THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

THE Eleventh Annual General Meeting of the Section was held in Manchester on February 1st, 1936. The attendance was forty-four; the Chairman (Prof. W. H. Roberts) presided.

On the suggestion of the Chairman the members stood in silence as a mark of respect to the memory of the late King George V.

The Secretary read the report and financial statement for 1935, which were adopted.

The following appointments for the coming year were made:—*Chairman*, A. R. Tankard; *Vice-Chairman*, Professor T. P. Hilditch; *Committee*, J. Evans, A. O. Jones, C. H. Manley, S. E. Melling, Miss M. Roberts, C. A. Scarlett, R. W. Sutton, J. R. Walmsley; *Honorary Secretary and Treasurer*, J. R. Stubbs.

The following papers were read and discussed:—"The Gravimetric Determination of Sulphur in some Pharmaceutical Preparations," by A. N. Leather, B.Sc., F.I.C.; "The New Poisons List and Rules," by H. Humphreys Jones, F.I.C.; and "Note on the Chlorine-Content of Feathers," by F. Robertson Dodd, F.I.C.

SCOTTISH SECTION

A JOINT Meeting of the Section with the Food Group of the Society of Chemical Industry was held in Glasgow on January 22nd, 1936.

The following papers were read and discussed:—"A System of Judging Flavour in Bread," by A. M. Maiden, B.Sc., Ph.D., A.I.C.; "The Determination of the Gel Strength of Weak Gels," by L. H. Lampitt, D.Sc., F.I.C., and R. W. Money, M.Sc., A.I.C.; "Some Observations on the Appreciation of Flavour in Food Stuffs," by H. C. Moir, B.Sc., A.I.C.; and "Milk in Adult Nutrition," by Miss Mary Andross, B.Sc.

Death

THOMAS HENRY POPE, Assistant Editor of THE ANALYST, on January 12th, 1936.

The Publication Committee wish to place on record their sorrow at the loss of a greatly valued colleague.

An obituary notice will be published later.

Testing for the Presence of Formaldehyde in Salt-cured Ling

By GEORGE A. REAY, M.A., B.Sc., Ph.D.

The object of this investigation has been to ascertain if tests usually recommended and employed for detecting the presence of formaldehyde in a foodstuff are, in the particular case of dry salt ling, suitable for determining whether formaldehyde has been applied as a preservative. If no formaldehyde is applied as a preservative of the fish at any stage of the curing process, and yet the ordinary tests on the same fish show a positive reaction, it would appear either that the tests are directly responsive to some substance present other than formaldehyde, or that, the test being specific for formaldehyde, formaldehyde is naturally present in the fish, or is formed from naturally occurring substances by the chemical process involved in applying the test.

Survey of the Literature.—The tests for formaldehyde used in the work now reported were Schryver's test[1]; the phenylhydrazine hydrochloride test; the phenylhydrazine hydrochloride and ferric chloride test; the phenylhydrazine hydrochloride and nitroprusside test; Hehner's test; and the phloroglucinol test[2] Schryver's test is usually applied to a warm phenylhydrazine hydrochloride extract of the flesh; the others to distillates of the flesh with phosphoric acid.

Schryver claimed that all the formaldehyde present in meat—free, bound, and polymerised—is quantitatively determined by his extraction method. He pointed out that steam-distillation of formaldehyde leads to the formation of non-volatile polymers (see Auerbach and Barschall[9]). That the distillation method for this reason affords, at best, only a qualitative test is made clear by the work of Dill and Clark[4] and of Rossmann.[10]

The specificity of some of these tests is discussed in the literature. While there is no record of salt-cured fish having been examined, it has been found that fresh cod, haddock, mackerel and herring give a colour equivalent to a few parts of formaldehyde per million parts of flesh when Schryver's method is employed.[3] The distillate from certain fresh and canned crustaceans acidified with phosphoric acid has been found to give positive reactions in the Schryver's, Hehner's, phloroglucinol, and nitroprusside tests, the intensity of the reaction being increased after canning.[4] Tankard and Bagnall[3] suggest that the substance responsible for these positive reactions is trimethylamine. They found that a weak solution of trimethylamine gave a positive Schryver's test, which was intensified eight times by oxidation of the original solution by hydrogen peroxide. They suggest that, in carrying out Schryver's test, trimethylamine is oxidised to formaldehyde and dimethylamine, which latter substance is in turn further oxidised to formaldehyde and methylamine. More recently, Hattori and Hasebe[5] have shown that the "lysine" fraction of the extractives of squid muscle contains trimethylamine oxide which, on distilling with water or on heating with water in a sealed tube, is converted into formaldehyde and dimethylamine. Suwa,[6] earlier, had isolated trimethylamine

oxide (0·06 per cent.) from the fresh muscle of *Acanthias vulgaris*. Komarov,[7] who examined extractives of haddock flesh, comparing them with those of mammalian flesh, found that the "lysine" fraction is much greater in amount in fish than in mammals. It is significant that in the literature there is no evidence of mammalian muscle giving a positive Schryver's test. Schryver[1] dealt exclusively with formalinised carcases of meat, and in the deepest portion of these he records that negative reactions to his test were obtained. It appears probable, therefore, that fish flesh contains a relatively large amount of trimethylamine oxide, as compared with mammalian flesh, and that this substance, as well as volatile amines, gives rise to formaldehyde as a result of oxidation of amine. Tankard and Bagnall[3] found, also, that a dilute solution of trimethylamine gave a negative reaction in Hehner's test, but on oxidation with hydrogen peroxide a positive one. Lunde and Mathiesen[8] consider that, whilst trimethylamine gives a positive reaction with Schryver's test, formaldehyde as such is present in aqueous extracts of canned fish, yielding a positive reaction with Hehner's test, which they found to be unaffected by trimethylamine. From the results of Hattori and Hasebe it seems likely that trimethylamine oxide would give rise to formaldehyde during the process of canning. Lunde and Mathiesen state that positive reactions obtained with any of the formaldehyde tests—Schryver's included—applied to the distillate obtained from flesh acidified with phosphoric acid are to be interpreted as due to the presence, in the distillate, of formaldehyde as such, and, since they do not believe that this is formed during distillation, the positive reactions which they obtained for the distillate from fresh herring are, presumably, interpreted by them as due to formaldehyde naturally occurring in the fish.

Experimental

1. The Application of Tests to Amines and Formaldehyde.—Interference with the tests for formaldehyde in fish may arise to some extent from the presence of trimethylamine oxide and volatile amines, and, during the application of the tests, formaldehyde, trimethylamine, dimethylamine and methylamine are probably all present. Stale fish contain more volatile amines than fresh fish, and methylamine, dimethylamine and trimethylamine have all been detected in decomposing fish. It is not known whether small amounts of formaldehyde also are produced during post-mortem decomposition. The reaction to formaldehyde tests of formaldehyde and the amines mentioned was therefore studied. From 33 per cent. solutions of the pure amines (Hopkin & Williams, Ltd.) solutions of molarity 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4} were prepared with dilute sulphuric acid, so that all had a final pH of approximately 5·4. The reactions of these solutions in six formaldehyde tests are given in Table I.

The results show that, for all three amines, Schryver's test is the most sensitive. The three phenylhydrazine tests and Hehner's test have much the same smaller sensitivity, whilst the phloroglucinol test does not react with amines. On comparing the three amines one with another, it will be seen that dimethylamine reacts most strongly, whilst methylamine reacts somewhat more strongly than trimethylamine. Schryver's test, two phenylhydrazine tests (C and D), the phloroglucinol test, and (possibly) Hehner's test, were found to detect one part of

formaldehyde per million. The phenylhydrazine hydrochloride test (B) gave negative reactions to one part in a million. Solutions of methylamine, dimethylamine, and trimethylamine of $10^{-1}M$ contain, respectively, 3106, 4508, and 5910 parts of amine per million. From the two tables it will be seen that amines are many times less sensitive to the tests than formaldehyde. For example, $10^{-3}M$

TABLE I

METHYLAMINE, DIMETHYLAMINE, AND TRIMETHYLAMINE IN FORMALDEHYDE TESTS

Molarity of amine solution	Methylamine	Dimethylamine	Trimethylamine
	A. Schryver's Test		
10^{-1}	+ Somewhat <10F.	+ Equal to 10F.*	+ Equal approx. to 5F
10^{-2}	+ ,, <1F.	+ Somewhat >5F.	+ Much <1F.
10^{-3}	—	+ Much <1F.	—
10^{-4}	—	—	—
	B. Phenylhydrazine Hydrochloride Test		
10^{-1}	+	+ >methylamine	+
10^{-2}	+ Very faint	+	—
10^{-3}	—	—	—
	C. Phenylhydrazine Hydrochloride + Ferric Chloride Test		
10^{-1}	+	+ Somewhat <methylamine	+ <Dimethylamine
10^{-2}	+ Very faint	+	+ Very faint
10^{-3}	—	—	—
	D. Phenylhydrazine Hydrochloride + Nitroprusside Test		
10^{-1}	+	+ >Methylamine	+ <Dimethylamine
10^{-2}	+ Very faint	+	+ Very faint
10^{-3}	—	—	—
	E. Hehner's Test		
10^{-1}	+	+	+
10^{-2}	∓ Doubtful	+	∓ Doubtful
10^{-3}	—	—	—
	F. Phloroglucinol Test		
10^{-1}	—	—	—
10^{-2}	—	—	—
10^{-3}	—	—	—

* Under Schryver's test, the most suitable test for quantitative work, "<10F" means "less intense colour than is produced by 10 parts of formaldehyde per million." The sensitivity of the same tests to formaldehyde, itself, is given in Table II.

TABLE II

SENSITIVITY OF FORMALDEHYDE TO FORMALDEHYDE TESTS

Parts per million	Test A	Test B	Test C	Test D	Test E	Test F
10	+	+	+	+	+	+
5	+	+	+	+	+	+
1	+	—	+	+	±	+

dimethylamine, containing 45 parts of amine per million, produced with Schryver's reagent a colour much less intense than that produced by one part of formaldehyde per million. From these results, and from the evidence in the literature, it is probable that in the process of carrying out the five tests that are sensitive to amines, a small amount of formaldehyde is formed, giving rise to a positive reaction, the tests being really specific for formaldehyde as such. Since the phloroglucinol test does not react with the amines used, it would appear that the chemical process involved in this test does not give rise to formaldehyde. It is clear that Schryver's test may not be used in the presence of unknown amounts of volatile amines to prove qualitatively the presence of formaldehyde.

Lunde and Mathiesen[7] appear, in their examination of distillates, to interpret a positive reaction to any of the formaldehyde tests as proof of the natural occurrence of that substance in the flesh. To investigate this, a mixture of the neutralised amines containing each amine in a concentration of $M/150$ was distilled under the following conditions, and the first 50 ml. of the distillate were tested:

(A) 200 ml. of amine solution + 10 ml. of water.

(B) 200 ml. of amine solution + 10 ml. of phosphoric acid.

(C) 200 ml. of amine solution + 10 ml. of water + 3 g. of magnesium oxide.

In (C) the amines distilled were collected in an excess of sulphuric acid, and the solution was neutralised.

All the distillates and the original amine solution were examined by Schryver's and the phloroglucinol tests. The original amine solution developed a colour with Schryver's reagents equivalent to 1·25 parts of formaldehyde per million, whilst the corresponding figures for the distillates (A), (B), and (C) were, respectively, 1·67, 2·5 and 1·11. On applying the phloroglucinol test, the original amine solution and distillate (C) gave negative reactions, whilst distillates (A) and (B) gave positive reactions, (B) giving the stronger. In (C) nearly all the amine must have been distilled, and the distillate gave almost the same Schryver figure as the original solution. The negative phloroglucinol reactions and the Schryver figures for these two solutions suggest that, during distillation of (C), any formaldehyde formed must have been immediately destroyed by the alkali. In both (A) and (B), although only a trace of amine was distilled as indicated by Nessler's test, the Schryver figures were higher than for the original solution, suggesting that formaldehyde was present in these distillates. This is confirmed by the positive phloroglucinol reactions. More formaldehyde was apparently produced in the acid than in the neutral distillation. Steam-distillation, carried out so that the volume of fluid in the flask remained constant, also gave positive reactions for formaldehyde in the distillate. The amine solution, "refluxed" for the duration of a normal distillation, gave a negative phloroglucinol reaction, since, presumably, the formaldehyde formed could not remain free in the presence of excess of amines.

These results shown that distillation of amines in neutral or acid solution may bring about oxidation of amine to formaldehyde, which appears in the distillate. In the presence of an undetermined amount of volatile amine, it is therefore not permissible to interpret a positive reaction of the distillate to any formaldehyde test as indicating that formaldehyde was present in the original solution.

Solutions of amines, of formaldehyde, and of both together were tested by Schryver's and the phloroglucinol reagents. When Schryver's test was applied, the result obtained for the mixed solution was approximately additive of the separate effects of amines and formaldehyde. With the phloroglucinol test the mixed solutions gave either negative reactions or positive reactions weaker than formaldehyde solutions of corresponding strength, denoting the complete or partial binding of formaldehyde by the amines. These results suggested that the phloroglucinol reagent might be used to detect free formaldehyde in extracts of fish obtained in such a way that no constituent of the fish was converted to an extent sufficient to produce free formaldehyde.

2. APPLICATION OF FORMALDEHYDE TESTS TO LING.—Various kinds of fresh fish have been reported as giving weak positive reactions in formaldehyde tests; the application of formaldehyde tests to ling only is here considered. From the results of the experiments with pure amines, it is clear that, in setting out the results, distinction must be made between different methods of obtaining from the fish the fluids to which the formaldehyde tests are finally applied.

Quantities of 100 g. of ling, fresh or salted, were distilled with 130 ml. of water and 20 ml. of phosphoric acid, and the first 50 ml. of distillate were tested with Schryver's and phloroglucinol reagents. The distillates from fresh fish varied from fish to fish in their reaction to the tests, the majority giving positive phloroglucinol reactions. The Schryver figures varied from less than 1 to 1·67 p.p.m. of distillate. The distillates from salted fish were strongly positive to phloroglucinol, and the Schryver figures were always greater than 10 p.p.m.

Extracts of fresh or salted ling were made under various conditions, and tested with Schryver's and the phloroglucinol reagents. A negative phloroglucinol reaction was taken as evidence that no free formaldehyde was present in the extract. Ten g. of fresh ling were extracted in all cases with 40 ml. of fluid by grinding with sand and filtering, and the filtrate was tested. Extracts were made with cold water, hot water, 5 per cent. trichloroacetic acid, and warm dilute phenylhydrazine hydrochloride (0·09 per cent.), as used in Schryver's method. It was found that trichloroacetic acid, when neutralised, did not interfere with the formaldehyde tests. The phloroglucinol test could not, however, be satisfactorily applied in the presence of phenylhydrazine hydrochloride. Extracts made with cold water, hot water, and trichloroacetic acid gave negative phloroglucinol reactions, indicating the absence of free formaldehyde. All the extracts gave positive Schryver's reactions, varying from slight traces to 1·4 p.p.m. of extract (6 p.p.m. of flesh). Two g. of fully-cured, salt ling were extracted in the same manner as the fresh fish, 80 ml. of the various extractants being used. In addition, an extract was made by boiling the fish with water under reflux for 15 minutes. As with fresh fish, the extracts made with cold water, hot water and trichloroacetic acid gave negative phloroglucinol reactions. The extract made under reflux gave a faint positive reaction. The extracts made with cold water and trichloroacetic acid gave a Schryver's figure of much less than 1 in a million. Heating the former extract increased the figure only slightly. The extracts made with hot water gave approximately the same Schryver figures as those made with phenylhydrazine hydrochloride, *viz.* 5 p.p.m. (200 p.p.m. of flesh)—a much higher figure than was

obtained for fresh fish. The difference between the cold and hot extracts may be due to the greater extractive power of hot water for precursors of formaldehyde, possibly together with the formation, during extraction, of some formaldehyde, which, being mostly combined in the cooled extract with nitrogenous substances, may give a weak phloroglucinol reaction.

In testing fresh ling by Schryver's direct method, 10 g. of fish were heated for 5 minutes on the boiling water-bath with 24 ml. of 0·09 per cent. phenylhydrazine hydrochloride solution, cooled and filtered, and the filtrate was tested with ferricyanide and hydrochloric acid. The colour obtained was estimated by matching it against formaldehyde standards ranging in concentration from 1 to 10 p.p.m. Above this concentration, aggregation of particles makes matching difficult. Where the colour obtained in a filtrate was too strong, the filtrate was suitably diluted with 0·09 per cent. phenylhydrazine hydrochloride solution. The results with triplicate samples of fish agreed closely. Results were expressed as parts of formaldehyde per million parts of flesh. Eight fresh ling, so examined, gave figures ranging from 4 to 32 p.p.m. Eight ling which had been stowed in ice for 12 days gave figures ranging from 20 to 160 p.p.m. Salt ling, which were taken at various stages of the curing process, were examined. To obtain a suitable colour in the filtrates, the method, recommended by Schryver, of varying the ratio of weight of fish to volume of extractant was adopted. This ratio was varied from 1 in 50 to 1 in 2·5. Separate experiment showed, however, that such variation produced variation in the estimated parts of formaldehyde per million (*e.g.* 90 to 240 p.p.m.). This is partly due to the fact that, when this ratio is large, a yellow tint interferes with the matching of colours. Dilution of such extracts so that equal volumes are equivalent to the same weight of fish, while greatly increasing facility in matching, still gives variation in the final figure. For comparative work, it would appear to be necessary to keep a constant small ratio of extraction, and, when colours are too strong, to dilute the filtrate. Fifty salted ling gave Schryver figures ranging from 4 to 480 p.p.m. Since some of these figures less than 120 were obtained at a high-extraction ratio, they are probably too low.

One hundred g. of salt-cured ling, which gave a Schryver figure of 480 p.p.m. of flesh, were distilled with magnesium oxide and water, and the volatile bases (83 mg. of N) were collected in acid. The solution of bases gave a Schryver figure of 2 p.p.m. of solution, or 10 p.p.m. of flesh. The phloroglucinol reaction was negative. The solution of bases was distilled with excess of phosphoric acid and five 50–ml. portions of the distillate were examined. All five gave strongly positive phloroglucinol reactions and Schryver figures of 3 to 5 p.p.m. of distillate.

Since no formaldehyde was added to the fish used in these experiments, the positive Schryver reactions obtained with distillates and extracts of fish must be ascribed to substances normally present in the fish, fresh or salted. In the literature the figures obtained by Schryver's method directly applied to fresh fish do not exceed 5 p.p.m. Some of the figures reported here are considerably higher, and for salt ling the figures obtained are very much higher. To some extent these high figures may be explained by the difficulty, already mentioned, of getting good quantitative results with Schryver's method, This can hardly explain, however, the great difference between fresh and salted fish. The results of the experiments

with the methylamines and with fish amines show that volatile amines alone cannot account for the high figures obtained for salt fish. The results of the distillation experiments cannot safely be interpreted quantitatively, but here, too, it is improbable that volatile bases alone are responsible for all the formaldehyde obtained in distillates of salt fish. The experiments with the methylamines and with fish amines do show clearly, however, that distillation is useless as a method of qualitatively detecting formaldehyde in fish. The Schryver figures being still unexplained quantitatively, further work is required to make clear the influence of the curing process and the part played by trimethylamine oxide, which, so far as is known, does not contribute to the volatile bases obtained by distillation with magnesium oxide. Little is yet known as to how much of this substance is present in fish, of how it is affected by curing, and to what extent it is oxidised by Schryver's reagents.

The possibility that formaldehyde is picked up, to some extent, from the coke fires used in drying salt ling has not been investigated. Little formaldehyde can be produced from coke, which is coal already destructively distilled, and what little may be produced cannot be regarded as "formaldehyde added as preservative" in the legal sense, since coke-fire drying is part of the customary manufacturing process. In this respect, coke-drying of salt fish is analogous to wood-smoking of fresh fish, in which process a considerable amount of formaldehyde is produced during combustion.

3. THE DETECTION OF FREE FORMALDEHYDE IN FORMALINISED SALT LING.—Formaldehyde was added to salt ling to give concentrations of 50, 100 and 150 p.p.m. of flesh; the treated fish were thoroughly ground for five minutes and extracted with cold water at extraction ratios varying from 1 in 10 to 1 in 40, and the extracts were filtered and tested with phloroglucinol. In every instance the filtrates gave a positive reaction, which, however, was always weaker than that given by pure formaldehyde in corresponding concentrations. Extracts of fish to which no formaldehyde had been added gave, as already reported, negative reactions. While some of the added formaldehyde had obviously combined with the fish, in every instance free formaldehyde was detected.

The phloroglucinol reagent thus gives a specific means of testing for free formaldehyde in the presence of fish flesh, if this is extracted with cold water. Free formaldehyde was also detected by this method in extracts of smoked codling, the formaldehyde in this case being attributable to the smoking process.

CONCLUSION.—It has been shown that ling (fresh or salted), to which no formaldehyde has been added as preservative, may give a positive reaction in Schryver's test applied directly to the flesh, and positive reactions with all the formaldehyde tests, as customarily applied to distillates of the flesh. The usual methods of testing, interpreted qualitatively, are therefore quite unsuitable for proving that formaldehyde has been applied to salt ling as a preservative. Evidence has been presented to show that quantitative data obtained by applying Schryver's method to non-formalinised salt ling are not fully explained, and therefore the method cannot be used for quantitative detection of added formaldehyde. It has been shown that the phloroglucinol reagent may be employed

qualitatively to detect free formaldehyde in fish. The possible relationship of amine bodies to the positive reactions given by non-formalinised fish is discussed.

There is no evidence to show that formaldehyde is a normal constituent of fresh or salt-cured ling.

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TORRY RESEARCH STATION
DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH
ABERDEEN

Air-damped Balances

BY W. N. BOND, M.A., D.Sc., F.INST.P.

(*Read at the Meeting, December* 4, 1935)

INTRODUCTION.—During the last few years balances have been constructed, by various makers, enabling the process of accurate weighing to be carried out more rapidly and with greater ease than was formerly possible. The improvement is achieved by attaching to the beam of the balance a damping mechanism consisting of light metal pistons which move in fixed metal cylinders. There is a "clearance" space of about 1 mm. between the pistons and the cylinders, and the damping is due to the motion of the air produced by the motion of the pistons. Owing to the viscosity of the air, the oscillation of the balance beam is rapidly reduced; the damping may even be made so great that the balance beam moves gradually to its new equilibrium position without executing any oscillations.

As a consequence of the rapidity with which the beam becomes steady in its final position, it is no longer necessary to estimate this position by reading three successive extreme positions of a pointer on a scale. Moreover, because the final position of the beam may be observed at leisure, it has been possible to incorporate another feature in the design. The tip of the pointer is replaced by a small transparent scale, or graticule, rigidly attached to the beam. A small electric lamp and an optical system project an enlarged image of this graticule on to a ground glass plate, across the centre of which is a fiducial line. If the sensitivity of the balance has a fixed value, independent of the load on the balance, the graticule may be so constructed that each scale division represents some simple sub-division of a gram. It is then unnecessary to use any riders or weights less than, say, 0·1 g., the smaller weights being read *directly* on the ground glass.

These balances, provided that they do not introduce or increase errors, have many advantages. More weighings can be done in a given time. The balances are pleasanter to use, and there is less liability to mistakes in counting and arithmetic. There is also the psychological effect that the ease in using the balances induces a desire to carry out a weighing whenever it may be at all useful. When rapid chemical or biological action is taking place, the time that could be devoted to a weighing might be so short as to preclude the use of any but an air-damped balance. The rapidity of the weighing with an air-damped balance may decrease some errors, such as any that are due to gradual changes in the temperature of the room. Finally, the shorter time required for a weighing enables repetitions to be made, to check and improve the accuracy of the measurements.

THE DAMPING SYSTEM.—When weighing to a high degree of accuracy, it is not advisable to use *liquid* to produce damping, for the somewhat erratic surface-tension forces would prevent the beam from reaching its true final position. No such error can occur when air-damping is used. In fact, air-damping seems to be the only satisfactory method, with the possible exception of electro-magnetic damping.

The balance should be constructed so that there is no possibility of the pistons rubbing against the cylinders. The pistons should be light in construction, and not too far from the central knife-edge, in order that the moment of inertia of the beam be not unduly increased. They must be rigid, for if they were bent at any time, the position of the centre of gravity of the beam would be changed, and the sensitivity of the balance would be altered. In some balances this last disadvantage is avoided by fixing the pistons to the stirrups from which the pans are suspended, instead of attaching them rigidly to the beam. Change of temperature should not displace the centre of gravity of the beam sideways. This possible error is most simply avoided by making the whole system symmetrical, a piston and cylinder being provided for each arm of the balance.

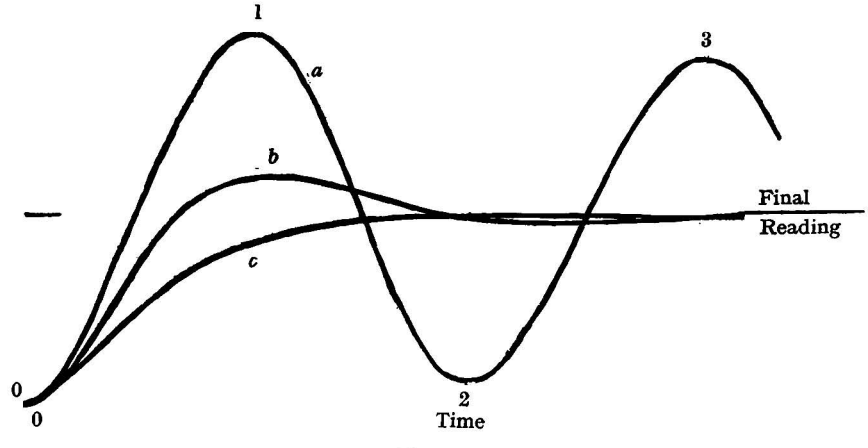

Fig. 1

The advantage of the damping can be seen by reference to Fig. 1. Curve (*a*) shows the slowly decaying oscillations of an ordinary balance. Curve (*c*) shows

the gradual movement to the new position that takes place when the same balance is "critically damped." In this case no oscillations occur. When the damping is not quite so great, the motion is such as is indicated in curve (*b*), the oscillations rapidly decreasing in amplitude.

In using an ordinary balance and "weighing by swings," readings would be taken at points (1), (2) and (3) of curve (*a*). By the time reading (3) is taken, the pointer of a similar balance *that was "critically damped"* would have moved 99·8 per cent. of the way towards its final reading. With the ordinary balance, we have still to calculate the value of

$$\frac{\frac{(1)+(3)}{2}+(2)}{2}$$

and multiply it by the sensitivity. In the meantime the damped balance would have proceeded on the remaining 0·2 per cent. of its journey, and the fraction of 0·1 g. could be read direct on the ground glass scale. The definite advantage of the damping is at once evident.

The advantages of the air-damped balance have been slightly overstated above, the increase in moment of inertia due to the presence of the pistons having been neglected. On the other hand, in using an undamped balance it is unlikely that reading (1), curve (*a*), will be taken on the very first swing.

If the damping is greater than in the critical case [curve (*c*)], the beam will be slower in reaching its final position, which is a disadvantage. It is probably better to have slightly *less* than the critical amount of damping, because the small oscillations [curve (*b*)] enable the observer to judge how soon the final position may be considered attained. With critical damping, the observer is apt to keep wondering if the reading will eventually creep much further. If the damping is nearly critical for small loads, the balance will be somewhat under-damped when the load is larger. The damping pistons are sometimes provided with small holes partly covered by adjustable flaps, so that the amount of damping may be adjusted by moving the flaps to a suitable position.

EXPERIMENTS WITH AIR-DAMPED BALANCES.—The results of experiments that I have carried out on five air-damped balances, made by four different makers, are described below. The experiments were designed to test the speed and accuracy of the balances. The results indicate how such balances may be expected to function under ordinary working conditions, and the experiments may be useful as a guide to anyone who wishes to test an air-damped balance.

Rapidity of Weighing.—After the weight had been adjusted to the nearest 0·1 g., the time required to release the beam, wait for a steady reading and record it to an accuracy of 0·0001 g. (or less) varied from 50 seconds to 20 seconds. The shortest time was found with a small balance designed for a maximum load of 20 g. In this balance, used at half its maximum load, a single swing (or half oscillation) occupied about 4 seconds, and each excursion of the beam was of about $\frac{1}{8}$ of the amplitude of the preceding excursion. This corresponds to a curve about mid-way between curves (*b*) and (*c*) in Fig. 1. If 4 seconds are taken in releasing the beam, the amplitude will decrease during the next 16 seconds to

about $\frac{1}{8} \times \frac{1}{8} \times \frac{1}{8} \times \frac{1}{8}$ or 0·0003 of the original amplitude, and the beam can be considered at rest in its new position.

Constancy of Zero.—Good air-damped balances, in a room where the temperature does not change rapidly, seem to be subject to a change in zero corresponding to about 0·0001 g. in half-an-hour of weighing. For a badly-designed balance, or when the temperature changes are rapid, the zero may change by as much as 0·0001 g. in 10 minutes of weighing. Even under very adverse conditions, however, error can be avoided by taking a weighing with the object in the left-hand pan, a second weighing with the object in the right-hand pan, and averaging the two results. This takes little extra time, and the procedure is advisable where a high degree of accuracy is required.

Inequality of the Lengths of the Two Arms of the Balance.—In a good balance the lengths of the two arms should not differ by more than about 1 part in 100,000. To find the inequality in the arms, we find the zero and then weigh a body first in one pan and then in the other. Let the lengths of left and right arms be a and b; the true weight of the body be W; the apparent weights when the body is in the left- and right-hand pans, W_1 and W_2, respectively. Then, if a and b are nearly equal, we have, to a close approximation,

$$W = \frac{W_1 + W_2}{2}$$

and

$$\frac{a - b}{b} = \frac{W_1 - W_2}{2\,W_2}$$

For the balances that I tested the fractional error, $\frac{a - b}{b}$, had values of between 0·000,013 and 0·000,001. Hence, neglect of any correction would have caused the weighings to be in error by only about 0·001 per cent. or less. However, the method of double weighings, mentioned at the end of the section on "constancy of zero," will give a weight that is not only free from the effect of "zero error," but is also free from any error due to the arms of the balance being of slightly different lengths.

Accuracy of Weighing.—In order to test the accuracy of weighing, three weights of nominally 1 g. each were compared in pairs on five balances. In every experiment a reading was taken, and a second reading with the weights on the pans interchanged. The two results were then averaged, thus eliminating error in zero and effect due to inequality in the arms. No other corrections were applied. The results obtained were:

Weights.	Difference in weight, in grams, using balance number:—				
	I	II	III	IV	V
1*–1	0·000,83$_5$	0·000,86	0·000,85	0·000,8$_5$	0·000,83$_5$
1**–1	0·000,47	0·000,49$_5$	0·000,48	0·000,4$_5$	0·000,53$_5$
1*–1**	0·000,32	0·000,35	0·000,36	0·000,3$_5$	0·000,39$_5$

By comparison of these results it can be concluded that the maximum error of any one of the 15 experiments (each of which was the mean of two weighings) was about 0·000,05 g. The "probable error" of a single experiment was

$\pm 0{\cdot}000{,}016$ g. Hence the balances can be used to weigh 1 g. to an accuracy of about 1 part in 50,000.

A few similar experiments were carried out with 10-g. weights, and the probable error of a single experiment was found to be $\pm 0{\cdot}000{,}01_6$ g., corresponding with an uncertainty of 1 part in 500,000.

Testing the Graticule.—If the graticule and optical system are arranged so that the scale-readings represent simple fractions of a gram when the balance is used for small loads, it is to be expected that at greater loads the sensitivity of the balance will be slightly different, causing the scale-readings no longer to represent the fractions of a gram quite accurately.

It is found that, for a load of 50 g., the sensitivity of these balances may differ from the sensitivity at zero load by as little as 0·2 per cent. or by as much as 2 per cent. The scale will usually be employed to estimate about 0·05 g. of the total load. This 0·05 g. (or so) may therefore be in error by as much as 2 per cent., giving an error of 0·001 g. in 50 g. Complete data cannot be given, as the error will depend on the particular balance and will not be directly proportional to the load.

When weighing masses of as much as 50 g. to an accuracy of 0·001 g., it is certainly desirable to calibrate the graticule by means of a 0·05-g. weight at *each* load that is used. The need of this calibration seems to be the only real trouble in using these balances. It may, however, be noticed that a similar calibration is necessary when "weighing by swings" with an undamped balance, and the correction is much easier to determine when using an air-damped balance.

The divisions on the graticule should be almost uniformly spaced, a slight allowance being made because the difference between the loads on the two pans is proportional to the tangent of the angle of deflection. The scale may be tested by weighing (say) a 0·02-g. weight, weighing another that may be denoted 0·02*, and then weighing them together. Whenever I tried such an experiment, I found that the reading for (0·02 + 0·02*) agreed with the sum of the separate determinations within the experimental error, indicating that the graticules were satisfactorily graduated.

The optical system should be rigid, or "changes in zero" may occur.

Finally, it may be remarked that the balance room should be suitable, the weights should be standardised, and a buoyancy correction should be applied (which is often a correction of 1 part in 800 and may be even greater).

My thanks are due to Captain John Golding for suggesting this investigation and giving me facilities for using the air-damped balances at the National Institute for Research in Dairying, Shinfield, Berks.

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DISCUSSION

Captain J. GOLDING said that their experience at the National Institute for Research in Dairying was in accord with Dr. Bond's conclusion. They had found that a balance air-damped at each end of the beam gave the most satisfactory results. This balance weighed up to 20 grams, and, for the routine determination of total solids in milk, aluminium capsules differing but little in weight were used,

so that the balance weights seldom required adjusting. The graticule was graduated over its whole length in fifths of a milligram.

Mr. F. G. TATE said that in some of the work at the Government Laboratory they had to do a very large number of routine weighings, and as something in the nature of a damped balance was necessary, they had tried various types. The oil-damped balances were open to grave criticism. For example, the oil was inclined to creep, and the zero of the balance might be affected by the temperature and age of the oil and the condition of the rod supporting the piston. The air-damped balance with the piston under the pan was liable to get out of gear very easily.

Some time ago Captain Golding had brought to the notice of the Society a balance with damping at one end of the beam. Mr. Tate had criticised this and, at subsequent meetings at the Government Laboratory between himself and the balance makers, a scheme to have an air damper at each end of the beam had been evolved. This had been found to be very satisfactory, and on one such balance they were now doing about 200,000 weighings per annum. He agreed with Dr. Bond that the best scaling was from one end of the graticule to the other.

Mr. P. BILHAM remarked that he had had experience with eight of these balances over a period of six years. If he might advise prospective users, he would urge them to deal with those balances with dampers in an elevated position. As these balances were used by people in a hurry, sooner or later they would spill something, which would enter the dampers if they were beneath the pans and necessitate dismantling in order to clean the balance. He added that with these balances it was possible to weigh substances which were almost hydroscopic.

Dr. J. GRANT said that he had had an opportunity of comparing a chainomatic and an air-damped balance, and came to the conclusion that for speed of weighing the air-damped balance had the advantage, but that for accuracy, weight for weight, the chainomatic was more satisfactory. With the air-damped balance, it was found that, after being adjusted in the morning it was decidedly "out" by the evening. Finally, it was discovered that the light in the balance room was not hanging symmetrically between the pans and that the air between the damping-cylinders on one side was getting warmer than on the other. Therefore, it was necessary to see that any source of heat did not affect one side more than the other.

Dr. W. N. BOND, replying, said that he had not had any real working experience of chainomatic balances. If one were aiming at considerable accuracy, the air-damped balance did not seem to introduce any cause of error, whereas the chainomatic did. He felt that there was an advantage in having the graticule numbered from one end, whichever way one used it. It was easier than writing down plus and minus and then working it out, but he did not know anything about the actual accuracy.

Notes on Mendel and Goldschieder's Method for Determining Lactic Acid in Blood

By R. MILTON, B.Sc.

(*Read at the Meeting, November* 6, 1935)

In 1925 Mendel and Goldschieder[1] put forward a method for the determination of lactic acid in blood. This consisted in precipitation of proteins with metaphosphoric acid, removal of sugar by the copper and lime method, heating the filtrate with sulphuric acid, and colorimetric measurement of the red colour produced on addition of veratrol.

It is assumed that heating lactic acid with sulphuric acid causes formation of acetaldehyde and carbon monoxide.[2] Measurement of carbon monoxide for indirect determination of lactic acid has been suggested by some authors.[3,4,5]

The acetaldehyde formed in this reaction behaves in an atypic manner, since acetaldehyde normally distils at 21° C., whereas here the sulphuric acid solution is heated to 100° C. without any apparent loss of aldehyde.

Mendel and Goldschieder state that conditions must be rigidly observed. Using a concentration up to 25γ of lactic acid in 0·5 ml. of solution, they found that:—(*a*) The optimum concentration of sulphuric acid is 3 ml. in 3·5 ml. (*b*) The minimum heating time with sulphuric acid is 4 minutes, and no further change occurs if the heating time is continued up to 8 minutes. (*c*) The best colour is obtained with 0·1 ml. of 0·125 per cent. veratrol (in alcohol). (*d*) The optimum colour-development time is 20 minutes.

Nordbo[6] has also studied the method. He found that the colour-development is, in the main, a function of temperature, *e.g.* between 10° C. and 15° C. development is strongest after 20 minutes, and between 0° C. and 5° C., the colour is strongest after 60 minutes. Below 15° C. the colour is stronger with 0·05 ml. of veratrol than with 0·1 ml. He further concludes that the amount of veratrol necessary is proportional to the amount of lactic acid present. He confirms Mendel and Goldschieder's statement that the reaction is only possible if chemicals of the highest degree of purity are used. In particular, the sulphuric acid must be of full strength and free from the smallest trace of nitrites. Both investigators insist that water inhibits the reaction.

I have attempted to apply the method as originally put forward, but to use the Cambridge Photo-electrometer, in place of a colorimeter, for the optical measurement.[7]

Since the original paper insists upon complete freedom from nitrites, Hopkin & Williams' nitrogen-free sulphuric acid was used.

With the quantities specified by Mendel and Goldschieder I was unable to get even the faintest trace of colour, and assumed that this was due to the sulphuric acid—the concentration of water therein being too high and thus inhibiting the colour reaction. The acid was dehydrated, but without effect. Nor was any reaction obtainable after treatment with various oxidising and reducing reagents.

I was finally led to investigate the effect of increasing water-concentration, and the results were surprising, as shown in the following table:

TABLE I

VARYING AMOUNTS OF WATER CONCENTRATION

(0·1 mg. lactic acid in each)

Water-concentration			Colour	Photo-electric reading
ml.		Sulphuric acid ml.		
0·2	+	3	Straw	16
0·5	+	,,	Yellow	18
0·7	+	,,	Orange	33
0·9	+	,,	Magenta	37
1·1	+	,,	,,	36
1·3	+	,,	,,	35

This table shows that the most intense colour is obtained when the concentration of solution to sulphuric acid is 1 : 3. At this concentration the colour is comparable with that obtained by Mendel and Goldschieder, and represents a concentration of sulphuric acid of 75 per cent. The concentration of lactic acid solution is twice that of Mendel and Goldschieder, suggesting that the "special" sulphuric acid used by them has about 87·5 per cent. concentration.

At this point I decided to make a thorough investigation of all the conditions.

1. TEMPERATURE OF COLOUR REACTION.—Nordbo's work sufficiently emphasised temperature conditions to justify us taking a given fixed temperature and referring all other variables to this. I therefore took 20° C. as the development temperature, since this is never really far from room temperature, and can thus be easily controlled.

2. TIME OF HEATING WITH SULPHURIC ACID.—Owing to the conditions of acetaldehyde formation, it is suggested in the original technique that the sulphuric acid be added, drop by drop, with shaking, to the lactic acid solution, while the tube is held in iced water. I found that, unless extreme care is exercised at this stage, some loss is easily incurred, possibly owing to too rapid formation of

TABLE II

EFFECT OF TIME OF HEATING

1 ml. of lactic acid solution + 3 ml. H_2SO_4

(Development with veratrol at 20° C. for 20 minutes)

Time in boiling water-bath Minutes	Photo-electric reading
1	25
3	26
5	26
7	26
9	26
15	26

acetaldehyde. Introduction of the acid down the side of the tube proved more efficient. The acid forms a layer below the lactic acid solution, and, by carefully tilting the tube to an angle of 30° from the horizontal, the separation surface is increased to such an extent that mixing can be made with a gentle shake, without any evolution of steam. The tube is then placed in a boiling water-bath without delay.

Table II shows the effect of heating with sulphuric acid for varying periods.

This shows that the time necessary to form the colour-producing substance is less than 3 minutes, but that the intensity of the colour is not affected by considerable further heating.

3. Concentration of Veratrol.—With amounts of lactic acid such as are likely to be found in blood filtrates, it was found that the optimum concentration of veratrol was between 0·1 and 0·15 ml. of a 0·125 per cent. alcoholic solution.

Table III

Lactic acid used per 100 ml. mg.	Concentration of veratrol: 0·05 ml.	0·10 ml.	0·15 ml.	0·20 ml.
	Photo-electrometer readings			
10	10	12	12	11
25	16	22	22	23
100	31	52	72	87

If the concentration of lactic acid is in the region of 100 mg. per 100 ml., the amount of veratrol is insufficient.

Our optimum was taken as 0·15 ml., with the proviso that should the concentration of lactic acid be above 30 mg. per 100 ml., an initial half-dilution should be made before proceeding with the colour reaction.

4. Time of Colour Development.—The reaction of veratrol with the acetaldehyde complex tends to be continuous. The table given below shows findings obtained when conditions of temperature and concentration of reagents are fixed, time being the only variable.

Table IV

Time of Colour Development

Development time Minutes	Concentration of lactic acid: 10 mg.	25 mg.	100 mg.
	Photo-electrometer readings		
5	8	20	49
10	10	22	52
15	13	24	55
20	13	24	55
30	15	24	55
40	16	27	57
80	17	27	57
140	18	27	58

These results indicate that the continuous colour development tends to slow down between 15 and 25 minutes. If 20 minutes are taken as the optimum time for colour development, sufficient latitude to make a series of readings is allowed.

The Application of Method to Blood

Mendel and Goldschieder recommend metaphosphoric acid as a protein precipitant. The clear filtrate is then freed from sugar by the copper and lime procedure. In using their de-proteinising technique I found that the excess of metaphosphoric acid, which must be present in the filtrate, tends to interfere at the copper and lime stage. On addition of calcium oxide a metaphosphate is formed which is precipitated completely only after considerable delay. Thus, varying amounts of tricalcium phosphate are found in the final solution, and these have an appreciable retarding effect upon the development of the colour. I therefore applied Somogyis'[8] method of colloidal zinc precipitation of proteins, which has two advantages. It gives a protein-free filtrate not containing excess of precipitating reagent and a solution freer from substances originally present in the blood, which are likely to interfere with the reaction.

At the copper and lime stage we experienced difficulty in obtaining a clear filtrate. The excess of lime tended to cause a carbonate scum which could not be separated by centrifuging. This was overcome by using a filter-stick made from $\frac{1}{4}$-in. glass tubing. I first removed the bulk of the precipitate by centrifuging, and then forced the supernatant fluid through the small asbestos packing by gentle blowing with the lips.

The above considerations led me to adopt the following technique:

(*Note.*—The precaution of ensuring complete freedom from organic matter during the reaction cannot be over-emphasised. It is essential that all apparatus should be washed with conc. sulphuric acid before use.)

Technique for Lactic Acid in Blood.—*Reagents.*—(1) Zinc sulphate (10 per cent. solution). (2) $N/2$ sodium hydroxide solution. (3) Half-saturated copper sulphate (15 per cent. solution). (4) Finely-powdered lime. (5) Veratrol in absolute alcohol (0·125 per cent. solution). (6) Sulphuric acid (sp.gr. 1·84, nitrogen-free).

Technique.—Blood is collected in a tube containing 1 mg. of ammonium fluoride per ml. of blood. One ml. of the blood is pipetted into a centrifuge tube and mixed with 3 ml. of water. One ml. of zinc sulphate solution is added, followed by 1 ml. of the sodium hydroxide solution, drop by drop, with shaking. The mixture is then thoroughly shaken and allowed to stand for a few minutes before centrifuging at high speed for $\frac{1}{4}$ hour.

Three ml. of the clear centrifuged liquid are pipetted into another centrifuge tube with a 5-ml. graduation mark. One ml. of copper sulphate solution is added, and, after the addition of 1 g. of lime, the contents of the tube are again mixed by careful inversion before being made up to the 5-ml. mark with water. After a thorough shaking the tube is allowed to stand for half-an-hour, and is then centrifuged.

The supernatant fluid is poured into a filter-stick packed with a layer of acid-washed asbestos. Gentle blowing with the lips is sufficient to effect filtration.

The first few drops which pass through are discarded, and then the bulk of the fluid is collected in a test-tube.

One ml. of the filtrate (representing 0·1 ml. of blood) is pipetted into a clean dry test-tube, 3 ml. of sulphuric acid are introduced down the side of the tube, the contents are carefully mixed, and the tube is placed in a boiling water-bath for 5 minutes, and then cooled to 20° C.

After the addition of 0·15 ml. of the veratrol solution the contents are again mixed, and the tube is placed for 20 minutes in a beaker of water maintained at 20° C. The depth of the magenta colour is then read in the photo-electrometer. From this reading is subtracted that given by a blank reagent, and the result is read on a graph relating photometric difference to concentration.*

Preparation of Graph.—Dissolve 171 mg. of pure re-crystallised calcium lactate in 100 ml. of water. This will contain 1 mg. of lactic acid per ml. Dilute 5 ml. of this solution to 100 ml. with water, and from this make a series of dilutions from 0·005 up to 0·03 mg. of lactic acid per ml. Take 1 ml. of each dilution and treat them exactly as in the above technique from the stage following the copper and lime treatment. When plotted, the resultant graph may be used for subsequent readings, if the conditions of experiment are identical with those used during the construction of the graph.

The foregoing method has been tested on blood in comparison with the titrimetric distillation procedure. The Friedmann–Kendall modification of the Fürth permanganate-iodimetric method was chosen as being the more accurate of the volumetric techniques. In carrying out this technique, however, the Folin–Wu tungstate protein precipitation was replaced by Somogyi's zinc procedure, in order that comparison might not be complicated.

TABLE V

Blood	Lactic acid: Proposed method mg. per 100 ml.	Lactic acid: Friedmann and Kendall's method mg. per 100 ml.
A	14·2	15·2
	15·8	17·4
	15·4	16·2
	15·8	
B	14·2	14·0
	14·0	15·2
	14·2	15·8
	14·2	
	14·2	
	14·3	
	14·4	
C	10·4	10·6
D	5·6	7·2
	5·6	

* When a colorimeter is used to obtain an end-point, it is suggested that at least three standards be used, containing 0·005, 0·010 and 0·015 mg. of lactic acid per ml., respectively, and that comparison of the unknown solution be made with the most appropriate standard.

From this table it is evident that the results given by the proposed method are slightly lower, but more consistent, than those given by the aldehyde-bisulphite titration procedure. This is probably due to the fact that in the volumetric method, (*a*) substances other than lactic acid distil as acetaldehyde, and (*b*) some degree of over-oxidation with potassium permanganate can rarely be avoided.

This work was carried out in the biochemical laboratories of Dr. E. Obermer, and is published with his permission.

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The Risk of Error in Determining Traces of Arsenic in Organic and Inorganic Materials

BY W. A. DAVIS, B.Sc., A.C.G.I., AND J. G. MALTBY, B.Sc., A.I.C.

ALTHOUGH the literature dealing with the determination of traces of arsenic is already very voluminous, recent experience has convinced us that it is desirable to emphasise the considerable error that may arise unless special precautions are taken when the arsenic is present largely in the form of arsenic acid or arsenate. This is due mainly to the variable activity of different arsenic-free zincs on the market which make the complete reduction to the arsenious form slow and uncertain, and thus may lead to very low values being returned for the arsenic volatilised as arsine. As a result of our experiments we consider that it is necessary when arsenates are present *always to ensure their complete reduction to arsenious acid by a suitable method before carrying out the ordinary Gutzeit or Marsh test*, whether the latter be made electrolytically or by using zinc and acid.

The Gutzeit test, in particular, when carried out as generally prescribed (Brit. Pharmacopoeia, 1914, 1932; Analar Standards, 1934) works admirably when all the arsenic is in the arsenious form; but if arsenates are present, owing to their reduction by zinc and stannated hydrochloric acid being relatively difficult, very low values may easily be obtained. In dealing with organic materials, the organic matter is often first removed by ignition with pure calcium carbonate and the residual ash tested; during ignition much of the arsenic may be converted into arsenate. In other cases, oxidising agents are used, such as nitric acid or

chlorate, which produce arsenic acid. In testing certain chemicals oxidation precedes the actual test, for example, in the case of hypophosphites, to avoid the production of phosphine, which falsifies the result. There are also methods which involve distillation of the arsenic with hydrochloric acid, the distillate being then oxidised before evaporating, to prevent loss of arsenic by volatilisation. In all such cases the arsenic is present finally in the valent form.

So long ago as 1861, Bloxam,[1] when studying the determination of arsenic in human organs, used potassium chlorate and hydrochloric acid to destroy the organic matter and emphasised the point that the arsenic was completely converted to arsenate; he recommended the use of sulphurous acid to reduce this before making the test. The solution was heated for some time on the water-bath with sulphurous acid, and the excess of this then removed by evaporating until all smell of sulphur dioxide had disappeared. Alternatively, a few drops of sodium bisulphite solution may be used. As we show later, this method, properly carried out, is still the simplest and most effective means of reduction.

A careful survey of the extensive literature shows that numerous workers have found that the Marsh test (whether with the use of zinc and acid or electrolytic) and the Gutzeit test are liable to give very low results when arsenates are present. Prolonging the time of action or heating the reaction vessel has been suggested to overcome the difficulty, but the more general plan has been to add an "accelerator" to the reaction vessel. Platinic, stannous, antimony, iron, cuprous, cupric, zinc, cadmium or bismuth salts have been considered satisfactory by some, but condemned by others. In the electrolytic methods, a platinum electrode alone does not reduce the arsenates, and lead, zinc, iron, mercury and cadmium cathodes have been recommended; most of these cathodes have been condemned by other workers.

For the Gutzeit test the procedure generally adopted in this country (British Pharmocopoeia, etc.) is a slight modification of that suggested by Hill and Collins,[2] who found that the results were more uniform and accurate when the acid used contained a small quantity of stannous chloride. Hence the general adoption of "stannated" hydrochloric acid in the current processes.

Besides attempting to effect reduction of arsenates to arsenites in the reaction vessel during the course of the test, several workers have recommended that this reduction should precede the test itself. Many reducing agents have been suggested,* but most have been regarded as unsatisfactory by other workers. There is a general consensus of opinion,† however, that digestion with sulphurous acid or bisulphite on the water-bath, removing the excess by short boiling, completely reduces the arsenates to the arsenious form, and enables the whole of the arsenic to be easily volatilised in the subsequent test. Our own experiments have confirmed this, reduction being rapid and complete.

* Sulphurous acid, hydriodic acid, stannous chloride, hydroxylamine hydrochloride, ferrous sulphate and titanous sulphate.

† See, for example, Kirkby, *Chem. and Druggist*, 1901, **57**, 968; Gotthelf, *J. Soc. Chem. Ind.*, **1903**, **22**, 191; Sand and Hackford, *J. Chem. Soc.*, 1904, **85**, 1018; Trotman, *J. Soc. Chem. Ind.*, **1904**, **23**, 177; Sanger and Black, *J. Soc. Chem. Ind.*, **1907**, **26**, 115; Hefte, Inaug. Diss., Zürich; Roche Lynch (*Lancet*, 1923, **203**, 629. The only dissentients are apparently Lawson and Scott, *J. Biol. Chem.*, 1925, **64**, 23.

Experimental

In view of the uncertainty existing in the literature as to the best conditions to ensure complete reduction of arsenates and as lower results than we had expected were obtained in certain cases where known quantities were present, when using the ordinary Gutzeit test, we made a large number of experiments to ascertain the best means by which reduction could be assured.* Various materials were used in which, ultimately, known quantities of arsenic in the form of arsenate were present. Arsenate might be added directly as such, or the arsenic added in the arsenious form and subsequently converted into the arsenic form by oxidation. The quantities taken varied from 0·005 to 0·02 mg. It is unnecessary to give our results in detail, but we found that with ordinary types of arsenic-free zinc, without a *prior* reduction of the arsenate, and carrying out the ordinary Gutzeit test with stannated acid *at the ordinary temperature*, much or all of the arsenic present in the arsenical form might remain unrevealed in 40 minutes. With different samples of zinc only 0 to 40 per cent. was found by working at ordinary laboratory temperature. Prolonging the action did not materially increase the yield. Under the same conditions arsenic in the arsenious form was fully determined.†

It was found also that when a solution of 0·02 mg. of arsenious oxide in the form of arsenate was left with 25 ml. of "stannated" hydrochloric acid for 12 minutes before making the test, only 35 per cent. of the arsenic was revealed by the particular zinc used, so that reduction was very incomplete at the ordinary temperature by the stannous chloride present. In another experiment, a few drops of stannous chloride solution and 5 ml. of arsenic-free hydrochloric acid were added, and the mixture was heated for 15 minutes on the water-bath; the test then made showed only 40 per cent. of the arsenic present, so that reduction was still very incomplete, the Gutzeit test being made at the ordinary temperature.

On the other hand, a pre-treatment with stannous chloride and potassium iodide under the conditions of the A.O.A.C. method (1930, p. 308) showed 100 per cent. of the arsenic with the Gutzeit test made at the ordinary temperature.

Prior Reduction by Sulphurous Acid.—This method seems to be the simplest and most certain to ensure reduction of the whole of the arsenates, even when these are present in relatively large proportion. It is, however, very important to use a *sufficient excess*, of either sulphurous acid or bisulphite. Small quantities, such as 2 to 4 mg. of bisulphite, may not be sufficient when much arsenic acid is present, and it is possible to feel safe only when an excess (*e.g.* 0·05 g. of bisulphite) is used. The excess should produce a pronounced smell of sulphur dioxide and, after the reduction on the water-bath is complete, this excess is easily removed by boiling for 2 to 3 minutes.‡

* Complete reduction of As^{v} to As^{III} is, for the purpose of this paper, to be taken to refer only to the minute quantities of arsenic looked for in the Marsh and Gutzeit tests, not to larger amounts.

† Different samples of AsT zinc showed very different activities, as regards both rate of solution and reducing power. Some effected no reduction of arsenate at all, others up to 40 per cent.

‡ The procedure we have found to be generally reliable in the pre-treatment is as follows:— After adding 5 to 10 ml. of arsenic-free hydrochloric acid (sp.gr. 1·10) to dissolve the material to be tested (for example, the product from ashing organic material with calcium carbonate) and 30 ml. of water, 0·05 g. of sodium bisulphite is added and the mixture heated for 30 minutes on the water-bath in the Gutzeit flask, closed with a glass Kjeldahl bulb to prevent any evaporation. (It is unsafe to evaporate the acid solution to any considerable extent, as arsenious chloride may be volatilised.) The liquid is then boiled for 2–3 minutes, until the smell of sulphur dioxide has disappeared, and used for the actual test.

Effect of Temperature during the Actual Test.—It was found that samples of zinc vary widely as regards their activity, owing especially to their different states of granulation. Some are relatively massive and dense, presenting less surface, and these may give low results in the Gutzeit test *even when the pre-reduction with sulphur dioxide has been properly carried out.* It is *essential* in such cases, in order to expel the whole of the arsenic, to warm the flask gently during the action (to about 40 to 60° C.). There must be sufficient rate of action to ensure a vigorous evolution of gas. In the B.P., 1914, it is stated that "the action *may* be accelerated by standing the apparatus on a hot plate, care being taken that the mercuric chloride paper remains quite dry throughout the duration of the test." In 1932 this was amplified by the addition, "The most suitable temperature is generally about 40°, but as the rate of evolution of the gas varies somewhat with different batches of zinc AsT the temperature *may* be adjusted to obtain a regular but not too violent evolution of gas." We would recommend that during the test the Gutzeit flask be *always* heated to 40 to 60° C. to ensure complete determination. In the Analar Standards (1934) a temperature of 40 to 60° C. is recommended, but no pre-reduction with sulphur dioxide is prescribed. Whilst this is satisfactory when the arsenic is present in the arsenious form, when arsenates are present low results are often obtained in the 40 minutes' heating unless pre-reduction is carried out, reduction by zinc and stannated acid being generally incomplete.*

One specially interesting case may be cited. A sample of commercial zinc chloride solution which by the direct test (without prior reduction) showed only 0·9 part of arsenious oxide per million, after reduction with sulphurous acid disclosed 15 parts per million.

CONCLUSIONS.—(i) When arsenic is present in materials in the form of arsenate, or when these materials have undergone an oxidation treatment which converts the arsenic from the arsenious into the arsenic form, before the ordinary Marsh and Gutzeit test is made, great risk occurs of under-estimating the arsenic present.

(ii) This is due to the relatively difficult reduction of arsenic acid to the arsenious form. Many samples of commercial zinc when dissolving in hydrochloric acid, even when "stannated" or in presence of a "few drops" of stannous chloride solution, fail to reduce arsenic acid completely to arsenious acid. This is true, even when the action is carried out at 40 to 60° C.

(iii) To ensure complete reduction it is usually necessary to carry out a pre-treatment with sulphurous acid, as described. Prior reduction with stannous chloride and potassium iodide, as in the A.O.A.C. method (1930), is also effective.

(iv) As many samples of AsT zinc evolve hydrogen slowly at the ordinary

* Special care, therefore, is necessary in testing the following materials in which the arsenic is present as arsenate:

(1) Oxidising agents, *e.g.* bromine, hydrogen peroxide, nitric acid, potassium chlorate, perchloric acid.
(2) Bases (fusion mixture, alkali hydroxides, carbonates and bicarbonates, magnesia, zinc oxide) which are dissolved in brominated hydrochloric acid.
(3) Hydrochloric acid (in testing which, evaporation with bromine water precedes the test).
(4) Potassium metabisulphite, sodium sulphite (with which a preliminary oxidation with chlorate and acid is carried out).

temperature, it is nearly always necessary to heat the reaction flask to 40 to 60° C. during the Gutzeit test, to ensure complete estimation of arsenic.

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The Composition and Examination of Tanganyika Arrow Poisons

BY W. D. RAYMOND, B.Sc., A.I.C.

(*Read at the Meeting, December* 4, 1935)

THE poisoned arrows used by the natives of Tanganyika are sometimes produced in Court as exhibits. Although they present an analytical problem of some interest and importance, no method for their examination, so far as I am aware, has been described.

The examination of botanical specimens and information collected during the past two years indicate that the arrow poisons of this territory are prepared from the following plants:—*Acocanthera longiflora* Stapf (the wood, and twigs); *Acocanthera friesiorum* Mgf. (the wood); *Strophanthus eminii* Asch. et Pax (the root); *Adenium coetaneum* Stapf. (the stems).

Other species of these genera occurring locally may be regarded as suspect. All the above plants contain glucosides which are generally classified pharmacologically as belonging to the Digitalis group.

The method of preparing the poison varies from simple extraction with water and subsequent concentration, to the observance of complicated rites, which are jealously guarded tribal secrets. The following description, due to Emin Pasha,[1] may be regarded as typical of the more complicated formulae: "The arrow poison is prepared by the learned man far from the village in the full secrecy of the forest. He cooks the pounded root bark of the trees called 'Bungo-bungo' and 'Mwelle-mwelle' together, and adds lizards, snakes' heads, snakes' teeth and other dismal ingredients thereto. . . . The rising vapours are very deadly. After some time the pot is removed from the fire, and the poison, which now forms a dark pulpy mass, is allowed to cool overnight." Although subsequent writers[2] have identified Mwelle-mwelle with *Acocanthera*, it would appear to be *Strophanthus eminii*, which identification was recently independently suggested by Braun.[3] Bungo-bungo is, perhaps, *Landolphia parvifolia*, which may be added to increase the adhesive powers of the resulting poison.

The prepared poison is a sticky black mass, and is applied to the barb of the arrow. As received, a single arrow usually yields from 1 to 5 g. of scrapings.

A portion of this is dissolved in water, and the turbid mixture is filtered. If a quantity of the filtrate equivalent to 50–70 mg. of the original poison is injected subcutaneously into the thigh of a healthy monkey, death occurs within a few minutes—usually within fifteen. The symptoms are slight vomiting, muscular spasms and dyspnoea.

The potency of the poison naturally varies according to the method of preparation, and various subsidiary ingredients are often highly esteemed for their reputed powers of enhancing the toxicity of the arrow poison. *Euphorbia* sp. and *Sapium madagascariense* have been reported as being employed in this manner. Death in human beings wounded by poisoned arrows is stated to occur within 30 minutes to two hours. The symptoms are not usually described, but one case, admitted last year to the Sewa Haji Hospital, Dar-es-Salaam, was under complete observation. In this case there was a clean superficial wound on the thigh, and the symptoms were shivering and slow action of the heart. Post-mortem the heart was flabby and full of blood, but with nothing to suggest the cause of death. Examination of this arrow showed the poison to be derived from *Acocanthera*.

Various attempts to isolate the active principle from the arrow poisons of this territory have been made. The varying nature of the results obtained are summarised in a table by Krause,[4] and it is only in recent years that Jacobs and his co-workers have elucidated the structure of strophanthin and ouabain. However, by working with material from the botanical sources named, it has been possible to distinguish between *Adenium*, *Acocanthera* and *Strophanthus*. The problem is more difficult than differentiation between ouabain, strophanthin and echujin, as will appear below.

The arrow scrapings (or the botanical material) are extracted at room temperature (27° C.) with 70 per cent. alcohol. The filtrate is treated with basic lead acetate in slight excess, and, after filtration, the excess of lead is removed by means of hydrogen sulphide. The filtrate is evaporated *in vacuo*, to remove the bulk of the alcohol, and extracted twice with an equal volume of chloroform, and the chloroform extract is filtered and evaporated to dryness on the water-bath. This forms residue *A*. The aqueous layer is evaporated *in vacuo* to a syrup, which is dissolved in methyl alcohol, and the solution is evaporated to dryness on the water-bath. The residue is re-dissolved in the minimum quantity of warm methyl alcohol, and the glucoside is precipitated by adding excess of ether. The glucosidal nature of this precipitate may be demonstrated by suitable tests. The precipitate, referred to below as *B*, is usually hygroscopic. The reactions obtained with *A* and *B* are set out in the accompanying table. Various other reactions were also examined, including (on residue *A*) those considered to be characteristic of cymarin (Legal's, Liebermann's and the diazo tests). They did not appear to offer any advantage over the reactions described.

Acocanthera and *Strophanthus* are differentiated by the tests on precipitate *B* (see Columns I, II and III in the Table) as follows:

(*a*) The difference in intensity between the colours with concentrated and 75 per cent. sulphuric acid. Some of the glucoside from *Strophanthus* roots gave only faint colours with either reagent.

(*b*) The absence of a violet colour with the phenol reagent.

(*c*) The different intensities of colours obtained with the resorcinol reagent. The glucoside from *Acocanthera* behaved like impure ouabain, but a total absence of colour with this reagent was not obtained.

TABLE I

COLOUR REACTIONS OBTAINED WITH MATERIAL FROM VARIOUS BOTANICAL SOURCES

	I (*a*) Wood of *Acocanthera friesiorum* (*b*) Twigs *Ac. longiflora* (*c*) Native arrow poison from (*a*)	II Seeds of *Strophanthus eminii* (de-fatted)	III Fresh roots of *Strophanthus eminii*	IV Fleshy twigs of *Adenium coetaneum*
TESTS ON RESIDUE A.				
Kiliani's test*	Brown or greenish ring. Acetic acid layer: green	Brown ring. Acetic acid layer: green to blue	As II	Crimson ring. Sulphuric acid layer fine crimson, lower portions tinged with violet
Concentrated hydrochloric acid	Slight or nil	Slight or nil	Slight or nil	Green
TESTS ON PRECIPITATE B.				
Concentrated sulphuric acid	Reddish-brown	Reddish-brown, changing to violet	As II, but fainter	Crimson, slowly fading
Sulphuric acid, 75 per cent.	Slight or nil	Ditto	Reddish-violet, changing to green	Faint reddish
Resorcinol (0·1 per cent.) in HCl (*a*) 27° C. for 10 mins. ..	Nil or very slight pink	Immediate red	Red	Nil or greenish
(*b*) 50° C. for 3 mins. ..	Pink or red	Red-violet	As II, but fainter	Pink or red
Phenol (1 per cent.) in HCl at 50° C. for 1 min. ..	Faint brown	Violet even in the cold	Violet, but fainter than II	Greenish
Concentrated hydrochloric acid	Brownish	Brownish	Brownish	Greenish

* *Note.*—Kiliani's test is made by introducing ferruginous sulphuric acid (100 ml. of concentrated acid plus 1 ml. of water containing 0·05 g. of ferric sulphate) into the test-tube so as to form a layer beneath a ferruginous acetic acid solution of the substance (100 ml. of glacial acetic acid plus 1 ml. of water containing 0·05 g. of ferric sulphate).

Adenium is easily recognised by the characteristic crimson colour obtained with residue *A* (see Column IV above). This finding is confirmed by the colour obtained with hydrochloric acid, but it has not been possible to distinguish clearly the roots of *Strophanthus* from *Acocanthera* by tests on this residue.

The difficulty experienced in dealing with the root material is of importance, since the native shows marked preference for roots in his selection of material for poisons and medicines. In connection with the possibility of the use of other species of *Strophanthus*, reference may be made to a paper by Smelt.[5]

Jacobs and Hoffmann,[6] in their studies on strophanthin, have found that K strophanthin β was hydrolysed quantitatively into glucose and cymarin by strophanthobiase of *Str. courmontii*. Successful attempts were made to apply this principle to the present problem. Strophanthobiase was prepared from the seeds of *S. eminii* by Jacob's method,[7] and the final dry enzymic powder was washed with chloroform. Portions of precipitate *B* were dissolved in methyl

alcohol, the solution was evaporated to dryness, and the residue was washed with chloroform. This residue, dissolved in water, was incubated at 37° C. for about two days* with strophanthobiase in the presence of a little toluene, a small amount of fresh enzyme being added after one day's incubation. Finally, the liquid was extracted with chloroform, the extract was separated, filtered and evaporated, and the Kiliani test was applied to the residue. Positive results were obtained with the root and seeds of *Strophanthus*, but not with *Acocanthera*. It was found that the same test distinguished clearly between strophanthin K and ouabain (both B.D.H.), and this is, perhaps, the best test for their differentiation. Possibly the principle could be applied to the quantitative determination of strophanthin.

The arrows so far examined have belonged mainly to the *Acocanthera* class, but a few have shown the reactions of *Strophanthus*. No *Adenium* arrow poison has yet been encountered, but no attempt to survey materials used by the various tribes has been made. It may be possible to carry out this survey later. The native sometimes displays considerable ingenuity in the use of his poisons. In a case, recently brought to my notice, prickly seed pods were coated with the poison and placed in the path of the victim, who, it was anticipated, would be barefoot. The attempted homicide failed.

I wish to acknowledge the valuable assistance received from Dr. Middleton and Mr. P. R. Bally in the collection of native information, plants and other material, and from Mr. P. J. Greenway of the East African Agricultural Research Station, Amani, in the identification of all the botanical specimens. Finally, I gratefully acknowledge the permission received from the Director of Medical Services, Tanganyika Territory, to publish this work.

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* Preliminary experiments indicate that enzymic hydrolysis takes place more rapidly at 55° C.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A SUBLIMATION TUBE FOR THE DETERMINATION OF BENZOIC ACID

In the determination of benzoic acid by the Monier-Williams method, the sublimation of the benzoic acid is carried out in a test-tube, the bottom portion of which is later broken off to separate the sand and other residue from the sublimate.

Some difficulty may be experienced in breaking off the end of the tube, and the sand may mix with the benzoic acid and *vice-versa*. This difficulty can be overcome by the use of the tube shown in the diagram.* This consists of two parts—a tube with socket-ending and a small flat-bottomed flask with cone, which fits accurately into the socket; these are standard joints.

For the evaporation of the ether-petrol solution in the water-bath, the joint is kept tight by means of a thin application of vaseline. After the benzoic acid has been finally washed down into the flask and the solution evaporated, the tubes are taken apart, and the vaseline is wiped off. Enough sand is added to cover the deposit in the flask (the flask may be filled with sand if necessary), the benzoic acid is sublimed, and the flask is then removed.

The paper may be weighed with the tube before and after sublimation, or removed after the sublimation. As the paper rests on the shoulder of the cone, it is rather difficult to insert a wire for the purposes of withdrawal. The paper can be removed, however, by burning a hole through the centre with a red-hot platinum wire, to permit of the introduction of a wire with a right-angle bend at the end.

After the weight of the benzoic acid has been obtained, the clean tube may be again attached to the flask, and the whole re-heated if there is any doubt whether all the benzoic acid has sublimed. The tube has the advantage also of known weight and constant diameter.

A satisfactory device for the air-oven is a cigarette tin, 50 size, with holes bored of a suitable size for the thermometer and tube, and provided with a metal support inside, the whole standing on a six-inch asbestos tray.

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* Made by Quickfit & Quartz, Ltd., Triplex Works, King's Norton, Birmingham.

Report of the Milk Products Sub-Committee to the Analytical Methods Committee

MILK PRODUCTS. REPORT No. 4

THE DETERMINATION OF WATER, OF TOTAL SOLIDS, AND OF FAT IN DRIED MILK

THE Sub-Committee was convened by the Standing Committee on Uniformity of Analytical Methods whose functions were later taken over by the Analytical Methods Committee of the Society; it consists of the following members:

Nominated by the Government Chemist: A. More, A.R.C.S., F.I.C.

Nominated by the London Chamber of Commerce: E. R. Bolton, F.I.C., M.I.Chem.E., A. L. Bacharach, M.A., F.I.C., and *Ir.* W. J. P. Pelle.

Nominated by the Manufacturing Confectioners' Alliance: T. Macara, F.I.C.

Nominated by the Society of Public Analysts and Other Analytical Chemists: E. B. Anderson, M.Sc., F.I.C., G. D. Elsdon, B.Sc., F.I.C., E. Hinks, M.B.E., B.Sc. F.I.C. (*Chairman*), E. B. Hughes, D.Sc., F.I.C. (*Hon. Secretary*), and A. E. Parkes, F.I.C.

This report deals with the determination of water, of total milk solids, and of fat in dried milk to which no other substance has been added.

The Dried Milk Regulations[1] prescribe that all tins or other receptacles of dried milk of a gross weight not exceeding 10 lbs. shall on sale or exposure for sale be labelled with a declaration stating (*a*) the description of the dried milk, namely, full cream, three-quarter cream, half-cream, or skimmed, and (*b*) the equivalent of the contents of the package in pints of milk of the declared description. Minimum limits for the percentage of milk-fat in the dried milk and minimum percentages of milk-fat and of milk-solids (including fat) in the milk on which the equivalent is based, are prescribed for each of the first four named grades of dried milk, and the minimum percentage of milk-solids other than milk-fat in the skimmed milk is also prescribed.

It is, therefore, necessary for the purpose of these Regulations to determine the percentages of milk-fat and of total milk-solids.

In dried milk to which no other substance has been added, the total milk-solids, like those of fresh milk or unsweetened condensed milk, consist (after removal of water by evaporation) of the dry residue, and it is immaterial whether the process be called the determination of water or the determination of total milk-solids. For commercial purposes, knowledge of the water-content of a dried milk is a common requirement, and, as dried milk is markedly hygroscopic, the percentage of fat may have to be critically interpreted in conjunction with the water-content of the dried milk at the time of the fat determination.

PART I

Determination of Water

It is well recognised that the determination of water in many organic materials is difficult. Particular difficulty arises with dried milk because in this material there may be free moisture and also water in combined form in hydrated lactose, hydrated salts and hydrated protein.

As the regulations concerning the labelling of dried milk require that the volume (pints) of milk equivalent to the contents of the container shall be stated, it becomes important that the method employed for the determination of the total milk-solids of dried milk should give these solids in a condition as close as is possible to that in which they are obtained in the analysis of fresh milk. Accordingly the Committee first examined the determination of the total solids

of the milk after reconstitution with water; next the method of distillation with liquids immiscible with water, *e.g.* toluol, as prescribed by the International Association of Milk Dealers[2]; and finally the method of direct drying (which is a commonly specified method).

The vacuum-drying method of the Association of Official Agricultural Chemists (*Official and Tentative Methods of Analysis*, 1930) requires a vacuum-oven fitted for the passage of dry air at a regulated pressure, but, as the necessary apparatus may not be generally available, this method was not studied.

A. DETERMINATION OF TOTAL SOLIDS BY DRYING OF RECONSTITUTED MILK

In order to make this method strictly comparable with that adopted for fresh milk (*i.e.* drying of 5 g. of milk), the quantity of dried milk taken should be in the neighbourhood of 0·5 g. This is a small quantity to take, since the loss on drying will generally be of the order of 0·02 g., with the result that a limit of accuracy of 0·0005 g. in the final weight will correspond to 0·1 per cent. of moisture; there is also the difficulty of ensuring that so small a quantity as 0·5 g. is a representative sample of the bulk of the dried milk. Nevertheless, when 1 or 2 g. was taken the concordance obtained was not so good as with 0·5 g.; if this method were to be used, the smaller weight would be the more suitable.

Many trials indicated that, when a dried milk is reconstituted, the conditions of evaporation have more effect upon the weight of dried residue obtained than is the case with fresh milk. Little difficulty is experienced with fresh milk (or with solutions of lactose) in obtaining the lactose in the anhydrous condition; vacuum-drying of fresh milk even at atmospheric temperatures (Hawley[3]) results in the lactose being obtained in the same condition as in fresh milk dried by evaporation at 100° C., but crystallised lactose monohydrate alone, when dried *in vacuo*, remains hydrated. On the other hand, if lactose solution is evaporated at temperatures near to 100° C., there is little difficulty in obtaining the lactose in the anhydrous condition. Some evidence was obtained that the length of time during which lactose is allowed to remain in solution has some effect upon the readiness with which the anhydrous form is obtained on evaporation.

With reconstituted dried milk, however, the temperature of evaporation has a more marked effect on the weight of dried residue. In view of the results (referred to above) obtained with fresh milk and with lactose, it would appear that the difficulties encountered may be attributed, at any rate in part, to different states of hydration of the protein. Numerous trials established the fact that, in order to ensure that all the water is removed, the conditions of evaporation have to be carefully controlled. Maintaining the mixture of milk and water at a high temperature for some time before evaporation, and evaporation under a guard (*e.g.* an inverted funnel over the dish), in order to prevent local cooling by draught previous to the final drying in the oven at 98°—100° C., gave the minimum percentage of total solids. Satisfactory concordance between analyses by members of the Committee was not, however, always attained, and the simpler method, C, described later (direct heating of the dried milk at 102—103° C.), which gives results of the same order, is recommended for general use.

A higher water-content was obtained if the residue after evaporation was dried at a temperature of 102—103° C., but (contrary to the experience with direct drying) at this temperature the solids sometimes failed to attain constant weight within a reasonable time, probably owing to decomposition.

B. DIRECT DETERMINATION OF WATER BY DISTILLATION WITH IMMISCIBLE SOLVENTS

This is the principle of the Brown Duvel[2] Moisture Tester and also of the method specified by the International Association of Milk Dealers in its Laboratory Manual.

The method should, on general grounds, give good results. The Committee have confirmed the fact that lactose hydrate, distilled with benzene and toluene, yields all its water.

Experimental difficulties leading to inaccuracy of results were, however, encountered. During distillation traces of solid matter tend to be carried over with the distillate and so prevent perfect separation of the water in the capillary measuring tube, thus making impossible an accurate measurement of the small volume of water. Attempts were made to effect improvement; thus different liquids were tried, for example, toluene, xylene, heptane, tetrachloroethylene; the heating was made more regular by the use of a paraffin-wax bath, and also modification was made in the form of the graduated receiver. None of these proved satisfactory in overcoming the difficulties. To ensure complete evolution of the water, the time of distillation had to be extended up to several hours. In consequence, the method was considered unsuitable. Moreover, it is not considered advisable to specify a method which requires a large amount of the sample for the test.

C. DETERMINATION OF WATER BY DIRECT DRYING

Most of the published methods for the determination of the moisture-content of dried milk specify simple drying at 100° C. or in the water-oven.

This method gives satisfactory results with dried milk of comparatively low water-content, but with dried milk which has absorbed water on exposure it yields low results, the water not being all removed at this temperature; raising the temperature of drying to 102°—103° C. resulted in complete drying being attained. As a result of their tests the Committee conclude that simple drying of a sample of dried milk at this temperature (102—103° C.) gives as true and as consistent a representation of the water-content (or milk-solids), as does the method of reconstitution and evaporation (method A), and they accordingly recommend this method of direct drying described later. It was found that approximately 1 g. is the most suitable quantity to be taken for this determination.

During the course of this work, in order to obtain for purposes of testing milk powders of varying moisture-content, dried milk of high moisture-content was artificially prepared by exposing the powder in a humid atmosphere. It is known that milk powder absorbs moisture irregularly and that it is not possible to obtain perfect distribution of water throughout a bulk of milk powder so treated.[4] To this the Committee attribute their inability always to obtain, with dried milks of high moisture-content, results as concordant as with those of lower moisture-content.

The following results were obtained by members of the Committee from samples both of Roller Process Powders and Spray Process Powders.

Direct drying at 102–103° C.

	Sample 18 (Spray process)	Sample 19 (Spray process)
	5·53	2·68
	5·43	2·74
	5·48	2·87
	5·23	2·48
	5·41	2·55
	5·40	3·01
	5·62	2·61
	5·45	
Mean	5·44	2·71
Standard deviation	0·11	0·19

	Sample 20 (Roller process)	Sample 21 artificially moistened (Roller process)	Sample 24* (Roller-process "sweetened 10 per cent. fat" powder)
	2·89	8·10	3·04
	2·89	7·89	2·90
	2·84	7·58	3·29
	2·88	7·58	2·82
	2·98	8·21	3·00
	2·87	8·01	2·90
	2·81	8·06	3·00
	2·74	8·51	2·81
	2·98		
Mean	2·88	7·99	2·97
Standard deviation	0·08	0·31	0·15

METHOD OF DETERMINATION

PREPARATION OF SAMPLE.—The whole bulk of the dried milk should be transferred to a dry stoppered bottle of a capacity about twice the volume of the sample and then intimately mixed by rotating and shaking.

DISHES.—These should be of metal (aluminium is suitable) with close fitting but easily removable lids; diameter 2 in. approximately and depth 1 in. approximately.

PROCEDURE.—Uncover the dish, and place dish and lid in the oven at 102–103° C. for 1 hour. Place the lid on the dish, remove from the oven, cool in a desiccator for 30 minutes and weigh.

Transfer approximately 1 g. of the well-mixed sample to the dish, cover with the lid, and weigh accurately and rapidly.

Remove the lid, place both dish and lid in the oven and maintain at 102–103° C. for 2 hours.† Replace the lid, remove from the oven, and allow to cool in the desiccator for 30 minutes; weigh.

In the same manner heat again in the oven for 1 hour and repeat this process until the loss of weight between successive weighings does not exceed 0·0005 g. (generally, drying is complete at the end of the first two hours).

The maximum loss of weight found is the weight of water in the quantity of sample taken, and the percentage of total solids is 100 minus the percentage of water thus found; where the sample consists of a dried milk to which no other substance has been added, these solids will be the total milk-solids including fat, mentioned in the Dried Milk Regulations.

NOTES.

1. *The Drying Oven.*—Particular attention should be paid to temperature-control and ventilation of the drying-oven. As the prescribed temperature is above 100° C., it is presumed that electric drying-ovens will be generally used.

Adequate ventilation should be ensured, and the analyst should ascertain that the milk is actually being dried at the temperature registered by the oven thermometer; for this purpose the thermometer is preferably to be immersed in a dish of mercury or heavy oil. The oven should be tested for ventilation, which should be such as to prevent both stagnant areas and local cooling by the entry of cold air. Neither dish nor thermometer should be close to the sides, top or bottom of the oven, and direct contact of the dishes with metal shelves should be avoided.

† With samples of high moisture-content the first heating may be advisably extended to 3 hours.

2. *Desiccators.*—Attention is directed to the importance of efficient desiccators.

PART II

Determination of Fat

This determination need present no serious difficulty. Either of the well-known methods—the Werner–Schmid or the Röse-Gottlieb—can generally be employed satisfactorily, though the former is apt to result in some degree of decomposition, giving ether-soluble decomposition products, and is, for this reason, unsuitable for sweetened dried milk; the latter tends to give a somewhat low result, particularly with stale dried milk.

The method recommended is an acid extraction method,[5] and is fully described later. This method is rather more lengthy and necessitates the use of larger quantities of solvents than either the Werner–Schmid or the Röse–Gottlieb method, but it is applicable to sweetened as well as to unsweetened dried milk (spray process or roller process), and the Committee recommends its use as a reference method.

The following results were obtained by members of the Committee using the process prescribed:

	Spray process		Roller process	
	Sample 11	Sample 22	Sample 10	Sample 23
	27·20	26·88	26·68	27·00
	27·17	27·15	27·15	27·28
	27·05	26·84	27·17	27·26
	27·01	26·67	26·92	27·04
	26·81	26·74	26·89	27·02
	27·17	26·81	26·69	27·20
	27·17	26·91	26·78	27·30
	26·75	26·90	26·86	27·03
	27·22	27·06	27·16	
			26·82	
Mean	27·06	26·88	26·91	27·14
Standard deviation	0·17	0·15	0·19	0·13

	Roller process "sweetened 10 per cent. fat" powder	
	Sample 12*	Sample 24*
	10·26	10·87
	10·54	10·84
	10·18	10·69
	10·38	10·64
	10·20	10·63
	10·59	10·49
	10·45	10·57
	10·25	10·90
		10·69
Mean	10·36	10·70
Standard deviation	0·16	0·14

* Although this report is not intended to deal with sweetened dried milk, these analyses are given to indicate that the presence of sucrose does not interfere with the recommended methods. Samples Nos. 12 and 24 were dried milks containing nominally 10 per cent. of fat and 10 per cent. of sucrose which had been added before drying. An unsweetened dried milk which gave 27·70 per cent. of fat when no sucrose was present, gave 27·74 per cent. when 10 per cent. of sucrose was added to the weighed portion of the sample taken for the analysis.

METHOD OF DETERMINATION

REAGENTS.—*Hydrochloric Acid.*—Sp.gr. 1·16.

Concentrated Ammonia Solution.—Nominal 0·880.

Alcohol or Industrial Methylated Spirit.—About 95 per cent. by volume.

Ether (Methylated).—Sp.gr. 0·720.

Petroleum Spirit.—Boiling between 40° and 60° C.

These reagents should leave no appreciable residue on evaporation.

Preparation of Sample.—See under "DETERMINATION OF WATER."

PROCEDURE.—Transfer to a hard glass boiling-tube (8 in. by 1 in.) (*Note* 1) approximately 1 g., accurately weighed, of the well-mixed sample; add 8 ml. of water and 2 drops of the ammonia solution. Gently boil the mixture until all lumps are disintegrated. Add 10 ml. of the hydrochloric acid, and heat in a Bunsen flame with gentle agitation; after the liquid begins to boil, continue gentle boiling for 3 minutes. Cool; add 10 ml. of the alcohol, and mix well. Add 25 ml. of ether, close the tube with the water-moistened stopper (*Note* 2), shake well for 15 seconds. Cool (*Note* 3), remove the stopper; wash the stopper and the neck of the tube with petroleum spirit, and add, including the amount in the washings, 25 ml. of petroleum spirit. Replace the re-moistened stopper, shake vigorously for 30 seconds, and either allow the tube to stand or whirl in a centrifuge until the two layers of liquid are completely separated.

Transfer the ethereal layer as completely as possible to a suitable flask by means of a siphon or wash-bottle fitting. Wash the tip of the siphon-tube (into the flask) with ether; disconnect the siphon-fitting and wash down the inside of the extraction-tube with 5 ml. of ether; without further shaking, siphon off this ether, and wash the tip of the fitting as before.

Add 15 ml. of ether to the extraction-tube, using this ether to wash the cork and inner limb of the siphon-fitting before its removal. Replace the freshly-moistened stopper; shake for 15 seconds; add 15 ml. of petroleum spirit and shake for 15 seconds, taking the same precautions as to washing the neck and stopper as before. When the ethereal layer has separated transfer it to the flask as before.

Repeat the extraction with 15 ml. of ether and 15 ml. of petroleum spirit and the transference of the ethereal layer to the flask as in the last paragraph, and wash the tip of the siphon-tube.

Cautiously distil the solvents from the flask, and then dry the residual fat at 102° to 103° C. for 1 hour, removing all solvent vapour from the flask at the early stages of the drying by blowing air gently into the flask. Cool and weigh. Repeat the heating until there is no loss in weight.

Completely extract the fat from the flask by repeated washings with petroleum spirit, allowing any sediment to settle before each decantation, and washing off any fat which may have crept over the edges of the flask during the removal of the fatty solutions (*Note* 4). Dry the flask at 102° to 103° C., with removal of solvent vapour, cooling and weighing as before.

The difference in weight before and after the petroleum spirit extraction is the weight of fat contained in the quantity of dried milk taken for analysis, uncorrected for the blank.

Make a blank determination, using the specified quantities of reagents and distilled water, and deduct the weight found, if any, from the weight of fat obtained.

NOTES.—The success of the method depends upon close attention to detail.

(1) The use of a boiling tube, into which the dried milk is introduced and in which it is dissolved, avoids the possibility of loss during transference such as may occur when the milk is digested in one vessel and transferred to another vessel for extraction. A narrow neck to the boiling-tube permits the use of a small stopper for closing the tube and for the wash-bottle fitting. A funnelled

mouth facilitates the introduction of the sample into the tube, and has the additional advantage that any trace of solution which may pass the stopper, when it is released, is retained in the funnel and can be readily washed back into the tube. Funnelled tubes, with or without ground-glass stoppers, as in Fig. 1, have been found useful by members of the Committee.

(2) Sound well-fitting corks only should be used if the glass-stoppered tube is not available. Rubber bungs are not suitable. The stopper or cork should be moistened with water before insertion for each extraction.

(3) Before each operation of removal of stopper or cork a slightly reduced pressure in the tube should be induced by cooling, in order to avoid spurting of the solvent.

(4) The non-fatty residue carried over with the ethereal solutions should be very small. Difficulty lies in preventing the flotation of this residue in the petroleum spirit in the final operation. The addition of a few drops of water to the ethereal liquid before distilling off the solvents is of service in concentrating this non-fatty substance, if any, into a small compass and causing it to adhere to the flask.

Weighing the Fat and Flask.—The conditions of weighing the flask when containing the fat and after its re-solution should be strictly comparable, *i.e.* as to time of standing in desiccator or balance case or other treatment of the flask. Any trace of solvent vapour should be removed from the flask by a current of air.

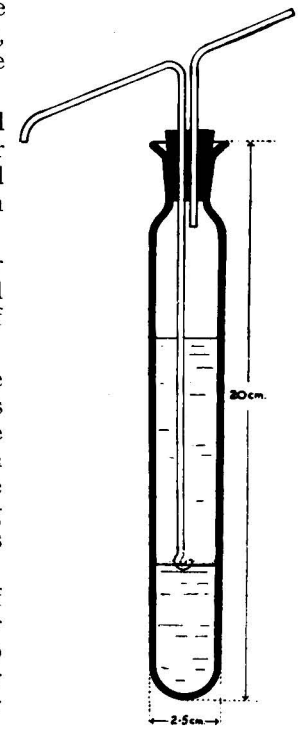

Fig. 1

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For and on behalf of the Sub-Committee

(*Signed*) E. HINKS (*Chairman*)
E. B. HUGHES (*Hon. Secretary*)

23*rd December*, 1935

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

MERCURIAL OINTMENT AND MERCURY OINTMENT

ON January 10th a firm of druggists was summoned by the Poplar Borough Council at the Thames Police Court for selling mercury ointment not of the nature, substance and quality demanded.

Mr. C. Hay Rickett, for the Council, said that one shillingsworth of mercury ointment was purchased, and that, when analysed, it was found to be deficient in mercury to the extent of at least 65 per cent.

Evidence was given by an assistant to the food and drugs inspector that, after the purchase had been made, he drew the manager's attention to the fact that the box was marked "Mercurial Ointment," whereas mercury ointment had been demanded.

In cross-examination the witness said that he would not dispute the fact that the manager had never been asked for mercury ointment by a member of the public, or that there was a steady sale in the neighbourhood for blue ointment or mercurial ointment.

The manager said that he never sold mercury ointment, except on a doctor's prescription, but he sold a good deal of mercurial ointment under the name of blue ointment. Mercury ointment was very strong and, if used by an unskilled person, might cause blistering or a rash.

In cross-examination the witness admitted that he had supplied something weaker than he had been asked for, but with the best intentions.

The Magistrate (Mr. John Harris) intimated that he was of opinion that the manager had made an honest mistake, but mercury ointment had been asked for, and mercurial ointment given.

Mr. Glyn-Jones (for the defence), however, submitted that, according to Section 4 of the Food and Drugs (Adulteration) Act, 1928, he had an answer in law. That Section provided that a person could not be guilty if the substance demanded were mixed with some non-injurious constituent, not calculated to increase the weight or bulk, and if, at the time of delivery, he supplied to the person receiving it notice by means of a legible label showing that it was mixed. That had been done by the manager, for it was admitted by the prosecution that the box was marked "Mercurial Ointment." The mercury ointment had been mixed with lard deliberately and not fraudulently, and the fact had been stated on the box in which it was served. Therefore, he submitted, it was a proper case for acquittal under Section 4. The manager did what 99 out of 100 customers would want him to do, and, if he had supplied mercury ointment, the defendants would probably have had to meet a claim for compensation because the ointment was too strong and had caused damage to the person using it.

The Magistrate said that, in his opinion, Section 4 of the Act, to which Mr. Glyn-Jones had drawn his attention, did not apply in this case. He thought that it applied to such things as coffee, which could be mixed with chicory, or butter, which could be mixed with margarine, not to such substances as ointments. It was not a mixed article that had been supplied, for every article of the nature was, in a sense, mixed, for they were compounds. There had to be a conviction, because one particular drug was asked for, and another was supplied. He did not, however, think that any fraud was intended, and the case would be dismissed under the Probation of Offenders Act, on payment of three guineas costs.

Department of Scientific and Industrial Research

BUILDING RESEARCH BOARD

REPORT FOR THE YEAR 1934*

THE present report, which contains 171 pages, gives a general outline of the progress of the work during the year by the Director, Dr. R. E. Stradling, followed by a detailed account of the general research and special investigations undertaken by the Board. Among the subjects discussed are the following:

WEATHERING QUALITY OF BUILDING STONE.—It is claimed that by the application of simple tests it is possible to determine the quality of samples of Portland stone. The desirability of some form of control of the output of the quarries is demonstrated by the occurrence of the inferior type of Portland stone in structures of recent date. Decay in such stone becomes noticeable in five or six years, and reaches an advanced stage in twenty-five years. Judging by results relating to quarries that have been systematically sampled, there is justification for the belief that the beds of quarries are sufficiently constant to warrant the application of tests to classify the various tiers in the several quarries in terms of their relative qualities.

STONE PRESERVATIVES.—The evidence cited indicates that in the relatively few instances in which the application of preservatives appears to have had a protective effect, there is no assurance that the treated and untreated stones were similar in character. Lack of visible alteration following preservative treatment does not necessarily imply that the treatment has been beneficial. In some places in a building experimentally treated in 1923 there was a thin, hardened skin on the surface of the stone, but, as a rule, this had blistered and rubbed off, leaving a thin layer of powdery stone beneath it. Observations of the effects of stone-preservative treatment of decaying buildings must be accepted with great caution, and it cannot be too strongly emphasised that stone of sound quality needs no preservative.

ATMOSPHERIC POLLUTION.—Comparative estimations of the "activity" of atmospheric sulphur gases by the lead peroxide and volumetric methods (ANALYST, 1933, **58**, 284) have shown that there is good correlation between the two methods. Activity, as measured by the lead peroxide gauges, may be considered to give a good indication of the relative level of pollution, and at the same time to afford a measure of the corrosive effects of the polluted atmosphere on building material, such as limestone.

A rough figure for the rate of sulphate deposit may be taken as represented by an addition of between 2 and 3 g. of ammonium sulphate per year on an area of 100 sq. cm. Presumably these sulphates have a contributing effect in causing decay.

Chlorides in Portland Stone.—Further instances of unusually rapid decay in Portland stone associated with the presence of chlorides have come to notice, and inquiries reveal that the possible consequences of chloride contamination are being widely recognised.

Crystallisation Test.—Sufficient progress has been made in an investigation into the principles of the test to warrant the hope of its complete standardisation. In order to obtain reproducible results, much will depend on the amount of anhydrous salt deposited during evaporation of the specimen after being soaked in a solution of determined concentration, and on the temperature at which re-hydration is made to take place.

* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. 1935. Price 3s. 6d. net.

Relation of Micro-organisms to the Decay of Stone.—It has been shown that scrapings from sound stone are as likely to carry sulphur-oxidising organisms as those from decaying stone. In the light of the information at present available, from investigations extending over a period of 10 years, there is no evidence that the presence of sulphur bacteria is related to the sporadic incidence of decay.

ASPHALTS AND BITUMENS.—A scheme of co-operative research has been arranged with the Natural Asphalte Mine-Owners and Manufacturers Council. Immediate work is being directed to the study of the physical characteristics and weathering properties of several types of mastic. In an investigation to ascertain the effect of repeated washing with water on bituminous films, it was found that there was no progressive breakdown of the film, for the reduction of the surface tension caused by contact with the film became inappreciable after five or six washings.

CEMENT.—Work on general problems relating to cement has made steady progress during the year. It is now possible to show, from an analysis of the results of the phase-equilibrium work, that the maximum amount of lime which can be combined under clinkering conditions in a mix of CaO, Al_2O_3, SiO_2, Fe_2O_3 of Portland cement composition is given by the formula:

$$\text{Maximum CaO} = 2{\cdot}80SiO_2 + 1{\cdot}18Al_2O_3 + 0{\cdot}65Fe_2O_3$$

Determination of Free Lime in Fresh Cement.—The only method of those studied which has been found to have any advantage over those previously described is that of Schläpfer and Bukowski (*Eidgenössische Material-prüfungsanstalt in Zurich*, Ber. No. 63, 1933), in which ethylene glycol is used as the extracting agent. The method has been found satisfactory for fresh cements, and to be more rapid and convenient than glycerin methods.

CALCIUM SULPHATE POWDERS.—X-ray work has confirmed previous conclusions and has shown that three distinct structures exist, *viz.* (i) that of gypsum, (ii) the hemihydrate type, and its dehydration product, soluble or α-anhydrite, (iii) that of natural anhydrite, and β-anhydrite (*i.e.* insoluble anhydrite, "hard-burnt" or "dead-burnt" plaster.

Corrosive Action of Calcium Sulphate Powders.—It has been found that a very small proportion of free lime, so long as it remains uncarbonated, will inhibit for long periods the corrosive effect of calcium sulphate powders on iron lathing.

FIRING OF CLAYS.—Work on the influence of firing conditions on the formation of soluble salts has been extended. It has been found that the sulphates of magnesium and sodium are the most dangerous salts from the point of view of the durability of the brick, and if they are present in appreciable amounts, a kiln temperature of at least 1000° C. is essential.

Crystallisation Tests of Bricks.—If the conditions are standardised, the crystallisation test can be made to give concordant results. Half-bricks give results comparable with those obtained with whole bricks, and it is advantageous to make two tests concurrently. In one, a weak solution is used to indicate the nature of the decay, and in the other a stronger solution to give measurable results within a measurable period.

CONTROLLING THE HUMIDITY OF AIR IN ENCLOSED SPACES.—A method suitable for use in enclosed spaces, such as containers, picture frames and rooms has been devised (B.P. 396,439). All entrant air is made to pass over a mixture of dry salts, either an anhydrous solid and its solid hydrate, or two solid hydrates of the same salt. At 60° F. the hepta- and hexa-hydrates of zinc sulphate, $ZnSO_4.7H_2O$ and $ZnSO_4.6H_2O$, for example, are in equilibrium with an atmosphere of relative humidity 55 per cent. In air drier than this some of the heptahydrate dissociates, giving up moisture and forming more hexahydrate, whilst if the humidity rises some of the hexahydrate takes up water from the air and forms

more heptahydrate. It is believed that the most important application of the method will be found in the preservation of valuable pictures, manuscripts and museum exhibits.

STRUCTURE AND STRENGTH OF MATERIALS.—This, the second part of the Directors' Report (pp. 68–128) gives an outline of the investigations carried out on various materials, including concrete and brickwork, and the measurement of existing stresses in masonry structures. Part III (pp. 128–141) deals with the study of the efficiency of buildings from the standpoint of the user. The subjects discussed include measurement of the rate of air change, heat requirements of a house, economy in factory heating, exclusion of solar heat, and dew collection on roofs.

INTELLIGENCE AND MINOR INVESTIGATIONS.—During the year the number of enquiries and special investigations increased to 2089. Among these were problems relating to the acoustics of buildings, asbestos cement products, bituminous materials, cast stone, cements, flooring, paints and waterproofing materials, and wallboards. Details are given (pp. 142–162) of some of the more important or interesting of these problems.

Home Office

CARBON BISULPHIDE

PRECAUTIONS AGAINST DANGERS OF POISONING, FIRE AND EXPLOSION*

CARBON disulphide (bisulphide) (b.p. 46° C., flash-point below −20° C.) has a very low auto-ignition temperature (125°–135° C.), so that even contact with a warm steam pipe may cause ignition of the vapour. The minimum explosive mixture in air is 0·063 g. per l. or 19 vols in 1000.

EFFECTS ON HEALTH.—The concentrations for acute effects are as follows:

Physiological response	Carbon disulphide in air p.p.m.
Slight symptoms after several hours' exposure	322 to 386
Maximum concentration that can be inhaled for 1 hour without serious disturbance	483 to 807
Dangerous after 30 minutes to 1 hour of exposure ..	1150

Exposure of several hours a day to concentrations lower than those given in the table soon leads to chronic poisoning (cf. *Noxious Gases*, Henderson and Haggard, 1927).

Inhalation of small quantities of the vapour over some weeks or months produces chronic effects, the first of which are nausea, headache and giddiness, characteristic odour of the breath, facial pallor, and pale and flabby tongue. Continued exposure produces mental disturbance with impaired memory and depression. Other signs of chronic poisoning are muscular weakness, tremor, loss of sensation and optic neuritis, and (in severe cases) paralysis. In advanced cases permanent effects may remain after removal of the subject from the toxic vapour. In acute poisoning symptoms of acute mental disturbance and sometimes of acute mania occur.

* Memorandum, Form 836. Factory Department, Home Office. November, 1935. H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 3d. net.

PREVENTION OF POISONING.—The preventive measures adopted are: (1) Efficient exhaust ventilation; (2) alternation and limitation of employment; (3) periodical medical examination of workers exposed to the vapours.

STORAGE AND PIPE CONVEYANCE.—A description is given of several safe methods for storing and conveying carbon disulphide. Tanks that have contained carbon disulphide should be cleansed with repeated charges of hot caustic soda solution—followed by hot water washes, and finally allowed to stand for several days before any worker is allowed to enter them. The use of an aluminium scraper for the removal of sludge is advised, and aluminium spanners are also recommended to avoid risk of striking sparks. As such sludge contains iron sulphide which in the dry state may become incandescent, it should not be dealt with except in the wet state.

NOTIFICATION.—Since carbon disulphide poisoning was made compulsorily notifiable in 1924 there have been 18 cases notified, *viz.* artificial silk works, 9; viscose paper works, 4; indiarubber works, 3; and manufacture of carbon disulphide, 3.

USE IN MANUFACTURE.—For information of methods of ventilation see Home Office Welfare Pamphlet, No. 5, "Ventilation of Factories and Workshops."

The use of carbon disulphide in any process of indiarubber manufacture is subject to certain requirements of the Indiarubber Regulation, 1922. Statutory Rules and Orders, No. 329.

PRECAUTIONS AGAINST FIRE.—Ordinary safety lamps which may have been certified for use in mines are not necessarily safe in atmospheres containing carbon disulphide. Extinguishers of (*a*) the foam type, or (*b*) those containing either carbon tetrachloride or methyl bromide are effective.

Under Regulation 27 of the Electricity Regulations (Statutory Rules and Orders, 1908, No. 1312) all conductors and apparatus exposed to inflammable surroundings must be so constructed as to prevent danger. Where carbon disulphide is used or stored, special precautions (described here in detail) are advisable.

TRANSPORT.—The Petroleum Acts have been applied to carbon disulphide by Statutory Rules and Orders, 1926, No. 1422, and the Regulations for its conveyance are contained in the Bisulphide of Carbon (Conveyance) Regulations, 1935 (S.R. & O., 1935, No. 583).

Hong Kong

REPORTS OF THE GOVERNMENT ANALYST FOR THE YEARS 1933 AND 1934

IN these Reports the Government Analyst (Mr. V. C. Branson) and the Acting Government Analyst (Mr. A. Jackson) lay stress upon the inadequacy of the amount of work done under the Food and Drugs Ordinance. For a Colony of the size of Hong Kong not less than 3000 to 4000 samples per annum should be examined, whereas the numbers in 1933 and 1934 were 104 and 139, respectively. The fact that in the former year only 3 samples (of milk) were found to be adulterated does not represent the amount of adulteration, since the samples are almost invariably taken by the sanitary inspectors in uniform, and usually they are taken on one day in each quarter.

LACHRYMATORY CARTRIDGES.—Cartridges, forming an exhibit in a case of armed robbery, were found to contain a lachrymatory substance. These cartridges could be fired from an ingenious pistol shaped like a fountain pen.

DETECTION OF ALCOHOL IN THE URINE.—In a murder trial it was alleged that the accused had taken alcohol prior to the crime; examination of a sample of his urine, taken shortly after the crime had been committed, showed that alcohol was present.

TOXICOLOGICAL CASES.—Ninety-one toxicological examinations were made in 1933 and 135 in 1934. In the former year there were 17 cases of opium poisoning, and in 1934, 26 cases. During the later months of 1933 there were 11 cases of lysol poisoning, and in 1934 there were 22 cases.

Gelsemium elegans Benth., a well-known Chinese poisonous herb, was used in two cases in 1934. This was the first instance of poisoning by this plant since 1929. Apparently in each case the deceased had chewed the leaves.

FUMIGATION WITH HYDROCYANIC ACID.—A small fumigation chamber has been constructed, and work is in progress to ascertain whether it is possible to deal with flour imported into the Colony on similar lines to those adopted by the Naval Authorities, who fumigate every batch of flour before issuing it to ships. This work is being done in consequence of the discovery of thousands of sacks of weevil-infested flour stored in the Colony.

Books and documents for the Law Courts and Colonial Secretary's Office have also been fumigated. Fumigation with hydrocyanic acid appears to be successful in keeping down the attacks of insects on books, and is cheaper and quicker than varnishing with a protective paint.

Mauritius

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1934

THE work of the Government Laboratory, under the direction of Mr. J. A. R. Stoyle, B.Sc., A.I.C., comprised routine services for the Medical and Health, Public Works, and the Police and Customs Departments. For the Public Health Department 471 samples of food and drugs and of water were examined, including 285 of fresh milk, 174 of water, 4 of butter, and 3 of medicinal tinctures, etc.

MILK.—Seventy-three of the 285 samples of milk were skimmed and 87 contained added water, 11 had been boiled, 2 contained sucrose, and 2 formalin. On August 4th the Milk Trade Regulations, 1934, came into force and raised the legal limit for milk-fat in fresh milk from 2·5 to 3·0 per cent. by vol. at 20° C. As the new figure more nearly approaches that for milk-fat in normal Mauritius milk, the raising of the limit has resulted in a sensible reduction in the practice of lightly skimming fresh milk before sale, which was formerly much in vogue.

It was suspected that the milk supplied to a Government Hospital was adulterated with banana sap, and a satisfactory test was devised which would detect less than 0·1 per cent. of the sap.

CLASSIFICATION OF VEGETABLE FIBRES.—True hemp (*Cannabis sativa*) is taxed for customs purposes at a much lower rate than other fibres, including other kinds of hemp. Samples of silk fabric and hemp cordage were submitted to microscopical and chemical examination for classification.

Palestine

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1934

IN his Annual Report the Government Analyst (Mr. G. W. Baker, F.I.C.) gives a summary of the work undertaken for different Government Departments, including advisory work for Customs, Excise and Trade. Laboratory demonstrations have been arranged as part of a C.I.D. course for the Police.

The number of samples of food examined for the Health Department was 10,933, including 3831 of milk, 2229 of edible fats and oils, and 146 of coffee. New legislation, consolidating and amplifying existing laws and giving power to impose regulations as to composition and labelling, has been drafted.

ADULTERATION OF OLIVE OIL WITH ARACHIS OIL.—Forty-three of 56 adulterated olive oils and 12 adulterated sesame oils were found to contain arachis oil. This is now the chief adulterant of the indigenous oils; it is pressed locally from imported nuts.

COMPOSITION OF "ARAK."—Under the Intoxicating Liquors Ordinance of 1927 "Arak" means spirits made from fruit and the aniseed plant by distillation, and is subject to a lower excise duty than other spirits. There has been evidence, however, that sometimes so little aniseed has been used that the resulting liquor could be readily converted into "Cognac" or other forms of spirit normally subject to a higher duty. It has therefore been necessary to add the proviso that the addition of water to the arak shall produce a marked opalescence. In practice, it has been found that the degree of opalescence due to the anise oils is influenced by the alcoholic strength and temperature, and, in order to have a uniform method of approximate measurement, Excise officers have been provided with sealed glass tubes containing liquor showing a standard minimum opalescence.

PALESTINE HONEY.—In 90 samples of local honey of known origin the natural sucrose-content has been found to range from 0·6 to 6·2 per cent., with an average of 3·2 per cent.

IDENTIFICATION OF HASHISH.—Two specimens sold as hashish were found to consist solely of henna. The police now employ Beam's test as an aid in their investigations, and the fact that petroleum spirit washings from a "Nargileh" ("hubble-bubble" pipe), in which hashish has been smoked, react to the test, has been of considerable value (*cf.* Lucas, ANALYST, 1933, **58**, 602).

CATTLE POISONING.—In 33 cases of suspected criminal poisoning of animals arsenic was found in 22 specimens. The poisoning of animals is a favourite form of revenge, especially in the Nablus and Jenin areas. White arsenic and the artificial sulphide, generally concealed in figs, are used.

SALINITY OF JORDAN WATER.—The degree of salinity tolerated by citrus would appear to depend upon factors, many of which require investigation. A preliminary survey in the Jaffa area has shown that in 18 groves, which have apparently been cultivated successfully for periods ranging from 20 to 80 years, the chloride-content of the irrigation water (expressed as chlorine) varies from 52 to 324 p.p.m. In 5 of these groves the salinity exceeds 200 p.p.m. Pending further knowledge on the subject, there appears to be some support for the opinion that, with good drainage, anything under 250 is likely to be tolerated by citrus, whilst 250 to 350 may be classed as risky, and anything above that as definitely dangerous to citrus. With regard to irrigation with Jordan water it is worthy of note that the salinity of the river between the southern end of Lake Tiberias

and the Allenby Bridge at Jericho is from 300 to 400 parts per million, whilst at the northern end of Lake Tiberias it is only 20 parts per million. The salinity is therefore derived from the Lake. Irrigation with Jordan water on low-lying land south of the Lake has resulted in adverse conditions. Bad drainage and rapid evaporation have, it seems, concentrated the salts of the Jordan water and also brought to the surface salt from underground sources.

Western Australia

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1934

IN Western Australia the examination of food and drugs and toxicological work are undertaken by a branch of the Mines Department (Government Analyst, Dr. E. S. Simpson). The total number of samples examined during the year was 726, of which 120 were toxicological exhibits, 56 were samples of human milk, and 36 of cows' milk.

TOMATO SAUCE ADULTERATED WITH STARCH.—A "tomato chutney sauce" and a "tomato sauce" were found to be adulterated with starch. Three other tomato sauces were condemned, one containing benzoic acid, another apple pulp, and a third both of these prohibited substances.

CRUDE FIBRE IN COCOA PRODUCTS.—The Food Standard Advisory Committee recommended that the allowable percentage of crude fibre in cocoa products should be raised from 6⅓ to 7 per cent. Regulation 36 (2) was amended accordingly and gazetted on August 11th.

"JELLY CRYSTALS."—Samples of "jelly crystals" (mixtures of gelatin, sugar, citric acid and essences in proportions ready for use) were submitted with tenders for Government contracts, but, as all proved unsatisfactory, the following specification was prepared and adopted by the Tender Board:

> "Jelly crystals, assorted, in packets to make one pint, best local. Gelatin-content to be not less than 19 per cent., and liquefied mixture to set firmly on standing overnight at 18° C. (64° F.). To be of full and true flavour, containing not less than 4 oz. of approved flavour in every 56 lb. of mixture."

BARIUM SULPHATE FOR X-RAY PHOTOGRAPHY.—Several samples of barium sulphate were examined to see whether they were safe to use as opacifiers for X-ray photography of the digestive tract. All but one were free from barium or lead compounds soluble in dilute acetic acid, but one contained an appreciable trace of copper and a trace of soluble barium.

POISONING WITH PHENYL-ETHYL-MALONYL-UREA.—In a case of suicide death was proved to be due to the swallowing of an unusually heavy dose (about 50 grains) of phenyl-ethyl-malonyl-urea. This was the first such case recorded in the States. Curiously enough the same drug was almost certainly responsible for the death in another case, direct proof however being unobtainable, owing to the rapid absorption and alteration of the drug in the digestive tract.

ABORTEFACIENT DRUG.—A sample of well-known "female ailment" pills, which were suspected of finding use for the purpose of procuring abortion, was found to contain aloes, the alkaloids of ergot, an oil resembling oil of savin, ferrous sulphate and liquorice, compounded with French chalk. As the label on the package did not comply with Regulation 72, section (1) of the Food and Drug

Regulations by declaring the presence of the two potent drugs, ergot and oil of savin, suitable action was taken by the Health Department.

LUMINAL POISONING.—The first case of luminal poisoning noted in this State occurred during the year, when a youth, an epileptic, who was receiving 3 grains a day in 1-grain doses, died by the self-administration of a number of 1-grain tablets. The exact amount taken could not be ascertained, but there was some evidence to show that not more than 50 grains were taken. The interval before the approach of symptoms was about three hours, and death took place during coma in 27 hours. The post-mortem appearances were fatty degeneration of the liver and some signs of irritation in the stomach. From the stomach washings three-twentieths of a grain of luminal were recovered. Luminal appears to be rapidly absorbed and changed in the human body.

CALORIFIC VALUE OF TIMBER USED FOR FIREWOOD.—Fifteen samples of timber, as supplied to the Goldfields Water Supply pumping stations, were examined for the Forestry Department. Determinations of calorific value on the dry and wet basis, nominal density and basic density (a figure calculated from the oven-dried weight and the volume when soaked, and considered to be the most useful density figure for the characterisation of timber species) were made. In connection with the supply of firewood, it had been contended that the calorific value of young re-growth did not compare favourably with that of firewood split from mature trees. Accordingly, samples of dry split wood from large trees, consisting of one billet from towards the heart and one towards the sapwood from each of three trees, and also samples of small round wood consisting of three billets of average diameter and three split billets were submitted for examination. The following results were obtained:

	Old jarrah billets (Mean of six samples) Per Cent.	Young jarrah round and split (Mean of six samples) Per Cent.	Marri (redgum) (Mean of three samples) Per Cent.
Moisture—			
Content when received	18·85	15·25	22·9
Calorific Value—			
B.T.U.'s gross, dry basis	8817	8822	8535
Calc. to original moisture-content ..	7156	7474	6580

The calorific values of woods, even of different species, apart from the presence of resins and essential oils, appear to approximate more or less to one another when calculated on the dry basis, and the main factor in buying wood is the moisture-content. In the present investigation the young wood, being thinner, had become air-dry more quickly than the heavier billets, with a consequently better fuel value before artificial drying.

FLUORINE IN PHOSPHATES.—Most of the rock phosphate, the source of all superphosphate made in the State, contains fluorine, amounting, in the raw rock, to 2·5 to 3·0 per cent. This constituent has recently been shown to have harmful effects upon stock and, to a less extent, on plants. Determinations of the fluorine-content of locally used rock phosphate, and of derived superphosphate and dicalcium phosphate (used as a constituent of stock licks) gave the following results:

	Fluorine Per Cent.
Rock phosphate	2·59 to 2·83
Superphosphate	1·49 to 1·78
Dicalcium phosphate	0·08 to 1·60

Dicalcium phosphate and superphosphate containing over 1 per cent. of fluorine are not suitable for use as ingredients of stock licks.

Authenticated samples of a natural rock phosphate from Ocean Island, and the superphosphate manufactured from it, gave, on analysis:

	Rock phosphate Per Cent.	Super-phosphate Per Cent.
Phosphoric oxide	39·76	23·54
Fluorine	2·80	1·52

The loss of fluorine in manufacture was thus 0·14 per cent., representing 5 per cent. of the total fluorine present in the natural rock phosphate.

Dicalcium phosphate	Per Cent.	Per Cent.
Phosphoric oxide	39·28	39·08
Fluorine	0·08	1·60

Poisons Lists and Rules

THE Poisons Lists and Rules relating to the Pharmacy and Poisons Act, 1933 (ANALYST, 1933, **58**, 548; 1934, **59**, 699), as approved by the Home Secretary, were issued on January 1st.* They confirm, with certain alterations, the final draft submitted by the Poisons Board.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Occurrence and Detection of Silica in various Foods. R. Strohecker, R. Vaubel and K. Breitwieser. (*Z. Unters. Lebensm.*, 1935, **70**, 345–353.)—Silica in foodstuffs is determined by converting it into the yellow silicomolybdate, the amount of which is measured colorimetrically with a step-photometer. For raw milk, cocoa products and eggs, the method is as follows:—The ash is fused in a platinum capsule with 0·5 g. of sodium carbonate or fusion mixture, and the fused mass is extracted with doubly-distilled water slightly acidified with about 1 ml. of sulphuric acid (50 per cent. by vol.). The acid extract is then treated with 1 g. of calcium carbonate, 0·25 g. of anhydrous sodium carbonate, 3 ml. of sodium phosphate solution (18·6 g. of $Na_2HPO_4.12H_2O$ in 200 ml. of water) and 3 ml. of calcium chloride solution (20 g. of $CaCl_2.6H_2O$ in 100 ml. of water). The solution containing the silica is filtered through a hardened filter-paper, and the filtrate and washings are made up to 50 ml., acidified with 0·2 ml. of 50 per cent. by vol. sulphuric acid, and 2 ml. of a 10 per cent. solution of ammonium molybdate are added. The yellow colour of the resulting silicomolybdate is measured by means

* Poisons Lists, Statutory Rules and Orders No. 1238 of 1935. Price 1d. Poisons Rules, S.R. and O., No. 1239 of 1935. Price 9d. net. H.M. Stationery Office, Adastral House, Kingsway, W.C.2.

of a Zeiss step-photometer (Katalog. Mess. 430, d and e: C. Pulfrich, *Z. Instrumentenkunde*, 1925, **45**, 35, 61, 109), the 3-cm. cell and the violet filter S.43 being used, and the measurement being made by comparison with the result obtained in a blank determination on the reagents. Using the ash from 50 ml. of milk for the determination, the authors found that the silica-content of 13 milk samples was less than 1 mg. per l. For condensed and dried milk, the amounts of the reagents used must be increased; the ash from 50 ml. of condensed, or 10 g. of dried, milk requires 2 g. of fusion mixture, 2 g. of calcium carbonate and 2 g. of calcium chloride, the other conditions being unaltered. Condensed and dried milks tend to give very high values for silica, and, as these are not proportional to the degree of concentration of the raw milk, it is probable that silica is introduced during manufacture. As an additional test, determination of the silica-content of raw milk may be used to detect and estimate added water, but the method is of value only when "appeal-to-cow" samples of the milk and a sample of the water suspected to have been added are available. For the determination of silica in meat and sausage products, 25 g. of the finely-minced substance, previously freed from adherent fat, are mixed with 5 ml. of 20 per cent. sodium carbonate solution, and evaporated to dryness, and the residue is ignited and fused. After fusion the procedure is as previously described. In general, the flesh of young animals yields less silica than that of older animals. Fish flesh has a higher content than mammalian flesh. "Black pudding" (Blutwurst) has an exceptionally high content (6·69 mg. of SiO_2 per 100 g.). This is in accordance with the observations of Gonnermann (*Z. physiol. Chem.*, 1917, **99**, 255) and others, *viz.* that blood has a high silica-content. Although silica determination is of some value for the detection of water added to minced meat, it cannot be used for the detection of water added to sausage products, as silica is introduced in the spices. The method may be applied to cocoa products, and the authors have found that, after allowance had been made for the presence of sand, cacao-shell contains from 2 to 10 times as much silica as the nib. The method was also used to show that, although the shells of eggs preserved in water-glass increased in silica-content, no silica penetrated into the interior of the egg. A. O. J.

Chemical Composition of Pig's Stomach. I. A. Smorodinzew and W. W. Palmin. (*Z. Unters. Lebensm.*, 1935, **70**, 365–366.)—The pig's stomach is used in the preparation of products such as cattle food, enzymes and bacteriological media. The stomachs of half-year to year-old pigs were removed about an hour after slaughtering, and, after separation of mucus, mucous membrane and visible fat, representative samples of the finely-minced material were taken for analysis. The average results (in percentages) were as follows, the figures in brackets being the percentage deviations from the mean:—Water, 80·92 (−1·6 to +6·3); total nitrogen, 2·44 (−12·3 to +15·9); protein nitrogen determined after precipitation of the protein with trichloroacetic acid, 1·79 (−23·4 to +26·8); residual nitrogen, 0·48 (−33·3 to +31·2); fat, 1·93 (−48·1 to +45·5); extractives, 1·85 (−34·0 to +39·4); and ash, 0·79 (−10·1 to +8·8); calorific value, 104·65. The fat-content shows the greatest deviation from the mean. The ash-content of the stomach is lower than that of the other organs. A. O. J.

Soya Bean Flour in Smoked Meat Products. C. H. La Wall and J. W. E. Harrisson. (*J. Assoc. Off. Agric. Chem.*, 1935, **18**, 644.)—The authors' test for soya bean flour (ANALYST, 1934, **59**, 552) has been applied successfully to sausages to which this flour was added to the extent of 1 to 10 per cent. of the meat present. Neither cooking nor smoking the sausage in its casing in the usual way affects the test, but if the soya bean flour is first made into a stiff paste and heated above 100° C. or under pressure, the urease is destroyed, and the test is vitiated; non-production of ammonia, therefore, does not necessarily indicate the absence of soya bean flour, and in any case it is always desirable to confirm a positive result by identifying the characteristic cell structures. Addition of soya bean flour does not affect the protein-water ratio to the same extent as addition of cereal. No substance normally used in meat products contains the positive urea-splitting enzyme, with the possible exception of dried mushrooms, the use of which is limited by their cost. J. G.

The Peroxidase Reaction as a means of Distinguishing Butter made from Pasteurised and Unpasteurised Cream. L. Waters and A. Zürn. (*Z. Unters. Lebensm.*, 1935, **70**, 353–355.)—A piece of butter, about the size of a hazel-nut, is placed in a test-tube with 2 ml. of saturated magnesium sulphate solution, 10 drops of an alcoholic 4 per cent. solution of benzidine are added, and the stoppered tube is shaken until a homogeneous mixture is formed. Five drops of 3 per cent. hydrogen peroxide solution are then added and, after further shaking, the mixture is agitated with about 5 ml. of ether and allowed to separate into two layers. If, immediately or in the course of half-an-hour, a blue colour appears in the aqueous layer, the butter was prepared from cream which had not been heated above 80° C. In no instance was the colour given by butter made from pasteurised cream or by unpasteurised butter which had been heated above 80° C. The tint and the depth of the colour varied from sample to sample, so that the reaction could not be used to determine the amount of unpasteurised butter added to pasteurised butter. The depth of colour, although varying in different samples, was constant for the same sample at the same time, but was found to change with time of storage. Butter from one source gave a positive result after 14 days; another, from a different source, gave no colour after 2 days. Different samples from the same source, however, tended to behave similarly. It is evident, therefore, that a negative result indicates the presence of either pasteurised butter or old unpasteurised butter; fresh unpasteurised butter, however, never fails to give a positive reaction. Strongly rancid and tallowy butter does not answer to the test, but the reaction is not hindered in fresh butter by the addition of rancid butter, and the peroxidase-content is not an indication of the degree of rancidity. Ether helps the reaction by removing butter-fat, thereby producing clearer tints. Other solvents may be used in the following descending order of efficiency:—Benzene, petroleum spirit, carbon tetrachloride, trichloroethylene, carbon disulphide. The presence of magnesium sulphate solution sensitises the reaction considerably. A. O. J.

Influence of the Degree of Maturity of Cheese on the Proportion of Fatty Matter. Ch. Brioux and E. Jouis. (*Ann. Falsif.*, 1935, **28**, 535–537.)—Since, in disputed cases, a delay of two or three months may occur before samples of cheeses are received for analysis, the examination of two Camembert cheeses was undertaken (*a*) when the cheese left the creamery; (*b*) after 3 weeks, when ready to be eaten, and again (*c*) 1½ months later, when maturity was well advanced and the cheeses were rather brown, with definitely alkaline reactions and showing vacuoles due to partial drying, with a slight loss of ammonia. The mean percentage figures for these three analyses were:—Dry matter at 100° C. (water-oven); (*a*) 43·14, (*b*) 48·40, (*c*) 64·31; fatty matter, (*a*) 20·34, (*b*) 22·80, (*c*) 32·55; fatty matter, per cent. on dry matter, (*a*) 47·19, (*b*) 47·30, (*c*) 50·61; total nitrogen, (*a*) 2·90, (*b*) 3·38, (*c*) 4·24; insoluble nitrogen (Trillat's method), (*a*) 2·65, (*b*) 2·26, (*c*) 2·59; ammoniacal nitrogen, (*a*) 0·25, (*b*) 0·55, (*c*) 0·85; soluble nitrogen as per cent. of total nitrogen, (*a*) 8·64, (*b*) 32·92, (*c*) 38·90. Increase in fatty matter takes place chiefly between the second and third periods, and is largely due to the changes occurring in the proteins, resulting in the formation of volatile gases or gases dissociated by heat. A total loss of nitrogen was found, amounting to 0·22 per cent. of fresh cheese. Actual losses during drying will vary according to the type of cheese. D. G. H.

Jaboty Fat. A. Steger and J. Van Loon. (*Chem. and Ind.*, 1935, **54**, 1095–1097T.)—Samples of commercial jaboty fat and of somewhat damaged kernels from Brazil apparently represented products from *Erisma uncinatum*, the "red-blossoming guaruba," rather than from *Erisma calcaratum*, the camarú tree. The kernels yielded 53 per cent. of fat on extraction with petroleum spirit, and the following constants were obtained for (*a*) the extracted and (*b*) the commercial fat:—M.p., (*a*) 41·5° C., (*b*) 43·0° C.; sp.gr. at 78/4° C., 0·8760, 0·8764; n_D^{77}, (*a*) 1·4360, (*b*) 1·4366; saponification value, (*a*) 233·0, (*b*) 236·1; iodine value (Wijs), (*a*) 5·4, (*b*) 4·8; Reichert–Meissl value, (*a*) 0·93, (*b*) 1·3; Polenske value, (*a*) 3·1, (*b*) 4·2; acid value, (*a*) 20·0, (*b*) 3·1; acetyl value, (*a*) 10, (*b*) —; unsaponifiable matter, (*a*) 0·7, (*b*) 0·35 per cent.; total fatty acids, (*a*) 93·0, (*b*) 92·9; glycerol (diff.), (*a*) 4·8, (*b*) 5·25 per cent. *Fatty acids*: M.p. (*a*) 41° C., (*b*) 42·1° C.; n_D^{70}, (*a*) 1·4269, (*b*) 1·4271; iodine value, (*a*) 4·9, (*b*) 3·9; neutralisation value, (*a*) 246, (*b*) 249; mean mol. wt., (*a*) 228, (*b*) 225. The neutral ethyl esters were prepared from the fatty acids and fractionated in a high vacuum, and the two largest fractions were re-distilled. The composition, calculated from the saponification and iodine values and the percentage of saturated acids, was as follows:—Acids of molecular weight lower than 200 were absent (except the small amount of volatile components), as was also stearic acid. About 21·6 per cent. of oleic acid was present, together with myristic, lauric and palmitic acids. Jaboty fat somewhat resembles ucuhuba fat, but is more unsaturated; when refined, it would be an excellent edible fat. D. G. H.

Estimation of Rape Oil in Edible Oils. J. Grossfeld. (*Chem.-Ztg.*, 1935, **59**, 935–936.)—An examination of the methods of Holde and Marcusson (*Z. angew. Chem.*, 1910, **23**, 1260; abst., ANALYST, 1910, **35**, 401) and of Tortelli

and Fortini (*Chem.-Ztg.*, 1910, 689; abst., ANALYST, 1910, **35**, 401), which are somewhat cumbersome, has led the author to devise an easy, practical, routine method depending upon the separation of erucic acid as its lead salt, and determination of the iodine value of this salt in its solution in alcohol and acetic acid. The experiments were made with mixtures of rape oil and linseed oil, and it was assumed that other oils not derived from the *Cruciferae* behave like linseed oil. A quantity of 0·6 ml. (0·5 to 0·55 g.) of the oil is saponified with 5 ml. of alcoholic potash (40 ml. of potassium hydroxide solution of sp.gr. 1·5, +40 ml. of water, made up to 1 l. with 95 per cent. alcohol) for 10 minutes, and the saponified solution is treated with 20 ml. of lead acetate solution (50 g. of lead acetate and 5 ml. of 96 per cent. acetic acid made up to 1 l. with 80 per cent. by vol. alcohol), 3 ml. of water and 1 ml. of 96 per cent. acetic acid, and the mixture is heated under a reflux condenser. After standing until the following day the mixture is filtered through a sintered glass crucible, and the precipitate is washed with 10 to 15 ml. of 70 per cent. by vol. alcohol. The crucible with the residue is extracted in a continuous extractor with 20 ml. of a mixture of equal parts of 95 per cent. alcohol and 96 per cent. acetic acid. The warm solution of the lead salt is washed into a flask with the mixture of alcohol and acetic acid, and its iodine value is determined by the method of Margosches, Hinner and Friedmann (*Z. angew. Chem.*, 1924, **37**, 334). This consists in adding 20 ml. of approximately 0·2 *N* alcoholic iodine solution, mixing well, diluting with 200 ml. of water, and titrating the excess of iodine with *N*/10 sodium thiosulphate solution. A blank is carried out upon 30 ml. of the alcohol-acetic acid solution, 20 ml. of the iodine solution being added to it. The titration may be carried out a few minutes after the water is added, but should not be delayed more than 2 hours. The factor for converting ml. of *N*/10 iodine into erucic acid is 16·9. The following are the results obtained for varying mixtures of linseed oil and rape oil:

Rape oil, per cent. ..	0	10	20	30	40	50	60	70	80	90	100
Iodine value (ml. of *N*/10 per 0·6 ml.)	1·0	1·9	3·8	5·5	7·0	9·4	11·6	12·1	13·4	15·0	15·9

Experiments (described in detail) show that the presence of 3 ml. of water is essential to reduce the solubility of the lead salt of erucic acid to a sufficient extent. Genuine samples of linseed oil gave an iodine value of 0·9 ml. of *N*/10 per 0·6 ml., corresponding with an apparent addition of 10 per cent. of rape oil. An addition of 10 per cent. or less is thus not detectable by this method. When the method was applied to certain samples of commercial linseed oil, amounts of rape oil ranging from 20 to about 60 per cent. were found. Experiments showed that amounts of rape oil of 5 per cent. or less could be detected by adsorption of the lead salt upon lead palmitate. For this purpose 0·25 g. of palmitic acid is mixed with 0·5 g. of the oil to be tested, and the mixture is saponified with 7·5 ml. of the alcoholic potash (*supra*). To the soap solution are added 2 ml. of 96 per cent. acetic acid, 30 ml. of the alcoholic lead acetate solution and 5 ml. of water. The mixture is warmed and allowed to stand over-night, and the precipitate is filtered off and treated as before. A. O. J.

Detection and Determination of Ephedrin. J. A. Sanchez. (*J. Pharm. Chim.*, 1935, **127**, 489–496.)—(i) Ethyl benzoate is formed by the oxidation of ephedrin in alkaline solution, and subsequent esterification. Ephedrin (0·02 g. or more) is evaporated to dryness with 30 per cent. sodium hydroxide solution (2 drops) and 1 per cent. potassium permanganate solution (5 drops) in a test-tube, the residue is dissolved in 2 ml. of water, and the solution is evaporated to a paste, which is warmed with 2 drops of ethyl alcohol and 5 drops of concentrated sulphuric acid, when the odour of ethyl benzoate is observed. (ii) Benzaldehyde and a fatty amine are formed when ephedrin is either (*a*) distilled with 5 ml. of 1 per cent. potassium permanganate solution, (*b*) heated in a test-tube with soda-lime, or (*c*) similarly heated with powdered zinc, 0·05 g. of ephedrin being used in each test, and the evolved vapours collected in about 2 ml. of water. Benzaldehyde is identified by its odour, by the usual condensation to a phenylhydrazone with phenylhydrazine, and by the formation of a deep green colour (malachite green) on warming gently with dimethylaniline (1 drop) and sodium hydroxide solution (1 drop), adding a few cg. of lead dioxide, and acidifying with acetic acid. Benzaldehyde is also formed by heating 2 ml. of 0·1 per cent. ephedrin solution with 1 drop of Labarraque's sodium hypochlorite solution (dry chloride of lime, 100 g., sodium carbonate, 200 g., water to 4500 g.). It is stated that distillation (*b*) gives dimethylamine and (*c*) methylethylamine; the amine formed by (*a*) is unspecified. All the distillates are strongly alkaline and form precipitates with the Bouchardat (iodine in potassium iodide) and Valser (potassium iodide + mercuric iodide) reagents, with Sanchez's molybdic and Bertrand's silicotungstic reagents, and with bromine water. A few drops of the solution, heated with 10 per cent. sodium nitroprusside solution (2 drops) and acetone (1 drop), give a red colour changing to violet on acidifying with acetic acid (Rimini reaction). (iii) Nitrosoephedrin is formed as a cheese-like precipitate on warming ephedrin (0·02 g. or more) with 10 per cent. sodium nitrite solution (20 drops), adding 1 drop of hydrochloric acid, and shaking vigorously. After extraction with ether, the nitrosoephedrin gives the Liebermann reaction. (iv) By heating 0·02 g. or more of ephedrin for a few minutes with nitric acid (5 drops) and conc. sulphuric acid (3 drops), diluting with 5 ml. of water, reducing in hot solution with granulated zinc, decanting, adding 10 per cent. sodium nitrite solution (2 or 3 drops) and shaking, the diazo-compound is formed; this gives the following colour reactions with phenols in alkaline solution:—Phenol, intense yellow; resorcinol and phloroglucinol, deep orange; thymol, intense red; β-naphthol, red. (v) Iodoform is formed by warming ephedrin with iodine and conc. sodium hydroxide solution. A few mg. of ephedrin may thus be detected.

Ephedrin is determined by reaction (v), which is quantitative. Exactly 10 ml. of 0·1 per cent. ephedrin solution, 3 ml. of sodium hydroxide solution, and 30 ml. of 0·1 *N* iodine solution are shaken in a 120-ml. flask closed with a ground-glass stopper; the mixture is warmed on a water-bath at 50° C. for 30 minutes, and then cooled, and 60 drops of conc. hydrochloric acid are added while the flask is kept cool with water. The remaining iodine is determined with 0·1 *N* sodium thiosulphate solution [4 g.-molecules of iodine ≡ 1 g.-molecule of ephedrin (165 g.)]. E. B. D.

Microscopy of Powdered Endocrine Glands. H. W. Youngken. (*Amer. J. Pharm.*, 1935, **107**, 463–471.)—The following microscopical standards are suggested as a means of detecting adulteration of powdered desiccated endocrine glands; the descriptions given apply to powdered desiccated glands from cattle and hogs (also to thyroid and pituitary from sheep):

(i) Thyroid contains (*a*) smooth to striated, hyaline fragments of colloid, and (*b*) irregular follicular epithelium fragments, both being stained brown with a mixture of (I) Mallory's stain and (II) 1 per cent. phosphotungstic acid solution.

(ii) Suprarenal gland exhibits stellate to irregular chromophil (chromaffin) cells, stained brown with (III) chromic acid test solution, and (*b*) cortical cells giving blue nuclear and red to purple protoplasmic stains with (IV) Delafield's haematoxylin and (V) alcoholic eosin.

(iii) Pituitary (whole) shows (*a*) large, polyhedral chromophil cells, possessing coarse granules, stained in presence of acid (red with acid fuchsin), (*b*) chromophobe, rounded, cubical, or pyriform cells giving blue nuclear and paler blue cytoplasmic stains with (IV) or a mixture of eosin and methylene blue solution, (*c*) mossy neuroglia cells visible in a mixture of (II) and (IV), and (*d*) bipolar nerve cells. In anterior pituitary (*c*) and (*d*), and in posterior pituitary (*a*) and (*b*), are absent.

(iv) Ovary (whole) shows (*a*) distorted cubical to columnar epithelial cells, giving deep blue nuclear and pale purple to pink cytoplasmic stains with (IV), (*b*) rounded to irregular masses of primary oocytes surrounded by connective tissue elements, (*c*) rounded to oval interstitial cells containing granules and fat droplets stained bright red with red acid dyes, (*d*) forked fibroblasts, (*e*) lutein cells, yellowish in water mounts, (*f*) narrow collagen fibres swelling in, and coloured yellow by, a mixture of 1 per cent. picric acid and 1 per cent. acetic acid solution. In ovarian residue very little (*e*) is present.

(v) Corpus luteum contains lutein cells, groups of which are mixed with fine collagen fibres and are yellowish or greenish-yellow in aqueous mounts.

E. B. D.

Microscopic Methods for the Detection of Karaya Gum, Gum Tragacanth and Agar-Agar. J. D. Wildman. (*J. Assoc. Off. Agric. Chem.*, 1935, **18**, 637–638.)—*Karaya.*—One drop (*e.g.* of catsup) is diluted suitably on a slide with water, and a mount is made and examined under a magnification of ×100. Owing to adherence of protoplasmic particles, the insoluble portions of the gum appear as billowy masses of various shapes and sizes which are resilient when pressed under a cover slip; in water the particles are almost invisible. Addition of a drop of a mixture of zinc iodide and potassium iodide solutions produces a blue colour with the cellulosic matter and a green colour with the gum masses. *Tragacanth* has a similar appearance, except that the masses are more uniform in shape and size, but to identify this gum with certainty it is essential to find its characteristic striations. *Agar-Agar.*—For mayonnaise or salad dressing, 50 g. of sample should be shaken with 2 volumes of alcohol, and the fat is removed from the residue after filtration by extraction with ether. The residue is dried in air, the soluble gums, residual sugars and dextrin are removed by suspension in 50 ml. of cold water, and the final residue is suspended in 25 ml.

of water, which is then heated rapidly to boiling to dissolve the gum and to precipitate the proteins. The liquid is filtered while hot, and, if starch is present, the filtrate is cooled to 65° C., and 5 ml. of malt extract (*cf.* "Methods of Analysis," *A.O.A.C.*, 1930, **26**, 282) are added, followed, after 5 minutes, by a further 5 ml. of extract. The liquid is concentrated by heat until it gels on cooling, and the colour obtained when a speck of the gel is treated with a solution of 0·05 g. of iodine and 0·2 g. of potassium iodide in 15 ml. of water on a slide is observed under the microscope. Agar gives a distinct red colour, but if blue is present, the digestion of starch should be repeated. If the egg-content is high, unseparated proteins may mask the colour; if so, the gel is repeatedly frozen (to precipitate the agar), and the new gel is washed in the centrifuge, re-dissolved, and re-precipitated. Curried chicken should be extracted with hot water, the mixture being filtered while hot, and the agar separated from the frozen filtrate by centrifuging, re-dissolving in boiling water and re-freezing a further 3 times. The final precipitate is dissolved in a little boiling water, and the resulting gel is stained as described. Irish moss, quince seed, tragacanth, Karaya and acacia gums do not react, but gelatin gives a yellow colour which masks the reaction, and it should be separated by freezing the solution and then melting it in a bath at 60° C. The liquid is centrifuged, the residue being washed with water at 60° C., re-centrifuged, and finally dissolved in 10 to 25 ml. of boiling water. The filtered solution should now contain only agar; if any yellow colour appears, the procedure is repeated, but this should be unnecessary if less than 0·1 per cent. of agar is present in a 5 per cent. solution of gelatin. J. G.

ERRATUM: **African Beeswax**:—The figure for Gambia wax in Salamon and Sieber's test should be "59·5" not "69·5."

Biochemical

Haemolytic Reaction for Testing the Removal of Bitterness from Soya Beans. M. Krajčinović. (*Z. Unters. Lebensm.*, 1935, **70**, 391–394.)—Raw soya beans must be deprived of their bitter principles before they can be used for human food. Since all the saponins are simultaneously removed, a haemolytic test may be used to determine the efficiency of the process. The soya beans (or meal) are dried and ground. About 0·5 g. of the meal is mixed with 10 ml. of physiological salt solution in a test-tube, and the mixture is allowed to stand for an hour, with frequent agitation. A drop of defibrinated ox-blood is placed upon a microscope slide, and a drop of the solution is added. The presence of saponin can be observed under the microscope, since it acts haemolytically upon the corpuscles, causing them to lose their irregular shape and to become spherical and uniform in size. It is advisable to make a control observation upon a drop of the defibrinated blood mixed with a drop of physiological salt solution. By this means the author has followed the course of the removal of the saponins from shelled and unshelled soya beans and from bread made from raw soya meal. The process was studied while taking place in ordinary water at 75°, 85°, 95°, and 100° C., then in

weakly acidulated water containing 0·05 per cent. of hydrochloric acid at 100° C., and finally in saturated steam at 100° C., and in saturated steam under pressure at 115° C. The results show that the rate of hydrolysis of the saponins by water increases with increasing temperature, that the saponins in soya bread are decomposed rapidly at 100° C., that raw soya meal, having a large contact surface, is hydrolysed very rapidly, and that in the dried shelled beans the saponins are hydrolysed more rapidly than in the unshelled. The presence of the stated amount of hydrochloric acid in the water increases the rate of hydrolysis, and, whilst saturated steam at 100° C. is a slower hydrolysing agent than boiling water, saturated steam under pressure at 115° C. is the most rapid of the hydrolysing agents tried. A. O. J.

Modified Nessler's Reagent for the Micro-Determination of Urea in Tungstic Acid Blood Filtrate. J. F. Barrett. (*Biochem. J.*, 1935, **29**, 2442–2445.)—When urea is determined in blood filtrates by direct nesslerisation, interference may be experienced from reducing substances, particularly glucose and creatinine. The author has found that, if an oxidising agent, such as sodium hypochlorite, be added to the Nessler's reagent, the reducing substances no longer exert their effect. The following micro-method for urea determination is based on this principle:—A urease solution is prepared by suspending 1 g. of "Arlco" jack bean meal in 50 ml. of water, shaking for several minutes and filtering. The solution, which should be clear, will keep for several days in a refrigerator. The purified urease is prepared by placing 10 ml. of this extract in a centrifuge tube, adding 2 drops of 10 per cent. acetic acid, and centrifuging for a few minutes. The supernatant fluid is discarded, and the residue is thoroughly mixed with about 2 ml. of sulphate-tungstate solution and diluted with the same solution to 10 ml. One ml. of the urease solution is placed in a conical centrifuge tube, and followed by 0·2 ml. of blood, the pipette being washed out in the solution. The tube is stoppered and kept in water at 30° C. for 15 minutes, after which 5 ml. of water and 0·5 ml. of $N/3$ sulphuric acid solution are added. Finally, 0·5 ml. of a 5 per cent. solution of sodium tungstate is added, and the whole well mixed and centrifuged for 5 minutes. By means of a 5-ml. pipette, which is pressed by the finger against the wall of the tube so that the tip of the pipette is about 2 mm. above the protein precipitate, 5 ml. of the clear supernatant fluid are withdrawn and transferred to a 6 × 1 in. test-tube. To this is added 5 ml. of water and 0·5 ml. of a 1·5 per cent. solution of sodium citrate, followed by 1 ml. of Nessler-hypochlorite solution, which should be added rapidly while the liquid is rotated in the tube. The solution is then compared in a colorimeter with standards prepared from a solution containing 1·833 mg. of pure ammonium sulphate per 100 ml. The sulphate-tungstate mixture is prepared by dissolving 5 g. of anhydrous sodium sulphate in water, adding 15 ml. of 5 per cent. sodium tungstate solution and diluting to 1 l. The Nessler-hypochlorite reagent is prepared by the addition of 0·1 ml. of sodium hypochlorite solution, containing 10 to 13 per cent. of available chlorine, to 20 ml. of Nessler's reagent (Koch and McMeekin, *J. Amer. Chem. Soc.*, 1924, **46**, 2066; Abst., ANALYST, 1924, **49**, 604). This solution should be freshly prepared. S. G. S.

Further Observations on the Constituents of the Unsaponifiable Fraction of Wheat Germ Oil with particular reference to Vitamin *E*. J. C. Drummond, E. Singer and R. J. MacWalter. (*Biochem. J.*, 1935, **29**, 2510–2521.)—Several definite fractions have been separated from the unsaponifiable matter of wheat germ oil. One fraction appears to consist of a hydrocarbon with a probable formula $C_{18}H_{38}$. Although similar to *iso*-octadecane (pristane), differences in some of the analytical figures point to a separate compound. A highly unsaturated hydrocarbon was also obtained. The formula of this appears to be $C_{45}H_{76}$. The fraction containing vitamin *E* contains a new sterol, having a probable formula $C_{29}H_{48}O_2$. Some data concerning it have been accumulated and further work on it is in progress. S. G. S.

Vitamins *A* and *D* in Common Foods. K. Coward and B. G. E. Morgan. (*Brit. Med. J.*, 1935, p. 1041 [Nov. 30th].)—Vitamins *A* and *D* were estimated in a variety of common foods. The standard of reference for vitamin *A* was a sample of cod-liver oil containing 1500 international units per gram, and this was compared with each individual food. The following table indicates the values obtained for vitamin *A*:

Milk (1 sample)	3 units per ml.	1700 units per pint
Jersey milk (1 sample)	5 units per ml.	2850 units per pint
Butter (17 samples)	26 to 200 units per g. (average 60 units)	730 to 5000 units per oz. (average 1700 units)
Egg-yolk (1 sample)	30 units per g.	600 units in a yolk of 20 g. ($\frac{3}{4}$ oz.)
Bone marrow (1 sample)	8 units per g.	220 units per oz.
Carrots, fresh or boiled (1 sample)	19 units per g.	2000 units per portion of about $\frac{1}{4}$ lb.
Cabbage, fresh or boiled (1 sample)	9 units per g.	1000 units per portion of about $\frac{1}{4}$ lb.
Runner beans, fresh or boiled (1 sample)	6 units per g.	600 units per portion of about $\frac{1}{4}$ lb.
Cod-liver oil (24 samples)	600 to 4000 units per g., a few outside this range (average 2000 units)	2000 to 13,000 units per teaspoonful (average 6400 units)
Halibut-liver oil (5 samples)	30,000 to 360,000 units per g. (average 160,000 units).	600 to 7200 units per drop (of 20 mg.) (average 3200 units)

The following are the figures obtained for vitamin *D*. Calf liver contained no vitamin *D*, even when tested as 10 per cent. of the diet; milk (20 samples) not more than 50 units per pint; butter (17 samples), 10 to 100 units per oz. (average 34 units); cream (1 sample), 80 units per gill; egg yolk (2 samples), 30 to 100 units per yolk of 20 g.; cod-liver oil (240 samples), 190 to 1000 units per teaspoonful (average 480 units); halibut-liver oil (10 samples), 40 to 80 units per drop (20 mg.) (average 48 units); olive oil contained none, even when tested as 20 per cent. of the diet. S. G. S.

Relation of Micro-Organisms to Carotenoids and Vitamin *A*. The Production of Carotenoids by *Mycobacterium phlei*. M. A. Ingraham and H. Steenbock. (*Biochem. J.*, 1935, **29**, 2553–2562).—The effects of a number of factors on the gross pigmentation of the cells of *M. phlei* are reported. When grown on a synthetic glucose-asparagine medium a relatively low pigment-content was obtained, and, although the colour increased as growth proceeded, this was

not due to the age of the cells or to the influence of the heavy pellicle. By lowering the concentration of potassium or phosphate ions in the medium, pigmentation was increased, but an increase of ferric ions tended to prevent pigment formation. The substitution of glycerol for glucose caused a greatly increased pigmentation, and under these conditions the concentration of potassium ions had no effect, although phosphates, ferric or cupric salts decreased the colour of the cells. The only carbon compounds which caused an increase in pigmentation were alcohols and glycols. If asparagine was present in excess, autolysis followed rapidly and the carotenoids were destroyed. When the reaction of the medium was kept below *p*H 8·6, ammonium salts, urea, peptones and other sources of nitrogen could be substituted for asparagine, but if the *p*H rose above this value, the cells had a pale colour. It was also found that ethylene, salts of sodium, lithium, calcium, magnesium and selenium, the oxidation-reduction potential, light intensity and the incubation temperature had no specific effect on pigmentation. When the colouring matter was resolved on a magnesium oxide column, the following pigments were recognised:—α-carotene, β-carotene, kryptoxanthin and esters of lutein, zeaxanthin and azafrin. The increased pigmentation in the presence of glycerol and the glycols was due to a pigment resembling phthiocol, which appeared to be an end-product of metabolism. S. G. S.

Toxicological and Forensic

Method of Rendering Latent Finger-Prints Visible. M. Wagenaar. (*Pharm. Weekblad*, 1935, **72**, 1265–1271.)—Methods previously suggested are reviewed. Theoretically, Mitchell's osmium tetroxide method (ANALYST, 1920, **45**, 127) is the best, but, in practice, it has the drawback of slow reaction. The hydrofluoric acid etching method gives fairly good results with finger-prints on glass, but methods involving the use of dyestuffs (such as Sudan-3, eosin or fuchsin) or of mercurous nitrate, silver nitrate, palladium chloride or tannic acid are not considered practical. The iodine method is the best, principally because it does not disturb the finger-prints, but the difficulty in the past has been the production of clear and permanent copies of the finger-print, silver acetate, silver nitrate, gallic acid, or calomel followed by hydrogen sulphide, being all unsatisfactory fixing agents for various reasons. The author, therefore, prefers to cover the object, on which the finger-print has been left, with the lid of a petri dish, inside which is placed a crystal of iodine, which is slowly vaporised by gentle heat. If this is impossible, owing to the irregular shape of the article, the finger-print may be sprayed with iodine vapour by means of an apparatus resembling a scent-spray, and containing a crystal of iodine which may be vaporised. The "printing reagent" is prepared by adding a solution of 2 g. of potassium iodide in a little water to a paste containing 1 g. of rice starch preserved with 0·3 g. of finely-powdered thymol. The mixture is diluted to 20 ml., which is then stable for a long period if stored in the dark. The surface of a piece of a thin, good-quality typewriting paper is coated with the paste, and, just before it is dry, a print is taken by contact, the image being preserved by coating it with a 3 per cent. solution of dammar resin in benzene.

The depth of the colour of the print depends on the time of contact; several prints may be taken. Very good results are obtainable from finger-prints on glass, metal, shoes, notepaper, linoleum, stamps and photographs, and even rough wood or leather gives a visible image. J. G.

Agricultural

Determination of Small Quantities of Mercury in Leafy Vegetables by means of Diphenylthiocarbazone (Dithizone). W. O. Winkler. (*J. Assoc. Off. Agric. Chem.*, 1935, **18**, 638–644.)—The method depends on the solubility of the mercury-dithizone complex in chloroform, and the difference in colour between the green of the reagent and the orange or yellow of the complex enables the mercury to be titrated with dithizone. The minced sample (150 to 200 g.) is placed in a 2-litre Pyrex digestion flask fitted with a cylindrical internal condenser with a closed cone-shaped base (cf. *J. Amer. Chem. Soc.*, 1926, **48**, 1816), and 50 ml. of nitric acid and 300 ml. of water are added, this being sufficient to dissolve the mercury without subsequently reducing the permanganate. The mixture is then gently heated under reflux for 25 minutes, the flask is cooled thoroughly (to prevent loss of mercurous salts), and the contents are filtered rapidly on a large Buchner funnel. The filtrate and washings are re-digested in the flask under reflux with 10 g. of potassium permanganate for 15 minutes; the flask is then cooled, 8 g. of potassium permanganate are added, and the boiling is continued. The process is repeated, after the addition of 5-g. portions of permanganate and 20 ml. of nitric acid, until all organic matter is destroyed and the colour of the permanganate persists at 70° C. This may take a long time (especially with lettuce), but it is an essential operation, because nitrites interfere with the extraction of the mercury. A 30 per cent. solution of hydrogen peroxide is then added to dissolve the oxides of manganese, followed by gentle heating and addition of 0·5 g. of crystalline hydroxylamine sulphate and, if antimony is present, by 15 ml. of a 10 per cent. solution of tartaric acid which has previously been extracted with a solution of dithizone (cf. *infra*). The liquid (less than 425 ml.) is shaken for 20 seconds with 20 ml. of a fresh mixture prepared by diluting a 0·05 per cent. solution of purified dithizone in carbon tetrachloride ten-fold with chloroform. Mercury and oxidation products are removed from commercial dithizone by extracting 50 ml. of a 2 per cent. solution in chloroform with 3 successive 100-ml. portions of 1 per cent. ammonia. The aqueous layer is acidified, and the purified dithizone is extracted with chloroform, the extract being subsequently evaporated and the last traces of solvent removed in a vacuum below 50° C. (cf. *id.*, 1934, **17**, 117). If the extract from the sample is yellow (indicating insufficiency of dithizone to react with all the mercury), the extraction is repeated with 15 ml. of reagent until a green (mercury) or (if copper is present) a red extract results, when one final extraction is made. The yellow oxidation product of dithizone resembles that of the mercury-dithizone complex, but the latter only is removed from the chloroform by a 1 per cent. solution of potassium cyanide. The combined extracts (*A*) are shaken vigorously with 50 ml. of water, 10 ml. of a 5 per cent. solution of potassium permanganate and 1 ml. of sulphuric acid (1 : 1), sufficient of the

hydrogen peroxide to clear the solution then being added. The hydrochloric acid test for silver may be applied at this stage. Two burettes are then each filled with a fresh 0·00125 per cent. solution of dithizone in carbon tetrachloride (prepared from the stock solution *supra*, so that 1 ml. ≡ approximately 0·005 mg. of Hg), and 10 ml. of a standard solution of pure mercury in nitric acid (1 ml. ≡ 0·01 mg. Hg) are diluted to 100 ml. with water containing a little sulphuric acid in a separation funnel; a similar funnel contains the whole, or an aliquot portion, of the extracts from the sample. The liquids in the funnels are then titrated simultaneously, with vigorous shaking, with the dithizone solutions, about 4 ml. being added at a time at first; the colours of the carbon tetrachloride layers which separate on standing are compared. These layers are removed after each addition, the end-point being the change in colour from the orange-yellow of the complex to the green of the reagent. A more exact titration is then made in each case after re-oxidation of the combined extracts with permanganate, as already described; a fading end-point indicates oxidation (cf. *supra*). If copper is present in large quantities, it is removed from the extract (*A*) by shaking it for 20 seconds with 60 ml. of a solution in water of some crystals of potassium iodide and a few drops each of a 5 per cent. sodium arsenite solution and sulphuric acid (1 : 1); the mercury is thus transferred to the water phase, which may finally be washed with a little chloroform. The solution may then be made ammoniacal and titrated roughly to a red end-point with dithizone, the titration being repeated more accurately after liberation of the mercury in acid iodide solution, as described above. Alternatively, the mercury may be extracted from the acid solution containing iodides by adding 2 ml. of a 1 per cent. solution of sodium diethyldithiocarbamate and using several 10-ml. portions of chloroform; the extracts are then oxidised and titrated as described above. Copper can be extracted with dithizone in the presence of iodides, but mercury cannot, unless the solution is ammoniacal; if the solution is acid, the sodium diethyldithiocarbamate solution must be used. Bismuth, bivalent tin, antimony, gold or platinum interfere in acid solutions, but quadrivalent tin, potassium cyanide, acids (up to 6 *N*), and sodium hydroxide (up to 2 *N*) do not. Chlorides prevent interference in acid solution by silver, tartaric acid prevents the interference of antimony or bismuth, and 1 per cent. nitric acid that of bismuth, tin or cadmium. Gold and platinum may be precipitated by powdered copper, but the precipitate should be extracted with nitric acid in case some mercury has also been thrown out. Almost complete recovery of 0·01 to 0·04 mg. of mercury added to lettuce was obtained in the absence of interfering substances; in 5 out of 13 determinations made in the presence of phosphoric acid (25 mg.), calcium sulphate (100 mg.), copper (10 mg.), manganese (5 mg.), barium (5 mg.), silica (20 mg.), iron (15 mg.), and aluminium (5 mg.) the recovery of mercury was within 0·005 mg. in every instance. J. G.

Colorimetric Determination of Phosphoric Acid in Grass and Similar Materials by the Fiske and Subbarow Method. A. W. Greenhill and N. Pollard. (*J. Soc. Chem. Ind.*, 1935, **54**, 404–406T.)—An adaptation of Fiske and Subbarow's method (*J. Biol. Chem.*, 1925, **66**, 375; abst., ANALYST, 1926, **51**, 205) for determining phosphoric acid in biological material proved accurate, rapid

and easy of manipulation when the quantity of material available was too small for the ordinary methods of analysis. The extract is prepared by weighing 0·5 g. of the dried and finely-ground material into an evaporating basin, adding 4 ml. of approximately 0·25 *N* magnesium nitrate solution, stirring into a thick paste, evaporating to dryness on a sand-bath in about 15 minutes, and igniting at 500° C. for 15 minutes in a muffle-furnace. Ten ml. of 10 *N* sulphuric acid are then added to the cooled residue, and, after 15 minutes' digestion of the thoroughly disintegrated mass, the cooled mixture is diluted with water and filtered into a 100-ml. flask. The filter-paper (9 cm.) is washed with hot water, and the cooled filtrate is made up to 100 ml. Twenty or 25 ml. are pipetted into a 100-ml. flask, and sufficient 10 *N* sulphuric acid to bring the total amount of acid to 5 ml. is added from a burette. Water is added to about 75 ml., followed by 10 ml. of ammonium molybdate reagent, and, after shaking, by 4 ml. of aminonaphtholsulphonic acid reducing agent. After further shaking, the solution is made up to 100 ml. The standard is prepared at the same time from 10 ml. of the standard phosphate solution (0·1917 g. of monopotassium phosphate dissolved in 1 l. of water with 1 drop of chloroform) with the addition of 5 ml. of 10 *N* sulphuric acid as above. After ten minutes the comparison is made in a colorimeter. The range for the standard is from 2 to 15 ml., but with materials in which the P_2O_5-content is only about 0·5 per cent., 25-ml. aliquot portions should be taken, and the colour developed in a final volume of 50 ml. Although silica, iron and other substances, when present in large amount, affect the colour-development, they are not usually found in sufficient proportion in grass extracts to make any special procedure necessary. Contamination of the sample with soil, however, should be carefully avoided. The results obtained by this method agreed closely with those obtained by the modified Pemberton–Neumann method, and the ammonium phosphomolybdate method, especially the latter. D. G. H.

Determination of Iron and Aluminium in Natural Phosphates. R. Meurice and P. Martens. (*Ann. chim. anal.*, 1935, **17**, 313–314.)—Crispo's method (i) for the determination of iron and aluminium in phosphates gives too high results for phosphates containing more than 4 per cent. of ferric and aluminium oxides, as the iron and aluminium, weighed as oxides after elimination of phosphate by means of nitromolybdic reagent, always contain molybdic acid. A method (ii) is described, in which more iron is first added to the sample, the acid solution nearly neutralised, and iron, aluminium, and phosphate are precipitated by alkaline acetate, re-precipitated, ignited and weighed. The results are satisfactory when the ratio of iron (as Fe_2O_3) to phosphate (as P_2O_5) is at least 4 : 1; otherwise, phosphate is lost. Five natural phosphates were examined by (i) and (ii). Also (iii), iron was determined volumetrically, and (iv), aluminium was determined by Lasne's method (*Z. angew. Chem.*, 1897, 277; *cf.* abst., ANALYST, 1898, **23**, 83). The tabulated results differ considerably according to the method used. E. B. D.

Determination of Barium Fluosilicate in Insecticide Powders.—A. Bonis. (*Ann. Falsif.*, 1935, **28**, 461–463.)—The powder (0·5 g.) is fused with 8 g. of a mixture of equal parts of sodium and potassium carbonates, the fluoride

thereby forming sodium fluoride and part of the silica forming sodium silicate. The residue is taken up with hot water and filtered, and the filter is washed with boiling water, yielding a filtrate (A) and a residue (R). A is treated with 4 to 5 g. of pure ammonium carbonate, and digested at a gentle heat for several hours, and the flocculent precipitate of silica (S_1) thus formed is separated by filtration. The filtrate is treated with a few centigrammes of zinc oxide dissolved in ammonia, and evaporated almost to dryness, and the residue is taken up with hot water and filtered. The residue of zinc oxide, containing the last traces of silica, is treated with hydrochloric acid, and the solution is evaporated to dryness. The residue is treated with dilute acid, filtered off and washed, yielding a second portion of silica (S_2). The ammoniacal filtrate remaining after the treatment with ammonium zincate is slightly acidified to methyl orange, made slightly alkaline with 10 per cent. sodium carbonate solution, and heated nearly to boiling-point, and the fluoride and carbonate are precipitated together by means of calcium chloride solution. The precipitate, after filtration and washing, is treated with 10 per cent. acetic acid, and the insoluble residue of calcium fluoride is filtered off, washed, ignited, weighed and calculated to barium fluosilicate. The residue (R) from the original fusion is dissolved in dilute hydrochloric acid, the solution is evaporated to dryness on the water-bath, the dry residue is well crushed and treated with hydrochloric acid, and the residue of silica (S_3) is filtered off, washed and weighed. The sum of S_1, S_2 and S_3 gives the total silica. If the diluent mixed with barium fluosilicate is free from silica (*e.g.* barium sulphate, calcium sulphate, etc.) the silica found will correspond with the fluoride-content; if, however, the diluent is a siliceous substance (talc, kaolin, kieselguhr, etc.) the determination described above requires verification. The acid liquid resulting from the separation of S_3 is treated, while boiling, with sulphuric acid. The precipitate of barium sulphate should correspond with the fluorine-content. Iron and aluminium in the filtrate from this determination of barium sulphate in the presence, for example, of kaolin, may be determined by precipitation with ammonia and the amount of diluent thus obtained within the method gives results accurate. A. O. J.

Organic

Detection of Oxalic Acid. N. A. Tananaeff and A. A. Budkewitsch. (*Z. anal. Chem.*, 1935, **103**, 353–355.)—Oxalic acid is not acted upon by 0·1 N dichromate solution, neither is indigo solution, but oxalic acid induces decolorisation of indigo by dichromate. The speed of the reaction is determined by the oxalic acid concentration, a 0·0001 N solution acting after 10 to 12 minutes in presence of a few drops of sulphuric acid. In order to avoid possible interference of sulphide, sulphite, or thiosulphate, the procedure involves treatment of 2 to 3 ml. of the unknown solution with a slight excess of sulphuric acid and removal of hydrogen sulphide or sulphur dioxide by boiling. After filtration (if necessary), the solution is treated with 0·01 N dichromate solution and mixed with a little of the same solution blued with indigo. Decolorisation takes place after 1 minute with 0·1 N, and after 1 to 2 minutes with 0·01 N oxalate solution. The test, which can be carried out in 15 minutes, will detect as little as 0·03 mg. of oxalic acid.

W. R. S.

Rapid Identification of Methyl Anthranilate. S. Sabetay. (*Ann. Falsif.*, **1935, 28**, 478–479.)—Methyl anthranilate occurring in certain essential oils (neroli, orange-flower, petit-grain, bergamot, jonquil, jasmine, ylang-ylang, gardenia, etc.) can be identified by the crystalline compounds which it forms with certain organic reagents, as well as by its physical constants. The *N*-acetyl derivative does not appear to have been used for identification purposes, though it was prepared by Mehner (*J. pr. Chem.*, [2], **64**, 83), and by E. and H. Erdmann (*Ber.*, 1902, **35**, 24; abst., ANALYST, 1902, **27**, 125). It can easily be prepared by the method of Delaby and Sabetay (*Bull. Soc. Chim.*, 1935, **2**, 1716; abst., ANALYST, 1935, **60**, 838) by acetylating methyl anthranilate by means of an acetylating mixture composed of 1 part of acetic anhydride and 2 parts of anhydrous pyridine. Four drops of methyl anthranilate are heated for 5 minutes with 12 drops of the acetylating mixture in a boiling water-bath. A few ml. of water are then added, and heating is continued for a few minutes to destroy the excess of acetic anhydride. On cooling and stirring the liquid the *N*-acetyl derivative separates, and it may be purified by re-crystallisation from dilute alcohol. Its m.p. is 100–101° C. The reaction may even be effected by acetic anhydride alone. In order to saponify the *N*-acetyl and the ester groups of this compound simultaneously, benzylic potash must be used (Sabetay and Savadjian, *J. Pharm. Chim.*, 1931, **13**, 530; abst., ANALYST, 1931, **56**, 475), since alcoholic potash saponifies only the ester group. For the determination of methyl anthranilate in essences of neroli and in neroli water the method now usually employed is that of Hesse and Zeitschel (*Ber.*, 1901, **34**, 296; *cf.* ANALYST, 1902, **27**, 329), based on a quantitative separation of the sulphate starting from an ethereal solution of the essential oil. This procedure is long and requires a considerable quantity of the essence. The determination can be carried out by the Zeisel method (*cf.* Sabetay, *Documentation scientifique*, 1934, **3**, 248, and L. Palfray, *ibid.*, 1935, **4**, 1) on 0·5 to 2 g. of the oil, especially since neither the essence nor the neroli water contain substances likely to react with hydriodic acid to form alkyl iodides. The method gives results identical with those found by the Hesse–Zeitschel method. The calculation may be made by the following formula:

$$\text{Methyl anthranilate, per cent.} = \frac{151 \times 4 \times \text{ml. } N/10\ AgNO_3}{\text{g. substance} \times 100}$$

A fraudulent addition of ethyl alcohol can falsify the results obtained by this method, but so can the results of the Hesse–Zeitschel method be rendered inconclusive by the addition of synthetic methyl anthranilate. A. O. J.

Technical Products from Coconut-Oil Wax. S. S. Tanchico. (*Philippine J. Sci.*, 1935, **57**, 423–426.)—Coconut-oil deposits a sediment on standing in tanks. The exact amount of sediment is not known, but it was surmised in one mill that 500 tons of oil would deposit some 40 kg. of sediment in 3 months, whilst other estimates were higher. After purification of the sediment by treatment with kerosene and animal charcoal, crystals (m.p. 93 to 96° C.) separated from the clear solution. These were readily soluble in hot amyl alcohol, benzene, etc., and fairly soluble in hot ethyl alcohol, but only slightly so in benzyl alcohol, ethyl acetate, petroleum spirit, methyl alcohol, ether and acetone. No glycerol was

found in the saponification products, and, although insoluble in water the residue formed water emulsions. Crystals, melting at 88 to 90° C. and identified as myricyl alcohol, separated from an ethereal solution of the precipitate formed on adding water to the saponified product, and cerotic acid (m.p. 78–80° C.) was separated from the filtrate. The coconut-oil residue is thus a wax consisting largely of the myricyl ester of cerotic acid. A floor wax, a furniture polish and a leather polish were prepared from the residue. D. G. H.

Separation of Selacholeic Acid from Cod-liver, "Sukeso-Dara" Liver, Sei-Whale and Pilot-Whale Oils. Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 684–687B.)—Selacholeic acid ($\Delta^{15:16}$-tetracosanic acid), a mono-ethylenic acid, $C_{24}H_{46}O_2$, has already been found in the liver-oils of *Narcacion tokionis*, *Chimaera barbouri* and *Squalus sucklii*, and in sardine oil; it has now been separated by methanolysis from cod-liver, "sukeso-dara" liver, sei-whale and pilot-whale oils. It may thus be described as a fatty-acid component of common occurrence in marine animal oils. It is the same compound as the "nervonic acid," isolated by Klenk (*Z. physiol. Chem.*, 1927, **166**, 287). D. G. H.

Acidic Components of Wool Grease. E. E. U. Abraham and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1935, **54**, 398–404T.)—The acidic components of many samples of fresh neutral wool grease, wool grease recovered from waste liquors, and grease obtained by extracting crude merino wool with solvent, were separated, and the neutral methyl esters were submitted to fractional distillation in the vacuum of a "Hyvac" pump. An attempt was made to resolve the acids produced by hydrolysis of individual ester fractions, by fractional crystallisation from various solvents, but the mixture was very complex and quite different in variety from that found in similar analyses of a natural fat. The chief component acid was found to be a waxlike solid, m.p. 73 to 75° C., not "cerotic" (*n*-hexacosoic) acid, but of similar formula. This confirms other workers' results, and the old view, that palmitic, stearic and oleic esters of cholesterol and *iso*cholesterol are absent from wool grease, is also endorsed. In fact, wool grease is a mixture of sterol and not of glycerol esters, and the sterols are regarded as in combination with acids of types not met with in the natural glycerides and in a number of which the carbon-content is probably a multiple of C_5. They may thus be derived from an isoprene or terpenoid skeleton, and, from the m.p. and other properties, the acids of formulae corresponding with $C_{15}H_{30}O_3$, $C_{30}H_{60}O_4$ and $C_{30}H_{60}O_3$ are regarded as identical with the "lanopalmic," "lanoceric" and "lanoceric acid lactone" acids of Darmstädter and Lifschütz. The acid of lowest m.p. (about 22° C.) and of greatest solubility could not be purified, but in its impure state it gave analytical figures in close conformity with those demanded by the formula $C_{14}H_{28}O_2$.
D. G. H.

Separation of Physeteric Acid from Sardine and Pilot-Whale Oils. Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 680–684B.)—Tetradecenoic acid was separated by the sodium soap and acetone method from sardine and pilot-whale body oil, converted into dihydroxymyristic acid by Hazura's method, and then into methyl dihydroxymyristate, which was oxidised by

potassium permanganate in acetone. After saponification of the acid ester in the oxidation products, *n*-nonoic acid and glutaric acid were identified, so that the tetradecenoic acid in sardine and pilot-whale oils is shown to be physeteric acid [$\Delta^{5:6}$-tetradecenoic acid, $CH_3.(CH_2)_7CH{=}CH(CH_2)_3.COOH$.] Although $\Delta^{9:10}$-tetradecenoic acid was not found, it does not necessarily follow that physeteric acid is the only tetradecenoic acid, in addition to the widely occurring $\Delta^{5:6}$ acid, present in marine animal oils. D. G. H.

Unsaponifiable Matter of Sei-Whale Oil. Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 687–690B.)—Recorded data for the proportion of unsaponifiable matter in sei-whale oil vary somewhat, and it is possible that, in samples containing over 10 per cent., there may have been contamination with sperm oil. The unsaponifiable matter used in the present investigation was the unsaponifiable residue from the distillation of the methyl esters obtained from the oil. The unsaponifiable matter was heated with acetic anhydride, and the resulting acetates were fractionated, selected fractions being saponified, and the free alcohols examined. Oleyl alcohol ($\Delta^{9:10}$ octadecenol) together with a small proportion of cetyl alcohol and cholesterol were identified; also a lower homologue of saturated alcohols (possibly octadecanol) appeared to be present, and the presence of some highly unsaturated alcohols was indicated. D. G. H.

Cress Seed Mucilage. K. Bailey. (*Biochem. J.*, 1935, **29**, 2477–2485.)—The mucilage obtained from cress seed (*Lepidium sativum*), like that from white mustard and quince seed, contains a dispersible cellulose component, and, on acid hydrolysis, gives rise to *l*-arabinose, *d*-galactose, *l*-rhamnose, *d*-glucose (from the cellulose component) and *d*-galacturonic acid, all of which have been isolated in crystalline forms. During the hydrolysis it was possible to obtain the uronic acids in a portion which is probably formed by the linkage of two aldobionic acids. Except for the reducing power, the barium salt of the uronide conforms with the analytical requirements of a barium aldobionate. When this salt was hydrolysed, β-*d*-galacturonic acid, *l*-rhamnose monohydrate and the *as*-methylphenylhydrazone of galactose were isolated from the hydrolytic products. It is uncertain whether the two sugars constitute part of one or of separate units. It has also been found that the two cellulose-containing mucilages of white mustard seed and the non-cellulosic mucilage of linseed are heterogeneous polysaccharide systems which are capable of fractionation. S. G. S.

Inorganic

Determination of Bismuth with *o*-Hydroxyquinoline. F. Hecht and R. Reissner. (*Z. anal. Chem.*, 1935, **103**, 261–269.)—The nitrate or sulphate solution is treated with 3 ml. of 50 per cent. tartaric acid solution per 0·01 g. of bismuth, a few drops of phenolphthalein and methyl red indicators, and ammonia until faintly red. Acetic acid (10 per cent.) is then added until the methyl red turns from yellow to pink, followed by enough acid to ensure an acidity of 0·5 to 1 per cent. after addition of all the reagents. The solution is then treated with ammonium acetate to give a solution with a concentration of not more than

3 per cent., and, after being heated at 60° or 70° C., it is treated with 4 times the required amount of 4 per cent. hydroxyquinoline solution in 8 per cent. acetic acid, added, drop by drop, during constant stirring. The liquid is heated just to boiling and left to cool. The precipitate is collected in a tared porous porcelain crucible, washed with hot water, dried by suction, and weighed as $Bi(C_9H_6ON)_3.H_2O$ (containing 31·71 per cent. of metal). Alternatively, the precipitate may be dried at 100° to 105° C. (1 to 1½ hours). The results are shown to be accurate in macro- as well as in micro-work. The authors have re-investigated Berg and Wurm's method (precipitation as hydroxyquinoline tetraiodobismuthate, *Ber.*, 1927, **60**, 1664), but could not obtain concordant results. W. R. S.

Determination of Small Amounts of Mercury and Lead by Photometric Titration. S. Hirano. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 646B–650B.)—With the aid of a technique for photometric titration, in which a cuprous oxide photo-electric cell is used (*id.*, 1934, **37**, 177B; ANALYST, 1934, **59**, 573; 1936, 67), the following processes have been worked out. *Mercury.*—To the mercuric salt solution (1 to 5 ml.) contained in a 150-ml. tall beaker, 5 to 10 ml. of 1 per cent. gum arabic solution and 5 to 10 ml. of 0·2 *N* potassium cyanide solution are added, and the liquid is titrated with sodium sulphide solution, previously standardised by a similar photometric titration with standard bismuth chloride solution (*id.*, 1935, **38**, 598B). The end-point is given by an inflexion in the curve of galvanometer-readings plotted against the amount of sodium sulphide added; *M*/100 sodium sulphide solution is used for 0·002 to 0·01 g. of mercury and *M*/1000 solution for smaller amounts down to 0·2 mg. The results were, in general, accurate within a few units per cent. Arsenic and copper (in the presence of an excess of potassium cyanide) had no effect. For the determination of mercury in anti-fouling paint and amalgamated electrode-zinc, the sample was dissolved in nitric acid, and the mercury was deposited on copper gauze, which was subsequently dissolved in nitric acid, the solution was neutralised, and the mercury determined by the above method. *Lead.*—The lead solution, to which has been added 5 to 10 ml. of 1 per cent. gum arabic solution, is titrated with sodium sulphide solution as for mercury; the amount determinable and the degree of accuracy are similar. The presence of up to 2 ml. of 15 per cent. acetic acid, 10 g. of ammonium acetate and 20 g. of ammonium sulphate has little effect. No interfering metals were present in the test experiments. The method was used for determining lead in crude sulphuric acid; the lead sulphate, precipitated by the addition of alcohol, as in the ordinary process, was filtered off, dissolved in ammonium acetate solution and titrated with sodium sulphide. For the determination of lead in flint glass, the powdered sample was decomposed with hydrofluoric and sulphuric acids, and the lead sulphate formed was dissolved and titrated as before. S. G. C.

Notes on the Chemistry of Tin Surfaces. A. Kutzelnigg. (*Z. Elektrochem.*, 1935, **41**, 450–453.)—When dipped in 10 per cent. ferric chloride solution, pure tin remains white, whilst tin containing antimony or bismuth is rendered grey or black in colour; 0·1 per cent. of antimony or 1 per cent. of bismuth gave a grey colour, and 1 per cent. of antimony gave black. Antimony in tin causes

a considerable acceleration in the rate of solution in hot concentrated hydrochloric acid; bismuth, on the other hand, causes a marked retardation; antimony and bismuth remain undissolved as black or reddish-grey residues, respectively. A tin surface in presence of air is only very slowly attacked by iodine vapour owing to the existence of a protective oxide film; attack starts at local spots where the oxide film is porous. Tin which has been freed from oxide film by treatment with hydrochloric acid and potassium chlorate mixture and kept in a vacuum, rapidly reacts with iodine vapour, acquiring a greyish-yellow colour. The oxide film on tin-foil was revealed by allowing iodine vapour to act on it for about 1 month, when all the tin metal became converted to iodide; the tin iodide was dissolved in carbon disulphide, leaving the oxide film as a thin skin. This demonstration could be achieved more rapidly by the use of bromine vapour. S. G. C.

Colorimetric Determination of Manganese in presence of Titanium. G. J. Hough. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 408–409.)—Titanium interferes with the silver nitrate-ammonium persulphate colorimetric method for manganese. When titanium is present in the test-solution in amounts exceeding 1 per cent., the method is useless, as no permanganate colour is developed unless excessive amounts of reagents are used, and even then there is no certainty that the full colour has been obtained. It is recommended that, in presence of titanium, potassium periodate or sodium bismuthate should be used to oxidise the manganese to permanganate, as titanium is stated not to interfere in these processes.

S. G. C.

Bismuthate Method for Determining Manganese. B. Park. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 427.)—Tests have been made of the titration of permanganate with standard arsenite solution in the presence of catalysts which have been claimed to cause the interaction to proceed according to the equation $2\,Mn^{VII} + 5\,As^{III} \rightarrow 2\,Mn^{II} + 5\,As^{V}$. It was found that osmium tetroxide was a satisfactory catalyst, rendering it possible to modify the usual bismuthate method for manganese in steel, as follows:—After the excess of bismuthate has been filtered off on a Jena-glass filter, a measured excess of standard sodium arsenite solution, containing 3 drops of 0·01 *M* osmium tetroxide solution, is added, and the solution is back-titrated with standard permanganate solution; an electrometric method of titration was used similar to that described by Kassner, Hunze and Chatfield (*J. Amer. Chem. Soc.*, 1932, **54**, 2278). Test results on a standard steel and on iron ore (both Bureau of Standards samples) were in close agreement with the certificate values. S. G. C.

Colorimetric Determination of Molybdenum. L. C. Hurd and H. O. Allen. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 396–398.)—A study has been made of the influence of various factors in the colorimetric thiocyanate method. To solutions of molybdenum (100γ as sodium molybdate) were added hydrochloric acid, stannous chloride solution (2 per cent.) potassium thiocyanate solution (10 per cent.) and water to a vol. of 50 ml. Values of intensity of colour were determined by means of an Eastman colorimeter after definite intervals of time. In solution containing less than 0·6 per cent. of potassium thiocyanate marked

fading occurred, but with larger amounts (in presence of 0·8 per cent. of stannous chloride and 5 per cent. of hydrochloric acid) the colour remained constant for at least 50 minutes. With low concentration of hydrochloric acid (0·5 per cent.) the colour reached a maximum at the end of 8 minutes, and faded to less than its initial value at the end of 25 minutes; with 5 per cent. of hydrochloric acid some fading occurred in the first few minutes, but thereafter the colour reached an almost constant value; with larger amounts of hydrochloric acid progressive fading occurred (these tests of effect of acid were in presence of 1 per cent. of potassium thiocyanate and 0·8 per cent. of stannous chloride). With sulphuric acid instead of hydrochloric acid, the colours rapidly reached steady values, provided not more than 10 per cent. was present; below this amount the full development of colour was not produced. In presence of 5 per cent. of hydrochloric acid the addition of more than 0·5 per cent. of sulphuric acid caused steady fading. [*Abstractor's Note.*—the strengths of hydrochloric acid given are, presumably, percentages of hydrogen chloride, since it is stated that "the hydrochloric acid solution was prepared by diluting constant-boiling acid with water."] The reaction was not noticeably sensitive to fluctuation in stannous chloride concentration above 0·1 per cent. In tests of the extraction of the colour with solvents, it was found that butyl acetate gave anomalous colour effects, but ether or *cyclo*hexanol was satisfactory. Extraction of the colour should be made 5 minutes after adding the reagents. S. G. C.

Determination of Small Quantities of Selenium in Sulphur. G. S. Marvin and W. C. Schumb. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 423–425.)—The following method is proposed for the determination of 0·001 to 0·1 per cent. of selenium in sulphur; arsenic and tellurium in amounts comparable with that of the selenium cause no interference. The sulphur (100 g.) is placed in a boat of Pyrex glass and ignited at one spot. The boat is then introduced into a prepared combustion tube consisting of a glass tube, about 1 inch in diameter and 2 ft. long, there being sealed on at one end a narrower tube, about ½ inch in diameter and 6 inches long, packed with asbestos (previously purified by heating with conc. hydrochloric acid) and provided with a water-jacket for cooling. The open end of the wider tube, through which the boat has been introduced, is closed with a rubber stopper carrying a leading tube, and oxygen is passed in, causing combustion of the sulphur; no external heating of the tube is required. (It is desirable that the end of the leading tube projecting into the combustion tube should be blown into a bulb only a little smaller in diameter than that of the combustion tube, the bulb having a small hole near the point of attachment to the leading tube; the oxygen thus has to pass through the annular space between bulb and interior of combustion tube; this device was found necessary in minimising back-diffusion of sulphur dioxide, which attacks the rubber stopper.) After the combustion, the boat, the interior of the combustion tube, and the asbestos packing are washed with hot conc. nitric acid and then with water. These washings, containing the selenium as selenious acid, are concentrated by evaporation to a vol. of 10 ml. The solution is made ammoniacal to precipitate any ferric hydroxide, which is filtered off, washed, and rejected. The solution is

neutralised with nitric acid, 10 ml. in excess of conc. nitric acid are added, and the liquid is diluted to 50 ml. After addition of about 3 g. of urea, to destroy nitrous acid, the liquid is heated gently for 2 to 3 minutes, cooled, and diluted to 300 ml.; 3 g. of potassium iodide are added, and, after an interval of 1 to 2 minutes, the iodine liberated according to the equation $SeO_2 + 4HI \rightarrow Se + 2H_2O + 2I_2$ is titrated with standard sodium thiosulphate solution. The results of tests on synthetic mixtures of selenium and sulphur were in close agreement with the amounts of added selenium. No selenium was found in commercial Texas flowers of sulphur, crude Louisiana sulphur, or crystal sulphur from Garginti, Sicily, but a volcanic sulphur deposit of Sicilian origin contained 0·054 per cent. of selenium. S. G. C.

Rapid Gravimetric Determination of Silica. N. A. Tananaeff and M. K. Buitschkoff. (*Z. anal. Chem.*, 1935, **103**, 349–353.)—The procedure utilises strong nitric acid for the precipitation of the silica, and gelatin solution (0·1 per cent.) for facilitating filtration.

Determination in Limestone (Dolomite).—The powder is treated in a covered beaker with nitric acid (3, 5, 7, 9, or 11 ml. for 1, 2, 3, 4, or 5 g., respectively). When effervescence has ceased, the cover and sides of the beaker are rinsed down, and the volume is made up to 25 to 50 ml. The silica is left to settle, collected on a small filter, and washed with 3 per cent. nitric acid. The wet paper is cautiously ignited, with the apex uppermost, in a platinum crucible, and fused with potassium and sodium carbonates. The product is treated with strong nitric acid (2 ml. per g. of fusion mixture). When the action is over, the crucible is heated on a steam-bath, the cover is rinsed, and 5 to 10 ml. of hot gelatin solution are stirred in, the nitric acid being diluted to not less than 5 times its volume. Should the crucible be too small, dilution of the acid must be carried out in a beaker. The vessel is left on a steam-bath for 5 minutes, and the precipitate is collected on a loose filter, washed with hot 3 per cent. nitric acid, ignited wet, and weighed.

Determination in Quartzite, Glass, Clay, and Kaolin.—A considerable excess of fusion mixture is used, and the fusion is conducted at low temperature, since otherwise the melt is refractory to acid treatment. The material (0·5 g.) is fused with 4 to 5 g. of fusion mixture and 0·1 to 0·2 g. of potassium chlorate. Quartzite and glass require 15, clay and kaolin 30, minutes. The fluid melt is poured out as thinly as possible on to a clean nickel or steel surface or the flat lid of a platinum crucible, left to cool, and treated with 7 to 8 ml. of strong nitric acid in a covered beaker. When the violent reaction has abated, the beaker is placed on a steam-bath and the cake is manipulated with a rod until disintegrated. Meanwhile 2 to 3 ml. of strong nitric acid are poured into the covered crucible, and the remainder of the melt is dislodged therefrom by means of the glass rod. The contents of the crucible are added to those of the beaker, and the crucible is rinsed with a little nitric acid. When decomposition is complete, 3 to 5 drops of strong hydrochloric acid are added for the solution of the sesquioxides, and the beaker is left for another 15 minutes on the steam-bath. The clockglass and sides of the beaker are rinsed down with hot water, and 15 ml. of hot gelatin solution are added, followed by hot water to dilute the nitric acid to 5 times its volume. The

assay is completed as in the preceding determination. Filtration and washing occupy 10 to 15 minutes, and the whole determination requires 2 to 2½ hours. Preliminary experiments failed to indicate interference of the gelatin in the precipitation of the sesquioxides. The results agree well with those obtained by the classic method. W. R. S.

Detection of Bromate. I. M. Korenman. (*Z. anal. Chem.*, 1935, **103**, 269–271.)—The solution to be tested (2 ml.) is treated with 1 ml. of 4 *N* HCl and 1 to 2 drops of 0·015 per cent. methyl orange solution. Bromate causes rapid bleaching of the colour. The sensitiveness is 14γ of potassium bromate in 2 ml. The reaction may also be carried out as a spot-test. As iodates, chlorates, persulphates, etc., decolorise methyl orange only in solutions acidified with strong acid, the above reaction may be used, *e.g.* for the detection of bromate in potassium chlorate. The salt (0·1 g.) is dissolved in 10 ml. of water, and 2 ml. of the solution are treated as described; if 0·1 per cent. of bromate is present, the colour is bleached in a few seconds. Nitrite at concentrations below 1 : 2000 acts much more slowly than bromate. For the detection of bromate in potassium bromide, 0·2 g. of the salt is dissolved in 2 ml. of water, and the solution is acidified and tested as described. Rapid decolorisation is brought about by as little as 0·01 per cent. of bromate. W. R. S.

Microchemical

Volumetric Modification of the Pregl Halogen Micro-Combustion Method for Organic Iodine. P. L. Kirk and K. Dod. (*Mikrochem.*, 1935, **18**, 179–181.)—The method is a slight modification of Leipert's method described by Pregl (2nd edition, p. 136), in which the Pregl combustion in oxygen is used and the iodine subsequently converted to iodate with bromine, and titrated with 0·01 *N* thiosulphate. The differences from Leipert's method are that the absorbing medium for iodine is 2 ml. of saturated sodium carbonate solution and 3 drops of strong sodium bisulphite solution (free of halides), instead of sodium carbonate only, and that 2 ml. of glacial acetic acid are used, instead of sulphuric acid, for the neutralisation. Instead of steam being blown through the flask to remove excess of bromine, the solution is boiled. It is important not to boil at once, otherwise up to 50 per cent. of the iodine may be lost, but no loss occurs if the solution is not boiled until it is uniformly brown. An advantage of boiling is that excess of water is removed and the end-point is correspondingly sharper. A little salicylic acid or, preferably, phenol, is added to remove the last traces of bromine, the solution is then made definitely acid by the addition of 2 ml. of 10 *N* sulphuric acid, after which 2 ml. of 1 per cent. potassium iodide solution are added, and the liberated iodine is titrated with standard thiosulphate solution. The errors in a number of analyses quoted are mostly of the order of 0·3 to 0·5 per cent. J. W. M.

Quantitative Determination of Components of Mixtures of Explosives by applying the Micro Carbon-Hydrogen Analysis. M. Furter and J. L'orange. (*Mikrochem.*, 1935, **17**, 38–42.)—The components of mixtures of

the two high explosives, trinitrotoluene and tetranitro-penta-erythritol, may be determined with an error of 0·5 to 1·2 per cent. by calculation from the carbon-content of the mixture, as the Pregl method achieves an accuracy of 0·2 per cent., or rather better (0·05 per cent.) with suitable material. The samples are mixed in the boat with ignited kieselguhr, to ensure slow combustion, and slightly more lead peroxide filling than usual is used in the combustion tube, otherwise the usual Pregl technique is closely followed. In testing the method, it was found that a mechanical mixture ground in an agate mortar was not sufficiently homogeneous. It was, therefore, necessary to weigh the two components directly into the combustion boat, the results then obtained being of the desired accuracy, 0·5 to 1·2 per cent. This method was applied to the analysis of mixtures made by solution in acetone, precipitation with water, and drying the precipitate *in vacuo* over phosphorus pentoxide. J. W. M.

Microscopy of the Amino-acids and their Compounds. I. Phosphotungstates and Phosphomolybdates. B. Bullock and P. L. Kirk. II. Picrates and Flavianates. B. L. Crosby and P. L. Kirk. (*Mikrochem.*, **1935, 18**, 129–136; 137–143.)—I. Details are given of the microscopic appearance and optical constants of a number of phosphotungstates and phosphomolybdates of the amino-acids, prepared on the microscope slide. The general method of preparation of the phosphotungstates is as follows:—A small drop of concentrated sulphuric acid is added to a large drop of phosphotungstic acid, and any precipitate formed is dissolved by stirring or by the addition of a little water. This reagent solution is diluted with 1 to 5 drops of water, and either a crystal, or a drop of a solution, of the amino-acid is added. The mixture is then heated almost to boiling, and the phosphotungstate usually crystallises out on cooling. The optimum dilution of the reagent (empirically determined) is somewhat variable. The hexone bases, which yield particularly insoluble phosphotungstates, require the most dilution, 4 or 5 drops of water being added to the reagent. With the exception of the phosphotungstates of proline and hydroxyproline, the preparations are improved by re-crystallisation. Fine precipitates unsuitable for identification were yielded by aspartic acid, norvaline, α-amino-*n*-valeric acid, leucine, valine, hydroxyvaline and isoleucine. No precipitates could be obtained with tryptophane, norleucine, glutamic acid, tyrosine, di-iodotyrosine, norvaline, methionine, or dibromotyrosine. Successful preparations were obtained with the following:—alanine, glycine, lysine, arginine, cystine, histidine, isoserine, serine, proline, and hydroxyproline. The phosphomolybdates are prepared exactly as the phosphostungstates, but the conditions of precipitation are less critical. Solutions of amino-acids yielded poorer preparations than the solid amino-acids. The crystals formed with phosphomolybdic acid were, with the exception of isoserine, always yellow. The same amino-acids which gave satisfactory preparations with phosphotungstic acid were successful with phosphomolybdic acid. Eighteen photomicrographs are given.

II. The picrates may be prepared on the slide by mixing a drop of a saturated solution of picric acid with a crystal of solid amino-acid. The drop is stirred to dissolve the amino-acid, with slight warming if necessary. Sometimes oily drops

form at the margin and crystals appear in these droplets. With the exception of aspartic acid, cystine and tyrosine, crystals were obtained with all the amino-acids tried. Successful preparations of picrates of the following amino-acids were made:—alanine, arginine, dibromotyrosine, dichlorotyrosine, diiodotyrosine, glutamic acid, glycine, histidine, hydroxyproline, hydroxyvalene, isoleucine, isoserine, leucine, lysine hydrochloride, methionine, norleucine, norvaline, phenyl-alanine, proline, serine, tryptophane, and valine. The compounds of leucine, isoleucine and norleucine crystallised very slowly from the dry oil-film (only after 5 to 6 hours), and are thus of little value for a systematic scheme of identification. Flavianates may be prepared in the same way as picrates, and for optical crystallographic examination the compound is re-crystallised once or twice from water and allowed to dry on the slide, from which the crystals can be scraped. The following yielded no crystals:—alanine, glycine, cystine, dibromotyrosine, proline, hydroxyproline, phenylalanine, hydroxyvaline, norvaline, serine and isoserine. The following formed good crystals and photomicrographs are given:—arginine, aspartic acid, dichlorotyrosine, diiodotyrosine, glutamic acid, histidine, isoleucine, leucine, lysine, methionine, norleucine, tryptophane, tyrosine, and valine. J. W. M.

Microchemical Detection of Cholesterol, Urea and Glycerol, etc., based on the Formation of Liquid Crystals. P. Gaubert. (*Compt. rend.*, 1935, **201**, 1202–1204.)—In previous work the author has described the formation of liquid crystals by fusing cholesterol with various substances (*Compt. rend.*, 1907, **144**, 761; 1907, **145**, 732; 1908, **147**, 632; 1909, **149**, 608; 1913, **156**, 149; and *Bull. Soc. Min.*, 1909, **32**, 62, 438; 1913, **36**, 614.) Either cholesterol itself, or, alternatively, the substances giving characteristic liquid crystals with cholesterol, may be identified by their formation and appearance. The urea-cholesterol anisotropic liquid may be formed by adding a small crystal of urea, either to a crystal of cholesterol, or to the residue left after evaporation of a solution, on a microscope slide and covering with a watch glass. The preparation should then be heated on a hot plate. An electric hot plate, provided with thermometer and suitable for placing on the microscope stage, enables the formation of liquid crystals to be observed under the microscope. In this manner urine may readily be distinguished from other biological fluids. The urea in 20 mg. of urine, or even less, may be identified by heating the liquid with a crystal of cholesterol to the m.p. of the latter (148·5° C.). Similarly, glycerol may be identified in wine and in certain toilet preparations. A drop of lemon juice gives liquid crystals with cholesterol, owing to the citric acid. These crystals differ in appearance from the liquid crystals obtained from urine or wine. J. W. M.

Physical Methods, Apparatus, etc.

Nature of the Nucleus in Hygroscopic Droplets. J. H. Coste and H. L. Wright. (*Phil. Mag.*, 1935, Ser. 7, **20**, 209–234.)—The concentration of nuclei in a closed cubical wooden box (vol. 72·5 litres) was determined by means of an Aitken nucleus counter before and after the combustion of various fuels or heating by electrically-heated metal surfaces. Various substances which, it was

thought, might be possible sources of nuclei, were also introduced. Combustion was produced by coal gas before and after a week in contact with strong sodium hydroxide solution, absolute alcohol, and a mixture of this with carbon disulphide containing the same amount of sulphur as ordinary coal gas. In general, the number of nuclei produced depends on the duration of combustion and is decreased, although not eliminated, if sulphur compounds are absent. Combustion (even of absolute alcohol) increases the number of nuclei, although this decreases subsequently, and formation of nuclei was found to occur under suitable conditions of temperature, even if the source of heat was electrical and if the air was free from pre-existent nuclei and from sulphur dioxide and other acid gases. Various hypotheses in explanation of this were tested by observing the effect on nuclei-formation of the introduction of appropriate substances, and it is concluded that droplets of nitrous acid are formed from constituents of the air under suitable conditions of temperature. Nitrous acid was, in fact, detected by the Griess–Ilosvay reagent in nucleus-free air in which a platinum surface was heated, and in the condensates collected from the various flames. The effects of sprays of various liquids (without heat) were also examined, and sulphuric acid and sea-water were found to be active producers of nuclei, whilst hydrochloric acid, caustic alkalis, calcium chloride and tap-water were inactive or, at the most, only feebly active. Reasons are given for the belief that, although chlorides (from sea-water) are the chief natural constituent of nuclei, most of the nuclei produced by human activities (*e.g.* fires) are droplets of nitrous acid, some droplets of sulphuric acid being also formed, probably by oxidation of sulphur dioxide by existing nitrous acid nuclei (as in the chamber process). It is calculated that both acids exist in air in quantities sufficient to produce 100,000 nuclei (average radius 5×10^{-6} cm.) per ml. (*i.e.* 10^{-10} to 10^{-11} g.); and that for the same humidity, fire-produced and sea-water nuclei have radii of 8×10^{-6} and 8×10^{-7} cm., respectively. J. G.

Colour Testing of Bitumen. D. M. Wilson. (*J. Soc. Chem. Ind.*, 1935, **54**, 1040–1042.)—The colour of a bitumen is a valuable guide to its quality, *e.g.* pure Trinidad epuré may be distinguished from the less expensive asphalt bitumen, which is sometimes used partly or wholly to replace it; it also provides a valuable means of testing a delivery against a specification (cf. *Chem. and Ind.*, 1934, **53**, 924). The solvent used is important, because some (*e.g.* carbon disulphide) penetrate the protective layer which is supposed to surround carbon particles and carbon compounds dispersed in an oily medium, and dissolve the nucleus, whilst others (*e.g.* benzene) do not, and so produce a paler solution. If, therefore, two samples appear to be the same in colour in one particular solvent, another solvent should be tried, especially if the bitumen-content is low. It is preferable with samples cut from a road to dissolve out the bitumen directly rather than to recover it in the usual way and then to take a portion of this for the colour test, as in the latter procedure the product is apt to become contaminated with water, which deepens the colour. Mineral matter should be removed by filtration in a sealed funnel through a No. 5 Whatman paper (cf. *id.*, 1931, **50**, 599) after it has stood for a specified period of time, and after a further 24 hours it should be diluted

and the colour matched. Exposure to light or the presence of impurities (particularly chlorine in trichloroethylene, etc.) have a marked influence on the colour. A skilled operator can distinguish between solutions differing by only 0·1 neutral tint, although sometimes the number of red units is a safer guide (*e.g.* in distinguishing between mixtures containing 50 and 30 per cent. of Trinidad epuré in Panuco crude oil); the operator should spend at least 10 minutes in a dark room before making a test. A description is given of a photo-electric colorimeter, in which the light from a 250-watt Osram AI projector lamp (compact filament type) passes through a condensing lens to a mirror. This reflects it downwards through a glass vessel (3 × 3 × 3 cm.) containing 10 ml. of a 0·5 per cent. solution of the standard bitumen in benzene, and thence to a Weston 594 photo-electric cell. The rheostat which controls the intensity of the lamp source is adjusted until the microammeter records a current of, say, 200 microamperes from the Weston cell, and a solution of the bitumen under examination is then substituted for the standard and the reading noted. If Trinidad epuré is the standard, some other typical readings are Mexphalte, 35 to 39·5; D.X. bitumen, 8; Utaphalte, 18; Panuco Spramex, 46; and Venezuelan Spramex, 21. A reference table of this kind should be made for each photo-electric cell used, and care should be taken that this cell is not illuminated other than through the solution. The sensitiveness may be increased (*e.g.* so as to enable differentiations to be made between mixtures of Trinidad epuré and Spramex with an accuracy of 10 per cent.) by taking the lighter solution as standard and adjusting the illumination or volume of the solution so as to obtain a reading of 200; the reading for the other solution is then determined under the same conditions. Alternatively, the volume of solution required to give the same deflection as a fixed volume of standard may be measured, and typical values based on this method are tabulated. The instrument, which is independent of the human eye, may be used to check the Lovibond tintometer values, and if coloured screens are used in the manner described by Bolton and Williams (ANALYST, 1935, **60**, 447), the transmission may be measured for rays of different wave-lengths. J. G.

Reviews

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY. Vol. XIV. By J. W. MELLOR, D.Sc., F.R.S. Pp. 892. London: Longmans, Green & Co. 1935. Price 3 guineas.

The first volume of Mellor's Treatise was published thirteen years ago; we have now before us the fourteenth volume, and, according to the publishers' notice, the completing two volumes are in the press. To have undertaken so great a work and to have accomplished it in so short a time are remarkable achievements, and place the author in the foremost rank of chemical writers.

The first half of the present volume is devoted to the chemistry of iron compounds, the isolation and metallurgy of iron having been discussed in the previous two volumes. The remainder of the book deals with cobalt and its compounds. It is undoubtedly the most exhaustive account, particularly of

the complex cobalt compounds, available in the English language. Both the treatment and arrangement of the subject-matter follow the lines adopted in the earlier volumes, but here and there one finds the author exercising a keener criticism of dubious claims made by the writers of original memoirs. A serious difficulty confronting anyone writing a critical survey is the fact that the existence of many compounds, described in the original chemical literature, is based on very slender evidence, and until the existence of such compounds has been confirmed, the compiler finds himself in a quandary as to which to accept and which to reject. This is particularly the case with the multitude of basic salts, the individuality of which has been claimed, and it is gratifying to note that in such instances the author has often used his powers of criticism, *e.g.* on p. 328 in connection with the basic ferric sulphates. On the other hand, it is somewhat irritating to find highly conjectural formulae representing the structures of complicated inorganic compounds and especially of doubtful basic salts.

The new volume is fully up to the very high standard of usefulness so characteristic of the preceding volumes of the treatise, and in conclusion, the reviewer wishes to thank and heartily to congratulate Dr. Mellor on the publication of yet another invaluable volume. H. T. S. BRITTON

AUSGEWÄHLTE UNTERSUCHUNGSVERFAHREN FÜR DAS CHEMISCHE LABORATORIUM. Neue Folge (Zweiter Teil). L. W. WINKLER. Pp. 159. Stuttgart: Ferdinand Enke. 1935. Price RM.15.8 (less 25 per cent. for foreign countries).

With the book under review, which makes the thirty-fifth volume in the well-known series first brought out by Dr. Margosches, Prof. Winkler adds a supplement to his previous book on general laboratory practice. In some respects this new work follows the lines of his earlier one, but much new matter is added, and the section devoted to physical methods includes several chapters on the determination of the absorption co-efficients of gases in various solvents. In the chemical part more space is now devoted to colorimetric methods of analysis. Although, no doubt, mainly intended for students or those engaged in the pharmaceutical laboratory, much of the matter in this book, especially that contained in the later chapters, is of interest to chemists generally. The early part of the book—like that of Part I—deals briefly with the measurement of density, melting-point and boiling-point of various substances, and there are a number of chapters on solubility determinations. Tables of results obtained by various workers are included, but these take up rather much space, and many of the figures given would seem to be of little interest.

In the chemical section some space is allotted to the examination of oils, methods for the determination of iodine, ester and acid values being described in considerable detail. Much of the book is, however, concerned with the various determinations required in the analysis of potable waters. As a rule, standard practice is followed, although, for the determination of free chlorine in water, the *o*-tolidine method would be more favoured in this country than that depending on the use of methyl red as described by the author. The question of hardness is fully dealt with, and it might be mentioned that the use of potassium

palmitate with alkali is favoured. The various methods involving the use of colorimetric matching include the determination of silica and ammonia in water. For the latter determination it is to be noted that potassium persulphate in acid solution is recommended as the oxidant for organic nitrogen. Of the metallic elements, iron, copper, manganese and lead are dealt with, and here, again, the methods described are well known. In this connection some mention might, with advantage, have been made of the various organic reagents now available. For example, two methods involving the use of ferrocyanide are given for copper, but no mention is made of that useful material, sodium di-ethyldithiocarbamate. Greater accuracy of working would also be obtained if a weaker standard than that described, *viz.* 0·1 milligram per ml., had been employed, and the addition of the standard solution to the reagents in the matching cylinder is certainly not to be recommended, especially when determining lead as sulphide.

The remainder of the book contains some general exercises in gravimetric separations involving half-micro methods of working, for which, provided a good ordinary laboratory balance is available, speed and accuracy are claimed. Figures for the ash-content of a number of crude drugs are also given. F. A. HATCH

DIE CHEMISCHE ANALYSE. XXXIV Band. DAS *O*-OXYCHINOLIN. RICHARD BERG. Pp. 94. Stuttgart: Ferdinand Enke. 1935. Price (bound) RM.10.20, (paper) RM.8.80.

This excellent monograph provides a comprehensive survey of the available information on the applications of 8-hydroxyquinoline. Despite the fact that the reagent was introduced less than 10 years ago, the large number of investigations which have already appeared have made a book of the present type greatly needed.

8-Hydroxyquinoline is not a "specific" reagent like dimethylglyoxime. On the contrary, its uses depend on its forming relatively insoluble co-ordination compounds with a wide variety of metals. In many instances the metal may be determined by weighing the precipitate after drying, or, more expeditiously, by means of a bromometric titration of the combined hydroxyquinoline. For microchemical purposes methods exist for determining the combined hydroxyquinoline colorimetrically. In the following periodic table, the metals which may be determined by means of 8-hydroxyquinoline are shown enclosed in squares (□); the metals shown in brackets give difficultly-soluble hydroxyquinolates which, for various reasons, have not been found of practical value. By suitable choice of conditions, in particular the *p*H of the solution, the metals sort themselves into groups which form the basis of methods of separation. Some of the separations may, of course, be effected as well, or better, by the usual processes, but, in the reviewer's experience, there are some separations in which the use of 8-hydroxyquinoline offers considerable advantages, notably in that of magnesium from lithium. The reagent has few applications in the qualitative field.

The general validity of hydroxyquinoline methods appears to have been well established. It may be pointed out, however, that the precipitate may tend to adsorb reagent, and since the issue of the present book it has been shown by Knowles (ANALYST, 1935, **60**, 777) that, owing to this cause, slightly high results were obtained for aluminium, and that for strictly accurate results it was necessary

to decompose the aluminium hydroxyquinolate, to destroy the organic constituent by wet oxidation, and then to precipitate the aluminium as hydroxide in the usual manner.

I	II	III	IV	V	VI	VII	VIII		
H									
Li	(Be)	B	C	N	O	F			
Na	[Mg]	[Al]	Si	P	S	Cl			
K	[Ca]	Sc	[Ti]	[V]	Cr	[Mn]	[Fe]	[Co]	[Ni]
[Cu]	[Zn]	[Ga]	Ge	As	Se	Br			
Rb	Sr	Y	[Zr]	[Nb]	[Mo]	Ma	Ru	Rh	[Pd]
(Ag)	[Cd]	[In]	Sn	Sb	Te	I			
Cs	Ba	(Rare earths)	Hf	(Ta)	[W]	Re	Os	Ir	Pt
(Au)	(Hg)	Tl	[Pb]	[Bi]	Po	—			
	Ra	Ac	[Th]	Pa	[U]				

The main part of the book is taken up with clear and concise descriptions of methods, together, in many instances, with notes of the author's personal experience. With the aid of this book, therefore, chemists will be able to take the opportunity of testing new methods and forming an opinion of what advantages they have to offer.

S. G. CLARKE

A SHORT MANUAL OF SYSTEMATIC QUALITATIVE ANALYSIS BY MEANS OF MODERN DROP REACTIONS. By C. J. VAN NIEUWENBURG and (Miss) G. DULFER. Second Edition. Pp. 96. Amsterdam: D. B. Centen's Utg. Maatschappij (N.V.).

The first edition of this book has already been reviewed in this journal (1934, p. 66). The new edition is almost identical with the first, except that a few new tests have been added and that, for the separation of the alkaline earths, the "old" ammonium carbonate method is recommended as an alternative, when the detection of small amounts of these elements is not the aim of the analyst.

The book is intended as a laboratory manual for students and other laboratory workers, and not as a book of reference. It is, therefore, assumed that the general methods of working are known, and these are merely referred to in the "general remarks." The tests, however, are intended to be carried out on the semi-micro scale, with the use of 100 to 300 mg. of material for a complete analysis, and, of course, less for the individual tests, and the authors lay down the rule "never use a test-tube when a drop plate or an object glass could be used."

Under the heading of the individual ions, which include the rarer elements, an extremely useful summary of identification tests is given. This comprises both

the well-known old-fashioned tests and the newer "spot" tests. Abbreviations are used to save space and, naturally, details, such as sensitivity or methods of preparing reagents, are omitted.

There is a chapter on dry methods of analysis and another on a systematic course of analysis. The latter is extremely useful, as it shows how the newer "spot" methods may be incorporated in routine analysis which adheres to the classical methods of separation, and thus the book is to be recommended to those teachers who wish to introduce a few "spot" methods into a general course of analysis.

As suggested by Dr. Ward, in the review of the first edition (*loc. cit.*), the proofs of this edition have been submitted to an English (or rather Scottish) chemist, without, however, eliminating all of the language and printing errors and the foreign use of the hyphen and exclamation mark. JANET W. MATTHEWS

HANDBOOK OF CHEMISTRY AND PHYSICS. Editor-in-Chief, CHARLES D. HODGMAN, M.S. Twentieth Edition. Pp. xiv + 1951. Chemical Rubber Publishing Co., Cleveland, Ohio. Price, $6.

The problem of including a comprehensive work of reference for chemical, physical and mathematical data within the limits of one handy volume becomes increasingly difficult with the progress of the sciences. It has been solved in the present instance by the use of thin paper and small print, but it may be suggested that subsequent and, presumably, larger editions should be published in two volumes.

Successive editions of the book have been published annually since 1914, with the lapse of only one year (1921), and it might be expected that, with such opportunities of revision and amendment, the present edition should attain a high standard. This expectation is confirmed by a scrutiny of the data in which the reviewer is especially interested. Two slight errors of omission may be mentioned. In the directions for preparing laboratory reagents on pp. 840–841, the concentrations in most cases correspond to those of normal solutions, but this is not stated. In the table of "Physical Constants of Organic Compounds" (pp. 505–742) one would expect to find the specific rotatory powers of the sugars; the values are given for many compounds, but not for the more important sugars, although they appear in a later section of the book, and the specific rotations of inulin and raffinose are not to be found anywhere. Such errors of omission are, of course, trivial, and the book, as a whole, is remarkably free from errors of any kind.

The table referred to above is prefaced by an article on the Rules for naming organic compounds adopted by the Council of the International Union of Chemistry in 1930, and names in the table approved by the Union are starred; the table is followed by a useful formula-index of organic compounds. LEWIS EYNON

FORENSIC CHEMISTRY AND SCIENTIFIC CRIMINAL INVESTIGATION. By A. LUCAS, O.B.E., F.I.C. Third Edition. Pp. 376. London: Edward Arnold & Co. 1935. Price 18s. net.

It falls to the lot of few scientific books to reach a third edition within the short space of four years after the publication of the second, and the author is to

be congratulated on having achieved this deserved success. One need not be surprised at this, however, for the book has established its position as a standard work both for reference and for practical use.

The new edition follows the plan of its predecessors (*cf.* ANALYST, 1921, **46**, 529; 1932, **57**, 135), the fifteen chapters following the Introduction being arranged in the alphabetical order of their subject-matter—a method that has been found to add greatly to convenience in use. The whole work has been thoroughly revised, and a large amount of new material has been added, especially in connection with the examination of documents and of firearms and ammunition, so that there are now 376 pages, as compared with 324 in the last edition.

The scientific literature of the world has been thoroughly sifted to find new information bearing upon the several subjects discussed under the different headings, and, as full references to the original sources are given at the foot of each page, in addition to the bibliographies at the end of the chapters, we are provided with the means of investigating almost any chemico-legal problem that may present itself.

In short, the book continues to justify its claim to be a general practical treatise on forensic chemistry, which need no longer be regarded as a subsidiary branch of medico-legal work. EDITOR

LA CHIMIE DES FERMENTATIONS. By MARC H. VAN LAER. Pp. 342. Paris: Masson. 1935. Price 75 fr.

This book is, in condensed form, the subject-matter of a course of lectures given at the National Institute for Fermentation Industries, Brussels. Its scope is the biochemistry of fermentation, in the field which is applicable to the fermentation industries. It does not, however, include any technology, and does not describe raw materials used in industry. For instance, although the author is an authority on malt and hops—raw materials of the brewing industry—these materials are not discussed.

The book is written by an author who is clearly familiar with all work that is going on throughout his field, and in consequence it is quite up-to-date. In dealing with so comprehensive a subject within the compass of a book of ordinary size the author is confined to matters of general importance, and brevity of treatment is enforced. Assuming, as he does, but little preliminary knowledge on the part of the reader of such matters as the constitution of sugars and proteins, the nature of enzymes, etc., the presentation of the subject is rather steeply graded. With these qualifications, the book is an excellent text-book for students and others interested in the field. Indeed, specialists and research workers would obtain a review of the general position, to date, in each part of the subject, but the book is not really intended for such, as no references to the literature are made, except that there is a bibliography of scientific text-books.

The various chapters deal with general biochemistry, sugars, polysaccharides, fats and phosphatides, proteins, enzymes, and micro-organisms. There is a useful seven-page treatment of oxidation–reduction potential, rH, and its measurement. In each chapter the author builds up from elementary principles to just the stage of knowledge of theory that is required by the technical chemist engaged in industry. R. H. HOPKINS