Further expts. showed that it was unnecessary to pre-form the amalgam, equally satisfactory results being obtained by direct addition of silver sulphate soln. to the test soln. before electrolysis (Expt. 30). There was also some evidence that the proportion of silver in the mercury for any particular

surface area of cathode was fairly critical. In Expt. 29 the addition represented approximately 0·006% of silver by weight in the mercury, or 0·0003 g of silver per sq.cm. of exposed mercury surface.

(8) *Effect of rotating anode.*—Our method differs from that of Etheridge in that we use a stationary platinum cylinder, and he uses a rotating gauze anode. In Expt. 22 a Sand's gauze electrode was substituted for the platinum cylinder, and it was rotated during electrolysis. A large amount of the black metallic chromium was deposited on the mercury and separation was incomplete. In Expt. 23 the same electrode was kept stationary in an identical expt. and electrolysis was found to be complete in 60 min., with formation of only a slight film. No explanation is offered for these effects.

(9) *Effect of reducing agents.*—In Expts. 24 and 25, 0·5 g of hydrazine hydrochloride and 1 g of sodium bisulphite respectively were added to the chromium soln. before electrolysis. In both instances the black layer of chromium was formed and separation was incomplete after 135 min.

Discussion.—*Acidity.*—The results of the expts. show that in presence of large quantities of ammonium sulphate chromium is not readily separated over a mercury cathode unless the acidity of the soln. is reduced to a minimum. In this general conclusion we are in complete agreement with Etheridge, but the other limitations to which he has referred are not found to apply with our design of apparatus and method of operation.

Current density.—Present conditions do not allow of a fundamental investigation into the mechanism of electrolytic deposition on a mercury cathode, but some tentative suggestions will be made to account for the differences in our results from those of Etheridge. The successful deposition of so many metals on mercury is, of course, due to its high hydrogen over-voltage. There is no very obvious reason why it should be so difficult to deposit chromium in presence of ammonium salts. E. F. Smith[3] stated that chromium amalgam was not very stable, and that water rapidly decomposed it with separation of metallic chromium as a fine black deposit on the surface of the mercury. This does not appear to be an adequate explanation for the formation of the black deposit of chromium in the expts. just described, as the deposit only occurs when the ammonium salt and/or the sulphuric acid concn. exceed certain values, nor for its occurrence in Etheridge's apparatus at lower values. We believe that the difference is due largely to the difference in design and operation of the two forms of apparatus. It is known generally that in electrolysing very dilute solns. spongy metallic deposits are frequently obtained even when high current densities are employed. The cause may lie in the arrival of considerable numbers of hydrogen ions with the metal ions at the cathode surface. Current density is also of great importance. The classical expts. of Bunsen[4] on the decomposition of chromic chloride yielded hydrogen, chromium trioxide, chromium sesquioxide or metallic chromium according to the current density employed. He noted, too, that, in order to obtain metallic chromium, "the concentration of the solution must receive attention as it has considerable influence on the result." By the use of high current densities and hot saturated solns. he even succeeded in obtaining smooth metallic deposits from the chlorides of calcium, barium and strontium. For this purpose he used an amalgamated platinum wire as cathode so as to lessen the evolution of hydrogen.

The figures for the Etheridge apparatus have been calculated on the assumption that a 1000 ml Hysil beaker is used and that 200 ml of solution are electrolysed. These may not be strictly correct but the figures will be of the right order. The acidity used by Etheridge is between those used in our expts. and no direct comparison is therefore possible. The current density he used is much lower than those used by the other workers, and it is possible that this may have had some influence in retarding the deposition of chromium.

Concentration.—Our own experience with nickel has shown that the current efficiency during deposition increases with increasing concn. of nickel, *e.g.*, using 8 amps. 0·5 g of nickel and 2·0 g of nickel were removed in 25 min. and 75 min. respectively. Pavlish and Sullivan[6] carried out extensive investigations on the deposition of iron under various conditions. They found that the current efficiency for 1 g of iron/litre was 11·6%, whilst at 13·3 g./litre it was increased to 32·8%; the vol. throughout was maintained at 150 ml. Again this suggests that the more dilute solns. used by Etheridge may have been a contributory factor in the difficulty with chromium deposition.

Temperature.—Another important difference not yet mentioned lies in the fact that

we begin with boiling solns. which are maintained by the passage of the current at 65° C. when 4 amps. are passed, or at 90° C. with 8 amps. In our earlier communication we drew attention to the great increase in rate of deposition obtained by this means (*cf.* Table I, Expt. No. 26).

TABLE I

Vol. of electrolyte, 150 ml; vol. of cathode mercury, 12 ml; current, 4 amps.; temp. of electrolyte, 65° C.

Expt. No.	0·5 g Cr present as:	Strength H_2SO_4	$(NH_4)_2SO_4$ g	K_2SO_4 g	Other metals g	Time for complete deposition, min.	Remarks
1	4·8 g Cr alum	*N*/8	Nil	0·87	Nil	70	
2	,,	,,	3	,,	,,	65	
3	,,	,,	5	,,	,,	75	
4	,,	,,	10	,,	,,	Incomplete after 4 hrs.	Black deposit
5	,,	,,	20	,,	,,	,,	
6	,,	*N*/80	Nil	,,	,,	45	
7	,,	,,	5	,,	,,	55	
8	,,	,,	10	,,	,,	60	
9	,,	,,	20	,,	,,	75	
10	,,	,,	30	,,	,,	75	
11	3·4 g $Cr_2(SO_4)_3.18H_2O$	*N*/80	Nil	Nil	Nil	45	See Expt. 6
12	4·8 g Cr alum	*N*/8	,,	10·87	,,	75	,, 1
13	,,	,,	10	0·87	0·22 Ni	95	
14	,,	,,	10	,,	0·11 Ni	90	,, 4
15	,,	,,	10	,,	0·05 Ni	80	
16	,,	*N*/80	10	,,	0·10 Ni as amalgam.	60	,, 8
17	,,	,,	20	,,	,,	65	,, 9
18	,,	*N*/8	10	,,	0·20 Fe	240	,, 4
19	,,	*N*/80	20	,,	0·15 Cu as amalgam	65	,, 9
20	,,	*N*/8	20	,,	,,	105	,, 5
21	0·74 g ferro-chrome	?	15	Nil	0·24 Fe	95	
22	4·8 g Cr alum	*N*/80	10	0·87	Nil (rotating gauze anode)	Incomplete after 90 mins.	Black deposit
23	,,	,,	10	,,	Nil (stationary gauze anode)	60	Very slight deposit
24	,,	*N*/8	10	,,	Nil (0·5 g hydrazine HCl)	Incomplete after 135 mins.	Black deposit
25	,,	,,	10	,,	1 g $NaHSO_3$	,,	,,
26	,,	*N*/80	10	,,	Nil (8 amps.)	40	See Expt. 8
27	,,	*N*/8	20	,,	Hg cathode (spect. trace Ag)	100	,, 5
28	,,	,,	20	,,	Ag-free Hg cathode	Incomplete after 8 hrs	Black deposit See Expt. 5
29	,,	,,	20	,,	Hg cathode (trace Ag added)	90	
30	,,	,,	20	,,	Ag-free Hg cathode (Ag_2SO_4 added to electrolyte)	90	

We have made some calculations of the operational details of various forms of mercury cathodes described in the literature and they are given in Table II.

TABLE II

Name	Vol. of electrolyte ml	Approximate cathode area sq.cm.	Cathode current density amp./sq.cm.	Acidity H_2SO_4
Etheridge[5]	200	86	0·046	*N*/20
Chirnside *et al.*[1]	150	28	0·14 (4 amps.)	*N*/8, *N*/80
			0·28 (8 ,,)	
Pavlish and Sullivan[6] ..	150	38	0·13	*N*/20–10 *N*
Brophy[7]	100	25	0·16	*N*/10
Cain[8]	70	26	0·15 (4 ,,)	"minimum amount"
			0·23 (6 ,,)	
U.S. Steel Corporation[9] ..	75	44	0·11	*N*/20

Addition of nickel or silver.—Perhaps the most important practical outcome of our work has been the discovery that such limitations as there are to the successful deposition of chromium on the mercury cathode can be largely overcome by addition of small amounts of nickel or extremely small amounts of silver to the mercury, either by the preformation of an amalgam or by addition to the electrolyte. With silver the effect is very marked and is so far unexplained. It is interesting to note that E. F. Smith[10] records a difficulty in the removal of thallium over a mercury cathode. The amalgam on washing gave up part of its thallium content to the water. The trouble was overcome by a technique somewhat analogous to that we have used, *viz.*, by simultaneous deposition of a trace of zinc; 0·7 mg of zinc was used for 0·13 g of thallium, and it was suggested that its function was to prevent oxidation of the thallium. It is hoped, when opportunity permits, to polarograph chromium solns., using as cathode pure mercury and mercury to which silver has been added respectively.

SUMMARY.—An investigation has been made into the conditions necessary for the separation of chromium over a mercury cathode. In particular, the factors affecting the rate of deposition of chromium in presence of ammonium sulphate have been studied. High current density, elevated temperatures, concentrated solutions, minimum acidity have all been found to increase the rate. Rotation of the anode, or addition of reducing agents, appears to prevent the deposition. Alkali metals are without effect.

When ammonium sulphate is present in amount such as to inhibit, partially or completely, the deposition of chromium, the difficulty may be overcome by addition of small quantities of nickel or very small, but critical, amounts of silver to the electrolyte.

It has been found also that the deposition of chromium takes place readily in presence of copper or iron, such as might be encountered in copper-chrome or ferro-chrome.

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RESEARCH LABORATORIES OF THE GENERAL ELECTRIC CO., LTD.
LONDON

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Notes

ESTIMATION OF OAT FLOUR IN MIXTURES WITH WHEAT FLOUR

THIS note is based on experience gained in estimating the percentage of oat flour which may be present as a diluent in National Flour. Oat endosperm contains a proportion of compound starch grains which are not found in wheat endosperm. They are easily recognised and counted under the microscope, and by preparing standards containing definite amounts of oat endosperm a curve can be made showing relationship of number of compound grains to the oat endosperm content of the mixture.

Wallis, "*Analytical Microscopy*," has described a general technique which might be expected to apply to this problem. He adds a known weight of lycopodium to his control and experimental sample in order to fix the volume in which he counts the number of particles. Difficulties were, however, experienced in applying this method to wheat flour mixtures, mainly due to the lycopodium spores being caught up in the gluten strands. The method described below was found to be simpler and quicker.

A suspension is prepared of flour in a mucilage in order to avoid rapid settling. A satisfactory mucilage, as described by Wallis, is a thin solution of gum tragacanth; to this is added 0·05% of Congo red and also a trace of ammonia to prevent pptn. of the dyestuff. The protein, cell wall material and damaged starch grains are stained pink, whilst the single starch grains of the wheaten flour remain uncoloured and the compound grains in the oat flour assume a greyish appearance. The mucilage is first cleared by centrifuging. Two ml are then added gradually to 30 mg of the material under examination and mixed thoroughly. One drop of the mixture is placed on a haemacytometer slide and covered with a cover slip. A definite volume of liquid is thus enclosed within a marked square and all compound grains lying within this square are counted. On plotting the average counts against the % of oat flour in a series of known mixtures, a straight line passing through the origin was obtained.

The following figures taken from the standard curve illustrate the nature of the results. They are the number of compound oat grains counted within a 3-mm square, the depth of liquid being 0·1 mm. Each figure represents the average count of 8 fields, 4 from each of 2 suspensions: 3%, 20; 6%, 40; 10%, 68.

nt sizes occur in similar proportions in all oats. It is, therefore, of interest to note
n curve has been found to apply to 3 entirely different samples of groats. A further
oat endosperm next to the bran contains relatively few large compound grains, but
o be unimportant in the present connection.
It is usual to find fragments of broken large grains, recognisable by their broken, jagge
number of broken grains varies from sample to sample according to its method of pre
ld not be ignored completely, but at the same time each fragment should not be counted
esent work, they were weighted according to size and shape, but this assessment is a n
idual worker, having in mind his analysis of the control samples forming the standard c
Occasionally a number of large well-formed compound grains are found which do not
istic reticulate markings very clearly, especially at low magnification. This is due, pre
anules being cemented closely together; at low magnifications, these grains appear d
an the ordinary wheat starch grains, sufficiently so to make them recognisable with ex
tion under higher magnification always brings up the reticulate markings clearly and i
any grain of this type. Care must be taken not to push a high-power examination to th
a very close examination may distinguish some wheat starch with reticulate markings
are always very shadowy markings, possibly the result of enzyme action on the grain
impression of being surface markings, whereas in the compound grains they obviously
roughout the grain. It is helpful to examine oat endosperm alone before beginning the
o get experience of these points.
It was noted that the compound grains disintegrate and disappear if allowed to sta
for many hours, *e.g.*, overnight.
in the range in which this method has been used, *i.e.*, between 3 and 10% of oat endosp
ch figure on the average of 8 fields, the error to be expected is about ±0·2%—*i.e.*, 5%
as 4·8 or 5·2%.
time taken by an experienced worker to make an estimation on a single sample is abou

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Apr

THE ASSAY OF SOLUTIONS OF STILBOESTROL DIPROPIONATE IN OIL

e introduction of synthetic oestrogens into medicine the estimation of these drugs ha
t. For stilboestrol, colorimetric,[1] spectrographic,[2] and volumetric[3] methods of assay
l, but the assay of solns. of stilboestrol dipropionate in oil has presented special difficu
rience, most of the vegetable oils now available exhibit such general absorption in the u
to render unreliable any direct spectrographic determination of stilboestrol dipropionat
eved no more success in attempts to saponify the oily solns. with alcoholic potassium
we were unable to separate the stilboestrol from the resulting saponification mixture in a s
n for analytical work. (*Cf.* Elvidge's[4] work on the assay of oestradiol benzoate in oil.)
a result of an observation by our colleague, Dr. E. Walton, who informed us that stilb
te, when crystallised from alcohol containing acid, was partly decomposed owing to a
oped the assay process described below; it has given satisfactory results in our hands
estrol dipropionate in arachis oil.

RACTION OF STILBOESTROL.—Treat 1 ml of the soln. of stilboestrol dipropionate in oil (
ng per ml) with 10 ml of alcohol (96%) containing 2 to 3 drops of conc. sulphuric acid ar
under reflux for 2 hrs. Cool the reaction mixture, wash it into a separating funnel w
ether and extract 3 times with *N* sodium hydroxide (10 ml), making sure that sufficien
the first extraction to render the extract alkaline in reaction to litmus. Wash the
extracts with ether (25 ml) and, after separating, wash the ethereal washing with 5 ml of
le. Add the alkaline washing to the main alkaline extract and acidify with dil. sulph
twice with ether (25 ml), wash the combined extracts with 5 ml of water, and evaporate
am-bath.

ORIMETRIC ESTIMATION.—*Solution A*.—Dissolve 7 mg of stilboestrol (≡ 10 mg of s
nate) in 2 ml of 20% sodium hydroxide soln. and dilute the mixture to 100 ml in a
ric flask.

ution B.—Dissolve the residue from the extraction process, as described above, in 0·4
le soln. so that the dilution will correspond to 10 mg of stilboestrol dipropionate in 100
, the residue from a soln. containing 5 mg of stilboestrol dipropionate in 1 ml of oil would
l of 20% sodium hydroxide soln. and made up to 50 ml. The resulting soln. is usual
nt.)

gent.—Folin–Ciocalteu phenol reagent.[5] For use, dilute 1 vol. of strong stock soln. w
.

our Reaction.—Treat 5 ml of the test soln. (A or B) with 3 ml of reagent and add 2 ml of 20
te soln. Mix and heat in a boiling water-bath for 5 min. Cool, wash the reaction mixt

The accuracy of the method is below that usual in colorimetric work, but we have had no difficulty in obtaining, with solns. containing 10 mg and 5 mg of stilboestrol dipropionate in 1 ml., results within an error of 10% of the theoretical. With the soln. containing 1 mg of the dipropionate per ml, low results were sometimes obtained, but the figures are more reliable if 5 ml instead of 1 ml of the soln. are used in the extraction process. We have found that sesame oil contains sufficient naturally occurring phenolic bodies to interfere with the estimation of stilboestrol dipropionate in this oil, and a correction must be applied to the colorimeter reading for the colour due to the oil.

The method appears to be suitable for routine work in a laboratory where stilboestrol dipropionate solns. of the usual strengths are examined, and we hope that our work may help others to overcome what we ourselves found to be a real difficulty.

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W. R. DRACASS
G. E. FOSTER
THE CONTROL LABORATORIES
WELLCOME CHEMICAL WORKS, DARTFORD

February 28th, 1943

DETERMINATION OF CHROMIC OXIDE IN PRESENCE OF CHROMIUM TRIOXIDE

ONE method of determining chromic oxide in presence of chromium trioxide is to determine the latter in the soln. by reduction with ferrous ammonium sulphate, and then to take a similar quantity of the soln. and oxidise the chromic oxide therein with potassium permanganate at b.p., destroy the excess of permanganate with manganous sulphate, by boiling for *ca.* 30 min., cool, filter and determine the total Cr_2O_3. This figure gives the total chromium, and from the initial figure for the CrO_3, the difference gives the Cr_2O_3; since, however, the difference in titration values is very small, there may be doubt whether the difference is not really due to experimental error.

In the preliminary expts. described in the following note, the principle of the new method was tested with relatively large amounts of chromic oxide. Twenty ml of $N/10$ potassium dichromate were taken, and 4 ml of $N/10$ potassium dichromate which had been reduced in a separate beaker with excess of $N/10$ ferrous ammonium sulphate, and then oxidised with nitric acid, were added to it. The chromic oxide and the iron were pptd. in slightly ammoniacal soln., filtered off on asbestos and washed well with hot water. The ppt. of iron and chromium was dissolved in 20 ml of 1 : 3 sulphuric acid, the asbestos was washed with hot water until a vol. of approx. 200 ml was reached, and the CrO_3 in this was determined by reducing with ferrous ammonium sulphate and titrating the excess with permanganate. This gave a blank which was allowed for in the final determination; it was due possibly to some chromium chromate or adsorbed dichromate. Then the total chromium was determined by diluting the soln. to *ca.* 600 ml, oxidising with permanganate, destroying the excess with manganous sulphate at b.p., boiling for *ca.* 30 min., cooling and titrating.

For example,

Taken $N/10$ $K_2Cr_2O_7$	Taken reduced from $N/10$ $K_2Cr_2O_7$	Blank	Total Cr	Cr_2O_3 from $N/10$ $K_2Cr_2O_7$ reduced
20 ml	4·0 ml	2·85 ml	6·95 ml	4·10 ml

It will be observed that the blank was rather high, and further expts. were made to reduce this blank to a minimum. Finally it was found that if the chromium were pptd. in a soln. just acid to litmus, the desired effect was attained.

Taken $N/10$ $K_2Cr_2O_7$ ml	Taken reduced $N/10$ $K_2Cr_2O_7$ ml	Blank ml	Total Cr found ml	Cr_2O_3 from $N/10$ $K_2Cr_2O_7$ reduced ml
10	0·50	0·05	0·55	0·50
10	1·00	0·10	1·10	1·00
10	2·00	0·10	2·05	1·95
10	3·50	0·20	3·70	3·50
20	3·00	0·45	3·35	2·90

From these results it appears that chromic oxide can be estimated tolerably well in presence of chromium trioxide by this modified method.

A "blank," determined by reducing 20 ml of $N/10$ potassium dichromate with ferrous ammonium sulphate, diluting to 600 ml containing 20 ml of 1 : 3 sulphuric acid, re-oxidising with permanganate, etc., was found to be nil, showing that under these conditions of high dilution there is no blank due to undecomposed permanganate.

Permission has been granted by A.D.Tech.A. (Tech.A) (4A) to publish this note.

ARMAMENT RESEARCH DEPARTMENT
W. J. AGNEW

January, 1943

DILUTION PROCESS FOR DETERMINING HYDROGEN ION CONCENTRATION WITH ONE-COLOUR INDICATORS

THE dilution procedure for determining *p*H values by means of two-colour indicators (McCrae, *J. South African Chem. Inst.*, 1935, **18**, 62; 1937, **20**, 10) is applicable, when slightly modified, to determinations made with one-colour indicators.

For the determination, two test-tubes of equal diam. (5/8 or 3/4 in.) are required, and the colours or depths of colour are conveniently matched in a comparator which permits equal cross-sections of the two tubes to be viewed.

Into one tube introduce 10 ml of the test soln. and into the other 9 ml of the soln. and 1 ml of approx. *N*/10 sodium hydroxide. It is essential that the liquid in the tube containing alkali shall have a *p*H well above the range of the indicator to be used, and this higher value must be maintained throughout the determination.

To the liquid to be tested add such an amount of appropriate indicator soln. as will produce a rather weak colour, and then add precisely the same amount of the indicator solution to the liquid in the other tube. The colour developed in the alkalised soln. will be more intense than in the liquid under test because the indicator is fully transformed into indicator salt (coloured ion), whereas in the test soln. only part of the indicator is so transformed.

It has to be established what proportion of the indicator in the test soln. has been changed to ionised indicator salt, and this is determined by diluting the comparison alkalised soln. until a colour match between the two solns. is attained. The concn. of indicator salt is then the same in both solns., and the ratio of the concns. of indicator salt (coloured ion) to indicator acid (uncoloured) in the test soln. can be derived from the extent of the dilution that had to be made of the comparison soln. If the dilution (D) is expressed as the final vol. divided by the original vol., the concn. of indicator salt is reduced by the dilution to 1/D of the original quantity. This is also the concn. of indicator salt in the test soln., the concn. of indicator acid being 1–1/D. The ratio of indicator salt to indicator acid in the test soln. is, therefore, (1/D)/(1–1/D), which is equal to 1/(D–1).

Michaelis and Gyemant (*Biochem. Z.*, 1920, **109**, 165) and Michaelis and Krüger (*id.*, 1921, **119**, 307) have shown that when the one-colour nitrophenol indicators are used, the *p*H value of a soln. is related to the proportion of indicator transformed into indicator salt (x) according to the formula $p\mathrm{H}=p\mathrm{K}+\log(x/[1-x])$ where *p*K is the *p*H value at the half transformation point of the indicator. Since $x/(1-x)=1/\mathrm{D}-1$) the formula becomes $p\mathrm{H}=p\mathrm{K}-\log(\mathrm{D}-1)$.

This formula is valid for the mono-acidic nitrophenols, and Michaelis gives the following *p*K values at 20° C.: 2,6-dinitrophenol, 3·68; *p*-nitrophenol, 7·16; 2,4-dinitrophenol, 4·05; *m*-nitrophenol, 8·32.

The one-colour indicators phenolphthalein and Salicyl Yellow (Alizarine Yellow GG) are poly-acidic, and the simple formula given above is not applicable when they are used. Michaelis and Gyemant have determined degrees of colour (proportion of indicator transformed into indicator salt), x, for these two indicators at specific *p*H values. Their calibration, together with the corresponding dilution values, D, are given in the following table:

Phenolphthalein						Salicyl Yellow		
x	D	*p*H	x	D	*p*H	x	D	*p*H
0·01	100	8·45	0·40	2·5	9·50	0·13	7·7	10·00
0·014	71	8·50	0·45	2·22	9·60	0·16	6·25	10·20
0·30	33	8·60	0·50	2·0	9·70	0·22	4·55	10·40
0·047	21	8·70	0·55	1·82	9·80	0·29	3·45	10·60
0·069	14·5	8·80	0·60	1·67	9·90	0·36	2·78	10·80
0·090	11	8·90	0·65	1·54	10·00	0·46	2·17	11·00
0·12	8·3	9·00	0·70	1·43	10·10	0·56	1·79	11·20
0·16	6·25	9·10	0·75	1·33	10·20	0·66	1·51	11·40
0·21	4·75	9·20	0·80	1·25	10·30	0·75	1·33	11·60
0·27	3·7	9·30	0·845	1·18	10·40	0·83	1·20	11·80
0·34	2·95	9·40	0·873	1·145	10·50	0·88	1·14	12·00

RAND WATER BOARD, JOHANNESBURG, SOUTH AFRICA J. MCCRAE

April, 1943

COLORIMETRIC ESTIMATION OF PHOSPHORUS BY REDUCTION OF PHOSPHOMOLYBDATE TO MOLYBDENUM BLUE

BY controlling the amounts and proportions of the reagents used, Truog and Meyer (*Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 136) have shown that phosphomolybdate is reduced to molybdenum blue by stannous chloride without reduction of the ammonium molybdate or of silicomolybdate when silica is present in amounts up to 700 p.p.m. The colour reaches its max. intensity almost immediately and begins to fade after about 10 min., but can be regenerated by adding more stannous chloride. A change to green is soon detected, however, corresponding with the development of a yellow colour in the "blank."

In a determination of traces of phosphine in acetylene by oxidation to phosphate with sodium hypochlorite soln. it was noted that phosphomolybdate was immediately reduced to molybdenum blue by stannous chloride in presence of hypochlorite or chlorate, and that no greenish colour developed on standing. Standards prepared from solns. of phosphate (0·00025–0·005 mg of phosphorus in 50 ml), to which 0·1% of potassium chlorate had been added, showed no change to green over a period of several hrs., while the "blank" remained colourless. A drop of stannous chloride soln. was added occasionally to regenerate the blue colour, which was readily detected in a soln. containing 0·005 p.p.m. of phosphorus.

Addition of chlorate to test samples and standards to prevent the development of the disturbing colour helped considerably in the task of matching without reducing the sensitivity of the reagents.

I wish to thank the Government Chemist, Dr. J. J. Fox, C.B., O.B.E., F.R.S., for permission to publish this note on work carried out at the Government Laboratory, London.

GOVERNMENT LABORATORY, CLEMENT'S INN PASSAGE, LONDON, W.C.2 P. J. HARDWICK

May, 1943

Ministry of Food

STATUTORY RULES AND ORDERS*

1943—No. 236. The Vegetable and Vegetable Products (Canning, Bottling and Freezing) (Control and Maximum Prices) Order, 1943. Dated February 15, 1943. Price 3d.

In this Order "vegetable" includes tomatoes and edible fungi and any vegetable—(a) whether or not mixed with any other article, and (b) whether fresh, or dried, wholly or partly cooked (including vegetables in vegetable rolls or similar products), and vegetable juices and purees. It does not include rhubarb or soups or vegetable extracts or vegetable jams or manufactured vegetable products other than those mentioned in the Order.

The minimum weight of vegetable or vegetable product per can, specified in Schedule II, shall be the wt. in the form specified exclusive of the weight of sauce or other added specified substances and of any covering liquid. If the wt. has to be ascertained when covering liquid is already present, this shall first be drained off for at least 1 min. The weight of the vegetable or specified vegetable product shall be the weight immediately after being placed in the can; if the weight is taken subsequently, an adjustment shall be made for estimated gain or loss in weight. Except where expressly provided, no vegetable or vegetable product shall be mixed with any other vegetable (whether mentioned or not in the Order) or with any other specified vegetable product. Specified vegetable products include: Beans (baked or steamed in a sauce blended from tomatoes or other fruit or vegetables, or in a gravy containing meat extract or yeast extract and with or without pork). Macaroni (cooked in cream sauce with cheese). Spaghetti (cooked in tomato sauce). Vegetable salad (with mayonnaise).

— **No. 497. The Fish (Maximum Prices) Order, 1943. Dated March 30, 1943.** Price 3d.

"Fish" means any fish found in the sea (whether fresh, frozen, smoked, cured, salted, pickled or otherwise processed) other than shellfish, sturgeon, salmon,† trout, eels (except conger eels, smelt, shad and whitebait, but does not include canned fish or processed fish packed in advance ready for retail sale in containers made wholly or partly of metal, glass or earthenware, or any manufactured product containing fish.

"Fresh" in relation to fish means fish which has not been frozen, smoked, cured, pickled, wet salted or dry salted.

"Frozen" in relation to fish means fish which by way of trade has been subjected to a temperature of or lower than 18° F.

— **No. 509. The Milk (Maximum Prices) (England and Wales) Order, 1943. Dated March 31, 1943.** Price 2d.

In this Order "Channel Islands milk" means milk—(a) produced from cows of the Channel Islands breed, and (b) containing not less than 4% of butterfat, and (c) which the producer sells by retail or in respect of which he receives a premium from the Milk Marketing Board premium contract.

"Homogenised milk" means milk that has been subjected to a process whereby the butterfat globules are broken up in such a way as to remain uniformly distributed throughout the proportionate vol. of milk, thus preventing the butterfat from rising to the surface; this process is in addition to the normal process of pasteurisation.

"Specially designated milk" means accredited milk (cf. S.R. & O., 1936, No. 356; 1938, No. 218), Channel Islands milk, homogenised milk, sterilised milk, kosher milk and tuberculin-tested milk.

"Sterilised milk" means milk which having been put into bottles capable of a vacuum seal is subjected to treatment for such a time as will ensure that it will remain fit for human consumption for at least 7 days; sterilised milk must first be homogenised.

— **No. 514. Order dated April 2, 1943, amending the Feeding Stuffs (Rationing) Order, 1942.** Price 1d.

The Order S.R. & O., 1942, Nos. 156, 337 and 1696 is further amended as follows: (a) In Art. 1 after "Distributing dealer" the following definition is inserted:—

" 'Grain or pulses' means any of the following cereals or pulses, namely, barley, beans, dredge corn, oats, rye, threshed home-grown peas, feeding peas and wheat, but does not include any such cereals or pulses which have been subjected to any process other than one or more of the following:—threshing, drying, cleaning, screening or dressing."

(*b*) In Art. 1 after "Retailer" the following definition is inserted:—

"'Wheat by-products' means any by-products obtained in the production of flour by milling and includes millers' offals and wheat offals, both as defined in Part II of the Fourth Schedule of the Fertilisers and Feeding Stuffs Act, 1926, as amended; and fine wheat feed, straight run bran, coarse bran, pollards, middlings and wheat germ."

This Order *came* into force on May 1, 1943.

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

† The price of salmon (including grilse and sea salmon) is controlled by S.R. & O., 1943, No. 110.

1943—No. 545. The Cereal Fillers (Control and Maximum Prices) Order, 1943. Dated April 8, 1943. Price 1d.

"Cereal filler" means any rusk, meal or crumbs of a description commonly used as a filler in the manufacture of articles of food containing meat or fish. "Flour" has the same meaning as in the Flour Order, 1943 (S.R. & O., 1943, No. 11).

The Order prohibits the manufacture by way of trade or business of cereal filler except under licence by the Minister or except from bread alone by a licensed baker. No soya flour or other soya product and no colouring matter may be used in the manufacture of cereal filler. Cereal fillers may not be used or bought or sold except for use in the manufacture or preparation of an article of food.

The max. prices specified are on the basis that the moisture content is 5% or less; if more moisture is present, the max. price shall be calculated on the basis of 5%.

Ministry of Health

THE PHOSPHATASE TEST FOR HEAT-TREATED MILK*

THIS leaflet describes in detail the laboratory technique for the application of the phosphatase test, including precautions, preparation of buffer substrate and of Folin and Ciocalteu's phenol reagent and other reagents, method of determination and of making control tests, and interpretation of results.

The colour in a blank test should not exceed 0·5 Lovibond blue unit. If the reading is 2·3 units or less the milk should be classified as "giving a negative phosphatase test," or as "sufficiently heat treated"; milks giving readings between 2·4 and 6·0 units as "insufficiently heat treated"; those with readings greater than 6 units as "grossly underheated."

A form (C) preferred for recording the results is appended to the leaflet.

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 FOURTH QUARTER, 1942

OF the 1463 samples submitted under the Food and Drugs Acts, 9 were taken formally.

FORMALIN TABLETS.—Three samples were deficient in formaldehyde. One contained only 2·4 mg instead of 9·7 mg. The tablets had been supplied by a reputable firm of manufacturing chemists, and it was suggested that there might have been partial volatilisation of the formaldehyde owing to the tablets having been kept in an ordinary stock bottle instead of an air-tight container. The entire stock was withdrawn from sale.

The second sample, also from a reputable manufacturer, was 58% deficient in strength. The tablets had been in stock for 10 months and, prior to that, had been delayed in transit for 3 weeks, during which time they had been packed in cardboard boxes. The stock was returned to the makers and replaced by new. The third sample was 80% deficient in strength. Here, too, volatilisation appeared to be the explanation. The stock was withdrawn from sale.

A sample of a proprietary brand of tablets was labelled as containing 0·15 grain of formaldehyde per tablet, whilst the actual strength was only 0·08 grain. These tablets had been in stock for about 2 years, and this probably accounted for the deficiency.

H. H. BAGNALL

Midland Agricultural College: Chemistry Department

SILAGE COMPOSITION

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

THE data prepared for the information of the Ministry of Agriculture (*cf.* ANALYST, 1942, **67**, 328) have been extended and improved by the inclusion of analyses up to May 1, 1943, so that they now represent the composition of the products from 390 silos. With the exception of 7 (not included) all the samples were considered reasonably normal in appearance, odour, wetness and *p*H and in the description by Silage Officers. In the present report the two main crops—grass and seeds—have been classified into (*a*) Good quality and Poor quality, and (*b*) Young and leafy, Medium maturity and Full mature. The new "average compositions do not differ significantly from those previously reported, and it may suffice to give here only a selection of the results.†

Ensiled crop	Number of silos	Dry matter %	Percentage composition of dry matter: Crude protein	Sol. carbohydrates	Crude fibre	Ash	Oil	Protein in fresh silage as fed, %
Permanent grass (all grades)								
Good quality	85	22·3	14·0	41·6	30·4	10·4	3·6	3·12
Poor quality	71	22·7	12·6	43·5	30·1	9·7	4·1	2·86
Temporary seeds (all grades)								
Grass and clover	87	22·6	16·0	41·4	29·7	9·7	3·2	3·62
Clover only	23	23·4	17·0	37·4	30·6	10·8	4·2	3·98
Lucerne (mainly medium maturity)	19	22·9	17·5	35·8	30·1	10·4	6·2	4·01
Pea haulm and cannery wastes	20	23·4	14·9	40·0	28·1	13·0	4·0	3·49
Sugar-beet tops	20	24·5	10·9	34·5	10·7	42·1	1·8	2·67
Cereal-legume mixtures (oats—beans—tares)	10	24·3	12·0	43·6	32·1	9·2	3·1	2·92

* Addendum to Memo 139/Foods. H.M. Stationery Office, 1943. Price 1d. net.

† The authors will be pleased to send a complete copy of the new table to any reader on application.—EDITOR.

The figures for protein in fresh silage were based on analysis of material dried in the laboratory oven and some of them are subject to minor corrections to allow for loss in drying.

The new classification, in terms of maturity condition, has not revealed quite the substantial differences in protein level anticipated, as is shown below.

	Number of silos	Crude protein (%) in dry matter		
		Young, leafy	Medium maturity	Fully mature
Permanent Grass				
Good quality	85	15·1	13·0	12·4
Poor quality	71	12·8	13·1	10·9
Temporary seeds				
Grass and clover ..	87	16·5	15·8	15·3
Clover only	23	18·1	17·1	13·3

SUTTON BONINGTON, LOUGHBOROUGH *May*, 1943

British Standards Institution

TEMPERATURE MEASUREMENT

BRITISH STANDARD CODE. 1041—1943*

THIS code is issued as a provisional specification to be improved when international conditions permit. It aims at assisting operators to select the most appropriate methods of temperature measurement for each industrial process, at indicating the sources of error and limitations in each method, and at formulating precautions to be taken. Tentative suggestions are also made for the standardisation of measuring instruments and procedure.

The definitions and explanations of the International Temperature Scale are those employed at the National Physical Laboratory. The technical methods described are classified into Contact Methods and Non-Contact methods. The former are explained and discussed under the following headings: (A) Thermal Expansion of Testing Bodies, (B) Electrical Resistance Thermometers, (C) Thermo-electric Junctions, (D) Radiations from Testing Body placed in the Gas, (E) Change of State of Testing Body, (F) Calorimeter Pyrometers, (G) Special Methods to obtain Equilibrium between Testing Body and Hot Body. The non-contact methods include (A) Black Body Radiation Methods, (B) Instruments to give the Temperature of a Grey Body, (C) Electro Excitation Radiations from Solids and Gases.

Calibration methods are described in detail in a section of 5 pages, and the Code concludes with Temperature Conversion and Fourth Power Tables, a bibliography and a full index.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Spectrophotometric Study of the Green Colour in Peas. H. Fischbach and S. H. Newburger. (*J. Assoc. Off. Agr. Chem.*, 1943, **26**, 127–134.)—Blair and Ayres (*Ind. Eng. Chem.*, 1943, **35**, 85) have developed a canning procedure by which 60% of the natural colouring matter of peas is retained. The peas are maintained in a mildly alkaline condition throughout the process by controlled treatment with very dil. solns. of sodium carbonate ("presoak"), calcium hydroxide ("blanch") and magnesium hydroxide ("brine"), the change of chlorophyll to phaeophytin being thereby inhibited. The green pigment of the fresh pea, the ordinary canned pea and the Blair-processed pea have been examined spectrophotometrically, the transmission curve of the extracted pigment in ethereal soln. being obtained with a General Electric recording spectrophotometer having an 8$m\mu$ slit. Owing to difficulty in interpreting data from the crude extracts, saponification derivatives were prepared and examined similarly. The samples used were fresh peas (sweet variety), Blair-processed peas (sweet variety), Blair-processed peas (Alaska variety, containing a number of olive-green and pale yellow peas) and ordinary canned peas. Before analysis all samples were stored at 40° F. *Method.*—Wash 150–200 g of shelled fresh peas or drained canned peas with copious quantities of water to remove soluble matter, especially traces of metallic salts. Draw air through the peas for 5 min. and to an aliquot portion (100 g) in a Waring blender add 100 ml (125 ml for fresh peas) of cooled (40° F.) 95% ethanol containing 0·5 g of sodium carbonate and a sheet of filter paper to facilitate filtering. Stir at high speed for 5 min., filter and wash the residue with two 25-ml portions of ethanol. Shake the filtrate vigorously with 50 ml of ether, add 125 ml of brine (40 g of sodium chloride and 5 g of sodium carbonate per litre of double-distilled water) and shake the mixture carefully. Discard the aq. layer and wash the ethereal layer with 100 ml of brine. Examine the ethereal layer in the spectrophotometer. To prepare the cold saponification product, treat the ethereal extract with 5 ml of sat. potassium hydroxide in methanol, shake vigorously, leave overnight at 40° F. and transfer to a separator with double distilled water. Discard the ethereal layer, wash the aq. layer with 25 ml of ether, dilute the extracts from the various samples to approx. the same intensity of colour and examine them in the spectrophotometer. The absorption peaks were found to occur at wavelengths increasing in the order fresh peas, sweet variety Blair peas and

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ordinary canned peas. The cold saponification products showed significant shifts to shorter wavelengths for the fresh and sweet variety Blair peas, but not for the ordinary canned peas. This shift is still observed if the sweet variety Blair pea is artificially aged by preheating the closed container for 1 hr. at 80° C., but not after heating for 16 hrs. The Alaska variety Blair pea used showed no indication of absorption at a shorter wavelength when its ethereal extract was saponified. Blair and Ayres have shown that, as the organically combined magnesium of the green pigment diminishes, the colour of the pea changes towards olive-green and that the olive-coloured ordinary canned pea contains no magnesium. This corresponds with the chemical change of chlorophyll to pheophytin. The following conclusions can be drawn from the spectrophotometric data. If both the ethereal extract and the saponification product have absorption peaks at 658·5–666·5$m\mu$, the canned pea has an olive colour, and little, if any, organically combined magnesium was originally present. It, however, the ethereal extract has an absorption peak at 661·5–662·5$m\mu$ and the saponification product one at 640·5–645·0, the presence of organically combined magnesium is indicated and the original colour has undergone little change. The Alaska variety pea has less chlorophyll than the sweet variety. The spectrophotometric data substantiate the conclusion of Blair and Ayres, *viz.*, that the new canning procedure inhibits the change of chlorophyll to pheophytin. A. O. J.

Determining Free and Acetylated Sulphanilamide. S. Anderson. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 29–30.)—The extinction coefficients of free and acetylated sulphanilamide in aqueous soln. were measured photographically on an Eastman Panchromatic process film over the wavelength range 320–260$m\mu$, a Cenco replica grating spectrograph provided with an Allen-type hydrogen arc being used. Solns. equiv. to 0·2–1·25 × 10^{-3} mg per ml were measured in a cell 13·7 mm long. A step-plate was used for calibration, and the relative light intensities were determined with a Leeds and Northrup Speedomax recording microphotometer. The curves reproduced show that these substances have almost equal extinction coefficients in the range 282–260$m\mu$, but that they absorb all light of wavelength less than 310 and 286$m\mu$, respectively. These differences in behaviour are used in a method of determination more rapid than that of Bratton and Marshall (ANALYST, 1939, **64**, 524); to determine the total amounts of sulpha-drugs present by the latter method, it is necessary to hydrolyse the acetyl compound by heating it in boiling water for 1 hr. In a convenient apparatus light rich in lines of wavelength 310–260$m\mu$ passes successively through one of two filters and a quartz lens which focusses it on the more distant wall of a cell with 2 laterally-adjacent 3·5-ml rectangular compartments separated by a thin glass wall, which contain 2 ml of the soln. of the sample and of a standard soln., respectively. The terminal wall contains a glass (Corning 014) which fluoresces blue when absorbing light of the above range, and it is common to both compartments. The concn. of the standard soln., therefore, is varied until the fluorescence of the glass in the wall of its compartment matches that of the glass in the wall of the compartment containing the soln. of the sample. The transmission spectra of each component of the instrument, with each of the 2 drugs in the cells, are reproduced in the paper. Two filters are used, *i.e.*, transmitting only the light absorbed by free sulphanilamide and by both drugs, respectively, and the match is made by adding free sulphanilamide to the standard compartment with each filter in position in succession, in the above order. If it can be assumed that both drugs have the same extinction over the range transmitted, then the total sulpha-drug content and the free sulphanilamide content are obtainable from the 2 readings; the amount of acetylated compound may then be found by difference. Data are tabulated for standards solns. containing 0·0375–0·0625 mg of total sulpha-drugs (singly and as mixtures) per ml; recoveries were 94–111 (sulphanilamide) and 86–110% (total sulpha-drugs). With 0·05 mg of sample per ml the accuracy is ±10 and 15% for the free and total sulphanilamide contents, respectively. The total time for each analysis was 3–5 min. With samples of blood, pptn. of protein or prevention of coagulation by addition of reagents whose absorption spectra overlap, the range 320–260$m\mu$ (*e.g.*, sodium oxalate soln.) must be avoided; dil. chloroacetic acid and sodium citrate solns., respectively, are satisfactory. J. G.

(Determination of) Phenolphthalein in Chocolate Preparations. M. H. Hubacher. (*J. Assoc. Off. Agr. Chem.*, 1943, **26**, 194–196.)—The method is a slightly improved modification of the method of the A.O.A.C. ("*Methods of Analysis*," 5th Ed.). The 0·5 *N* iodine reagent is prepared by dissolving 12·7 g of potassium iodide in 10 ml of water, adding 6·35 g of iodine and, after soln. of the iodine, 12 ml of 5 *N* potassium hydroxide, and finally diluting the soln. to 100 ml. Extract the fat from 1 g of shavings of the sample (≡ 0·1 g of phenolphthalein) in a Gooch crucible with successive portions of 5 ml, 4 ml and 3 ml of carbon tetrachloride, using slight suction towards the end. Extract the phenolphthalein with 30–45 ml of hot alcohol in small portions, finally washing the underside of the crucible free from phenolphthalein. Evaporate the alcoholic soln. on the water-bath and dissolve the residue at room temp. in 1–1·5 ml of 5 *N* sodium hydroxide. Add *ca.* 25 g of ice, 7–8 ml of the iodine reagent and conc. hydrochloric acid, drop by drop, from a burette, with stirring, until pptn. is complete. If the ppt. (as well as the supernatant liquid) is not brown, add more iodine reagent until an excess is ensured. Dissolve the ppt. by adding 5 *N* sodium hydroxide, drop by drop. Repeat the process of pptn. and redissolving 3 more times, adding a small piece of ice, if necessary, to keep the soln. cool. To the blue alkaline soln. add 1–1·5 ml of sodium sulphite soln. (12·6 g of anhydrous salt per 100 ml) and filter the mixture through a Gooch crucible, washing several times with water. Acidify the filtrate with conc. hydrochloric acid, collect the white or greyish ppt. in a tared Gooch crucible, wash with water until free from chloride and dry the tetraiodophenolphthalein to constant wt. at 110°–130° C. Wt. of ppt. × 0·3872 = wt. of phenolphthalein. The alkaline phenolphthalein soln. is unstable in air and should be converted into the tetraiodo-compound within 2 hrs. The accuracy of the method is 99·2% with a mean deviation of ±0·8%. A. O. J.

Biochemical

Colorimetric Determination of Aliphatic Nitrate Esters. H. Yagoda. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 27–29.)—The method is based

on the hydrolysis of the ester by sulphuric acid and the nitration of *m*-xylenol by the nitric acid so liberated; the resulting compound is then separated by steam-distillation and determined colorimetrically by addition of alkali (*cf.* Werr, ANALYST, **1937, 62,** 577). Prepare the sample (*e.g.*, blood, urine or stomach contents) by extracting with ether, wash the extract with 10% sodium sulphate soln. until the wash liquor gives no chloride reaction with silver nitrate, and dilute the extract to a known vol. Evaporate an aliquot portion (equiv. to *ca.* 3 mg of the ester) almost to dryness in a 300-ml conical flask in a gentle stream of cold air (to avoid volatilsation of certain esters), add to the residue 1 ml of a 2% soln. of *m*-xylenol in acetone, and then 15 ml of 62·5% (by vol.) sulphuric acid (sp.gr. 1·63); the use of acetone as the solvent is important, as it facilitates the nitration of certain esters. After 30 min. at room temp., add 100 ml of water and steam-distil, in presence of a boiling-rod and some porous tile if fatty matter is present. Collect the distillate directly in a tall 50-ml Nessler cylinder, which stands in a larger cylinder of cold water and contains 5 ml of 2% sodium hydroxide soln; the end of the delivery tube should be slightly above a 20-ml mark made on the Nessler cylinder. In this way solidification of the nitroxylenol in the tube is prevented. The walls of the Nessler cylinder should be wetted by the alkali, and when the soln. boils, reduce the height of the flame to 2–3 cm. and collect 15 ml of distillate. Rinse the delivery tube into the Nessler cylinder, cool the contents to room temp., and dilute to the 50-ml mark. Match the deep yellow colour in a Duboscq colorimeter (5-mm cups) against a standard soln. of nitroxylenol. Prepare this by evaporating, *e.g.*, 5 ml of a standard 0·02% potassium nitrate soln. almost to dryness, cool, add the reagent and acid, and proceed as described; 1 mg of potassium nitrate ≡ 0·7486, 0·7470 and 0·7817 mg of nitroglycerin, erythritol tetranitrate and pentaerythritol tetranitrate, respectively. Results are tabulated for 0·01 to 3·00 mg of these 3 substances, and the max. recorded differences between the amounts taken and recovered are −0·06 and +0·04, −0·03 and +0·02, and −0·03 and +0·06 mg, respectively; Beer's law applies over this range. The reaction is stoichiometric within the limits of visual colorimetry, and analyses of successive aliquot portions of extracts of the digestive tracts of animals fed on the esters were reproducible to within 3%. The min. colour visible (in a Nessler cylinder having a 50-ml mark at a height of 23 cm) is equiv. to 5μg of ester, but with quantities of this order it is advisable to use a 1% soln. of *m*-xylenol, as the colour of the blank test soln. is otherwise influenced by this reagent. This method was used to determine the solubility of these esters in water or oil. The preliminary extraction processes remove halogen salts, metals that liberate hydrogen with the acid, nitrites, sulphides and inorganic nitrates, which may interfere. However, they do not remove hydrogen peroxide completely, and, although its presence in samples of biological origin is unlikely, it will interfere if present. The method may be tested on standard solns. of these esters in acetone, after purification as follows. Evaporate a commercial 10% soln. of nitroglycerin in acetone at room temp. and dry the residue to const. wt. in a vacuum desiccator. Purify the other esters by adding water at 50° C. to filtered solns. in warm acetone; filter off the resulting granular ppts., wash them with 25% (by vol.) acetone, and dry them to const. wt. over calcium chloride *in vacuo*. J. G.

Acetoin. Polarographic Determination. Disappearance from the Blood after Administration. L. A. Greenberg. (*J. Biol. Chem.*, 1943, **147**, 11–17.)—Determination of acetoin by the polarographic method is specific and quantitative, and acetoin in concns. as low as 0·5 mg per 100 ml can be determined in *ca.* 1 hr. on a 2-ml sample of blood. Prepare a 1 : 10 tungstic acid protein-free filtrate from 2 ml of blood by the Folin-Wu method, and to 10 ml of the filtrate in a 125-ml distillation flask add 10 ml of 50% ferric chloride soln. Connect the flask to a small vertical condenser, the lower end of which dips into a receiver calibrated at 10 ml, and immerse the distillation flask in a hot water-bath for 30 min. Remove the bath and heat directly with a micro-burner until exactly 10 ml of distillate have been collected. Determine diacetyl in 2–3 ml of this distillate by the polarographic method, using a 5-ml cell. The reduction potential and diffusion current of diacetyl are influenced by the *p*H of the soln. and by the nature of the supporting electrolyte. A convenient electrolyte is sodium sulphite, which gives a large diffusion current at a half-wave potential of −0·86 volt; add an excess of sodium sulphite crystals to the soln. The reduction potential of sodium does not interfere, and the use of sulphite makes the removal of oxygen from the soln. unnecessary. The relation between the diffusion current and concn. is not linear, and a reference curve is required. One mg of diacetyl ≡ 1·023 mg of acetoin. The error involved in the determination of acetoin was estimated by adding known amounts to water, blood and urine. With 1 mg per 100 ml the max. error was ±0·2 mg per 100 ml; with 10 mg per 100 ml the error did not exceed +0·2 and −0·5 in water, +0·2 and −0·4 in blood or 0·0 and −0·5 in urine; with 75 mg per 100 ml it did not exceed +1·1 and −1·2, +0·6 and −1·0, and −0·9 mg per 100, respectively. F. A. R.

Iron Content of Crystals of Human Haemoglobin. F. W. Bernhart and L. Skeggs. (*J. Biol. Chem.*, 1943, **147**, 19–22.)—The iron content of dialysed dried human haemoglobin has previously been reported to be 0·305 to 0·338%. A somewhat different value has now been obtained by the following method. Weigh 2–5 g of haemoglobin into a tall porcelain 50-ml crucible, taking precautions against absorption of moisture. Add 2 ml of sulphuric acid and heat in an electric oven, first at 80° C. and increasing to 135° C. after 8 hrs. Transfer the crucible to a hot plate, and leave it until the contents cease to bubble. Finally, place it in a cold muffle furnace, raise the temp. to 590° C. in about 2 hrs. and continue the heating for 8 hrs. Add 2 ml of 12 *N* hydrochloric acid to the dry ash, cover the crucible with a watch-glass, evaporate to *ca.* 0·2 ml, add 1·5 ml of water and heat almost to boiling on a hot plate. Add, drop by drop, a freshly prepared solution of stannous chloride (2 g of the iron-free dihydrate in 100 ml of 6 *N* hydrochloric acid). Continue the addition until the yellow colour of the ferric iron disappears and then add 1 more drop. Cool to 25° C. and add 1 ml of 5% mercuric chloride soln. all at once. If the ppt. is white, silky and small in amount, add as rapidly as possible 15 ml of 85% phosphoric acid and 0·04 ml of a 0·2% soln. of barium diphenylamine sulphonate; otherwise discard and start again. Titrate at once with standard potassium dichromate soln. (*ca.* 0·028 *N*), with mechanical stirring, until a violet tinge appears. By this method the iron content of human haemoglobin dried at 105° C.

was found to be 0·340%. The constants generally used in haemoglobin estimations are therefore 1·5% too low. F. A. R.

Micro-determination of Iodine in certain Biological Materials. B. K. Shahrokh. (*J. Biol. Chem.*, 1943, **147**, 109–113.)—A method of estimating iodine, which is especially useful for the analysis of thyroid preparations containing less than 1% of iodine, comprises digestion of the material with potassium chlorate in sulphuric acid (which at the same time oxidises iodine to iodic acid) and liberation of the iodine with potassium iodide. Put 2 ml of conc. sulphuric acid, diluted with an equal vol. of water, in a micro-Kjeldahl digestion flask, and then 1 ml of the liquid to be analysed. Add solid potassium chlorate equiv. to 0·25 g for each 10 mg of dry matter in the sample, but not in excess of 0·75 g. Heat the flask gently until the liquid becomes green, continue for a further 2 min., and then gradually increase the heat. Boil until the colour fades and white fumes are evolved and heat for 1 min. at the same rate. After cooling, add 10 ml of water, and transfer the soln. to a 50-ml conical flask, marked at the 15-ml level. Rinse the flask twice with 5 ml of water and transfer the washings to the conical flask. Boil until the level of the liquid reaches the 15-ml mark, cool and add a crystal of phenol. Add 1 ml of 0·5% potassium iodide soln. and titrate immediately with 0·001 *N* sodium thiosulphate, using starch as indicator. A microburette is advisable, but, if an ordinary burette is used, the loss of accuracy is partly compensated by the increased speed of titration. It is important that the titration be completed rapidly, as small amounts of iodine are liberated slowly from the potassium iodide. A more accurate end-point can be obtained as follows. After cooling the digest, ppt. the salts with 5 ml of 85% alcohol, centrifuge and wash twice with 5 ml of 85% alcohol, add 1 ml of water to the supernatant liquid containing the iodate, and evaporate to remove the chlorine, taking care not to ignite the alcohol vapour. Both methods give slightly high values, and a series of controls should be carried out, preferably with known amounts of either iodoacetic acid or iodopropionic acid. From the result a correction figure is obtained, which can be applied to the estimation of iodine in unknown samples. F. A. R.

Determination of Aluminium in Biological Material. J. Cholak, D. M. Hubbard and R. V. Story. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 57.)—Prepare nitric acid solns. of the dry-ashed (500° C.) samples and adjust to volumes approx. as follows. For ashed urine samples, make up the soln. so that each ml corresponds to 10 ml of fresh urine, for faeces ash make up to a total vol. of 100 ml, and for solns. of ashed mixed food samples make up to 500 ml. Incorporate in these solns. a suitable quantity of a standard soln. containing bismuth, so that the prepared test soln. contains 15 mg of bismuth per 100 ml. Bismuth serves as an internal standard. Dry a 0·2-ml portion of the soln. in the crater (10 mm deep, 3 mm diam.) of a pure graphite rod (37·5 mm long, 6 mm diam.). Burn the dried rod as positive electrode in a 10-amp. d.c. arc, and adjust the arc gap so that there is a 50-volt drop across the electrodes. Use a similar cratered but untreated graphite arc as the negative electrode. The craters in the electrodes help to improve the steadiness of the arc. Photograph the spectra on a large quartz spectrograph. The bismuth lines 2993A and 3024A are of suitable intensity to serve as standard lines for the evaluation of aluminium (3082A) in the respective ranges of 0·01–0·10 mg per 100 ml, and 0·05–2·00 mg per 100 ml of the prepared sample. Construct a calibration curve by adding known amounts of aluminium to the standard bismuth soln. It is claimed that in the low range the average error of a single analysis is ±0·014 mg of aluminium per 100 ml of soln. and, in the high range, approx. ±10% of the amount present. During the course of the investigation a chemical method was developed which involves the isolation of the aluminium as the phosphate, the removal of iron with cupferron, the subsequent development of an aluminium lake with Alizarin Red S, and the measurement of the optical density of this lake at wavelength 580$m\mu$. This method was found to equal the spectrographic method in precision. B. S. C.

Ascorbic Acid Values of Fruits and Vegetables for Dietary Surveys. M. Olliver. (*Chem. and Ind.*, 1943, **62**, 146–148.)—Examination with 2 : 6-dichlorophenolindophenol of several thousand samples of fruits and vegetables as normally consumed indicated the following average amounts (mg per 100 g) of vitamin C. Freshly harvested vegetables and fruit were also examined after ageing and when cooked under controlled but normal conditions; *e.g.*, green vegetables were added to boiling water and root vegetables to cold water just sufficient to cover them; salt was added to the water. The fruits were stewed until tender with an equal quantity of water and sugar to sweeten. Apple, cooked 4, raw 8; apricot, canned 5, dried, cooked <2; asparagus, cooked 30; banana* 10; bean, broad, cooked 10; bean, French or runner, cooked 6; bean, stringless, cooked 4; beetroot, cooked 5; bilberry, cooked 7; blackberry, cooked 8, raw 20; cabbage, cooked 16, raw 70; carrot, cooked, young (July–Sept.) 7; carrot, cooked, old (Oct. onwards) 3; carrot, raw 9; cauliflower (white head), cooked 30; celery, 7; cherry, cooked 3, raw 6; cucumber, 9; currant: black, cooked 90, red, cooked 23, white, cooked 23; damson, cooked 3; gooseberry, cooked 20, raw 40; grapefruit* 40; greengage, cooked 2; horseradish 136. Jams (*ca.* 30% fruit)—apple, <2; apple jelly, <2; apricot, <2; blackberry, 5; blackberry jelly, 2; blackcurrant, 50; blackcurrant jelly, 25; damson, <2; gooseberry, 10; greengage, <2; marmalade, 10; plum, <2; raspberry, 8; redcurrant jelly, 6; rhubarb, <2; strawberry, 10. Kale, cooked, 23; leek, cooked, 15; lemon*, 46; lettuce, 16; loganberry, cooked, 20; marrow, <2; melon,* 3; mushroom, cooked, 3; mustard and cress, 37; onion: cooked, 6, spring, raw, 25; orange (sweet),* 58; parsley, 154; parsnip, cooked, young (Feb. onwards) 10, cooked, old (Nov.–Jan.), 4; peach, canned, 3; pear, cooked, <2, raw, 3; pea, cooked, 14; pineapple, canned, 8; plum, cooked, <2, raw, 3; potato, cooked, new, 16, cooked, old, 4; prune dried, cooked, <2; pumpkin, cooked, <2; radish, 29; raspberry, 25; rhubarb, cooked, 4; spinach, cooked, 25; sprouts, brussels, cooked, 30; strawberry, 61; swede, cooked, 17, juice, raw, 40; tomato, 22; turnip, cooked, 13; watercress, 61. The variety and degree of maturity do not affect the values. Storage, however, has a marked effect and for most green leafy vegetables and peas in pod a 10% correction should be applied for each day's storage after harvesting. The rate of destruction is lower with root vegetables, but is important, as they are

* Stored after picking.

stored for longer periods. The vitamin C content of potatoes eaten in different months of the year may be assumed to be: Aug.; Sept. (assumed to be freshly dug), 16; Oct., 12; Nov., 9; Dec., 7; Jan., 5; Feb., 3; March and onwards, 2. For broken or soft fruits 10% should be deducted if the period after picking exceeds 24 hrs. For steamed vegetables 25% should be added to the value for the boiled material. Chips contain 20% more vitamin C than is in boiled potatoes, owing to loss of water. Most of the ascorbic acid lost during cooking is extracted in the cooking water. When this is used for soup, the extracted vitamin C (*ca.* 50% of that in the cooked vegetable) is consumed. The rate of boiling affects the ratio of water to vegetable at the end of cooking, but the time of boiling is generally immaterial. Addition of salt or soda does not affect the ascorbic acid content unless the food is subsequently kept hot; then the presence of soda accelerates destruction. Keeping food hot after cooking destroys vitamin C; *e.g.*, in cabbage kept hot for 15, 30, 45, 60, 75 and 90 min. the loss was 25, 40, 50, 60, 70 and 75% respectively. Since stewed fruit is invariably consumed with the juice produced, no loss of vitamin C occurs through extraction in the cooking water. The vitamin C content of canned and bottled foods is similar to that of controlled household-cooked foods. The loss on treatment and storage of frozen foods is small, provided that they are subsequently cooked in the normal way. In ordinary methods of household drying there is almost complete loss of vitamin C, and the amounts in dried figs, sultanas, raisins, currants and dates are only negligible. Some fruit and vegetable juices lose activity rapidly; others do not. Ten per cent. are lost from the initial ascorbic acid value of jam after 6 months' and 20% after 12 months' storage. F. A. R.

Stability of Ascorbic Acid in Metaphosphoric Acid Extracts. L. W. Mapson and C. A. Mawson. (*Nature*, 1943, **151**, 222–223.)—Since it is often impossible to determine the ascorbic acid content of a food immediately after sampling, measurements have been made of the rates of oxidation of the pure acid and of extracts containing it from potato, swede or cabbage in 5% metaphosphoric acid soln. and in a soln. containing 2% of metaphosphoric and 5% of trichloroacetic acids. Activity-time curves are plotted illustrating the effects of exposure to ultra-violet light and daylight at 20° C., and of storage in the dark at 20° C. and at 0° C. The conclusion reached is that such extracts should always be stored in the dark; they are then sufficiently stable for the purposes of the assay for 2 days and 24 hrs. at 0° and 20° C., respectively. The stability is greater if, after centrifuging, the supernatant liquid is separated from the ppt. It is believed that substances such as copper, iron and riboflavin in the food catalyse the oxidation of the ascorbic acid in light at 20° C. Under all of the conditions of exposure used, pure ascorbic acid proved to be more stable than the acid present in the extracts; in daylight at 20° C. this difference amounted to 200–300%. J. G.

Bacteriological

Occurrence of Salmonella in Retail Meat Products. W. B. Cherry, M. Schèrgo and R. H. Weaver. (*Amer. J. Hygiene*, 1943, **37**, 211–213.)—Various types of meat products obtained from retail markets were examined by means of the tetrathionate enrichment method of Kauffmann and the selenite enrichment method of Leifson. Of the 250 samples examined, 13 (5·2%) contained Salmonella. The samples included: *Pork.*—Salt bacon ($^0/_1$), smoked bacon ($^0/_6$), brains ($^1/_{10}$), chops ($^2/_{21}$), ham ($^0/_{17}$), kidney ($^0/_{10}$), liver ($^6/_{30}$), loin ($^0/_8$), fresh sausages ($^1/_{44}$), smoked sausages ($^0/_5$), shoulder ($^0/_8$), and tenderloin ($^0/_3$). *Beef.*—Hamburger steak ($^2/_{24}$), kidney ($^0/_5$), liver ($^0/_{14}$), sirloin ($^1/_3$), spleen ($^0/_1$), sweetbreads ($^0/_5$) and veal ($^0/_3$). *Lamb.*—Chops ($^0/_8$) and fries ($^0/_3$). *Chicken.*—Liver ($^0/_3$). The numerators and denominators of the figures in brackets indicate positive findings and number of specimens respectively. The serological types found were *S. typhimurium*, *S. give*, *S. derby*, *S. anatum*, *S. newport*, *S. bredeney*, *S. seftenberg* and *S. newington*. The absence of *S. enteritidis* contra-indicates infection from the droppings of rodents, and the authors consider the most probable source to be the animals from which the meats were obtained. D. R. W.

Agricultural

Leaf Analysis as a Guide to Soil Fertility. H. Lundegårdh. (*Nature*, 1943, **151**, 310–311.)—Since the amount of nutrient salts absorbed by a plant reflects the amounts of the salts available in the soil, the % of nitrogen, potassium, calcium and phosphoric acid in the dried leaves collected at the flowering stage is a measure of the concns. of these substances in the soil. The method has been confirmed over 5 years by numerous pot experiments, which showed that the growth and yield of the plant is regulated by the actual amounts of nutrient salts in the green assimilating parts. Leaf analysis is thus an integration of all the factors that affect the availability of the salts in the soil; in particular, it avoids the misleading deductions from analyses of soil for nitrogen, due to available nitrogen being continuously produced by micro-organisms which obtain part of their nitrogen from the atmosphere. Other advantages of the method are that it takes into account methods of extraction of nutrients peculiar to the plant; it not only gives an instantaneous picture of the situation in the soil, but it can also be used to sum up the extraction of salts during several weeks, since the samples are taken when the vegetative parts of the plant are fully grown but still vigorous. This latter point is important from the viewpoint of substances (*e.g.*, potassium and calcium) which are extracted from soil by the joint action of the roots and soil micro-organisms. A curve illustrates ion antagonism between calcium and potassium in oats, showing that an increase of the latter in the plant suppresses absorption of the former, with a consequent decrease in yield. A curve also shows the interaction of potassium and phosphorus; thus, if soil is deficient in phosphorus (as indicated by leaf analysis), fertilisation with potassium salts alone gives a lower yield than if superphosphate is used. Similarly, leaf analysis indicates whether the use of superphosphate is advantageous without simultaneous use of a nitrate fertiliser. An approx. inverse relationship exists between the concn. of a particular element in the leaves and the increase in yield resulting from adding to the soil a fertiliser consisting principally of that element. A disadvantage of the method arises from the variability of environmental factors, especially rainfall and temp. Thus a dry summer tends to raise the concn. of nutrient elements in the leaves, and *vice versa*, but the resulting variations in the results of leaf analysis are not unduly high. J. G.

Teart Pastures of Somerset. I. Cause and Cure of Teartness. W. S. Ferguson, A. H. Lewis and S. J. Watson. II. Relation between Soil and Teartness. III. Reducing the Teartness of Pasture Herbage. A. H. Lewis. (*J. Agric. Sci.*, 1943, **33**, 44–51; 52–57; 58–63.)—I. The scouring of cattle and sheep caused by the teart pastures of central Somerset is due to the presence of molybdenum in the herbage in amounts ranging from *ca.* 20 to 200 p.p.m. in the dry matter. Scouring can be prevented and cured by feeding or drenching with copper sulphate. A daily dose of 2 g for cows and 1 g for young stock is sufficient on very teart land; less may suffice when the land is only mildly teart.

II. Teart soils contain from *ca.* 0·002–0·010% of molybdenum in the surface horizon; they are neutral or alkaline in reaction and often calcareous. The molybdenum content increases down the soil profile. Teart soils are developed from Lower Liassic materials, but not all soils so formed are teart. Those acid in reaction in the surface horizon are not teart even when the molybdenum content is high. Others which contain little molybdenum are also not teart; such soils cover a large area in Glamorgan. Molybdenum appears to be concentrated in the (uppermost) argillaceous component of the Lower Lias. The limestone contains very little. The soils of Somerset are largely derived from the argillaceous component; those of Glamorgan largely from the lower limestone component. This may explain why the soils of Somerset contain much more molybdenum than those of Glamorgan. Somerset soils formed from Keuper, Middle Lias, Upper Lias and Cretaceous material generally contain little molybdenum and are not teart. The relation of teartness to calcium carbonate content and *p*H of the soil indicates that molybdenum uptake by plants might be reduced by application of acidic materials to the soil. Application of lime or basic slag to soils of high molybdenum content might make them teart. Osmond's maps (*Ann. Rep. Long Ashton Res. Stat.*, 1934, 272–7) show clearly the areas concerned.

III. In expts. to determine the uptake of molybdenum by various species of pasture plants, 10 common pasture grasses and 2 types of clover were grown in teart soil in pots. The soil contained 0·0018% of molybdenum and 5·3% of calcium carbonate; its *p*H was 7·5. Four pots of each species were sown. The herbage was cut when *ca.* 3–4 in. high, and its molybdenum content was determined by the method of Marmoy (*J. Soc. Chem. Ind.*, 1939, **59**, 275). The results (p.p.m. on the dry substance) were as follows. Yorkshire fog, 36–83; fiorin, 9–14; timothy, 4–8; meadow fescue, 6–15; cocksfoot, 9–17; rough-stalked meadow grass, 11–18; smooth-stalked meadow grass, 6–8; crested dogstail, 5–10; indigenous perennial ryegrass, 11–11; Italian ryegrass, 10–13; wild white clover, 57–109; wild red clover, 59–103. Clovers and Yorkshire fog were thus outstanding in their ability to absorb molybdenum from teart soil. Many teart pastures contain a fair amount of clover, but Yorkshire fog is only a very minor component of the herbage. Acidic nitrogenous fertilisers decrease teartness by suppressing clovers, and by reducing molybdenum uptake by grasses. Acidification of the soil by regular applications of sulphur would reduce the availability of molybdenum in the soil. On the other hand, the application of basic materials increases molybdenum uptake by grasses on acid soils containing a fair amount of molybdenum. The proportion of molybdenum in newly sown grasses is low, but it increases with age. Thus a system of short leys consisting largely of grasses would give an increased output of material of low molybdenum content.

Water

Spectrophotometric Determination of Magnesium by means of Titan Yellow. E. E. Ludwig and C. R. Johnson. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 895–897.)—A rapid spectrophotometric method for the determination of magnesium in natural and treated waters is described. Preliminary removal of iron and calcium is unnecessary and sulphides do not interfere if the colloidal sulphur formed on exposure to air is allowed to settle. Magnesium hydroxide pptd. in presence of Titan Yellow forms an orange-red lake which, in dilute soln., can be kept in suspension for long periods by addition of calcium sulphate and starch. The transmission of the suspension is measured in a commercial spectrophotometer and the method is recommended for control work. *Reagents.*—Titan Yellow: 0·05%. Calcium sulphate: 5 g is stirred with 1000 ml of water for 4 hr. and filtered. Soluble starch soln.:—1%, freshly prepared every few days. *N* sulphuric acid. 2 *N* sodium hydroxide. *Procedure.*—Allow any colloidal sulphur and ferric hydroxide to settle, and then measure accurately a suitable amount (not more than 49 ml and containing between 0·1 mg and 1·1 mg of magnesium) into a 100-ml standard flask. If the water contains less than 2 p.p.m. of magnesium, acidify slightly with hydrochloric acid and evaporate to suitable bulk, preferably in platinum. To the sample in the standard flask add in order the following solns.: 1 ml of *N* sulphuric acid, 10 ml of starch, 20 ml of calcium sulphate, 10 ml of Titan Yellow, and 10 ml of 2 *N* sodium hydroxide. Make up to 100 ml, pour into a 250-ml glass-stoppered conical flask and shake well for 5 min. Transfer a portion of the suspension to the spectrophotometer cell and, as soon as air bubbles have disappeared, measure the transmission relative to a blank at a wavelength of 525$m\mu$ (renew the blank daily). Determine the amount of magnesium present by reference to a previously prepared calibration curve. C. F. P.

Organic

Pseudo-saccharin Chloride, a Reagent for Identification of Alcohols. J. R. Meadoe and E. E. Reid. (*J. Amer. Chem. Soc.*, 1943, **65**, 457–458.)—Pseudo-saccharin chloride, when heated with primary or secondary alcohols or with phenols until evolution of hydrogen chloride ceases, forms derivatives readily purified by crystallisation from organic solvents. Excess of alcohol or of chloride used with the lower or higher alcohols respectively are removed by evaporation or by washing the product with dil. sodium hydroxide soln. Heating is for 10 min. at 100–125° C. (primary alcohols) or longer (secondary alcohols). The m.p. and mol. wt. (calc. and found) of 31 *o*-alkyl derivatives are tabulated. The m.p. of typical examples are: *iso*propyl, 136·8° C.; *n*-hexyl, 59·7° C.; *s*-amyl, 38° C.; *n*-heptyl, 55° C.; *n*-octyl, 46° C.; *n*-octadecyl, 74·5° C. Phenol derivatives are formed by heating excess of the phenol with the pseudochloride to 125–140° C. for 15 to 20 min. and washing the product with sodium hydroxide soln.; m.p. are tabulated. The reagent, first prepared by Jerurum (*Ber.*, 1893, **26**, 2287) is made by heating 2 mols. of phosphorus pentachloride with slightly more than 1 mol. of saccharin for 1½ hr. at 175° C. and then

applying suction to remove phosphorus oxychloride. The product (yield *ca.* 80%) is pressed on a porous plate and recrystallised from benzene (m.p. 141°–144° C.). E. B. D.

Isolation of Linolic Acid from Vegetable Oils by Low Temperature Crystallisation. J. S. Frankel, W. Stoneburner and J. B. Brown. (*J. Amer. Chem. Soc.*, 1943, **65**, 259–262.)—The technique (Frankel and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 1483) is as follows. Dissolve the mixed fatty acids of the oil in acetone (75 g per litre) and cool to −20° to −25° C. Remove the crystals by inverted suction filtration. Cool the filtrate to −50° C. with slow stirring and filter as before. Cool this filtrate to −70° C. and again filter off the crystals. Calculated from the iodine number as a binary mixture of oleic and linolic acids, this crystal fraction is *ca.* 90% linolic acid. Dissolve the crystals in 30–60° light petroleum, 65 g per litre, and cool to −48° C. The crystals at this temp. are usually 95% linolic acid. At −48° C. the solubilities of oleic and linolic acids are more nearly equal in light petroleum than in acetone, so that relatively larger amounts of the oleic acid remain in soln. Dissolve the 95% acid in light petroleum, 6·25 g per litre, and cool to −60° to −62° C. This time the crystals are practically pure linolic acid. Use sufficient solvent to keep all the oleic acid in soln.; very low concns. also tend to minimise mixed crystal formation. Results of the application of this process to 5 types of oils are shown in the table.

Analyses of Crystallisation Linolic Acids from Vegetable Oils

Oil	I. val.	Tetrabromide val.	m.p. °C.	n_D^{20}	Purity from I. val.(*a*)	Purity from T. val.(*b*)
Maize	180·6	100·6	−5·4	1·4699	100	98
Sesame	178·4	95·1	−5·8	1·4692	97	92
	178·2	96·0	−5·2	1·4692	97	93
Cottonseed	179·9	99·4	−5·8	1·4697	99	97
Grapeseed	180·0	97·5	−5·8	1·4692	99	95
Poppyseed	179·4	95·2	−5·8	1·4697	98	92
Poppyseed, recrystallised	180·8	97·8	−5·2	1·4697	100	95
Linolic acid by debromination	181·0	102·0	−5·2	1·4699	100	100

(*a*) Calculated from iodine val., therefore total octadecadienoic acid.
(*b*) On the basis of the tetrabromide val., using the factor 102·9.

With olive oil fatty acids there were obtained preparations of somewhat lower purity, max. purity being 95·8%. M.p. were −9·0° to −17·4° C. Tetrabromide vals. were very low, two products being 95·2% and 95·8% pure by the iodine val., but only 76% and 56% pure, respectively, by the tetrabromide val. It is concluded that olive oil linolic acid is a mixture of two or more isomeric octadecadienoic acids, linolic acid itself (*cis*, *cis*-9.12-octadecadienoic acid) being present in somewhat larger amounts than the others. E. M. P.

Amylose and Amylopectin Content of Starches determined by their Iodine Complex Formation. F. L. Bates, D. French and R. E. Rundle. (*J. Amer. Chem. Soc.*, 1943, **65**, 142–148.)—Solns. of amylose and amylopectin were titrated potentiometrically with iodine, and the combined iodine was determined, to investigate differences in the capacity of amylose and amylopectin to bind iodine. Curves illustrating the results show that the activity of iodine in an amylose soln. remains essentially constant upon addition of iodine until complex formation is complete, whilst with an amylopectin soln. there is a continual rise in the iodine activity. Starches containing both components show a break in the curve; thus, plotting potential against iodine added, the point of inflexion might be expected to give a measure of the amylose fraction present in the starch.

Analyses of various whole starches are shown in curves and in the tables below. Preliminary results indicate that the affinity for iodine varies inversely with the degree of branching and directly with the length of the starch chains; the amylose content of any one starch appears fairly homogeneous in chain length. The authors conclude that most starches have 2, and only 2, components differing significantly in the degree of branching. The sharp breaks in the iodine titration curves certainly indicate that the molecular species that may possibly be present in starch have a marked discontinuity in their ability to react with iodine. Components with intermediate degrees of branching would almost certainly have intermediate properties and do not appear to be present in the starches studied.

The analytical procedure recommended is as follows. Disperse 0·01–0·04 g of starch in 10 ml of 0·5 *N* potassium hydroxide; alkali works most effectively on dry material. When dispersal is complete, dilute the mixture with water, neutralise to methyl orange with hydriodic acid, and dilute to 100 ml; this soln. is 0·05 *N* in potassium iodide. The amount of iodine taken up by amylose decreases with increasing iodide concn., so that a standard iodide concn. must be adopted. Titrate the soln., which must be slightly acid, with 0·001 *N* iodine containing potassium iodide of the same normality as that of the soln. being titrated. The exact value of the *p*H is not important, since the potential of the iodine-iodide half cell is nearly independent of

Table I.—Comparison of Methods for the Determination of Amylose in Starch

Starch	Amylose, % Iodine titration	Amylose, % Butanol fractionation by Schoch*	Amylose, % Butanol fractionation by authors
Corn	21	22	—
Potato	22	22	22·5
Lily bulb	34	—	31
Waxy corn	none	none	negligible

* Schoch, *J. Amer. Chem. Soc.*, 1942, **64**, 2957.

Table II.—Amylose Contents of Starches Determined by Iodine Titration

Starch	Amylose,%	Starch	Amylose,%
Waxy rice	0	Corn	21
Waxy sorghum	0	Potato	22
Waxy corn	0	Popcorn	23
Waxy barley	0	Wheat	24
Tapioca	17	Sago	27
Rice	17	Lily bulb	34
Banana	20·5		

*p*H. If the starch is well dispersed, equilibrium is nearly always reached 2–5 min. after addition of 1 ml of 0·001 *N* iodine, the shorter interval being usually sufficient. If the change of potential near the end of the interval is at a rate exceeding a few tenths of a millivolt per min., allow more time between successive additions of titrating soln.
E. M. P.

Determination of Mannan and Starch in Paper. J. W. Dijk. (*Chem. Weekblad*, 1941, **38**, 329; through *Paper Ind.*, 1943, **24**, 1080).—To remove the starch selectively, extract 5 g of the sample with a mixture of 200 ml of water and 5 ml of glacial acetic acid at b.p., filter, and hydrolyse the filtrate by boiling it for 30 min. with 10 ml of conc. hydrochloric acid; determine the glucose so formed in the usual way. After filtration remove the mannan from the residue by means of a hot approx. 40% soln. of chloral hydrate, concentrate the extract so obtained and ppt. the mannan with alcohol. Separate the ppt. by filtration, dry, extract with ether to remove any rosin, and weigh the final residue. J. G.

Scheme for Identification of Common Commercial Plastics. H. Nechamkin. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 40–41.)—Hold the sample (preferably in strip- or rod-form) at one side of a Bunsen flame until it catches fire, but not for more than 10 sec. (I) No flame results, the shape is retained and the odour of formaldehyde is apparent.—(A) No other odour: *urea formaldehyde*; (B) strong fishy odour: *melamine formaldehyde*; (C) phenolic odour: *phenol formaldehyde*. (II) The sample burns but is extinguished on removal from the flame. (A) Green zone on holding the sample at the edge of the flame, with odour of (1) burnt rubber: *pliofilm* (pronounced green area), *neoprene* (small green area, over-shadowed by a yellow area); (2) acrid: *vinyl chloride derivative*; (3) sweet, with heavy black ash: *vinylidene chloride derivative*. (B) Odour of burnt milk protein: *casein plastics*. (C) Sparks from the flame of the burning sample, and acetic odour: *cellulose acetate*. (III) The sample continues to burn after removal from the flame.—(A) Rapid burning, with an intense white flame: *celluloid* (odour of camphor), *cellulose nitrate* (no camphor odour). (B) Predominantly blue flame, possibly with a small white tip and odour—(1) sweet, floral and fruity: *methacrylate*; (2) resembling burning vegetation or celery: *nylon* (this resin is sol. in 60% v/v hydrochloric acid); (3) weak, and slightly sweet: *polyvinyl formal*; (4) like rancid butter or cheese: *cellulose acetobutyrate* (sparks produced), *polyvinyl butyral* (no sparks, burns steadily). (C) Flame surrounded by a bright green mantle; odour of burnt rubber: *pliofilm* (*vide infra*). (D) Flame surrounded by a purple mantle; sparks and an acetic odour: *polyvinyl acetal*. (E) Yellow-white, luminous flame and odour.—Butyric acid: *cellulose acetobutyrate*; burnt milk protein: *casein*; sweet marigold odour and smoky flame: *polystyrene*; weak, slightly sweet: *polyvinyl formal*; burnt paper: *cellulose*; burnt rubber, with a weak flame having a small green mantle overshadowed by yellow, with white flashes: *neoprene*. (F) Flame surrounded by a yellow-green mantle. (1) Burns with difficulty, producing sparks and an acetic odour; heavy, black-brown, foamy granules or flakes are produced on allowing the molten, burning plastic to drip into water: *cellulose acetate*. (2) Once burning has started it continues readily, evolving a slight sweet odour, but on letting it drip into water flat discs result which are light-tan in colour when the plastic is clear, and of the same colour as the original when the plastic is coloured: *ethyl cellulose*. When making the olfactory tests, blow out the flame immediately after removing the sample from the Bunsen flame, and smell the rising vapour very cautiously 2 sec. later. If the sample ignites readily remove it from the flame at once; if it melts and draws away from the flame, move it into the flame again but for not more than 10 sec. The identification is facilitated by making comparison tests against authentic specimens. *Note.*—Pliofilm is a thermoplastic resin produced by addition of hydrogen chloride to the sat. linkage present in rubber; it is used as a protective covering (*cf.* also Powers, *Ind. Eng. Chem., News Ed.*, 1942, **20**, 536).
J. G.

Inorganic

Semi-micro Determination of Silver. S. Reznek. (*J. Assoc. Off. Agr. Chem.*, 1943, **26**, 155–157.)—Digest the sample (≡ 1–5 mg of silver) in a 100-ml Kjeldahl flask with 2 ml of conc. sulphuric acid, 5 ml of conc. nitric acid and a few glass beads until oxidation is complete, adding more nitric acid if necessary. Heat until most of the nitric acid has been driven off and transfer the cooled, slightly diluted soln. with water into a beaker to a vol. of 40–50 ml. (Alternatively, if the type of sample allows, dissolve the ashed sample in dil. sulphuric acid.) Neutralise the soln. to methyl red with ammonia, add 2–3 drops in excess, heat nearly to b.p. and add *ca.* twice the amount of 0·1% potassium iodide soln. equivalent to the silver present. Neutralise the cooled liquid with 10% sulphuric acid, add 5 ml in excess and leave the soln. in the dark for 2–3 hr. with occasional stirring. Filter through an asbestos pad in a crucible with a removable bottom (Caldwell crucible), transferring and washing the ppt. with dil. nitric acid (1+100). Transfer the bottom of the crucible and the pad to a flask, rinse out any remaining ppt. from the crucible with water, add 40–50 ml of sat. bromine water and a few drops of bromine and swirl the flask until the pad has dispersed. Boil gently until the bromine has been removed, add 1 ml of 5% phenol to the hot liquid to remove the last traces, cool, add 10 ml of 10% sulphuric acid and *ca.* 0·1 g of potassium iodide and titrate the liberated iodine with 0·01 *N* sodium thiosulphate soln. using starch indicator. Each ml ≡ 0·00018 g of silver. This procedure involving the conversion of silver iodide to silver bromide and iodic acid by action of bromine has the advantages of an iodate method, *viz.*, the 6-fold liberation of iodine and the sharp starch iodide end-point. With amounts of silver of the order of 1 mg the error is about 2%. A. O. J.

Polarographic Determination of Lead in Lead-bearing Steels. G. Haim and W. C. E. Barnes. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 867–).—Lead may be determined in 25 min. or less by polarographic comparison of a hydrochloric acid soln. of the sample with standards prepared either from steels of known lead content, or by adding lead acetate soln. (1 ml ≡ 0·001 g of Pb) to solns. of lead-free mild steel. The method is not successful with 18–8 stainless steel. *Procedure*—Dissolve 1 g of millings in 10 ml of warm conc. hydrochloric acid in a 50-ml graduated flask passing nitrogen through the soln. Add 2 ml of 2% gelatin soln., cool to room temp., dilute to the mark with boiled water and polarograph from 0·1

to 0·7 volt. The ferrous chloride in the soln. acts as supporting electrolyte; the lead step occurs at about 0·45 volt. Precision ("tolerance") to 0·01% for lead contents from 0·1 to 0·4% is claimed.
L. A. D.

Qualitative Thallium Reactions. P. Wenger and R. Duckert. (*Helv. Chim. Acta*, 1943, **26**, 338–345.)—The more familiar of the 26 reagents not recommended include: hydrochloric acid, ammonium thiocyanate, ammonium molybdate, mercuric thiocyanate, calcium ferrocyanide, bromine and potassium hydroxide, tartaric acid, sodium cobaltinitrite, picric acid, quinalizarine, rhodamine B, sodium sulphide, thiourea, dithizone, sodium azide. Recommended reactions. *For thallous salts.*—(*A*) With the microscope: (i) potassium iodide. Yellow ppt. at $1 : 3{\cdot}33 \times 10^5$. Elements of the first qualitative group interfere. (ii) Chloroplatinic acid. Yellow ppt. at $1 : 1{\cdot}25 \times 10^6$. Beryllium and alkali metals interfere. (iii) Ammonium dichromate: yellow ppt. at $1 : 1{\cdot}67 \times 10^4$. Silver, mercurous, lead, barium, and strontium salts interfere. (*B*) Spot plate tests: (i) Potassium iodide, as (*A*, i), at $1 : 5 \times 10^4$. (ii) Phosphomolybdic with hydrobromic acid: blue ppt. at $1 : 5 \times 10^4$. Reducing substances interfere. (*C*) Spot test on filter-paper: as (*B*, ii), at $1 : 5 \times 10^5$. (*D*) Test-tube reactions (micro and macro): (i) As (*A*), i; (ii), As (*B*, ii). *For thallic salts.*—(*A*) With the microscope: Martius yellow (5% soln. of the dye in pyridine + water (1 : 3). Golden-yellow ppt. in neutral soln. at 20° C. at $1 : 1{\cdot}5 \times 10^5$; distinction from thallous salt. Cobalt reacts similarly. (*B*) Spot plate test: Benzidine or *o*-tolidine in acid acetate soln. gives blue ppt. at $1 : 3{\cdot}33 \times 10^5$. Silver, ceric, manganous and cobaltous salts and oxidising agents interfere. (*C*) Spot test on filter-paper. As (*B*, i). (*D*) Test-tube reaction. As (*B*, i), at $1 : 5 \times 10^6$.
W. R. S.

Polarographic Determination of Manganese as Tri-dihydrogen Pyrophosphatomanganate. I. M. Kolthoff and J. M. Watters. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 8–13.)—A number of possible polarographic methods for the determination of manganese possess marked disadvantages. For example, the presence of an excess of ferric, ferrous, cobaltous, nickel, zinc, or copper ions interferes with the polarographic determination of bivalent manganese, whilst the permanganate ion produces a poorly defined wave not suitable for analytical purposes. The use of the tri-dihydrogen pyrophosphatomanganate has the advantage that the only interfering substances are chromium, vanadium and cerium. The procedure involves the quantitative oxidation of the manganese, with lead dioxide, to the tervalent state in a medium which contains a large excess of pyrophosphate at a *p*H less than 4. Over the range 1 to 100 mg of manganese in approx. 50 ml of aqueous soln. it is shown that proportionality exists between the diffusion current and the concn.
B. S. C.

Colorimetric Determination of Cobalt with Terpyridyl. W. L. Moss with M. G. Mellon. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 74–75.)—The test soln. must be freed from copper, nickel, iron, cyanide, and dichromate. Adjust the *p*H to 2 to 10 with 20% ammonium acetate soln., 6 *N* ammonia and 6 *N* hydrochloric acid. Adjust concentration to 2 to 5 mg of Co per 100 ml. To 25 ml of the soln. add 5 ml of reagent, dilute to 50 ml, and mix. Match the orange colour against that of a standard cobalt soln. treated in the same manner. The reagent is 2,6-di-2′-pyridylpyridine dissolved in a minimum of 6 *N* hydrochloric acid and diluted to 0·1% with iron-free water. For visual comparisons fresh standards should be prepared daily. The colour may be determined photometrically with a recording spectrophotometer using a blue-green filter (Corning No. 428) and a 2-cm. transmission cell. Terpyridyl is not available commercially (*cf.* Morgan and Burstall, *J. Chem. Soc.*, 1937, 1649).
W. R. S.

Separation of Iron from Cobalt and Nickel. R. J. De Gray and E. P. Rittershausen. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 26–27.)—Treat the soln. (200 ml) containing 0·0005–0·0040 g of cobalt and not more than 10 times that amount of ferric iron, with 10 ml of 10% oxalic acid soln. Neutralise with, and add 5 ml excess of strong ammonia, boil, filter and wash. The ppt. is free from cobalt. If the Fe : Co ratio is greater than 10, extract excess of iron with ether from the acid chloride soln. Nickel may be separated from iron by the same process. The oxalic acid does not interfere with the colorimetric ferricyanide method for cobalt. (*Id.*, 1942, **14**, 858.)
W. R. S.

Electrographic Detection of Molybdenum in Steel Alloys. J. A. Calamari, R. Hubata and P. B. Roth. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 71.)—Fold an ashless filter into a wad (3–4 layers) and dip it into a filtered soln. of sodium nitrate (30 g per 100 ml). Make the sample the anode in the authors' electrographic apparatus (ANALYST, 1942, **67**, 373), place the moist wad on its surface, and press a graphite cathode (length, 7·5 cm; diam. 0·6 cm) firmly against the free side of the wad for *ca.* 1 sec. (3 sec. for alloys of molybdenum steel). Use an E.M.F. of 6–9 volts (produced by dry cells), and a current of 0·5–1·0 amp. Wash the end of the wad with a 1% aqueous soln. of lead acetate to remove some of the heavy metal ions and to ppt. the molybdate and fix it on the paper as the lead salt, and add to the face of the wad that was in contact with the sample *ca.* 3 drops of a fresh mixture of equal vols. of 1·0 *M* potassium thiocyanate and of a soln. of 30 g of stannous chloride in sufficient hydrochloric acid to make 100 ml. In presence of molybdenum a carmine red stain will be produced by the tervalent molybdenum thiocyanate complex formed. The colour intensity increases with the molybdenum content for amounts up to 0·2% alloyed with steel, if the current-density and electrolysis time are constant. Ferric ions form ferric thiocyanate, but are rapidly reduced, forming a pale green stain which does not interfere. The test takes only a few seconds.
J. G.

Spot Test for Zirconium. J. H. Yoe and L. G. Overholzer. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 73.)—The reagent is a soln. of sodium 1-amino-4-bromo-2-anthraquinone sulphonate in 1 : 1 acetone-water (2 mg per ml). The nitrate soln. to be tested must be free from phosphate, sulphate and fluoride. Transfer 0·05 ml to a depression in the spot plate, add 0·05 ml of 2 *M* nitric acid and 0·03 ml of reagent alongside a blank in distilled water. Shake the plate continuously for several min. The blank sometimes gives a slight, pale red scum; zirconium gives a granular darker ppt.

which settles to the bottom. A zirconium concn. of 10 p.p.m. is suitable. Hydroxide ppts. are dissolved in 2 *M* nitric acid. The limiting concn. for ions likely to interfere is: ceric 0·03, beryllium 0·25, aluminium, chromium, thorium, and titanium 0·1 mg per ml. W. R. S.

Use of Denatured Alcohol in Alkali Determinations. P. A. Webster and R. M. Crane. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 36.)—In the determination of alkalis in glass, the ppt. of sodium zinc uranyl acetate is washed with 95% ethyl alcohol, and that of potassium chloroplatinate with 80% alcohol. Check analyses proved that denatured spirits may be substituted for pure ethyl alcohol. One of the commercial spirits contained about 10% of ethyl ester, the other about 10% of acetone. W. R. S.

Colorimetric Determination of Carbonate in Presence of Bicarbonate. W. T. Sumerford with D. Dalton and R. Johnson. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 38–39.)—Neutral alkali carbonates tautomerise colourless *p*-nitrosothymol to the red alkali salt of thymoquinone monoxime; pure bicarbonates do not react. Prepare a series of standards from equal vols. of sodium carbonate solns. of increasing molarity and twice the calculated quantity of 0·35 *M* soln. of *p*-nitrosothymol in neutral acetone or dioxane. Shake the solns. for 10 to 15 min., and filter from excess reagent into Nessler tubes. Treat the test soln. in the same manner and match against the scale. The colour of a 0·0001 *M* carbonate soln. can be detected by this procedure; above 0·1 *M* strength the colour is too intense. Bicarbonate preparations usually give a slight yellow colour depending on the amount of carbonate present; this is discharged by treatment with carbon dioxide. The method can be applied to carbonates of potassium and lithium. The standard scale should be freshly prepared; if kept for a day or two, it should be stored in the dark. The method works best where the volumetric brocess is least exact, *i.e.*, with low carbonate contents. W. R. S.

Determination of Pyrophosphate by Precipitation with Cadmium and Polarographic Measurement of Cadmium in the Precipitate. G. Cohn and I. M. Kolthoff. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 886–890).—A method is described for the determination of pyrophosphate in presence of 4 to 16 times the molar concn. of orthophosphate and 8 to 32 times the molar concn. of calcium. Cadmium pyrophosphate is pptd. from a buffered soln. and the determination completed either by weighing the ppt. after dehydration at 250° C. or dissolving in hydrochloric acid and determining the cadmium polarographically; the second procedure is recommended. The method is claimed to be particularly useful for dealing with small samples and may be applicable to biological materials. If large samples are available, the method does not appear to be superior to existing methods. The effect of meta- and/or polyphosphate (often present in commercial phosphate) has not been investigated. *Procedure.*—To 25 ml of the neutral or slightly alkaline soln., which must be 0·002 to 0·01 *M* in pyrophosphate (≡ 7 to 35 mg of P_2O_5), add sufficient 0·2 *N* orthophosphate, if necessary, to make the final orthophosphate concn. approx. 0·03 *M*. Add 5 ml of buffer soln. (8 *M* acetic acid, 1 *M* ammonium acetate, *p*H 3·6) and 2 ml of 1 *M* calcium chloride soln. (less if calcium is present). Then add 15 to 20 ml of 0·4 *M* cadmium acetate soln. and shake gently for 5 to 6 hrs. When the gelatinous ppt. has become granular, filter or centrifuge it and wash with water (both orthophosphate and calcium facilitate the development of a well-crystallised ppt. of cadmium pyrophosphate). Dissolve the ppt. of cadmium pyrophosphate in a little hydrochloric acid (1 : 4), add 25 ml of 2 *M* potassium chloride soln., make up to 100 ml, and determine the cadmium polarographically. If the orthophosphate content is larger than stated above, dissolve the ppt. in a few ml. of hydrochloric acid (1 : 4) at room temp. Neutralise immediately with 6 *M* sodium hydroxide soln. (Tropeolin 00 is recommended as indicator) and dilute to about 25 ml. Re-ppt., adding the same amounts of buffer and cadmium acetate solns. as before. [No explicit indication that calcium chloride or orthophosphate should be added before re-precipitation is given.—Abstractor.] The authors measured the diffusion current at 25° C., applying 0·8, 0·9, 1·0 volts and obtained identical current readings at these potentials. The cadmium concn. of the soln. was determined by linear extrapolation after adding successively 3 known amounts of 0·1 *M* cadmium chloride soln. and measuring the increase of diffusion current. A correction was applied for the residual current. The results of expts. are discussed and several tables are given showing the effect of variations in the composition of the pyrophosphate soln. L. A. D.

Physical Methods, Apparatus, etc.

Spectrophotometric Determination of Lovibond Number in Brown Lovibond Glasses, Series No. 52, Brewers' Scale. G. F. Beyer. (*J. Assoc. Off. Agr. Chem.*, 1943, **26**, 164–171.)—Some of the brown standard glasses, No. 52 of the Lovibond series, used in the brewing and distilled spirits industries and recommended by the Amer. Soc. Brewing Chemists, vary appreciably in depth of colour, although they may have the same number. An attempt was made to correlate spectrophotometric transmission with the Lovibond number by means of a Coleman D.M. Model 10-S photoelectric spectrophotometer having a 30mμ exit slit. Preliminary expts. showed that the optimum wavelength for the recording of readings of the colour of beer, whisky, etc., is in the region 400–460mμ. A large number of values for T (transmission) were obtained at 430, 440, 450, 460 and 500mμ by using a 5mμ and a 30mμ slit, with water, air, 50% alcohol, a plain glass slide and the No. 1 Lovibond glass as references. Concentration-transmission (C–T) curves were constructed with T as logarithmic ordinate and C, the number on the Lovibond glasses, as abscissa on the uniform scale, to determine the degree of conformity with Beer's law. The neg. log. of these measurements was also plotted against the Lovibond number to show the scattering of the points, especially with the higher numbered glasses. The highest conformity with Beer's law was found at 430mμ. To test the suitability of the C–T curves as calibration curves, the transmission of different concns. of whisky, caramel solns., beer and wort was measured at the wavelengths previously mentioned. Absorption % was then read in a neutral wedge photometer by using a 1/2 in. cell and a blue

filter transmitting at 460$m\mu$, and, finally, visual readings were made in the Lovibond tintometer with the same cell. The only curve giving the required linear relationship between the optical density (*i.e.*, the negative log of the transmission) and the Lovibond number was the one referring to wavelength 430$m\mu$. This is therefore the wavelength at which coloured solns. and coloured glasses of this kind should be read when a 30$m\mu$ slit is used, and the negative log. of the transmission, multiplied by 10, is equal, within a small limit of error, to the Lovibond number. This linear relationship holds for the No. 52 series of Lovibond glasses up to glass No. 12. Above this number the relationship appears to fail, either owing to instrument errors at this low transmission or to difficulty of matching such glasses during their manufacture. The same is true of glasses having a very high transmission, *e.g.*, those with a Lovibond number less than 0·5.

A. O. J.

Spectrochemical Assay for Traces of Tungsten. A. G. Scobie. (*Ind. Eng. Chem., Anal. Ed.*, **1943, 15**, 79–80).—This method was developed to determine traces of tungsten in mineral ores. A check of the common methods in use for the isolation of tungsten showed these methods to give incomplete separation for trace amounts. The method finally adopted involves the chemical treatment of the ore to obtain the whole of the tungsten present as sodium tungstate soln. To this soln. is added a standard soln. of potassium aluminium sulphate and then satd. sodium bicarbonate soln. The hydrated alumina thus pptd. is found to collect the tungsten quantitatively. A 30-mg portion of the crushed dried alumina containing the tungsten is placed in a suitable crater in an 8-mm diam. pure graphite electrode and arced at 15 amps. The spectrum is photographed on a large quartz spectrograph and the density of the tungsten line 2896.45A measured. Calibration is effected by means of standard tungsten solns. given the same treatment. It is claimed that the lower limit of detection corresponds to 0·00002% of tungsten in an ore or concentrate.

B. S. C.

Measurement of Fibre Length. J. d'A. Clark. (*Paper Trade J.*, 1942, **115**, *T.A.P.P.I. Sect.*, 328–334.)—Disintegrate the sample in the usual way and prepare a dil. suspension of the resulting separated fibres (*e.g.*, *ca.* 0·1 g per litre for paper fibres). Transfer about 4 ml in a 6-mm diam. pipette fitted with a rubber bulb, to a cell made from a flat, flawless, glass plate on to which is cemented an annular ring of metal or glass (diam., 6–8 cm; depth *ca.* 1 cm). If the inner sides of the ring are painted with a water-repellant material (*e.g.*, aluminium stearate) the surface of the suspension remains fairly flat. Add to the cell 2–3 ml of a soln. prepared by heating 1 g of locust bean gum in 200 ml of water to 80° C., with stirring, and, after cooling, adding 3 drops of formalin as preservative; this both disperses and immobilises the suspended fibres. Then place the cell and its contents in a vertical projection apparatus, the magnification of which has previously been accurately adjusted so that a pair of parallel lines 5·0 ± 0·01 mm apart on a microscope slide in the projector, exactly coincide with 2 opposite sides of a 4-in. square (sub-divided into 1-in. squares) drawn on the screen which lies horizontally on the bench. Place on the screen a piece of thin translucent paper (*ca.* 8 × 10 in.) on which are lightly ruled in pencil a series of vertical lines, *ca.* 0·25 in. apart, and also, at the top and bottom, with 2 parallel horizontal lines, exactly 10 in. apart. Focus to obtain sharp images of the fibres, and, beginning at the top right hand 1-in. square on the screen, move the thin paper so that the tip of a fibre coincides with the point of intersection of the horizontal line and a vertical line; move the thin paper so that the latter line coincides as closely as possible with the fibre, and, if the fibre curves away from the line, place the fine point of a hard pencil on the spot at which the departure starts and, using it as a pivot, push or pull the paper until coincidence with the line is established. If this process is continued the image of any fibre, no matter how curved, may be "straightened out" accurately and measured along the fine line on the paper. Repeat the procedure for every fibre which has one end in the top right-hand small square and has more than 50% of its length inside the 4-in. square; use the point marking the end of one fibre on the straight line as the starting-point for the next measurement, so that there are no gaps between the lengths of the straightened fibres. Then proceed to the second top right-hand square, and measure the lengths of all fibres having ends in it and not already dealt with; similarly with the remainder of the 16 squares. Fibres which have an image 2 mm or less in length (equiv. to a fibre length of 0·1 mm or less) and fibre particles having an image area of less than 0·001 sq. mm., are regarded as "fibre debris," and are ignored. When the end of one of the fine pencilled lines is reached, continue at the top of the next such line. Move the cell to a new position (without looking at the screen), and in this way record the lengths of *ca.* 200 fibres which, if they are of average length, will be found in *ca.* 10 fields (for paper fibres). Measure the total length (in in.) of the fibres recorded (L) by counting the no. of 10-in. lines completely filled plus the partly-filled length of the last line, and divide it by the magnification-factor (0·8 under the conditions specified above, and by the no. of fibres examined, and so calculate the average fibre length in mm. The length of fibre per g of original sample (called the "titer") may also be calculated from L, the no. of fields used, and the area of the cell; it is of greater value as a measure of the "fineness" of a fibrous sample than are measurements of the average fibre width, and it is more easily obtainable. The method described is more accurate than ordinary microscopical mensuration, and requires only about 50% of the working time. Applications are described. Anomalies in reported "average" fibre-lengths (especially of paper pulps) are discussed, and are shown to be due to the inclusion of varying amounts of fibre debris, and to different interpretations of the term "average." The determination of the average fibre-length of fractions obtained by classification on standard screens is discussed mathematically.

J. G.

Reviews

THE EXAMINATION OF WATERS AND WATER SUPPLIES. By E. V. SUCKLING, M.B., B.S. (Lond.), M.R.C.S., L.R.C.P., D.P.H. Pp. x + 849. London: J. & A. Churchill, Ltd. 1943. Price £3.

Some books are one of a bunch, maybe the best of the bunch, maybe not: others are in honourable isolation, there being none other, dealing with the same matter in at all a similar way, with which to compare them: "Thresh," which it will now be a pleasure to call "Suckling," belongs to the latter class.

As is known to those who are familiar with previous editions, this book is far more than an analytical treatise on the chemical and bacteriological examination of water; it is a treatise on all aspects of water for domestic and industrial use. Without detracting in the least from its merits as an analytical text book, it may be said that the laboratory practice side is almost subsidiary to the consideration of the water itself—where it comes from, what to expect of it and to suspect in it, how to use it and to treat it in order to make it fit and safe for use, and finally, to complete the circle, how after use it affects, as sewage, fresh supplies. Analysis comes in, surely correctly, as one of the factors to be used in the provision of a water suitable for the purpose for which it is required. And the habits of water are exposed and judged as the outcome of an experience which, in this country at any rate, is unrivalled. In this way "Suckling" is a contrast to books on methods only, in which one can read directions as to processes but finds nothing as to why these should be performed or as to what the results mean.

This, the fifth edition, follows very closely the fourth in scope and plan: chapters are the same in number and deal with the same matters: the plates of the larger water organisms are the same; tabulated analyses of waters from various strata have increased from 727 to 790; format is the same and pages have increased only by 3 per cent.; it is a convenience to a user of the previous edition that there is so little re-arrangement.

From this it should not be thought that there is little new; quite the reverse. Naturally, in the main, established analytical processes stand as before, but improved methods and reagents have found a place; the reviewer suggests that a dithizone method for the detection and determination of lead might well be added in place of reliance solely upon the sulphide and chromate reactions; an acid-alkali titration method for determining total hardness is inserted, as an alternative to the soap titration method for determining total hardness, on p. 784 in the Appendix, and is indexed. There has existed some confusion as to the terms of McGowan's formula for calculating the strength of sewage liquors (not long aeration process) and it is suggested that McGowan's organic nitrogen should be taken as twice the albuminoid, not as numerically equal to it.

Fluorine, which in 1933 could only be mentioned as having some possible but doubtful significance, now has many pages devoted to it in several relevant sections. The chapters on chlorination and other water treatments have been completely re-written; they record and explain current practice; much attention is given to the exchange treatments. The preparation of feed water for high pressure boilers, which had a note in the last edition, is not pursued.

Corrosion by waters is more fully dealt with than before and changes of view as to the effect of chlorination upon corrosion and the effectiveness of silicate as a remedy for plumbo-solvency are to be noted; also a recommendation for higher dosages of chlorine for swimming bath waters in certain circumstances.

On the bacteriological side some fifteen or sixteen chapters, though bearing practically their old titles, have been almost entirely re-written. The relations between water and disease are fully treated and here, as elsewhere, instances abound of the author's experience both in the laboratory and in the field. Recent public happenings in the water world are recorded; amongst these are typhoid at Bournemouth, Croydon and Epping. A full history is given of the Croydon occurrence with quotations from the enquiry report; the author adds his own comments and does not fail to draw the moral.

In these pages will be found a most interesting consideration of the Ministry of Health Memorandum scheme for the presumptive coliform count and differential coliform identification. A record is given of the working out of 10,000 presumptive positives with the proportions of presumptives, shown to be false by differential tests, occurring in the various coliform groups. The author has a tilt at reporting as the probable number of coli a

number which is really only "the probable number of probable coliforms"; this appears to him to be a stretching of the theory of probability and a likely cause of unnecessary alarm.

Dr. Suckling says in his preface "It is hoped that the book will prove of increasing use to Waterworks Authorities, Civil Engineers, Medical Officers of Health, Bacteriologists, Analysts and all others interested in water supplies." Speaking for the analysts the reviewer says it surely will, and ventures to suggest that "Planners" should not find it beneath their notice.

In giving a cordial welcome to this edition, analysts will not be unmindful of the debt they owe Dr. Suckling for the labours which make its production possible and for the thought that inspires his labours, particularly in the difficult circumstances discreetly alluded to in the Preface. E. HINKS

CANNED FOODS: AN INTRODUCTION TO THEIR MICROBIOLOGY. By J. G. BAUMGARTNER. Pp. viii + 157. London: J. & A. Churchill. 1943. Price 10s. 6d.

In the canning of food the raw material is carefully sorted and prepared so that when the canned product is opened the contents are ready for consumption with little waste. The same careful sorting and selection of the material available has been carried out in the writing of this excellent book, with the result that, in conformity with existing economy regulations, no paper has been wasted. Yet little of importance has been omitted and, for those requiring fuller information, a useful list of references is given at the end of each chapter.

The book is principally intended for chemists and technologists engaged in the canning industry, and it is assumed that such persons will already be familiar with elementary bacteriological technique. Thus, apart from a good general account of bacteria, yeasts and moulds, very little space is taken up in dealing with those aspects of bacteriology commonly found in text books. Instead the author gives us the benefit of his wide and practical knowledge gained in the bacteriological laboratory of a modern canning factory, supplemented by a careful study of the research work which has been conducted over a number of years in this country and the United States of America.

The scientific principles underlying the preservation of food by means of heat are described in a clear and concise manner, and the public health aspects of canned foods are adequately dealt with. It is now generally recognised that owing to the application of scientific methods of sterilisation such as are outlined in this book there has, during the past decade, been a great improvement in the types and quality of canned foods packed in this country, and spoilage to-day is far more often due to infection of the canned product, subsequent to sterilisation, than to faulty processing. It is important, therefore, that the technologist should not only be able to ascertain the cause of spoilage by a bacteriological examination of the product, but he should—when the container is suspected—be able to make a detailed examination of the can seams to find how the spoilage bacteria gained entry. This is often the more difficult of the two examinations, and the last chapter gives a full account of the examination of can seams and summarises seam defects.

This is undoubtedly the best book on the subject which has been published in this country, and it will be specially welcomed by technologists engaged in the industry. It will also be of value to public health officers, food officials and others interested in canned foods. F. HIRST

Special Notice

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

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

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