# THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

## Deaths

WITH deep regret we record the deaths of the following members:

Mr. Frank George Edmed, a former Member of Council (January 22nd).

Sir Gilbert Morgan, Honorary Member (February 1st).

Dr. Frank T. Shutt, Formerly Dominion Chemist, Ottawa (January 5th).

## The Phytic Acid Content of some Poultry Feeding Stuffs

BY R. H. COMMON, PH.D., A.I.C.

IN view of the probable significance of phytic acid in the calcium-phosphorus metabolism of the fowl (Lowe, Steenbock and Krieger,[1] Common[2]) the phytic acid phosphorus content of a number of feeding stuffs as sold for poultry feeding has been determined in this laboratory. The method adopted was essentially that of McCance and Widdowson,[3] modified with a view to convenience when large numbers of analyses are being made simultaneously.

A quantity of the feeding stuff containing about 4 to 8 mg. of phytic acid phosphorus was dried at 100° C. and extracted for three hours with 100 ml. of *N*/2 hydrochloric acid in an end-over-end shaker. The extract was filtered, and 25 ml. of the filtrate were pipetted into a 50-ml. graduated flask, neutralised to phenolphthalein with 25 per cent. sodium hydroxide solution, re-acidified with a few drops of *N*/2 hydrochloric acid, made up to the mark and mixed. Aliquot portions (usually 20 ml.) for duplicate determinations were pipetted into 50-ml. centrifuge tubes and made up to 20 ml. with water when necessary. Four ml. of a solution of ferric chloride in *N* hydrochloric acid, containing 1·0 g. of iron per litre, were then introduced into each tube, and the tubes were heated in the water-bath for fifteen minutes. Each tube was then cooled and centrifuged, the supernatant liquid was decanted from the precipitate of ferric phytate, and the tube was drained and dried inside with filter-paper. The precipitate was broken up with 2 to 4 ml. of *N*/2 hydrochloric acid and re-centrifuged, the wash liquid being poured off and the inside of the tube drained and dried as before.

The precipitate was broken up by blowing in 2 ml. of water from a fine pipette, and decomposed by heating for fifteen minutes on the water-bath after further addition of 2 ml. of 2 per cent. sodium hydroxide solution. The contents of the tube were filtered through a 7-cm. filter-paper (Whatman No. 40) into a 50-ml. silica dish, hot water being used for washing. Two ml. of 20 per cent. w/v calcium acetate solution were then mixed with the filtrate, the mixture was dried at 100° C. overnight in the electric oven, and the residue was gently ignited in an electric muffle to a white ash. This was taken up by heating with about 6 ml. of 2 *N* hydrochloric acid and washed with hot water through a filter into a 100-ml. graduated flask. The contents of the flask were nearly neutralised with 25 per cent. sodium hydroxide solution and cooled, and phosphorus was determined directly by the method* of Fiske and Subbarrow.[4]

From time to time the silica dishes used in the determination should be cleaned with hydrofluoric acid.

TABLE I

COMPARISON OF PERCHLORIC ACID OXIDATION AND DRY ASHING TECHNIQUES IN PHYTIC ACID PHOSPHORUS DETERMINATIONS

| | Phytic acid phosphorus | |
|---|---|---|
| | By wet ashing with sulphuric and perchloric acids Per Cent. | By dry ashing with calcium acetate Per Cent. |
| Wheat meal .. | 0·264 | 0·262 |
| | 0·256 | 0·262 |
| Maize meal .. | 0·192 | 0·257 |
| | 0·213 | 0·259 |
| Pollard .. .. | 0·194 | 0·250 |
| | 0·209 | 0·254 |

The modified method was tested on a sample of pure sodium phytate prepared by Professor D. C. Harrison. The total phosphorus of the sample was found to be 10·8 per cent. and the phytic acid phosphorus to be 10·7 per cent., so that the method is capable of giving a recovery of phytic acid phosphorus of the order of 98 to 99 per cent.

* FISKE AND SUBBARROW'S COLORIMETRIC METHOD.—The following reagents are required:—(*a*) *Molybdate solutions.*—A solution of 25 g. of ammonium molybdate in 400 ml. of water is added to 500 ml. of 10*N* sulphuric acid and made up to 1 litre with water. (*b*) 1:2:4-*amino-naphthol sulphonic acid reagent.*—0·5 g. of the acid, 30 g. of sodium bisulphite and 6 g. of sodium sulphite (crystals) in 250 ml. of water. The standard phosphate solution is prepared by dissolving 0·3509 g. of potassium dihydrogen phosphate in water, adding 10 ml. of 10 *N* sulphuric acid and making up to 1 litre (5 ml. contain 0·4 mg. of phosphorus).

The aliquot part of the phosphate solution under examination, which should contain about 0·4 mg. of phosphorus, and be only slightly acid, is diluted to about 75 ml., treated first with 10 ml. of reagent (*a*) and then with 4 ml. of reagent (*b*), shaken and made up to 100 ml. The final acid concentration is about 0·5 *N*.

The standard for comparison is prepared by mixing 5 ml. of the original standard phosphate solution, 70 ml. of water and 10 ml. of the molybdate reagent (*a*), adding 4 ml. of reagent (*b*) and making up to 100 ml. The colorimetric comparison is made after about 30 minutes. If the aliquot portion contains up to 1·0 mg. of phosphorus the comparison is made against 10 ml. of standard phosphate solution.

The modified method was also tested against the original method of oxidation with sulphuric and perchloric acids. In some instances agreement was good, but in others the perchloric acid oxidation seemed to give more erratic results, as may be seen from Table I. This may have been due to the difficulty of removing the last traces of perchloric acid; traces of perchloric acid have been shown to interfere with colour development in the method of Fiske and Subbarrow (Snook).[5]

Experiments were carried out on the recovery of phytic acid phosphorus added to extracts of meals. The recovery was satisfactory, as may be seen from Table II.

TABLE II

RECOVERY OF ADDED PHYTIC ACID PHOSPHORUS FROM $N/2$ HYDROCHLORIC ACID EXTRACT OF WHEAT

| Solution | Phytic acid phosphorus found mg. |
|---|---|
| 20 ml. of $N/2$ HCl extract of wheat . . | 1·245 |
| 20 ml. of $N/2$ HCl extract of wheat + 5 ml. of sodium phytate solution | 1·760 |
| 5 ml. of sodium phytate solution . . | 0·525 |

$$\text{Recovery} = \frac{(1{\cdot}760 - 1{\cdot}245)}{0{\cdot}525} \times 100 = 98 \text{ per cent.}$$

Total phosphorus was determined by a modification of the method of Fiske and Subbarrow, which has been described elsewhere (Common[6]).

Table III gives maximum and minimum figures for the phytic acid phosphorus contents of samples of cereals and other feeding stuffs, and Table IV records the results obtained with typical samples of the different products. The origin of most of the samples was known.

TABLE III

| | Phytic acid phosphorus Per cent. on dry matter | | Total phosphorus Per cent. on dry matter | | Phytic acid phosphorus Per cent. of total phosphorus | |
|---|---|---|---|---|---|---|
| | Max. | Min. | Max. | Min. | Max. | Min. |
| Wheat (11 samples) . . | 0·305 | 0·111 | 0·418 | 0·204 | 77·6 | 52·9 |
| Oats (5 samples) . . . . | 0·312 | 0·218 | 0·505 | 0·365 | 74·3 | 59·1 |
| Barley (3 samples) . . | 0·217 | 0·178 | 0·369 | 0·328 | 59·2 | 54·3 |
| Yellow maize meal (3 samples) . . | 0·314 | 0·277 | 0·407 | 0·364 | 78·3 | 76·1 |
| Bran (6 samples) . . | 1·030 | 0·512 | 1·571 | 0·571 | 77·7 | 59·3 |
| Extracted soya bean (3 samples) . . | 0·388 | 0·341 | 0·671 | 0·644 | 53·9 | 52·9 |

Phytic acid phosphorus accounted for about two-thirds to three-quarters of the total phosphorus of wheat, oats, barley and maize. The samples of barley examined tended to have a lower proportion of their phosphorus in the form of phytic acid than did the samples of wheat. About the same ratio of phytic acid phosphorus to total phosphorus was found in bran as in pollard of grades

similar to "weatings." Both total phosphorus and phytic acid phosphorus were lower in the Australian wheats than in the British wheats, in agreement with the observations of Snook (1938).[5] Rice bran meal, tapioca root flour and hempseed all had about one-third of their phosphorus in the form of phytic acid phosphorus. Earthnut cake, extracted soya bean meal, maple peas, beans, millet and sunflower seed had from one-half to three-quarters of their total phosphorus in the form of phytic acid phosphorus. Dried grass contained only a very small proportion of its total phosphorus as phytic acid, alfalfa meal containing a greater proportion.

TABLE IV

| Feeding stuff | Place of origin | Crude fibre Per cent. on dry matter | Phytic acid phosphorus Per cent. on dry matter | Total phosphorus Per cent. on dry matter | Phytic acid phosphorus Per cent. of total phosphorus |
|---|---|---|---|---|---|
| Wheat meal | — | — | 0·301 | 0·458 | 65·7 |
| Oatmeal | Ireland | 11·24 | 0·242 | 0·355 | 68·3 |
| Oats | Ireland (Co. Down) | — | 0·272 | 0·434 | 62·7 |
| Sussex ground oats | Ireland | — | 0·218 | 0·365 | 59·7 |
| Pinhead oatmeal | Ireland | — | 0·299 | 0·495 | 60·5 |
| Barley meal | — | 5·03 | 0·216 | 0·355 | 61·0 |
| Yellow maize | River Plate | — | 0·276 | 0·368 | 75·0 |
| ,, ,, | N. America | — | 0·149 | 0·199 | 75·0 |
| Bran | Australia | 10·92 | 0·512 | 0·676 | 75·8 |
| ,, | Canada | 12·54 | 0·974 | 1·258 | 77·5 |
| ,, | Holland | 12·36 | 1·030 | 1·571 | 65·5 |
| Pollard | — | 10·43 | 0·277 | 0·350 | 79·1 |
| White sharps | — | 7·55 | 0·312 | 0·467 | 66·8 |
| Fine pollard | River Plate | 7·19 | 0·962 | 1·238 | 77·7 |
| Coarse pollard | River Plate | 10·53 | 0·760 | 1·044 | 72·8 |
| Middlings | Holland | 6·98 | 0·481 | 0·936 | 51·3 |
| Fine white sharps | — | 7·03 | 0·364 | 0·558 | 65·3 |
| Rice bran meal | (E. Indies?) | 6·66 | 0·577 | 1·558 | 37·0 |
| Tapioca root flour | — | 1·91 | 0·028 | 0·083 | 33·8 |
| Earthnut cake | — | — | 0·402 | 0·668 | 60·2 |
| Dried yeast | — | — | 0·058 | 1·514 | 3·8 |
| Alfalfa meal | Canada | — | 0·027 | 0·131 | 20·5 |
| Dried grass | Ireland | — | 0·007 | 0·351 | 2·0 |
| Millet | Smyrna | — | 0·206 | 0·289 | 71·2 |
| Sunflower seed | Hungaria | — | 0·374 | 0·453 | 82·8 |
| Hempseed | Manchuria | — | 0·285 | 0·692 | 41·2 |
| Beans | England | — | 0·501 | 0·662 | 75·7 |
| Maple peas | Tasmania | — | 0·194 | 0·334 | 58·1 |

Small amounts of phytic acid were found in dried yeast. This presumably came from the malt, since phytic acid has not been recorded among the phosphorus compounds present in yeast (Macfarlane[7]).

It is evident that in an ordinary poultry ration about three-quarters of the phosphorus derived from cereals will be in the form of phytic acid. Experiments designed to ascertain the minimum calcium and phosphorus requirements of poultry should take cognizance of this fact.

I wish to record my indebtedness to Mr. F. Dickinson, F.I.C., Chemical Research Division, Ministry of Agriculture for Northern Ireland, Belfast, who very kindly carried out the fibre determinations, and to those grain millers who furnished samples of known origin. I also wish to thank Professor D. C. Harrison, of Queen's University, Belfast, for his advice and helpful criticism.

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# The Precipitation of Aluminium Hydrous Oxide* and its Solubility in Ammonia

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THE precipitation of alumina by ammonia and its residual solubility should be explicable in terms of the electrochemical properties of the hydroxide and by theories of the colloidal state, but the position is by no means clear. Also, experimental data as to the solubility under analytical conditions, as well as in pure ammonia solution, are very scanty.

Precipitation from sulphate solutions by means of alkalis follows a course which is determined by the amphoteric ionisations of the hydroxide, but is complicated by colloidal phenomena (Britton[1]). Visible precipitation begins at about *p*H 4 but not until about *p*H 6·5 in chloride solutions.

This is attributed to the tendency of chlorides to form colloidal solutions, and the difference between the two salts may be accounted for by the accepted theories. Thus, aluminium chloride is hydrolysed in stages, the colloidal basic salt is then stabilised by aluminium ion and forms a positive micelle with a double layer of chlorine ions as figured in papers by Weiser *et al.*, Weiser and Gray.[2] If sulphate ion is present, it tends to discharge and precipitate the micelle as a basic salt. After precipitation is nearly complete, the *p*H rapidly increases, an inflection appears, at about *p*H 7, but this is *not* the isoelectric point of alumina itself, since the precipitate contains acid radicle. With further addition of alkali, the *p*H increases still further from 8 to 10·5, with solution of alumina as aluminate. In the precipitation by ammonia, which depends upon the almost complete hydrolysis of ammonium aluminate, well-known methods, referred to below, seem

* Since definite meanings are attached to the terms "hydroxide" and "hydrate," it seems that a more general term would be useful to cover these as well as the amorphous and colloidal hydrated oxides of uncertain composition. The term "hydrous oxide," however, as used by H. B. Weiser ("*Inorganic Colloid Chemistry*," Vol. II) refers only to those amorphous colloidal substances which are neither definite hydroxides nor definite crystal hydrates. Thus, under "hydrous oxides" are classified those of iron, aluminium and chromium, *i.e.* in their most usual form, and without reference to the possibility (realised for iron) of preparing definite crystal hydrates by special methods.

to aim at the isoelectric condition. Now, although the dissociation constants of alumina are not accurately known, there is no doubt that the basic is considerably greater than the acidic (ca. $1 \times 10^{-10}$); therefore the calculated isoelectric point should be definitely higher than *p*H 7. Regulation of the hydrogen ion concentration by the ammonium chloride and ammonia mixture proceeds according to the usual equation, the maximum buffer effect being at *p*H 4·64 or, if pKw = 14·14, at *p*H 9·5, and for any given mixture, $H^- = (NH_4Cl/NH_3) \times 10^{-9\cdot5}$. The calculated values of *p*H have been checked by us in a Lovibond comparator, using phenol red.

| Ratio: $\frac{\text{ammonium chloride}}{\text{ammonia}}$ | 8 | 16 | 32 | 64 | 128 | 256 | 512 |
|---|---|---|---|---|---|---|---|
| *p*H calculated .. | 8·6 | 8·3 | 8·0 | 7·7 | 7·4 | 7·1 | 6·8 |
| *p*H observed .. | 8·5 | 8·2 | 7·9 | 7·5 | 7·1 | 6·9 | 6·7 |

Since it is the practice to add considerable quantities of ammonium salt and only the slightest excess of ammonia, it is clear that the *p*H will never rise above 9·0 and may easily pass to the acid side of neutrality in hot solutions.

Some experiments designed to correlate the alumina left in solution with the *p*H values were made, in 1916, by Blum,[3] who added ammonia to 200 ml. containing aluminium equivalent to 0·1 g. of $Al_2O_3$ and 5 g. of ammonium chloride up to the change-points of various indicators:

| | *p*-Nitrophenol | Methyl red | Rosolic acid | Phenolphthalein |
|---|---|---|---|---|
| *p*H | 6 | 6·5 | 7·5 | 9 |
| $Al_2O_3$ in filtrate g. | 0·001 to 0·0012 | 0·0001 | 0·0001 to 2 | 0·0004 |

Hence it was concluded that dilute ammonia solution should be added to the nearly boiling solution until this was nearly alkaline to methyl red; it should then be boiled for not more than 2 minutes, and filtered at once. Further quantities of 0·5 to 0·2 mg. appear in the washings with 75 ml. of hot water, and 0·3 mg. in those made with 2 per cent. ammonium chloride solution. It is evidently difficult to establish *p*H conditions of minimum solubility by means of indicators, since the solution is poorly buffered at *p*H 6·5 to 7, and the solubility rises on the acid as well as on the alkaline side. The precipitate also coagulates poorly until a definite excess of ammonia is present. The small weights recorded might be affected by various errors. In the present investigation the solubilities under analytical conditions, as well as those of pure alumina, have been determined by one of the new colorimetric methods.

EXPERIMENTAL.—A solution of potash alum was made up to contain 0·9 g. of aluminium per litre, and 10 ml. of this solution together with 5 ml. of 4*N* ammonium chloride solution were taken for each experiment (*i.e.* 9 mg. of aluminium). In experiments 1 to 7, these 15 ml. of solution were heated to boiling in a beaker and 5 or 10 ml. of ammonia of various concentrations were added. In experiments 8 and 9, the ammonia solution was heated, and the alum and ammonium chloride solutions were added. In every instance the solution was quickly heated to boiling and filtered through a Whatman's No. 1 filter, the

operation lasting about 1 minute. The filtrate was boiled to remove excess of ammonia and frequently became turbid owing to decomposition of the alumina sol. The volume of solution remaining was then measured, and the amount of aluminium contained in each ml. was determined by the colorimetric method. B.D.H. spot test reagent, aurine tricarboxylic acid (0·4 g.), was dissolved in water, and excess of ammonia was added; it was then boiled to remove the excess of ammonia and made up to 200 ml., thus giving a 0·2 per cent. reagent. A standard solution of aluminium, containing 0·02 mg. per ml., was made from potash alum. The colorimetric determinations were made on standard and sample as described in the B.D.H. "*Reagents for Delicate Analysis including Spot Tests.*" Solutions containing more than 0·5 mg. of aluminium per ml. gave a red precipitate, and concentrations were therefore kept below this and arranged to show nearly equal colours for standard and sample.

The results are presented in tabular form.

TABLE I

| Expt. | $[NH_3]$ before filtration Moles per litre | $[NH_4Cl]$ | $(H^+) \times 10^{10}$ calc. | Total Al in filtrate mg. | Al per ml. mg. | Ratio $Al/NH_3$ | $\frac{Al \times 10^{-4}}{(OH)}$ |
|---|---|---|---|---|---|---|---|
| 1 | 0·467 | 1·0 | 6·77 | 0·168 | 0·0084 | 1·8 | 0·056 |
| 2 | 0·748 | 0·8 | 3·38 | 0·23 | 0·0093 | 1·24 | 0·031 |
| 3 | 0·935 | 1·0 | 3·38 | 0·27 | 0·0135 | 1·44 | 0·0455 |
| 4 | 0·972 | 1·0 | 3·25 | 0·34 | 0·0168 | 1·74 | 0·0545 |
| 5 | 1·556 | 0·8 | 1·625 | 0·46 | 0·0183 | 1·18 | 0·030 |
| 6 | 1·945 | 1·0 | 1·625 | 0·16 | 0·0082 | 0·42 | 0·0135 |
| 7 | 3·11 | 0·8 | 0·81 | 0·39 | 0·0156 | 0·50 | 0·0125 |
| 8 | 0·972 | 1·0 | 3·25 | 0·20 | 0·0101 | 0·20 | — |
| 9 | 1·556 | 0·8 | 1·63 | 0·65 | 0·026 | 0·40 | — |
| 10 | ammonia (0·880) | | about 18·3 | — | 0·198 | 1·28 | — |

The amount of alumina in solution increases with the ammonia, although not in strict proportionality, up to about 1·5 *N*. Above this concentration the amounts dissolved fall and tend to become irregular. The ratio of aluminium to ammonia is about the same in the strongest as it is in 0·75 *N* ammonia. The aluminium dissolved varies also very roughly with the hydroxyl ion concentration, since this, at nearly constant ammonium ion concentration is, of course, proportional to the free ammonia. The variability of these results is due not to experimental error, nor even principally to variable losses of ammonia from hot solutions, but much more to the fact that alumina, precipitated in this manner, is the most colloidal of all the forms, whose properties vary with the speed of coagulation, as is emphasised in "*The Theory of Quantitative Analysis,*" by H. Bassett. This author considers that the soluble part is not an ammonium aluminate, but a colloidal alumina peptised by the ammonia. If the concentrations of dissolved alumina given in column 6 of Table I are present in 100 ml. from which a normal amount, say, 0·2 g. of alumina, has been precipitated, then the percentage losses in 0·5 to 1·5 *N* ammonia vary from 0·4 to 0·9. The total losses (column 5) in the 20 to 25 ml. of filtrate of course form a much larger proportion of the possible weight of the precipitate, corresponding to 9 mg. of aluminium.

As shown later, these losses are mainly due to the hydrous oxide in a state of supersaturation or peptisation.

Solubilities of Aluminium Hydroxide in Ammonia.—A sample of the purest sheet aluminium, supplied by the courtesy of Mr. A. N. D. Pullen and the British Aluminium Company, had a guaranteed purity of 99·995 per cent. Pieces of uniform size and shape were amalgamated with mercury in excess, and placed in ammonia solutions of different concentrations. In the first series the ammonia solutions were kept in open tubes; in the second, redistilled ammonia solutions were allowed to react with the amalgam in closed tubes. In some of the experiments colorimetric determinations of alumina were checked by weight.

Any threads of precipitated alumina were, of course, removed by filtration before the determination of solubility.

The following results give the maximum initial solubilities in ammonia and in complete absence of ammonium salts:

| | | | | |
|---|---|---|---|---|
| Ammonia, Normality.. .. .. | 5·0 | 0·75 | 0·50 | 0·25 |
| Aluminium mg. per ml. (after 1 day) | 1·08 | 0·36 | 0·12 | 0·125 |

Concentrations of alumina were maintained for several days when ammonia solutions were in contact with precipitates. The filtrates, however, began to deposit alumina, and the concentrations progressively decreased, and more rapidly in those solutions having the lower concentrations, as follows:

Filtrate from 5 *N* ammonia, 1·3 mg. of aluminium per ml.

| | | | |
|---|---|---|---|
| Time (days) .. .. .. .. | 1 | 2 | 3 |
| Aluminium mg. per ml. .. .. | 0·8 | 0·45 | 0·25 |

Filtrate from 0·75 *N* ammonia, 0·36 mg. of aluminium per ml.

| | | | |
|---|---|---|---|
| Time (days) .. .. .. .. | ½ | 1½ | 2½ |
| Aluminium, mg. per ml. .. .. | 0·1 | 0·04 | 0·022 |

In the next series the effect of standing was investigated, when the concentration of ammonia was maintained, in contact with the precipitates. Pure redistilled ammonia interacted with aluminium amalgam in closed tubes furnished with Bunsen valves.

Concentration of ammonia, initial 5·84 *N*; final 5·37 *N*.

| | | | | |
|---|---|---|---|---|
| Time (days) .. .. | 1 | 2 | 5 | 6 |
| Aluminium, mg. per ml. .. | 1·1 | 1·1 | 0·18 | 0·10 |

Concentration of ammonia, initial 2·92 *N*; final 2·756 *N*.

| | | | | |
|---|---|---|---|---|
| Time (days) .. .. | 1 | 2 | 5 | 6 |
| Aluminium, mg. per ml. .. | 1·2 | 1·2 | 0·54 | 0·125 |

Discussion of Results.—When the metal dissolves with evolution of hydrogen in solutions that are well on the alkaline side of the isoelectric point it must be supposed that ammonium aluminate is formed at first. This can then decompose in the following ways:

(*a*) *By Loss of Ammonia.*—In the tubes that were left open it was noticed that the precipitates formed a very coherent skin on the surface.

(*b*) *By Hydrolysis of Ammonium Aluminate.*—This produces colloidal alumina which gradually gives a turbidity throughout the solution. In the experiments

with closed tubes precipitation is delayed, either because hydrolysis is diminished or because the resulting hydroxide is peptised by ammonia. The precipitate finally appears in thread-like forms, the presence of which does eventually lower the solubility, owing to the continued solution of the metal. Thus in 0·75 *N* ammonia the solubility after 2½ days is 0·022 mg., which is only about twice that in 0·75 *N* ammonia with much ammonium chloride. Although the initial solubilities in ammonia alone are 10 to 100 times those in presence of ammonium chloride, the final solubilities may be hardly greater. The effect of the salt, then, is principally to accelerate the formation of nuclei. These results also give a reason for the observation of Blum, that the presence of a small excess of ammonia is useful in aiding the coagulation of the precipitate. For this is then formed by way of ammonium aluminate, and not by way of the very gelatinous form obtained on first precipitation. The amalgam experiments show in every instance a precipitate which is dense and easily separated by filtration.

A procedure based on these facts is suggested. This is to add *N* to 2*N* ammonia to the solution containing the usual ammonium salt, then to digest the precipitate in a closed tube in the water-bath, and finally to remove the excess of ammonia and filter. It is hoped that further experiments will be made in these directions as opportunity offers.

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# The Analysis of Cadmium-plating Solutions

BY G. STANLEY SMITH, B.Sc., A.I.C.

CADMIUM is usually deposited from a cyanide solution which contains cadmium and potassium cyanides and caustic alkali. Baths that have been in use for a considerable period contain also large quantities of ferrocyanide and possibly copper.

The analysis of used solutions presents certain difficulties. The cyanide in the form of the comparatively stable ferrocyanide does not assist in the formation of a good deposit and should not be included in the figure for alkali or cadmium cyanide, yet a distillation with acid to obtain the cyanide in a form suitable for titration with silver nitrate yields in addition at least half the cyanide of the ferrocyanide. Methods involving distillation with excess of sodium bicarbonate or the passage of carbon dioxide through the hot solution have been found to give high results, for ferrocyanide is unstable in the presence of even such a weak acid as carbonic acid. Again, direct electrolysis of the solution to determine the total cadmium often yields a very poor, non-adherent deposit containing iron and takes many hours before the electrode ceases to gain in weight.

For determining total cyanide, excluding ferrocyanide, successful use has been made of the observation of Feld[1] that lead cyanide and magnesium cyanide are easily decomposed on boiling to give hydrocyanic acid and the hydroxides of the metals, whilst the ferrocyanides are stable. For cadmium, copper and iron, the original solution is decomposed with sulphuric acid, the cadmium and copper are deposited together electrolytically in a dilute sulphuric acid medium, the solution of the deposit in nitric acid is electrolysed for copper, and iron is precipitated as hydroxide in the former electrolyte. The details are as follows:

CYANIDE, EXCLUDING FERROCYANIDE.—Place 5 ml. of the solution in a 500-ml. flask fitted with a rubber bung carrying a tap-funnel and a trap connected with an upright water-condenser dipping into a flask or bottle containing 10 ml. of 20 per cent. sodium hydroxide solution and sufficient water to cover the outlet of the condenser to a depth of at least half-an-inch. Introduce into the flask 150 ml. of water and 50 ml. of 0·5 *M* solution of lead nitrate. (Lead nitrate is to be preferred to a magnesium salt, because with the latter a very slight decomposition of ferrocyanide is liable to occur.) Lead hydroxide and carbonate are precipitated, and the amount of lead nitrate added should be sufficient to destroy all the caustic alkali and carbonate. Distil the solution rapidly down to a small bulk and titrate the distillate with 0·1 *N* silver nitrate solution, using a little potassium iodide as indicator. If the distillation has been carried sufficiently far, no more cyanide should be evolved when a further 100 ml. of water is placed in the flask and the distillation continued. Even when the contents of the flask have been allowed to become almost dry, no decomposition of ferrocyanide has been detected.

The number of ml. of silver nitrate required, divided by 6, gives the cyanide-content, calculated as CN, in ounces per gallon.

CADMIUM, COPPER AND IRON.—To 5 ml. of the original solution, diluted to prevent undue frothing, add a slight excess of dilute sulphuric acid and boil down carefully until fumes appear, adding nitric acid to destroy organic matter. Cool, wash down with water and evaporate to fuming again. Take up the residue in water, neutralise with ammonia and add 10 ml. of dilute sulphuric acid (sp.gr. 1·2) per 100 ml. Add a few drops of hydrogen peroxide and electrolyse to deposit cadmium and copper, using platinum electrodes. The cathode may be coppered first, but it does not appear to be necessary. The electrolysis with a rotating electrode should be complete in half to three-quarters of an hour, but a test should be made to ensure that it is complete. Weigh the deposit, dissolve in nitric acid, dilute so that the solution contains about 10 ml. of dilute nitric acid (sp.gr. 1·2) per 100 ml. and electrolyse to deposit copper. Weigh and deduct the weight from that previously found to obtain the amount of cadmium.

CYANIDE.—Total alkali cyanide and "free cyanide" are obtained by calculation as follows:—*Total cyanide.*—From the figure for cyanide given by distillation deduct the equivalent of the cadmium and copper obtained from the formulae $Cd(CN)_2$ and CuCN and calculate to KCN. *Free cyanide.*—Since this is usually taken to be potassium cyanide in excess of that required to form a compound of the formula $K_2Cd(CN)_4$, a corresponding deduction from the total cyanide should give the free cyanide. It should be recognised, however, that any figure for free cyanide is somewhat arbitrary.[2]

RESULTS.—In Table I solution A represents a plating solution containing 8·5 g. of cadmium per litre, excess of potassium cyanide and no ferrocyanide; solution B represents a solution containing 11·3 g. of cadmium per litre and ferrocyanide, when expressed as potassium cyanide, equivalent to 3·95 ml. of 0·1 *N* silver nitrate per 5 ml. of solution, the volume taken for distillation; the cuprous cyanide solution contained 6·4 g. of copper per litre, and was obtained by dissolving cuprous cyanide in excess of potassium cyanide.

Distillation with sulphuric acid or, in presence of ferrocyanide, with sulphuric acid and cuprous chloride (Williams[1]), was used to obtain comparative figures for the titration of total cyanide, but in the case of solution B the result has been corrected for the quantity of ferrocyanide present and decomposed.

TABLE I

| Solution distilled | Method of decomposition | Silver nitrate (0·1*N*) required ml. |
|---|---|---|
| 25 ml. of solution A | Dilute sulphuric acid | 39·85 |
| ,, ,, | Magnesium chloride | 39·65 |
| ,, ,, | Lead nitrate | 39·8 |
| 25 ml. of *M*/30 potassium ferrocyanide | Magnesium chloride | 0·4 |
| ,, ,, | Lead nitrate | nil |
| 25 ml. of each of the solutions above | Lead nitrate | 39·9 |
| 5 ml. of solution B | Lead nitrate | 17·9 |
| ,, | Dilute sulphuric acid and cuprous chloride | 17·85 |
| 25 ml. of cuprous cyanide solution | Dilute sulphuric acid | 37·5 |
| ,, ,, | Magnesium chloride | 12·6 (plus 1·35 on second distillation) |
| ,, ,, | Lead nitrate | 36·0 (plus 1·55 on second distillation) |

A more rapid method for evaluating cadmium solutions would be useful, and it was thought that titrations with acid after adding formaldehyde to one portion and mercuric chloride to another might give (*a*) total cyanide, (*b*) cadmium, (*c*) hydroxide with carbonate, by calculation from these simple titrations. The method failed with the plating solutions used owing to the presence of ferrocyanide, but the principles are outlined in the event of someone finding it possible to adapt them.

On addition of formaldehyde, cadmium gives a precipitate of cadmium hydroxide, whilst potassium cyanide gives the potassium salt of glycollic nitrile, $CH_2(OK)CN$, which is soluble and reacts alkaline. After filtration, titration of the filtrate, or preferably, for speed, an aliquot portion, should give a figure for alkali hydroxide and carbonate plus alkali cyanide.

With mercuric chloride solution, containing sodium chloride to repress hydrolysis, cyanides form mercuric cyanide, which is neutral. A determination

of the alkalinity gives that due to alkali hydroxide and carbonate. After neutralising and adding an excess of potassium iodide, which forms a more stable mercury salt and sets free potassium cyanide equivalent to the original potassium cyanide plus cadmium cyanide, a further titration with acid gives the total cyanide.

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166, WICKHAM CHASE
WEST WICKHAM, KENT
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# The Routine Examination of Magnesium Trisilicate

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THE dispensing of substances for dealing with minor intestinal disturbances is the daily task of the pharmacist. Various alkaline powders, and materials such as chalk, charcoal and kaolin, are widely employed as antacids and as adsorbents* of toxins and alkaloids. Although a number of magnesium silicates have been used medicinally for a long time, it is only recently that they have been subject to critical examination and their uses defined. Mutch,[1] in an exhaustive survey, concluded that the most effective compound was an artificial silicate having the approximate composition $Mg_2Si_3O_8nH_2O$. The silicate combines effectively the action of an antacid with that of an adsorbent for a wide range of materials, including dyes, alkaloids, colloids and toxins; in each category, however, a selective action is noticed, some dyes, for example, being much more effectively adsorbed than others at similar concentrations. With the probable increase in demand for trisilicate, tests for controlling its composition and adsorptive capacity become desirable. Analytical figures and a methylene blue adsorption test were put forward by Mutch in a second paper,[2] and Glass[3] outlined further suggestions for analytical procedure, and gave a modified qualitative adsorption test.

The objects of the present investigation were: (*a*) to examine the chemical analytical procedure and to devise suitable routine tests; (*b*) to devise a modified quantitative adsorption test, capable, if possible, of correlation with Mutch's figures; (*c*) to determine whether or not the adsorption depends in any way on the physical condition of the trisilicate.

(*a*) ANALYTICAL PROCEDURE.—(1) *Magnesia and silica.*—The following methods were adopted after duplicate experiments on acid decomposition and fusion with alkali carbonate had shown fusion to have no advantage. The material (0·5 g.) was treated with hydrochloric acid, followed by evaporation, drying and boiling with dilute acid, and finally by filtration of the silica, which was ignited and weighed, as described by Treadwell and Hall.[4] Re-evaporation, however, was omitted,

* The term "adsorbent" has been preferred to "absorbent" throughout this paper.

as without it the figures obtained are sufficiently accurate for routine purposes. The filtrate was made up to 250 ml. and the magnesium was determined in duplicate —volumetrically as the 8-hydroxyquinoline complex, and gravimetrically as pyrophosphate. For the oxine procedure, 25 ml. of the solution were treated as described by Mitchell and Ward,[5] method (1), re-precipitation of the complex being unnecessary. To the boiling, faintly acid solution, was added 5 to 10 g. of ammonium acetate (AnalaR), followed by about 15 ml. of 2 per cent. oxine in 2 *N* acetic acid. The solution was then made faintly alkaline with ammonia (0·880) and the precipitate allowed to settle. The supernatant liquid was filtered off through a Jena G.3 glass filter, to which the precipitate was finally transferred and well washed with hot water. The precipitate was dissolved in 100 ml. of 2 *N* hydrochloric acid, 25 ml. of *N*/10 (*M*/60) potassium bromate and bromide solution were run in, and the excess was titrated back with *N*/10 thiosulphate solution after the addition of potassium iodide; 1 ml. of *N*/10 bromate ≡ 0·504 mg. of MgO. Results tend to be low in comparison with those obtained by the pyrophosphate method (usually 0·3 to 0·4 per cent. on the sample or 1 to 2 per cent. on the magnesium oxide), but this is offset by the greatly reduced time required, from ½ to 1 hour. Two hundred ml. of the filtrate from the silica determination were used for the determination of magnesia as pyrophosphate.*

TABLE I

| | | MgO | | | Moisture | | | |
|---|---|---|---|---|---|---|---|---|
| Sample | $SiO_2$ Per Cent. | Pyrophosphate Per Cent. | Oxine Per Cent. | Ratio MgO: $SiO_2$ | Free Per Cent. | Combined Per Cent. | Total Per Cent. | Basicity ml. of *N*/10 HCl per g. |
| 1*a* | 51·2 | 22·2 | — | 1 : 2·30 | 9·5 | 15·8 | 25·3 | 100 |
| 1*b* | 49·2 | 22·6 | 22·25 | 1 : 2·18 | 9·5 | 15·9 | 25·4 | 111 |
| 2 | 49·9 | 20·7 | 20·1 | 1 : 2·48 | 14·9 | 11·6 | 26·5 | 79·5 |
| 3 | 50·5 | 16·35 | 16·2 | 1 : 3·07 | 16·7 | 14·1 | 30·8 | 73·5 |
| 4 | 49·6 | 22·35 | 22·6 | 1 : 2·22 | 10·5 | 13·2 | 23·7 | 109·5 |
| 5 | 46·8 | 22·05 | 21·5 | 1 : 2·12 | 12·5 | 16·1 | 28·6 | 111 |

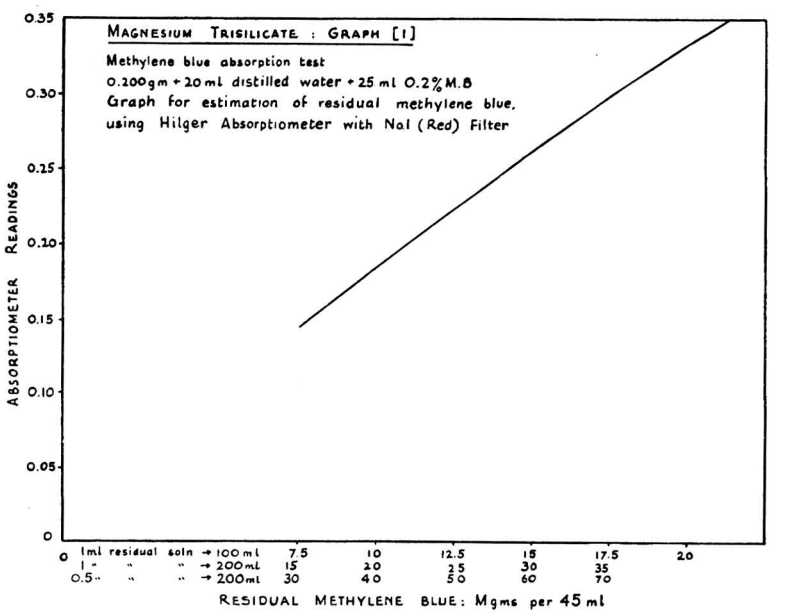
All results are calculated to sample "as received."

(2) *Moisture.*—The loss at 100° C. on 1 g. in about 4 hours was returned as free moisture, and the further loss on ignition as "combined" moisture.

(3) *Basicity.*—The procedure advised by Glass[3] was adopted. Fifty ml. of *N*/10 hydrochloric acid were added to 0·2 g. contained in a 100-ml. stoppered flask, and the whole was shaken occasionally over a period of two hours. At the end of this time the excess acid was titrated back with *N*/10 caustic soda, with methyl orange as indicator. Results were expressed as ml. of *N*/10 acid per 1 g. of sample "as received." For analytical results, see Table I.

* A similar procedure is possible in the examination of tablets, granules, etc., containing magnesium trisilicate as a major ingredient. The finely-ground sample (0·5–1 g.) is gently ignited, if necessary, to remove organic matter, and then treated with acid as described. If the magnesium is estimated by the oxine procedure alone, sufficient filtrate remains from the determination of silica for the estimation of other inorganic constituents, *e.g.* precipitated chalk, which may be present

(*b*) METHYLENE BLUE ADSORPTION.—(1) The method proposed by Glass[3] cannot give quantitative results, owing to the difficulty of assessing the end-point. This is due to the fineness of some of the silicate particles, stained blue, which do not settle, thus giving a pale blue suspension, and also due to the adsorption of the dye by the glass of the flask, which is especially pronounced with poor samples of trisilicate because these have a low adsorptive capacity for the dye, and therefore leave a relatively large amount free to be adsorbed by the glass. Attempts to reduce suspension by centrifuging or filtration were unsuccessful. Similar experiments carried out in 100-ml. graduated flasks were slightly more successful. The flasks were shaken every half hour and the neck was observed immediately before each shaking. The same troubles were encountered, however, and the method was abandoned.



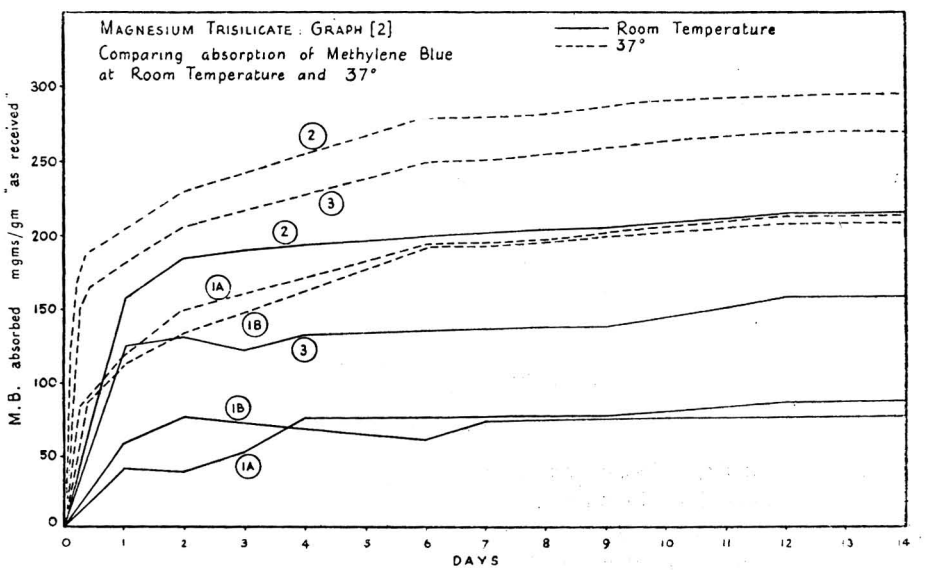

Graph 1

(2) A few experiments were made with a view to obtaining a figure that would represent the minimum amount of silicate required to adsorb a standard amount of dye in a standard time ($\frac{1}{2}$ hour). The relatively large quantitities of silicate required obscured the end-point, owing to the suspension of silicate particles.

(3) Examination of Mutch's method. This method[2] consists essentially in adding a standard amount of trisilicate to a standard amount of methylene blue in a given volume, and determining the residual dye after 14 days by a colorimetric method. For routine purposes a shorter test is desirable.

For this purpose investigations were made of (*a*) the relation between the adsorptions at room temperature and at a higher temperature—say, 37° C., and (*b*) the relation between the adsorptions in, say, 2 days and 14 days at room

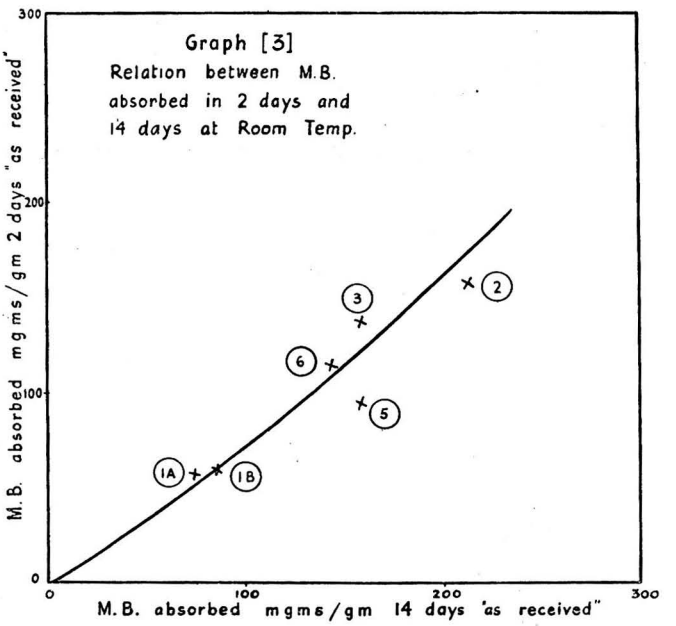
temperature. The procedures used were as follows:—The sample (0·200 g.) was placed in a 50-ml. rubber-stoppered boiling-tube. For experiments at room temperature, 20 ml. of water followed by 25 ml. of a 0·2 per cent. aqueous methylene blue solution (B.D.H. ⟨SS⟩) were introduced from a pipette, and the tube was closed and shaken periodically; 1 ml. or 0·5 ml. samples, depending on the observed degree of adsorption, were removed after shaking the tubes and immediately made up to volume, the unadsorbed methylene blue being measured on a Hilger Spekker Absorptiometer, using the No. 1 (red) filter. The experiments at 37° C. were made with 0·200 g. of material, 10 ml. of water and 35 ml. of methylene blue solution. The experiments at room temperature thus involved the use of 50 mg. of dye in 45 ml., and the experiments at 37° C., 70 mg. of dye in 45 ml. Graph 1 indicates suitable ranges of dilution for the determination of residual methylene blue. It is, however, necessary to calibrate each individual instrument separately.




Graph 2

(*a*) *Adsorption at Room Temperature and at* 37° *C.*—It was thought that, if a sample of trisilicate has a constant maximum adsorption of methylene blue, then this value might be more quickly reached at 37° C. than at room temperature. Four samples were examined, and it was found that the maximum adsorption figures (*i.e.* adsorption in 14 days) at the two temperatures were different. The time for the adsorption, at 37° C., of the amount of dye adsorbed in 14 days at room temperature was found also to be different with different samples; it was therefore concluded that the estimation of adsorption at 37° C. could not be correlated with the adsorption at room temperature (see Graph 2). During the course of this series of experiments, irregularities, especially with small degrees of

adsorption, *i.e.* high residual quantities of methylene blue, were observed in the graph. The cells were washed with distilled water before each determination, but it was observed that the methylene blue was adsorbed strongly on to the surface of the glass cell; ultimately it was found necessary to wash the cell with a few drops of conc. nitric acid, followed by distilled water, before each determination. Experiments were also made without the addition of methylene blue, after addition of an equivalent volume of water, to find the effect of the trisilicate suspension on the absorptiometer values. This was negligible and could be ignored.



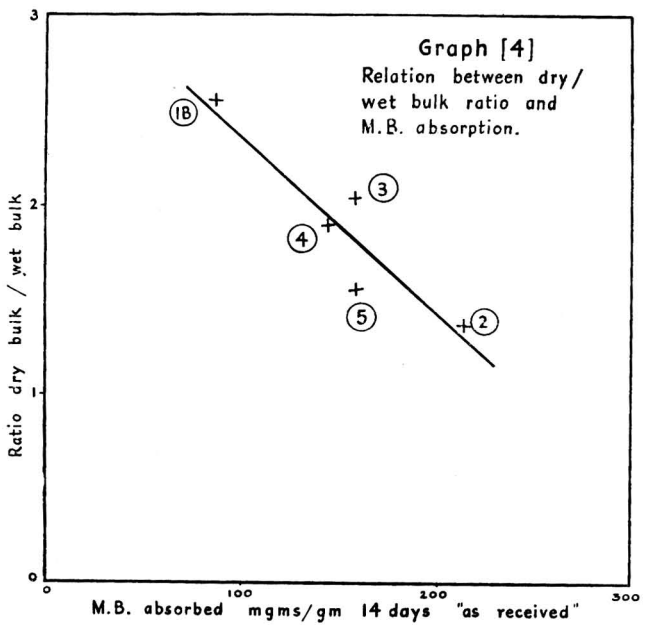

Graph 3

(*b*) *Relationship between Adsorption in* 2 *days and* 14 *days at Room Temperature.* —The results obtained in 2 days and 14 days at room temperature were plotted (Graph 3); whilst no mathematical relationship is obvious, a general tendency is observable for the final adsorption figure to be about $1\frac{1}{3}$ times the adsorption at 2 days. From the calculated ratios, omitting sample (5) (see Table II), it would seem that samples showing a low adsorption in 2 days tend to show a higher ratio of adsorption in 14 days to adsorption in 2 days than samples showing a high adsorption in 2 days; in other words, "good" samples reach their maximum adsorption more quickly than inferior samples. Graph 3 is therefore probably non-linear, but this can ultimately be decided only after a considerably larger number of samples have been examined. If this is so, the 2-day adsorption test, besides taking less time than the 14-day test, permits of better differentiation between good and poor samples. Similar remarks apply to the test at room temperature compared with that at 37° C.: there is considerably better differentiation between good and poor samples at room temperature than at 37° C. This is shown on Graph 2.

TABLE II

| Sample | Methylene blue adsorption, mg. per g. "as received" | | | | Ratio: room temp., 14/2 days | Ratio: 37° C., 14/2 days |
|---|---|---|---|---|---|---|
| | Room temperature | | 37° C. | | | |
| | 2 days | 14 days | 2 days | 14 days | | |
| 1*a* | 55 | 84 | 147 | 217 | 1·52 | 1·47 |
| 1*b* | 55 | 77·5 | 130 | 217 | 1·41 | 1·62 |
| 2 | 165 | 213 | 227 | 295 | 1·29 | 1·30 |
| 3 | 134 | 157 | 205 | 269 | 1·17 | 1·31 |
| 4 | 112 | 144 | — | — | 1·29 | — |
| 5 | 95 | 160 | — | — | 1·68 | — |

Some of the above figures are averages of duplicates.




Graph 4

(*c*) *Physical Properties.*—It was thought that adsorption might depend to some extent on physical condition, especially surface area per unit weight. The dry bulk of different samples was determined by weighing 10 g. on a slip of paper, breaking up lumps by smoothing with a watch glass, transferring to a 50-ml. graduated cylinder, shaking this vigorously for about 5 seconds, and then tapping it on a wooden bench about 25 times from a height of about $\frac{1}{4}$ inch; the volume was read after 1 minute. Water was introduced to bring the volume to the 50-ml. mark, with shaking, and the cylinder was allowed to stand for 2 hours: the wet volume was then read. In many instances no distinct line of demarcation was visible before two hours; after this period the apparent volume increased, possibly owing to hydration of the silicate. This is shown in Table III. No direct relationship between adsorption and either dry or wet volume is evident, but

samples with a high ratio of dry to wet volumes seem to have poor adsorption, and *vice versa*, as indicated by Graph 4.

TABLE III

| Sample | Dry bulk vol., ml. per 10 g. | Wet bulk, ml. occupied by 10 g. 2 hrs. | 5½ hrs. | 18 hrs. | 30 hrs. | 66 hrs. | Dry to wet ratio | 14-day adsorption mg. Meth. Blue per g. |
|---|---|---|---|---|---|---|---|---|
| 1*b* | 32 | 12·5 | 14 | 15·5 | 16 | 16 | 2·56 | 77·5 |
| 2 | 24·5 | 17·5 | 18·5 | 19·5 | 19·5 | 20 | 1·36 | 213 |
| 3 | 45·5 | 22 | — | 24·5 | 26·5 | — | 2·06 | 157 |
| 4 | 35·5 | 18·5 | 20·5 | 21·0 | 21·5 | 21·5 | 1·91 | 144 |
| 5 | 29·5 | 19 | — | — | — | — | 1·55 | 160 |

SUMMARY AND CONCLUSIONS.—(*a*) It is recommended that the analytical examination of magnesium trisilicate should include determinations of silica, magnesium, free and combined water and acid absorption. Methods are indicated for their determination.

(*b*) The merits of various times and temperatures for a methylene blue adsorption test are considered, and it is concluded that a two-day test at room temperature is of value. The figures thus obtained can be roughly correlated with those for adsorption after 14 days.

(*c*) The wet and dry bulks can be determined with advantage; the ratio of dry to wet bulk appears to have some relation with the results of the adsorption test.

I have to acknowledge the encouragement and help of Mr. A. F. Lerrigo, B.Sc., F.I.C., and to thank the directors of Glaxo Laboratories, Ltd., Greenford, for permission to publish this paper.

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# 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.*

## DETERMINATION OF FAT BY THE GROSSFELD METHOD

GROSSFELD'S method has been given particular prominence in recent German literature; special tables have been printed in connection with it, and arrangements have been made for the supply of the special apparatus for filtration without loss through evaporation. We recently tested the method, using the following simplified technique:—Five g. of maize meal were put into a 300-ml. Erlenmeyer flask, 50 ml. of trichloroethylene were accurately pipetted into it, and the flask was connected (rubber stopper) with a reflux condenser. The mixture was boiled for 7 minutes and then cooled, a little anhydrous sodium sulphate was added, and the contents of the flask were shaken and allowed to settle, after which 25 ml. were pipetted off through a cotton-wool guard plug, and filtered into a tared receiver, the paper being washed with a few ml. of the solvent. Two samples were worked on, and the results were checked by extractions with ether in a Soxhlet apparatus.

The dried fats from the Grossfeld process were appreciably darker than those from the Soxhlet extractions, and the Grossfeld results were very much higher.

A control test applied to the trichloroethylene (a "technical" product from a reputable firm) showed that it contained 0·065 g. of non-volatile matter per 100 ml. When allowance was made for this the results were as follows:

| | Refined meal Per Cent. | Straight-run meal Per Cent. |
|---|---|---|
| Soxhlet extraction .. | 1·2 | 4·2 |
| Grossfeld method .. | 2·2 | 6·2 |

The discrepancies are very serious, and one wonders if rubber stoppers are as unaffected by trichloroethylene as has been assumed.

We should be grateful to learn the experiences of others who have used the method or who have employed Leithe's refractive technique.

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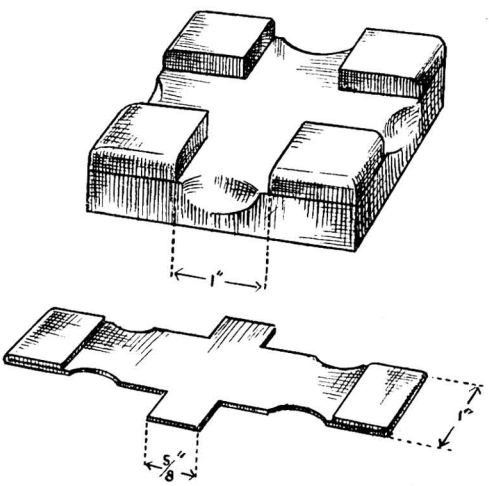
*December 5th,* 1939

## TECHNIQUE FOR THE PREPARATION OF A STANDARD MICROSCOPE SLIDE, WITH PARTICULAR REFERENCE TO CHOCOLATE

IN the manufacture of chocolate it is well known that the size of the particles of sugar greatly influences the quality of the finished product. Measurement of the sugar particles has been mentioned by Knapp[1] in 1920, and further described by Bywaters[2] in 1930. Jensen[3] described a microscope method he had applied successfully for a number of years, and a process is also given by Fincke.[4] In these methods it is assumed that the microscope slide is made up in a standard way, but personal judgment is always required for the original amount of material taken. The subsequent manipulation has always been open to the appreciable

variations in technique introduced by different workers. With a view to preparing a slide in a standard way as free as possible from these variations I have devised the following method, which is applicable as a routine test.

PREPARATION OF STANDARD SLIDE.—To ensure that a standard amount of plain or milk chocolate is taken, a plate of 22-gauge metal drilled in the centre with a 5/64 inch hole is used. The plate is placed on a microscope slide, and the hole is tightly packed with the material by means of the flat blade of a penknife. The excess of chocolate is removed by drawing the edge of the knife across the hole, any loose particles being removed by wiping with a finger or tapping the edge of the plate on the bench. The chocolate in the hole is poked out with a blunt steel tool which passes through the hole for $\frac{1}{2}$ to $\frac{3}{4}$ inch and is then stopped by a shoulder on the handle, which prevents the hole becoming enlarged in use. The chocolate should be deposited at the centre of the slide already used. The weight of chocolate given by this method is approximately 2·8 mg., but may vary by ±0·2 mg., according to the nature of the material.




The definition of the sugar particles is increased by mounting the slide in red-coloured oil as suggested by Phillips.[5] The oil is prepared by dissolving B.D.H. oil-soluble red in a small volume of trichloroethylene, filtering and adding the filtrate to arachis oil. The oil is added from a 5-mm. glass rod tapered to 3 mm. in a distance of 2 cm. and with the end rounded. In use, the first two or three drops are allowed to fall in the bottle and only a slow-forming drop which will fall clear of the rod is taken.

The slide is gently warmed, if necessary, excessive heating being avoided, and is then placed in the aluminium holder of the device shown in the diagram (Fig. 1), and the holder is moved until the oil and chocolate are in the centre of the "cross." A clean microscope slide is placed on top at right angles to the first slide and, without any additional pressure, the aluminium holder is moved six or seven times in each direction. The holder is designed so that the movement is $\frac{3}{8}$ inch

The aluminium holder and the two slides are lifted out of the wooden part. The lower slide is held with the left hand and the upper with the right. The slides are parted, and the oily material clinging to the top slide is transferred to the bottom one by scraping the top slide against the edge of the bottom slide at an angle of approximately 45°. The major part can be removed on one edge and the

residual traces on the other. The material, now practically completely on the bottom slide, is collected to the centre of the slide by means of the edge of a sharp penknife, and a final mixing is given, only the edge of the knife still being used. Any material on the knife is then scraped on to the edge of the slide and as much as possible is transferred to the middle. A round cover-glass, $\frac{7}{8}$ inch in diameter, is placed on the top and allowed to sink by its own weight without external pressure of any sort.

The amount of material taken should be sufficient to spread to the edge of the cover-glass. A clear field with the particles sharply separated should be obtained, but, if not, it is permissible to move the cover-glass in two or three directions, but not exceeding 1/16 in., by applying the point of a knife on the slide and not on the cover-glass. For ease of examination it is important that the cover-glass should be clean and free from smears, and industrial alcohol is recommended for the final cleaning.

If the cover-glass fails to sink down evenly, owing to the presence of a comparatively large particle of foreign matter, it is advisable to remake the slide from the beginning. It is important that no material be removed from the slide, and the details given must be strictly followed. Particular care should be taken in wiping slides and apparatus with a cloth, as the presence of fine hairs on the slide causes an uneven distribution of particles.

The amount of chocolate given by the plate described is suitable for finished chocolate, but for microscope examination during manufacture two other plates are used depending on the coarseness of the material. The three plates are as follows:

| No. | Thickness of plate Inch | Diameter of hole Inch |
|---|---|---|
| 1 | 0·028 | 5/64 |
| 2 | 0·048 | 3/32 |
| 3 | 0·048 | 9/64 |

The plates are made of stainless steel or other metal resistant to wear and, for convenience, measure 2 in. by 1 in. The capacities of plates Nos. 2 and 3 are approximately $2\frac{1}{2}$ and 6 times that of plate No. 1 respectively. The plate to be used depends on the average size of the largest particles in the chocolate and is fixed as follows:

| Plate No. | Average size of largest particles |
|---|---|
| 1 | less than 0·0030 inch |
| 2 | 0·0030 to 0·0060 ,, |
| 3 | above 0·0060 ,, |

The amount of oil required for plates 2 and 3 is best found by experience, but is generally given by one free drop and afterwards touching the slide with the rod to give half a drop.

NOTES ON EXPERIMENTAL WORK.—The method described for preparing a slide takes $1\frac{1}{2}$ minute, and this compares favourably with the ordinary technique. To find if particles were broken down by the process, the lower slide was given 50 backward and forward movements instead of 6 or 7, but no difference in the particle size was detectable. Another variation comprised placing a 100-g. weight on the top slide in the holder, but even this had no breaking-down effect on particles, while after another test the two slides were inverted and the movement carried out in the opposite way. No difference was recorded. It was not found possible to dispense with the after-manipulation of the material, as the particles were insufficiently separated for measurement.

Tests were carried out to find what percentage of the material originally taken was secured under the cover-glass. It amounted to 75 per cent. with

plate No. 1 and 85 per cent. with plates 2 and 3. The figures were reasonably constant and, with care, different operators should retain approximately the same proportions.

CONCLUSION.—The main advantages of the method are that the same amount of chocolate is taken by different operators and that each slide receives the same amount of mixing. It is considered that the method should find application in other industries where particle-size measurement is carried out as a rapid routine test or where standard slides are required.

I wish to thank Mr. R. V. Wadsworth and Mr. J. R. Johnson for their interest and advice, and Messrs. Cadbury Bros. Ltd. for permission to publish this method.

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*November 5th*, 1939

## THE REACTION BETWEEN 2.2'-DICHLORODIETHYL SULPHIDE (MUSTARD GAS) AND BLEACHING POWDER

IT has been observed that the reaction between mustard gas and bleaching powder is violently exothermic—so much so that the mixture frequently bursts into flame. It often happens, however, that a sample of the gas will inflame with one sample of bleaching powder but not with another. I recently tried a sample of specially good bleaching powder from a sealed tin freshly opened. This gave no sign of reaction at all with mustard gas, although several drops were added and even stirred in. On the addition of a few drops of water, however, the whole mass burst into flame. This seems to indicate that the failure of certain samples of bleaching powder to give a vigorous reaction is due to their having too low a moisture-content.

A. G. LIPSCOMB

68, BRIAN AVENUE
NORWICH
*December 21st*, 1939

## AN ANCIENT EGYPTIAN MARKING INK

SEVERAL years ago I examined the marked characters on the winding sheet of Tchehuti Sat in the British Museum (B.M. 37,105), and gave an account of the pigment in THE ANALYST (1927, **52**, 27). This fabric was the one to which Budge refers in his book *The Mummy* (p. 137), where he says: "It is noteworthy that Egyptian ladies marked their linen with indelible ink." The pigment in this marking contained neither metals nor lampblack, but consisted of an organic colouring matter, possibly bistre, attached to the fibres of the fabric.

A still more ancient marking ink than that mentioned by Dr. Budge has recently been discovered, and I am indebted to Mr. A. Lucas for the opportunity of examining it. Three small pieces of linen fabric were found by Mr. W. B. Emery in the rubble filling of the shaft of a tomb of the Second Dynasty at Saggara, near Cairo (the ancient capital Memphis). The dynasty ended about B.C. 2980, and the tomb is probably of a much earlier date than that; it is not known who was buried in it. In Mr. Emery's opinion it is probable that the

Fig. 1

MARKING ON ANCIENT EGYPTIAN LINEN (× 1·5).

markings had some ritual significance, for, although the letters can be read, their meaning is not known. The fragments were cut, not torn, and were probably put intentionally into the shaft of the tomb.

As will be seen in the photograph (Fig. 1) of one of the three fragments, the linen fabric is very coarsely woven, and two of the sides end in a long rough fringe. The marked characters are of a brownish-yellow colour and are placed towards the edge of the fragment. The pigment dissolved with difficulty in hot hydrochloric acid and gave the usual reactions for iron. No other pigment could be detected, and it was concluded that the markings consist of iron oxide deposited on the fibres. The unintentional production of "iron mould" by laundries on modern linen suggests the way in which the iron oxide may have been fixed. The markings behave like iron oxide pigments in ultra-violet light, giving a black "fluorescence."

I have to thank Mr. T. J. Ward for his help in the microchemical examination of these markings.

C. AINSWORTH MITCHELL

12, LIVERPOOL TERRACE
WORTHING
*January*, 1940

# Department of Scientific and Industrial Research

## WATER POLLUTION RESEARCH

### ANNUAL REPORT OF THE BOARD FOR THE YEAR ENDED JUNE, 1939*

THE Annual Report of the Water Pollution Research Board for the year ended June 30th, 1939, has been issued by the Department of Scientific and Industrial Research. In an introductory statement the Board points out that greater vigilance is required in protecting existing and future sources of water supply from undue contamination by the discharge of polluting substances; these measures are especially necessary during wartime, when there are movements of large numbers of people from one district to another. Research carried out under the supervision of the Board includes investigations on the treatment of water for domestic and industrial purposes, the treatment and disposal of sewage and trade effluents, and on problems of pollution of rivers.

BASE-EXCHANGE PROCESS OF WATER SOFTENING.—The base-exchange materials available for this purpose include natural glauconites, treated clays, synthetic zeolites, certain synthetic resins and materials prepared from carbonaceous substances such as coal. Of these materials, natural glauconites and treated clays have not hitherto been produced on a large scale in this country. Previous work under the Board has shown that satisfactory base-exchange substances can be obtained by treatment of fuller's earth, which occurs in large amounts in Great Britain. During the year under review, further work has been done on the examination of British minerals for the preparation of base-exchange materials. One of these minerals, a glauconitic sand, from a brick-works in Surrey, has a high base-exchange capacity and appears to be a suitable raw material for a base-exchange zeolite for the treatment of water. Other work on the base-exchange process has included the investigation of the effect of temperature on the base-exchange capacity of a number of representative base-exchange materials. Within the limits 4 to 20° C. temperature has no significant effect on the exchange capacity of any of the materials tested.

* Published by H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1940. Price 1s. net.

LEAD IN DRINKING WATER.—One method of treatment of water to reduce its corrosive action on lead and other metals consists in passing the water through beds of pieces of limestone, marble or similar substances. This method is particularly attractive for rural districts and remote localities, since the plant, when properly designed, should require little skilled supervision. Several such plants are already in use in this country in rural areas, but much further information is required on the design and methods of operation of this type of plant, if satisfactory results are to be obtained, particularly in the treatment of certain types of water. The Board is making a systematic investigation of this problem. Suitable apparatus and methods of analysis were first developed for the determination of small quantities of lead taken up by water in passing through service pipes. Visits were then made to water-works where water is treated by passage through beds of limestone, and samples of the raw water and treated water were taken for analysis. Arrangements were then made to carry out experiments on the treatment of water in filters containing pieces of limestone, both in the laboratory and on a large scale. Many of the experiments are being made at the Blackmoorfoot Works of Huddersfield, where facilities have been provided by the Huddersfield County Borough Council.

BACTERIOLOGY OF FRESH WATER.—An investigation on the bacteriology of freshwater lakes and streams was begun in May, 1938; this work is being carried out for the Board by the Freshwater Biological Association at the Association's research station at Wray Castle, Ambleside, Westmorland. Preliminary work has indicated that fluctuations in the numbers of bacteria in the upper layers of water in Windermere can be correlated with the rainfall over the drainage area during the period immediately before the samples are taken. The increase in the numbers of bacteria in the lake after heavy rain, however, appears to be due to multiplication of bacteria already in the lake rather than to the washing in of soil bacteria by the storm water, since the types of bacteria isolated from the lake water are, in general, different from the types found in soil.

MILK FACTORY EFFLUENTS.—The Board's investigation of the problems of treatment and disposal of the highly polluting waste waters from milk-collecting and distributing depots, and from the manufacture of cheese, butter, and other products from milk, was begun five or six years ago. In 1935 two large experimental plants were erected at the milk depot and cheese factory at Ellesmere, Shropshire, where facilities were afforded by United Dairies Limited. Methods of treatment of the waste waters which had previously been investigated in the laboratory were tested in the two large-scale plants. These experiments, which were completed during the autumn of 1938, have proved that it is practicable to purify the waste waters either by the activated sludge process or by treatment in two percolating filters in series with periodic change in the order of the two filters. The conditions necessary for the satisfactory operation of these processes in the treatment of the waste waters from the various branches of the milk industry have been ascertained. Under normal factory conditions, the process employing two percolating filters in series is more economical and requires less supervision than the activated sludge process, and it produces final effluents of high quality. The milk industry has shown great interest in this investigation and has contributed a total of £12,050 towards the cost of the work.

TREATMENT AND DISPOSAL OF SEWAGE.—The method developed by the Board for the treatment of dairy waste waters in two percolating filters in series, with periodic change in the order of the filters, is in some respects an elaboration of the method used at many sewage disposal works, where settled sewage is passed through a single percolating filter. For a given volume of filtering material, however, the volume of dairy waste waters which can be treated daily by the new method is considerably greater than the volume of sewage which can be treated by the method of single filtration, allowance being made for the difference in

strength of the two liquids. Moreover, the quality of the effluent from the double-filtration process was much better than is usual at many sewage disposal works. This at once suggested the desirability of experiments on the treatment of domestic sewage by the double-filtration process. If the amount of sewage which can be efficiently treated by double filtration with a given volume of filtering medium is only 50 per cent. greater than by single filtration, the adoption of the new process should lead to considerable reductions in the extensions required at many sewage disposal works.

In addition to this work on the treatment of sewage by biological filtration, experiments have been continued in the laboratory on the treatment of sewage by the activated sludge process. Among the factors investigated were the effect of temperature, proportion of activated sludge, and the acidity or alkalinity of the mixture of sewage and sludge. Experiments have also been made on the effect of acids and alkalis, mineral salts, and organic substances, on the rate of sedimentation of fine particles from suspension in water.

# Ministry of Health

## ANNUAL REPORT OF THE CHIEF MEDICAL OFFICER*

In the Twentieth Annual Report for the year 1938, Sir Arthur MacNalty reviews the nature of progress and the application of the conception to questions of health. This is followed by chapters on Vital Statistics, General Epidemiology Maternity and Child Welfare, The Relation of Food to Health and Disease, Milk, Control of the Purity of Food, Medical Intelligence and Research, Water Supplies, etc.

Food Standards.—In the chapter on the Control of the Purity of Food the question of food standards is fully discussed. It is suggested that where standardisation is undertaken in connection with marketing schemes the object of which is to promote the sale of the higher grades and qualities, it may be of material assistance to fix standards for the higher rather than for the lower grades. "It is, however, questionable whether, from the public health viewpoint, standards should take account of the higher grades and qualities of food where the considerations are mainly aesthetic. It may be held that the primary object of food definitions and standards should be to exclude all articles the consumption of which is clearly prejudicial to the public interest, but not to furnish the vendor with a "selling point" for the higher and more expensive grades of food.

"In demands for standards emanating from commercial interests there is often discernible a desire to stifle competition. Frequently the grades or qualities to which objection is taken are sound wholesome articles of food, the suppression of which would be a distinct loss to the poorer classes of consumers. In such cases the consumer's interest may involve a standard sufficiently low to include nearly all the grades of the food in question provided that they are wholesome and nutritious, and provided also that a system of labelling is adopted which will ensure that the consumer knows what he is buying."

A statutory standard which lays down the composition of an article in numerical terms must be capable of being fully supported by analysis. It has been represented that in all cases where a standard is fixed it should be accompanied by a prescribed method, so as to ensure the results of different analysts agreeing. On the other hand, there are several objections to prescribing analytical technique, and it would seem best that, whenever possible, the analyst should be allowed a free hand to adopt the methods that he has personally found to be the best for the purpose, or which the general body of analysts may have agreed among themselves to adopt.

* H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1939. Price 3s. 6d. net.

COPPER IN CONCENTRATED TOMATO PULP.—At a conference of Port Medical Officers of Health held in October, 1938, it was agreed that a tolerance of not more than 100 parts of copper per million in the dried total solids should be allowed until January 1st, 1940, and that a limit of 50 p.p.m. would have to be complied with on and after that date.

TOXICITY OF THE FLESH OF RABBITS KILLED BY HYDROGEN CYANIDE GAS.—At the request of the Ministry of Health laboratory experiments were made to ascertain if the use of hydrogen cyanide gas for the killing of rabbits would render the flesh unfit for human consumption. The rabbits were exposed for varying periods of time to high concentrations of the gas (up to 1 part in 200). The amounts of free cyanide in the blood and tissues varied with the time of exposure and the concentration. After exposure to a concentration of 1 in 2000 (which is quickly lethal) followed by exposure for 5 hours to the same concentration, small amounts of free cyanide were found in the edible portions of the rabbit. The highest amount found was 2 mg. in the body of a rabbit which had been exposed for 4 minutes to a concentration of 1 part in 200. It would appear that the flesh of rabbits exposed to concentrations of the gas probably higher than would ordinarily be employed cannot normally be regarded as unwholesome, but it would not be wise to say that in no circumstances would it be open to objection from the dietetic standpoint.

# Rothamsted Experimental Station

## REPORT FOR 1938*

THE Introduction to the Report contains a general account of the founding of the Experimental Station and of the development of its numerous activities. The Report itself gives a description of the work of the Station in the different laboratories and on the Woburn Experimental Farm. Among the interesting results discussed are the following:

USE OF TOWN REFUSE AS MANURE.—A prepared town refuse was compared with (1) sulphate of ammonia and (2) dung or rape dust, each given in single and double dressing, the nitrogen content being taken as the basis for comparison. The mean composition of the town refuse used was N, 0·82 per cent.; moisture, 30·3 per cent. The rates of application were: Single dressing of town refuse, about 5 tons per acre; rape cake, dung, 0·8 cwt. of N per acre. Single dressing of sulphate of ammonia, 0·4 cwt. of N per acre. Comparative tests with other nitrogenous manures were also made. The results (tabulated in detail) show that treated town refuse did almost as well as sulphate of ammonia providing half as much nitrogen, and was distinctly superior to sulphate of ammonia providing one quarter of the nitrogen, although it was much inferior to sulphate of ammonia supplying the same amount of nitrogen. The similarity in effectiveness to dung emphasises the desirability of further investigation (*cf.* E. Voelcker, ANALYST, **1939**, **64**, 510).

PHOSPHORUS COMPOUNDS IN SOIL.—Field experiments have indicated that, of the phosphate added as fertiliser, only about 25 per cent. is recovered in the crop in ordinary circumstances; the rest remains in the soil, but, in so far as can be discovered, in a form in which plants cannot easily take it up. Present evidence indicates that the soil is a poor storehouse for fertilisers.

MANGANESE DEFICIENCIES IN SOIL.—Three main types of soil are liable to manganese deficiency, as shown by characteristic crop troubles: (i) Neutral or alkaline soils, notably recently limed reclaimed heath soils, which do not contain

* Pp. 213. To be obtained from the Secretary, Rothamsted Experimental Station. Price 5s.

manganese mineral; these are liable to "grey speck" of oats. (ii) Alkaline fen soils; these are liable to "speckled yellows" of sugar beet. (iii) Heavily alkaline marsh soils, even if they contain manganese mineral; these are liable to "marsh spot" in seed peas. All these diseases have been remedied by suitable applications of manganese sulphate. It should be noted that they can all be brought on by over-liming.

COBALT DEFICIENCIES IN SOILS.—In the Chemical Department it has been shown that pastures of the Dartmoor area are deficient in cobalt; the sheep there suffer from a disease similar to that in New Zealand (*cf.* ANALYST, **1938, 63, 112**). The remedy is to give a cobalt lick, but it is clearly desirable to make a survey of other hill or moorland grazings.

X-RAY ANALYSIS OF SOIL MINERALS.—X-ray analysis is now used in the Chemical Department for the identification of the minerals in the different soil fractions, and special attention has been devoted to the clay fraction. The special properties of this fraction are largely due to certain components now under investigation. They are very complex, and their smallest particles are shown by X-ray analysis to consist of a lattice structure in which layers of silicon and oxygen atoms alternate sandwich-like with layers of aluminium and oxygen atoms arranged systematically. The particles are electrically charged and hence have associated with them various ions, of which the most important from the point of view of soil fertility are calcium, and, in the Rothamsted conditions, hydrogen and potassium, but in arid conditions sodium and magnesium. These cations are replaceable by others: the "souring" of soil is caused by the replacement of calcium by hydrogen; conversely the "sweetening" of soil by liming is due to the replacement of hydrogen by calcium. An account is given in the Report of the three ways in which the electric charges appear to originate.

COLOUR OF THE SOIL.—Soil surveyors use the colour of the soil as one of its properties for classification, but the estimation of soil colours is very vague. Dr. Schofield has devised an instrument for the exact measurement of colour, and this has been taken over by Tintometer Limited.

WATER SUPPLY TO PLANTS.—A method of measuring the intensity with which soils hold water has been worked out in the Physics Department. The underlying conception of water suction is being applied to a study of the pore size distribution in soils.

CROPS AND MICRO-ORGANISMS.—*Clover Nodule Bacteria.*—Some strains of clover nodule bacteria are much less efficient than others. One of the poorest, found on the Welsh hills, has been studied in detail. It is so inefficient that it can barely sustain its host plant. The reason for this has been traced to some incompatibility between them and their host. Evidence has been obtained that plants bearing inefficient nodules produce some substance toxic to the plant, so that while they begin by fixing nitrogen just as the more efficient forms do, in a very short time the nodules begin to disintegrate.

*The Denitrification Process.*—The process of denitrification whereby nitrates are reduced in the soil to gaseous nitrogen has hitherto been regarded as entirely anaerobic. It is now shown that this is not so, and that complete reduction of nitrate to gaseous nitrogen can take place under anaerobic conditions, with the difference that, for a C/N ratio of 10, the whole of the carbon supplied is used up under aerobic conditions, but part of it is left untouched under aerobic conditions.

THE CABBAGE APHIS.—It has been found that the rate of reproduction of cabbage aphides is dependent on the composition of the cabbage, and that the aphides themselves affect not only the yield but also the composition of the cabbage.

VIRUS DISEASES.—From plants infected with two strains of potato virus "X," nucleo-proteins have been isolated which in many respects resemble those previously obtained from plants infected with tobacco mosaic virus. When

precipitated from solutions with acids or salts these proteins are amorphous. From plants infected with tomato bushy stunt virus another nucleo-protein has been isolated; after precipitation with salts this crystallises in rhombic decahedra. It is the first virus to be isolated in a fully crystalline state. It differs from those previously studied in having spherical instead of rod-shaped particles; also in having a much greater nucleic acid content.

Other sections of the Report deal with Insecticides and Fungicides, Fungus Diseases of Crops, Statistical Control of Experiments, Field Experiments at Outside Centres, etc.

# The Sale of Milk Regulations, 1939

STATUTORY RULES AND ORDERS, 1939, No. 1417*

ADULTERATION. FOOD AND DRUGS ACT, 1938

THE Minister of Agriculture and Fisheries, in exercise of the powers conferred on him by Section 23 of the Food and Drugs Act, 1938, does hereby make the following Regulations:

*Milk*

1. Where a sample of milk (not being milk sold as separated, or condensed, milk) contains less than 3 per cent. of milk-fat, it shall be presumed for the purposes of the Food and Drugs Act, 1938, until the contrary is proved, that the milk is not genuine, by reason of the abstraction therefrom of milk-fat, or the addition thereto of water.

2. Where a sample of milk (not being milk sold as separated, or condensed, milk) contains less than 8·5 per cent. of milk-solids other than milk-fat, it shall be presumed for the purposes of the Food and Drugs Act, 1938, until the contrary is proved, that the milk is not genuine, by reason of the abstraction therefrom of milk-solids other than milk-fat, or the addition thereto of water.

*Separated Milk*

3. Where a sample of separated milk (not being condensed milk) contains less than 8·7 per cent. of milk-solids other than milk-fat, it shall be presumed for the purposes of the Food and Drugs Act, 1938, until the contrary is proved, that the milk is not genuine, by reason of the abstraction therefrom of milk-solids other than milk-fat, or the addition thereto of water.

*Commencement*

4. These Regulations shall come into operation on the first day of October, one thousand nine hundred and thirty-nine.

*Extent*

5. These Regulations shall extend to England and Wales.

*Short Title*

6. These Regulations may be cited as the Sale of Milk Regulations, 1939.

In witness whereof the Official Seal of the Minister of Agriculture and Fisheries is hereunto affixed this 1st day of October, one thousand nine hundred and thirty-nine.

(*Signed*) DONALD FERGUSSON
(*Secretary*).

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* H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1939. Price 1d. net.

# British Pharmacopoeia Commission

## REPORT OF THE COMMITTEE ON PHARMACY AND PHARMACOGNOSY*

SECTION I.

*The Sub-Committee on Crude Drugs* have reviewed the 82 monographs submitted to them by the Commission, and have rewritten them so as to present a more complete account of the microscopy of commercial drugs than has been given in previous Pharmacopoeias, and also to indicate in sufficient detail the diagnostic microscopical features of the powders. Four complete monographs (Belladonnae Folium, Belladonnae Radix, Cinchona, and Nux Vomica) are included in the Report in order to show the general scope and mode of presentation. As regards the other monographs it is thought that a concise statement of the standards and tests for purity should be sufficient for the present purpose.

TYPES OF STOMATA.—The Sub-Committee recommend that, for reference in relation to the microscopy of drugs, the following definitions (applicable only to mature stomata) should be included in an Appendix to the Pharmacopoeia.

*Ranunculaceous Type*—with no special subsidiary cells.

*Cruciferous Type*—often with three or more accessory cells, one of which is distinctly smaller than any of the others.

*Rubiaceous Type*—often with two subsidiary cells, with their long axes parallel to the pore.

*Caryophyllaceous Type*—often with two subsidiary cells, lying round the ends of the guard-cells.

STANDARDS AND TESTS FOR PURITY.—*Drying of Drugs.*—The Sub-Committee recommend that all determinations for ash, acid-insoluble ash and water-insoluble ash should be made on the drug as received (air-dried drug).

*Volatile Oil.*—A method has been published in Report No. 11.

*Powders.*—The revised monographs are arranged to give, in most instances, descriptions for the powders of crude drugs. For the present the assumption is made that it will be possible to apply the standards for foreign organic matter to the official drugs in the form of powder. It is thought advisable for the present to restrict the standards for volatile oil in crude drugs to the drugs in the unground condition, with the exception of powdered cinnamon, for which a minimum content of oil is proposed (not less than 0·7 per cent.). Investigations are in progress to ascertain the loss of volatile oil during powdering and storage of powders.

*Foreign Organic Matter.*—This term should be used, in preference to "other organic matter" to designate organic matter which does not form part of the drug as defined by the monograph.

SUMMARY OF THE REQUIREMENTS FOR INDIVIDUAL DRUGS.—Standards and tests for identity are given for 78 monographs of the current Pharmacopoeia.

SECTION II.

*The Sub-Committee on Extracts, Liquid Extracts and Tinctures* have reviewed the monographs in the current Pharmacopoeia and recommend that the general principles there followed should be continued, *viz.* that instructions should be given for the preparation of relatively small quantities of these galenicals, and that recognition of deviations from the strict details of the pharmacopoeial monographs should be given in General Notices to the Pharmacopoeia.

Certain changes are recommended in the following monographs:—Extractum Belladonnae Liquidum, Extractum Ipecacuanhae Liquidum, Extractum Sennae Liquidum, Tinctura Capsici, Tincturae Nucis Vomicae.

New monographs are proposed for Extractum Hamamelidis Siccum and Tinctura Gelsemii.

SECTION III.

*The Sub-Committee on Waters, Infusions, Solutions, Spirits and Syrups* recommend certain changes in 14 monographs. New monographs are proposed for Liquor Sodii Chloridi Compositus (Ringer's Solution), Spiritus Lavandulae, and Syrupus Codeinae Phosphatis.

SECTION IV.

*The Sub-Committee on Ointments and Miscellaneous Galenicals* recommends certain changes in 14 monographs. New monographs are proposed for Acriflavine Preparations, Emulsio Olei Morrhuae, Emulsio Paraffini Liquidi, Glycerinum Acriflavinae, Injectio Calcii Gluconatis,

* Report No. 13. Published by authority of the General Medical Council, 44, Hallam Street, London, W.1. September, 1939. Price 2s. 6d.

Injectio Procainae et Adrenalinae, Injectio Quininae et Urethani, Injectio Sodii Morrhuatis, Linctus Diamorphinae, Linimentum Aconiti Oleosum, Linimentum Methylis Salicylatis, Lotio Acriflavinae, Lotio Calaminae, Pasta Acidi Tannici, Pillulae Digitalis Compositae, Pulvis Bismuthi Compositus, Pulvis Catechu Compositus, Pulvis Kino cum Opio, Suppositoria, Suppositorium Adrenalinae, Unguentum Gallae cum Opio, Unguentum Hamamelidis, Unguentum Hydrargyri Dilutum, Unguentum Methylis Salicylatis Compositum.

*Mercury Ointments.*—The difficulties that have arisen from the use of various names and synonyms for ointments containing metallic mercury have been considered, and the Sub-Committee recommend:

(*a*) That the monograph on the Ointment of Mercury of the current Pharmacopoeia, containing 30 per cent. of mercury, should be continued without the synonym "Mercury Ointment."

(*b*) That a Diluted Ointment of Mercury, containing 10 per cent. of mercury, should be introduced with the synonym "Blue Mercury" and with the addition of a note explaining the application of the names "Mercury Ointment" and "Mercurial Ointment." The draft for "Blue Ointment" submitted contains one-third of Mercury Ointment and two-thirds of Benzoinated Lard.

When Mercury Ointment or Mercurial Ointment is prescribed or demanded, Diluted Ointment of Mercury shall be dispensed or supplied, unless, on enquiry, it is ascertained that Ointment of Mercury is required.

SECTION V.

*The Sub-Committee on Tablets* has explored the possibility of defining tablets and the general principles have been worked out, but further investigation is required before definite conclusions can be reached.

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

# Food and Drugs

**Freezing-point of Milk. L. M. Lampert.** (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 768–771.)—Hortvet (*J. Ind. Eng. Chem.*, 1921, **13**, 198) reported that the depression of the freezing-point of pure milk, as determined by the instrument he described, now widely used, ranged from 0·534° to 0·562° C., with an average value of 0·548° C. It would appear that the currently accepted average figure was obtained by rounding off this figure to 0·55° C. Bailey (*J. Assoc. Off. Agr. Chem.*, 1922, **5**, 484), reporting collaborative work on some 2700 samples, gave an average value of 0·544° C. Results from the Union of South Africa (ANALYST, 1937, **62**, 44) gave a range of 0·528° to 0·561° C. and an average of 0·541° C. Stubbs and Elsdon (ANALYST, 1934, **59**, 146) found for 1000 samples a range of 0·529° to 0·563° C. and an average of 0·544° C. The freezing-point depressions of 24 carefully authenticated samples from large and small herds in different parts of California were determined with minute attention to the details of the process and to the calibration and standardisation of the thermometers, and the average value found was 0·536° C. A survey of all the data obtained and other recently published data indicated that the accepted average depression of 0·550° C. is somewhat high. The authorities of New South Wales (ANALYST, 1937, **62**, 610) have considered it advisable to accept 0·535° C. and those of Western Australia (ANALYST, 1938, **63**, 890) to accept 0·540° C. as the average depression of pure milk. The data obtained by Hortvet, Bailey, and Stubbs and Elsdon were combined and examined statistically. The distribution curve was found to be normal and very

symmetrical, with a range of 0·523 to 0·566° C., a mean of 0·544° C., and a median of 0·543° C. Out of 1224 values, 54 per cent. showed a depression of 0·544° C. or less and 84·7 per cent. a depression of 0·550° C. or less. Since the depression of the freezing-point of milk from healthy cows has been proved to be unaffected by the season of the year or the feed, these values may be assumed to be characteristic of much of the milk produced. It is, therefore, suggested that, when control samples are not available, the value 0·540° C. be accepted as the average freezing-point depression of pure milk, especially when the results are to be used for the detection and determination of added water. A. O. J.

**Rapid Method for the Determination of Chlorides in Tomato Products. L. M. Beacham.** (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 765–766.)—The following method avoids such difficulties as slow evaporation in the official method for the determination of chlorides in tomato products ("*Methods of Analysis*," A.O.A.C., 1935, 500) and slow filtration in the tentative method for their determination in tomato juice (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 78) and gives excellent results. The tomato product (5 g.) is shaken with about 50 ml. of 80 per cent. alcohol, and after the addition of 1 ml. of conc. nitric acid and 25 ml. of $N/10$ silver nitrate solution the mixture is diluted to 100 ml. with the alcohol, thoroughly mixed, and centrifuged at 1800 r.p.m. for 5 minutes. A 50-ml. portion of the supernatant liquid is titrated with $N/10$ ammonium thiocyanate solution in presence of 2 ml. of saturated ferric ammonium sulphate solution in the usual manner. Results obtained by this method agreed well with those obtained by the official method. Tomato pastes and juices were prepared and their natural chloride-content was determined by this method. Known amounts of salt were then added, and the determination was repeated. The results obtained agreed closely with the known amounts of salt present. A. O. J.

**Estimation of Soya-bean Flour in Sausage by determining Non-fermentable Sugars. W. B. Hendrey.** (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 611–613.)—A direct carbohydrate method based on hydrolysis to reducing sugars and the determination of these by Fehling's solution is put forward for the determination of soya-bean flour in sausage. The sample should contain about 2 g. of soya-bean flour (50 g. of sausage). It is prepared as directed by the A.O.A.C. (grinding with alcohol, extraction with petroleum spirit and re-grinding), and the water-soluble sugars are remoyed by washing the weighed sample by decantation with neutralised 50 per cent. alcohol. The liquid is poured through an 11-cm. 42 Whatman paper coated with 0·3 cm. of washed Filter-cel, and most of the solid is transferred to the paper and washed five times with the alcohol. If desired, the determination of soluble added sugars may be made. The insoluble sugars are then determined. After partial drying the washed residue and Filter-cel are transferred to the original flask, and the paper and sides of the flask washed with 120 ml. of 2·5 per cent. hydrochloric acid. The flask is fitted with rubber-stoppered reflux air condensers and held in a boiling saturated salt-bath for 3 hours. The liquid is nearly neutralised with 10 per cent. sodium hydroxide solution and transferred to a 250-ml. flask, hot water is added nearly to the mark, followed by 2 ml. of 50 per cent. phosphotungstic acid, and the liquid is made up

to 250 ml. with water, shaken and centrifuged, and tested for complete precipitation. Two hundred ml. are then pipetted into a 250-ml. flask and potassium chloride is added in slight excess to precipitate the excess of phosphotungstic acid, followed by 1 drop of methyl orange solution, and the liquid is neutralised to methyl orange and litmus, cooled, made up to volume, shaken and filtered. If desired, the percentage of insoluble sugars may be determined in an aliquot portion by the A.O.A.C. method, and for soya-bean will be about 11 to 12 per cent. of invert sugar or 10·5 to 11·5 of dextrose. The non-fermentable sugars are determined by a quick fermentation method adapted from Bailey (*Conn. Agric. Expt. Sta. Bull.*, 1937, 401, 869). Bakers' yeast is washed 5 times by stirring with 3 times its volume of water and centrifuging, and a 25 per cent. suspension in water is kept at about 0° C. Ten ml. are placed in a 100-ml. centrifuge tube and centrifuged, the water is poured off, and the inside of the tube is dried with filter paper. About 60 ml. of the sugar solution are added (diluted if necessary so that not more than a 0·1 per cent. concentration of fermentable sugars is present), stirred and left for 45 minutes, preferably at 30° C., with one stirring during this period. The solution is centrifuged and filtered, and the sugar is determined as invert sugar by the A.O.A.C. method; the percentage of non-fermentable sugars, multiplied by 9·4, gives the percentage of soya-bean in the sample. If lactose is absent the method may be shortened, but the short method suggested for the determination of total non-fermentable sugars is at present only tentative, since sufficient data are not yet available for determining the general validity of the blank correction.

D. G. H.

**Indirect Volumetric Determination of Alkaloids. G. Auguste.** (*J. Pharm. Belg.*, 1939, **21**, 935–941, 961–964.)—Several attempts have been made to employ modifications of Mayer's reaction with alkaloids as quantitative methods, the most successful being that of Jonesco–Matiu and Varcovici (*J. Pharm. Chim.*, 1926, **8**, 533; Abst., ANALYST, 1927, **52**, 100) by which the alkaloidal iodomercurate is separated and decomposed by means of nitrous and sulphuric acids and its mercury-content determined by the procedure of Votoček and Kasparek (*Bull. Soc. Chim.*, 1923, **33**, 110; Abst., ANALYST, 1923, **48**, 192). Since the alkaloids tend to form more than one iodomercuric salt (François and Blanc, *Bull. Soc. Chim.*, 1922, **31**, 1208, 1304; *cf.* Abst., ANALYST, 1922, **47**, 440), such methods have obvious disadvantages. Potentiometric methods for the titration of the iodomercuric anion (*e.g.* that of Maricq, *Bull. Soc. Chim. Belg.*, 1929, **38**, 259; 1930, **39**, 496; Abst., ANALYST, 1930, **55**, 284; 1931, **56**, 120) have not found general acceptance. In the reaction between alkaloids and potassium mercuric iodide in an acid medium, formation of the alkaloidal hydriodide that combines with mercuric iodide must entail a reduction in the acidity of the system equivalent to the amount of alkaloid present. This principle has now been applied to the determination of alkaloids by an acidimetric method. The reagent was prepared by diluting a solution of 25 g. of potassium iodide and 36 g. of mercuric iodide in 200 ml. of air-free water to 1 litre and allowing the solution to stand overnight before filtering. Fifty to 100 mg. of atropine were dissolved in 10 to 20 ml. of *N*/10 sulphuric acid, and the reagent was added, drop by drop, from a burette,

coagulation of the yellow colloidal precipitate being induced by agitation after each addition. When precipitation was complete the amount of reagent added was noted, and an excess of four to eight times this amount was run in. The mixture was vigorously shaken, allowed to stand until the supernatant liquid became clear, and, after addition of a little barium sulphate, was filtered through a double or triple filter-paper. An aliquot portion of the filtrate was titrated with $N/10$ sodium hydroxide solution, phenolphthalein being used as indicator. The reagent (20 ml.) was then mixed with 10 ml. of $N/10$ sulphuric acid and titrated with $N/10$ sodium hydroxide solution in the same manner. The amount of atropine present was calculated from the reduction of acidity caused by the formation of the complex salt. Each ml. of $N/10$ acid is equivalent to 0·0289 g. of atropine. The burettes used in the final titrations were graduated in 1/50th and 1/100th ml. The relative error of the method was usually not more than 1 to 2 per cent.; in rare instances it reached 3 per cent. The results of the acidimetric and iodimetric methods agreed well, the relative errors being of the same order as that of the iodomercurate method. Further investigation is being made to apply the method to other alkaloids and to the determination of alkaloids in galenical preparations. A. O. J.

**Application of the Herapathite Reaction to Aristoquin. M. Wagenaar.** (*Pharm. Weekblad*, 1939, **76**, 1544–1545.)—Methods for the detection of aristoquin (diquinine carbonic ester), $CO(OC_{20}H_{23}N_2O)_2$, are based on the assumption that when this substance is dissolved in hydrochloric or sulphuric acid, carbon dioxide is evolved, and quinine chloride or disulphate is formed, respectively (*cf. id.*, 1934, **71**, 316). The author provides evidence that in practice this is not entirely correct. Thus quinine sulphate has an intense blue fluorescence, whilst a solution of aristoquin in sulphuric acid fluoresces with a greenish-blue colour. The difference is apparent without the aid of an ultra-violet lamp, and is conveniently demonstrated by focussing sunlight, with the aid of a lens, on to the test-tube containing the liquid. Similarly, the herapathite reaction (whether used to produce the complex sulphate or selenate) is difficult to demonstrate for a solution of aristoquin in acid, whereas it is very sharp for pure quinine salts. The author has shown (*id.*, 1929, **66**, 177) that the presence of acetone usually induces crystallisation in the herapathite reaction. This, however, does not apply to solutions of aristoquin in acid, unless the quinine salt so formed is first purified (*e.g.* by precipitation); the greater the degree of purity, the sharper the herapathite reaction. It is concluded, in fact, that the above dissimilarities between quinine salts and solutions of aristoquin in acids are due to the presence of impurities in the latter, and that these result from the method of preparation of aristoquin, namely, by the reaction of diphenyl carbonate and quinine; they may be due to the presence of an excess of the former or of the products of side-reactions. Another method of inducing the herapathite reaction is as follows:—The sample is evaporated slowly with a dilute solution of sodium hydroxide, and 1 drop of a solution of iodine in potassium iodide is added to a solution of the residue in dilute sulphuric acid. The brown precipitate which results is dissolved in acetone, and when the yellow solution so produced is evaporated the crystals of herapathite form rapidly. This method

serves satisfactorily as a test for aristoquin, and, although the crystals are not so well-formed as those produced from a pure quinine salt, they enable a strong dichroism to be detected. J. G.

**Reactions for the Identification of Isazin. M. J. Schulte.** (*Pharm. Weekblad*, 1939; **76**, 1256–1257.)—Isazin is diacetyldihydroxy-phenylisatin, and the reactions described indicate the presence of the phenol, isatin and acetyl groupings. (1) The phenolic group is shown by Ehrlich's diazo-reaction. A solution of 10 mg. of the sample in 1 ml. of conc. alcohol is made just alkaline with 1 drop of sodium hydroxide solution and, on the addition of 1 drop of a 0·5 per cent. solution of sodium nitrite, and sulphanilic acid, an orange-red colour develops if isazin is present. On acidification with sulphuric acid the colour becomes yellow, and, on warming, an odour of ethyl acetate is evolved. (2) To a solution of 10 mg. of sample in 1 ml. of conc. alcohol is added 1 ml. of 0·1 *N* sodium hydroxide solution. On warming, a pale violet colour is obtained, and, on subsequent cooling and addition of 1 drop of 0·5 *N* bromine water, a dark blue colour results. If the solution is then shaken with chloroform the blue colour appears in the chloroform layer, the water layer being violet. Evidence is provided in support of the view that the blue compound is a bromine substitution-product of isatin. The reaction is successful only in weakly alkaline solutions and, consequently, the bromine water must not be too old. In presence of acid the blue colour changes to yellow, and if an excess of bromine water is present the colour is dirty green, and a yellow-brown precipitate is deposited. The blue compound is an indicator, which turns violet in alkali and yellow in acid, and it may be obtained by evaporation of the chloroform. A solution of the residue in alcohol gives a sharp end-point in the titration of borax with 0·1 *N* acid. (3) If 1 drop of a 0·1 per cent. solution of potassium permanganate is added to the violet alkaline alcoholic solution (see above) a dark purple-red colour is developed. This is preferable to the reaction with bromine water, in that it is less affected by outside influences. (4) A solution of 10 mg. of isazin in 1 ml. of conc. sulphuric acid develops a purple colour. J. G.

# Biochemical

**Inactivation of the Enzymes of Gum Arabic. J. P. Kieft.** (*Pharm. Weekblad*, 1939, **76**, 1133–1136.)—The enzymes of gum arabic are usually inactivated by heating a solution of the gum to 100° C. or by preparing *Gummi arabicum resiccatum* by evaporation of the mucilage. Thus, according to Laursen (*Dansk Tidskrift for Farmaci*, 1932, p. 54) the oxidases and peroxidases are inactivated after 15 and 30 minutes, respectively, at 80° C. Since it has been accepted that, in general, enzymes are more stable to heat-treatment when in the dry state than in presence of moisture, the following experiments were carried out with the object of demonstrating the effect, on the inactivation, of variations in the technique of the method used. In each instance 500 mg. of the powdered gum (or an equivalent quantity of the mucilage) were dissolved in 3 ml. of water, and the solution was shaken with 4 drops of a 5 per cent. tincture of guaiacum; the

time that elapsed before a blue colour was produced was then noted, and these values are given below:—(1) Original gum arabic, 4 minutes. (2) Ten g. of gum were heated in a closed 15-ml. flask in a current of steam at 100° C. for 30 minutes, the flask being at 94° C. for 15 minutes; 70 minutes. (3) Experiment (2) was repeated, except that a boiling water-bath was used in place of the steam; 70 minutes. (4) The gum (50 g.) was heated in a 75-ml. flask on a water-bath, so that the temperature rose to 92° C. in 20 minutes, and was maintained at 92° C. for 2 hours; 105 minutes. (5) The powdered gum was heated in a flat dish in a drying-oven at 103° to 105° C., and the oxidase-values were determined after 0·5, 1, 2, 3·5 and 5 hours; 7, 20, 20, 25 and 25 minutes, respectively. (6) Gum arabic mucilage was heated for 1 hour at 70° and 100° C.; 35 minutes, and no change after 120 minutes, respectively. (7) *Pulvis Gummi arabici resiccat.* was prepared by evaporating the mucilage in air in a flat dish on a boiling water-bath at 65° to 80° C., this being completed in 1 hour; 70 minutes. (8) A portion of the product obtained in (7) was heated for 10 minutes at 103° to 105° C. in a drying-oven; no change after 120 minutes. (9) *Pulvis Gummi arabici resiccat.* was prepared by distillation in a vacuum, on a water-bath, in a stream of carbon dioxide for 1 hour at 75° to 85° C.; 30 minutes. J. G.

**Phytic Acid and the Rickets-producing Action of Cereals. D. C. Harrison and E. Mellanby.** (*Biochem. J.*, 1939, **33**, 1660–1680.)—It has long been known that certain cereals, especially oatmeal, promote rickets in young animals. This rachitogenic activity is not the result of a deficiency of calcium or phosphorus in the cereal, as oatmeal for instance contains large amounts of both these elements. At first the presence of an "anti-calcifying toxamin" was postulated, but later, Bruce and Callow suggested that the rickets resulted from the non-availability of the phosphorus, which in such cereals, is present chiefly in the form of phytin (calcium magnesium inositol hexaphosphate). These workers, however, used diets rich in calcium and poor in phosphorus, whereas it has now been found that oatmeal is equally rachitogenic when fed to puppies on a diet having a normal calcium/phosphorus ratio. Under these conditions an adequate amount of phosphorus is present, so that the above explanation no longer holds good. Similar rachitogenic activity is also possessed by sodium phytate and phytic acid, but not by commercial phytin (the calcium magnesium salt), which may even be slightly antirachitic. The rachitogenic factor was isolated as follows:—Defatted oatmeal was hydrolysed by diastase to destroy the starch and then extracted with cold hydrochloric acid. Phytic acid was isolated from this extract by precipitation as the insoluble iron salt, and this was converted into the sodium salt. The latter was found to have the same rachitogenic activity as the oatmeal from which it was prepared; moreover, the activity was not lost on purification. The rachitogenic activity of oatmeal and of phytic acid and sodium phytate was inhibited by adding sufficient calcium. The hypothesis is now advanced that the rickets is produced by the phytic acid immobilising the calcium in the oatmeal and possibly also in other food eaten at the same time, by inhibiting its absorption from the alimentary canal. F. A. R.

**Colour Reaction of Methionine. J. J. Kolb and G. Toennies.** (*J. Biol. Chem.*, 1939, **131**, 401–407.)—When a solution of cupric chloride in conc. hydrochloric acid is added to methionine a colour is produced which resembles that of iodine-iodide solutions, varying from a deep brown to a pale yellow according to the concentration of methionine. This reaction was not obtained with twenty other naturally-occurring amino acids, including cysteine and cystine, nor with the methionine derivatives homocysteine thiolactone and methionine sulphoxide. The following compounds, which like methionine contain the grouping $-CH_2-CH_2-S-CH_2-$, gave the reaction in its full intensity: ethionine, homomethionine, hexomethionine and homodjenkolic acid. Methyl-S-cysteine and ethyl thioglycollic acid gave a positive reaction, but less strongly than methionine; benzyl-S-cysteine and ethyl-S-cysteine gave the reaction faintly, and djenkolic acid very faintly. Carboxymethylcysteine and phenyl-S-cysteine gave negative reactions. Carbohydrates and alkaloids did not give a colour with the reagent, whilst some proteins, presumably containing methionine, gave positive responses. The coloured compound appears to be formed by the combination of 1 molecule of the sulphide with 1 molecule of cupric chloride. With an excess of the latter, green colours tend to be formed, and this reduces the sensitivity of the test. The addition of hydrogen peroxide destroys the colour, and affords a valuable method of confirming a positive result. For qualitative purposes, it is best to allow 1 or 2 drops of 0·1 *M* cupric chloride solution in hydrochloric acid to run down the side of a test-tube upon which a few particles of the substance have been scattered. If at the moment of contact an intense brown colour develops, then methionine or a closely related substance is present. F. A. R.

**Fluorometric Method for Determining the Riboflavin Content of Foodstuffs. A. Z. Hodson and L. C. Norris.** (*J. Biol. Chem.*, 1933, **131**, 621–630.)—A 5-g. sample of the material to be tested is weighed into a 500-ml. Erlenmeyer flask, and 50 ml. of 0·25 *N* sulphuric acid are added. After being thoroughly mixed the contents of the flask are gently heated under reflux for an hour and allowed to cool, after which the *p*H is adjusted to 7·0 to 7·5 with trisodium phosphate solution. The extract is diluted to 50 ml. with water and filtered after standing for 30 minutes. An aliquot part of the filtrate is pipetted into a 200-ml. volumetric flask and diluted to approximately 175 ml. with water. Then 2 ml. of sodium hydrosulphite solution (1 g. of pure sodium hydrosulphite and 1 g. of sodium bicarbonate in 20 ml. of ice-cold water kept in an ice-bath; the solution is stable for about 4 hours) and 2 ml. of stannous chloride solution (10 g. of stannous chloride in 25 ml. of conc. hydrochloric acid are diluted 200-fold with water) are added, and the solution is diluted to the mark. The mixture is allowed to stand for 10 minutes to ensure as complete reduction as possible of interfering pigments and fluorescent substances; it is then transferred to a 1-litre Erlenmeyer flask and shaken vigorously for 5 minutes with access to air. The riboflavin present, which is reduced to a non-fluorescent form together with the other substances, is re-oxidised by this procedure, whereas none of the interfering substances so far encountered is thereby affected. A definite volume of the solution is then introduced into the cell of a fluorometer and the fluorescence is

measured in the usual way. In addition, three other readings are taken: (*a*) with the unknown solution after addition of a known amount of standard riboflavin solution, (*b*) with the unknown solution after reduction with sodium hydrosulphite solution (2 per cent. of its volume), and (*c*) with a solution containing the same amount of riboflavin as that added to the unknown. The difference between the apparent riboflavin-contents before and after reduction gives the true riboflavin-content, except in so far as this is affected by the presence of stable interfering pigments. This effect is corrected for by multiplying by the factor:

$$\frac{\text{riboflavin content of the standard solution}}{\text{difference between the riboflavin contents before and after the addition of flavin to the unknown}}$$

The appropriate dilution factors must, of course, be employed where solutions of sodium hydrosulphite or flavin have been added to the unknown. In the extraction of bulky materials, such as alfalfa meals, the quantity of 0·25 *N* sulphuric acid should be doubled. Samples of milk by-products containing casein are preferably extracted with a mixture of acetone (3 volumes) and *N* sulphuric acid (1 volume) rather than 0·25 *N* sulphuric acid. Satisfactory results cannot be obtained with extracts containing large amounts of light-absorbing impurities, as, for instance, those obtained from molasses, but by means of the following modification most of the interfering substances are removed. To 10 ml. of the neutralised extract are slowly added 90 ml. of methyl alcohol and the mixture is filtered, with precautions to prevent evaporation. A suitable aliquot part of the filtrate is transferred to a 200-ml. volumetric flask and diluted to 175 ml. Subsequently the usual procedure is followed. The validity of the results obtained by this method should always be checked by determining the recovery of added riboflavin, since some flavin may be lost on the methyl alcohol precipitate. The riboflavin-contents found by the method were in close agreement with those obtained by a microbiological method, although variations up to 10 per cent. were observed in duplicate estimations. The following are some of the more important results, the riboflavin contents being expressed in $\gamma$ per ml.: dried alfalfa meal 15, white fish meal 10, liver meal 80, dried skim-milk 20, dried whey 20, dried yeast 30 to 50, wheat, yellow corn and oats (various forms) 0·2 to 1. F. A. R.

**Vitamin E Chemistry: Oxidation Products of α-Tocopherol and of Related 6-Hydroxychromans. L. I. Smith, W. B. Irwin and H. E. Ungnade.** (*J. Amer. Chem. Soc.*, 1939, **61**, 2424–2429.)—When α-tocopherol, 2,2,5,7,8-pentamethyl-6-hydroxychroman and similar substances are oxidised with ferric chloride, gold chloride, or, in certain circumstances, silver nitrate, the products are yellow *p*-quinones. When the action of silver nitrate is prolonged beyond this stage brilliant red solutions are obtained (John, Dietzel and Emte, *Z. physiol. Chem.*, 1939, **257**, 173; Karrer, Fritzsche and Escher, *Helv. Chim. Acta*, 1939, **22**, 661). Red solutions result also when nitric acid is the oxidising agent as in the photometric analysis of tocopherols (Furter and Meyer, *Helv. Chim. Acta*, 1939, **22**, 240; Abst., ANALYST, 1939, **64**, 217). The red crystalline substance (m.p. 109 to 110° C.) present in these solutions has now been obtained from 2,2,5,7,8-pentamethyl-6-hydroxychroman with either silver nitrate or nitric acid as oxidising

agent, and it is shown by comparison of the molecular extinction curves that it is responsible for the colour in the Furter and Meyer reaction. John, *et al.* (*loc. cit.*) showed that the red compounds differ from the *p*-quinones by 1 carbon atom and 4 hydrogen atoms, and Karrer *et al.* (*loc. cit.*) found a similar change when the quinone from 2,5,7,8-tetramethyl-hydroxychroman was converted into the analogous red compound $C_{12}H_{14}O_3$ (m.p. 140° C.). These authors proposed a tentative structure for this compound, and by analogy the red compound derived from the pentamethyl-chroman would have a *p*-quinonoid structure. It may be deduced from work on the colour of napthaquinone derivatives (Hooker, *et al.*, *J. Amer. Chem. Soc.*, 1936, **58**, 1163, 1168, 1179, 1181, 1198, 1202) that it is an *o*-quinone, and this is now confirmed by comparison of its absorption spectra curves with those of substances with an *o*-quinonoid structure.

Cook, Macbeth and Winzor (*J. Chem. Soc.*, 1939, 878) have shown that a maximum in the absorption curve at 400 to 440$m\mu$ is characteristic of *o*-quinones and does not occur with *p*-quinones. The fact that the red oxidation products show a maximum absorption around 480$m\mu$ is considered good evidence of their *o*-quinonoid structure. This is confirmed by their chemical behaviour. The red substance (m.p. 109° to 110° C.) forms a phenazine (m.p. 151° to 152° C.) with *o*-phenylenediamine and a tetramethyl phenazine (m.p. 204° to 205° C.) with tetramethyl-*o*-phenylenediamine. These phenazines are yellow with a pale green fluorescence in alcoholic solution. $\alpha$, $\beta$, and $\gamma$ Tocopherols give deep red solutions when oxidised in alcoholic solution with nitric acid. It was not found possible to crystallise these oily compounds, but that from $\alpha$-tocopherol gave a phenazine showing the greenish fluorescence previously mentioned. Formation of the red *o*-quinones is not limited to 6-hydroxychromans. According to Furter (private communication) and Smith, Irwin and Ungnade (*loc. cit.*) the reaction occurs with 5-hydroxycoumarans. Apparently the presence of an alcohol (or possibly a phenol) is essential for the production of the red compound, and experiments showed that the intensity of colour developed in a given time decreased according as the alcohol was primary, secondary or tertiary. Red solutions are not formed in petroleum spirit, acetic acid or acetone, although a mixture of alcohol and acetone may be used with the tocopherols. There is definite evidence that the alcohol is oxidised during the reaction, and that the oxidation is not due to the nitric acid. A. O. J.

**Vitamin A Content of "Light White" Casein. M. K. Maitra and T. Moore.** (*Biochem. J.*, 1939, **33**, 1648–1651.)—"Light white" casein (sodium caseinate) was extracted with various solvents, and the extracts were examined colorimetrically for carotene and vitamin A. Hot alcohol extracted fat amounting to 2 per cent. of the casein; the extract was coloured yellow and gave a blue colour when treated with antimony trichloride solution. The amount of carotene and vitamin A calculated to be present, corresponded to a biological activity of 1 i.u. per g. of casein. This was consistent with the activity found by biological test. Ether and ethylene dichloride extracted only a portion of the fat and of the vitamin A-active material. F. A. R.

**Curative Factor (Vitamin H) for Egg White Injury with Particular Reference to its Presence in Different Foodstuffs and in Yeast. P. György.** (*J. Biol. Chem.*, 1939, **131**, 733–744.)—Rats, and some other animals, develop a skin disorder when fed on a diet containing a high proportion of egg white. The egg white is deprived of its toxic properties by continued heat treatment or by digestion with pepsin or hydrochloric acid. The toxic effect is also neutralised by an organic protective substance, present in different foodstuffs, to which Boas gave the name "protective factor X" and György the name "vitamin H". A large variety of foodstuffs have now been examined for this detoxifying factor, and its main sources are shown to be liver, kidney, yeast and, to a less extent, cows' milk. The factor is absent from concentrates of the pernicious anaemia factor from liver, but present in the residues. It is insoluble in water and in fat, but is liberated in a water-soluble form by autolysis of yeast in presence of toluene. Chloroform reversibly inhibited this apparent enzyme reaction. F. A. R.

**Attempts to Isolate the Factor (Vitamin H) Curative of Egg White Injury. P. György, R. Kuhn and E. Lederer.** (*J. Biol. Chem.*, 1939, **131**, 745–759.)—Although vitamin H is obtained in a water-soluble form by autolysis of yeast (*cf.* preceding abstract) it cannot be obtained by autolysis of liver, nor do the enzymes of yeast liberate the factor. This can be accomplished, however, by digesting the liver with pepsin or, better, with papain, or by heating with sulphuric or hydrochloric acid under pressure. The simplest method of obtaining good yields of vitamin H was by autoclaving liver powder with water for 1 to 2 hours at 200° C. Fresh liver and kidney did not give the vitamin unless acid was present. The factor was concentrated by a series of processes, including precipitation with acetone or alcohol, which removed large amounts of inert material, precipitation with lead acetate, which also removed impurities, adsorption on charcoal followed by elution with a mixture of pyridine, methyl alcohol and water, and treatment with phosphotungstic acid or gold chloride solution, which precipitated the vitamin along with other substances. The last two reagents did not precipitate the vitamin from solutions relatively free from impurities. Vitamin H was irreversibly inactivated by benzoylation, by treatment with formaldehyde, nitrous acid and ketene, and by oxidation with hydrogen peroxide. F. A. R.

**Physicochemical Properties of the Factor (Vitamin H) Curative of Egg White Injury. T. W. Birch and P. György.** (*J. Biol. Chem.*, 1939, **131**, 761–766.)—A solution of vitamin H was distributed equally in the ten compartments of an electrodialysis apparatus, and the *p*H and biological activity of the solutions at the end of electrodialysis, carried out over a period of 20 to 48 hours, were determined. The experiment indicated that the factor is an ampholyte with an isoelectric point between *p*H 3 and 3·5. No appreciable loss of potency occurred during the operation, but a five-fold concentration was obtained in the cells to which the active principle migrated. In spite of its acidic properties, vitamin H could not be precipitated by alkaloids. Further concentration was effected by precipitating the barium salt in alcohol at *p*H 5 or the calcium salt at *p*H 8. The most active fraction obtained was free from sulphur and phosphorus.

F. A. R.

**Photometric Determination of Oestrogens. I. Modified Kober Reaction for Determining the Total Oestrogens in a Mixture of Oestrogenic Steroids. C. Bachman.** (*J. Biol. Chem.*, 1939, **131**, 455–462.)—Kober (*Biochem. Z.*, 1931, **239**, 209) devised a two-stage reaction for the identification of natural oestrogens. This consisted first in heating the oestrogen at 100° C. with phenolsulphonic acid, whereby a yellowish-brown colour was produced. The solution was then cooled, diluted and reheated, whereupon a characteristic pink colour developed. Besides the disadvantage that such a two-stage reaction cannot readily be made quantitative, it was found that the speed of the reaction was different for different oestrogens. Both these defects have been overcome by diluting the phenolsulphonic acid reagent with water, and by carrying out the reaction at 150° C. instead of 100° C. The reagent is prepared by mixing pure conc. sulphuric acid (5·6 volumes) and pure dry melted phenol (3·6 volumes), and then diluting the phenolsulphonic acid so formed with half its volume of water. One to 3 ml. of a solution (in alcohol) of the oestrogen, containing 10 to 60$\gamma$, are introduced into a series of test-tubes (200 × 18 mm.), and the solvent is evaporated in a current of air with the tubes immersed in a boiling water-bath. The residues left after evaporation are dried *in vacuo* for 1 hour. Corresponding volumes of alcohol are similarly treated, to serve as blanks. Into each tube are put 3 ml. of the reagent, and the series (not more than 8 tubes) is immersed, one tube at a time at 15-second intervals, in a bath of chlorinated diphenyl maintained at 150° C. The contents of each tube are stirred for 10 seconds, and again 2 minutes later for 10 seconds, each of the tubes being thus treated in rotation. After 9·5 minutes, the first tube is transferred to an ice-bath, the other tubes following at 15-second intervals. The same stirring technique is followed as with the heated tubes. After 5 minutes in ice, the solutions are made up to 15 ml. with dilute sulphuric acid (3 volumes of conc. acid to 7 volumes of water), and the colour of each is measured in an Evelyn photoelectric photometer, using a filter giving maximum transmission at 520$m\mu$. It was found that, although the pink colours obtained with the three oestrogens—oestradiol, oestrone and oestriol—developed at different rates, the absorptions become equivalent for equal concentrations of all three after heating for 9·5 minutes, thus making it possible to estimate the total content of a mixture of the three substances. The technique of heating and cooling outlined above must be strictly adhered to, and under these conditions, the absorption at 520$m\mu$ for all concentrations between 10 and 60$\gamma$ is linear. Various combinations of oestradiol, oestrone and oestriol were tested, and in the data recorded the variation is not greater than ±1 per cent. The applicability of the reaction to urine extracts was also verified. F. A. R.

**II. New Colour Reaction for Oestriol. C. Bachman.** (*Ibid.*, 463–468.)—When oestrogens were heated with a mixture of phosphoric acid and sodium *p*-phenolsulphonate at temperatures exceeding 100° C., a violet-pink colour formed with oestriol, whereas little if any colour developed with other steroids. The reaction has been made the basis of a quantitative method of assaying oestriol in the presence of other oestrogens. Into each of the tubes containing 10 to 60$\gamma$ of the oestrogen to be tested, and into accompanying control tubes, are introduced

15 ml. of reagent made by dissolving 2 g. of sodium *p*-phenolsulphonate in 100 ml. of 85 per cent. phosphoric acid. The series of tubes is immersed for 9 minutes in a bath maintained at 150° C., and then for 5 minutes in an ice-bath. The details of this procedure are the same as those described in the preceding paper. The colours of the solutions are measured directly without dilution by means of an Evelyn photoelectric colorimeter, using a filter with maximum transmission at 540$m\mu$. α-Oestradiol and oestrone had extinction values of approximately one-third and one-sixth that of oestriol, respectively. Consequently in estimating oestriol in presence of one or other of the other oestrogens, a correction has to be applied by means of the following equation:

$$y = \frac{\epsilon \text{ (mixture)} - \epsilon \text{ (1}\gamma \text{ oestrone)} \times \text{C}}{\epsilon \text{ (1}\gamma \text{ oestriol)} - \epsilon \text{ (1}\gamma \text{ oestrone)}}$$

Where $y$ is the amount in $\gamma$ of oestriol in the mixture, C is the concentration in $\gamma$ of total oestrogen determined by the modified Kober reaction, $\epsilon$ (mixture) is the extinction value of the unknown solution measured at 540$m\mu$, using the phosphoric acid reaction and $\epsilon$ (1$\gamma$ oestrone) and $\epsilon$ (1$\gamma$ oestradiol) are the extinction values observed with 60$\gamma$ of the pure oestrogens divided by 60. β-Oestradiol gave a very weak pink tint with a strong greenish fluorescence; equilin, 17-dihydroequilin and both 17-dihydroequilenins gave weak brown or orange-brown tints; dehydro-androsterone and $\Delta^5$-pregnenol-3-one-20 gave a succession of colours culminating in a pale dirty brown. Androsterone, iso-androsterone, testosterone, aetiocholanol-3(α)-one-20, progesterone, pregnandiol, and sodium pregnandiol glycuronide yielded weak yellow or yellowish-brown solutions. Diethyl stilboestriol gave a weak brown colour. With oestriol results agreeing within 2 per cent. of the theoretical value were obtained, whilst oestriol was estimated with a similar degree of accuracy in mixtures of oestriol and oestrone in varying proportions.

F. A. R.

**Root-forming Substances used for Propagation Purposes. M. A. H. Tincker and C. H. Unwin.** (*J. Royal Hort. Soc.*, 1939, **64**, 554–566.)—A further series of results is reported on the effect of 9 root-forming substances on cuttings of various plants, some being species that cannot normally be propagated by means of cuttings. The most generally valuable substances are indolyl butyric acid, 1:2:3:4-tetrahydronaphthylidene acetic acid (m.p. 92° C.) and a mixture of the latter with 3:4-dihydro-1-naphthylacetic acid. The first of these gave the best results with many species, but an equal number of other species gave better results with the second. The indolyl butyric acid produced a more fibrous root system, whilst tetrahydronaphthylidene acetic acid caused thicker roots to be formed, and is probably the most powerful agent causing cell division and root formation. A second group of very useful compounds comprised α-naphthyl acetic acid, 3:4-dihydro-1-naphthylacetic acid and 1:2:3:4-tetrahydro-1-naphthylacetic acid, and a third group 1:2:3:4-tetrahydronaphthylidene acetic acid (m.p. 163° C.) and indolylacetic acid.

F. A. R.

# Bacteriological

**Effectiveness of Heat Penetration in the Canning of Meat in the Home by the Pressure Cooker. C. I. Nelson and D. Berrigan.** (*J. Agric. Res.*, 1939, **59**, 465–474.)—A 12-quart home-type of pressure cooker was used in canning solid meat packs of various types, and a group of organisms such as are likely to occur in canned meats was chosen to test the effectiveness of the sterilising process: *Clostridium botulinum*, *Escherichia coli*, a heat-resistant strain of *Streptococcus faecalis* isolated from a can of spoiled meat, and *Bacillus mesentericus*. The variables experimented with were type of pack; steam pressure (10 lbs. and 15 lbs.); can size; duration of process, and methods of cooling. In general, for solid meat packs temperatures reached under 10 lbs. steam pressure were found insufficient to destroy the bacteria tested, and 65 minutes at 15 lbs. pressure (121° C.) appeared to be the minimum time and temperature that could safely be used to allow for the elimination of food-poisoning organisms in the tests on No. 2 cans; 90 minutes for No. 2½ cans, and 110 minutes for No. 3 cans. Cooling was best effected by cold dipping after removal of the cans from the retort. It was found, however, that temperatures attained at 15 lbs. pressure were not uniformly effective in destroying thermoduric organisms, such as *Bacillus mesentericus* and *Streptococcus faecalis*. Heat penetration occurred most readily where least interference with convection currents was met with, *i.e.* in the following order: liquid, chunk meat, ground-meat patties, ground-meat solid pack, and solid chunk. The surprisingly low ratio of efficiency is due to the lag in the heat curves, the gradient of the non-effective part of the curve varying in the order of the packs given above.

D. G. H.

# Toxicological

**Toxicology of Sodium and Potassium Permanganates. P. Cheramy and A. Lemos.** (*J. Pharm. Chim.*, 1939, **30**, 249–252.)—It has been shown by Lemos (*J. Pharm. Chim.*, 1939, **30**, 206–212; Abst., ANALYST, 1940, **65**, 63) that subcutaneous injection of a considerable amount of potassium permanganate into a rabbit produces an abscess which causes the death of the animal. The permanganate could not be administered with the food. Three intra-stomachic injections of potassium permanganate were made at weekly intervals into a rabbit, the amounts administered being 20, 40 and 40 ml. of 5, 5 and 10 per cent. strength. Water only was administered for 36 hours before each dose. Death occurred after the third dose, the animal having been almost unable to absorb nourishment during the three weeks. The stomach, which still contained permanganate, showed important lesions, and was strongly coloured and almost perforated, the kidneys showed signs of haemorrhage and the liver was congested. The manganese-contents (in mg. per 100 g.) of various organs were:—for sodium (*A*) and potassium (*B*) permanganate respectively: surrenals, 9·5 and 36·6; muscles, 8·0 and 1·2; lung, 6·5 and 5·6; marrow, 5·0 and 25·0; spleen, 4·4 and 21·2; bile, 3·1 and 45·5; brain, 1·5 and 4·0; genital organs, 1·2 and 3·4; blood, 1·1 and —; heart, 1·0 and 3·2; kidneys, 0·70 and 2·3; liver, 0·07 and 6·2. During treatment urea in the blood rose from (*A*) 0·40 to 0·65 g. per 1000 (when the animal was killed), and (*B*) from 0·50

to 1·42 g. per 1000 (after the second dose), indicating a lesion of the kidneys. In a case of human poisoning from manganese, in which the manganese-content of the blood was 2·25 mg. per 100 g., the urea in the blood of an anuric invalid was 3·50 g. per 1000. The distribution of the manganese in the rabbit treated was similar to that observed in acute cases of human manganese poisoning. It has been suggested that the toxicity of large doses, especially of the potassium salt, is due to the caustic action of the product, which causes fatal lesions. E. B. D.

**Toxicity of Coal Tar Naphtha Distillates. H. Taylor.** (*Chem. and Ind.*, 1939, **58**, 1078–1080.)—Coal tar naphtha distillates as used for fumigation against bed bugs, are complex mixtures of variable composition with a boiling range of 160–190° C., which may account for the disagreement in results obtained in the present investigation from those of Cameron, Paterson, de Saram and Thomas (*J. Path. and Bacter.*, 1938, **46**, 1, 95). Their vapours were found to have considerable narcotic action on rats at concentrations over 0·1 per cent. by volume in air, and in one instance exposure to a 0·16 per cent. concentration caused death in all the animals used. The narcotic effects were very similar for all samples, although these differed greatly in chemical composition, but the effects on the internal organs were widely different. Of the four samples used, two were capable of producing degenerative changes in the liver, and there were also suggestions of kidney damage. The determinations of the concentrations of vapour were made by means of the interferometer, by which any change in concentration is readily detected. It is suggested that possible hazards should be kept in mind in using this method of fumigation. D. G. H.

# Water

**Volumetric Determination of Sulphate in Water. J. Courtois and P. Bonjean.** (*Ann. chim. anal.*, 1939, **21**, 229–235.)—The process studied involves the reaction of a soluble sulphate with barium chromate yielding barium sulphate and a soluble chromate which is determined iodimetrically. A method based on this principle and described in "*Einheitsverfahren der physikalischen und chemischen Wasseruntersuchung*" (Berlin, 1936) was tested and found to give low results, owing to adsorption of chromate on the barium sulphate. A modification of this method in which the adsorption effect is minimised is now proposed. A 100-ml. sample of water is heated to boiling and 20 ml. of a solution containing 5 g. of barium chromate and 12·5 g. of hydrogen chloride per litre are added slowly. The boiling is maintained for 5 minutes, after which the liquid is allowed to cool for 15 minutes in order to secure complete precipitation of barium sulphate. The liquid is again boiled, ammonia is added, drop by drop, until the colour changes from reddish to greenish; and the boiling is continued for 5 minutes. This precipitates the barium chromate, leaving soluble chromate in solution proportionate to the sulphate originally present. The liquid is cooled, diluted to 200 ml. and filtered. To a 100-ml. portion of the filtrate 5 ml. of 25 per cent. sulphuric acid (by volume) and 5 ml. of a freshly prepared 30 per cent. potassium iodide solution are added, and after a 10-minute interval the liberated iodine is titrated with $N/100$ thiosulphate solution, with starch as indicator. It is necessary to make a correction

for the solubility of barium chromate, amounting to 0·85 ml. of $N/100$ thiosulphate solution to be deducted from the titration value of 100 ml. of test solution. Test-results obtained with solutions containing 38 to 510 mg. of $SO_4$ per 100 ml. were all consistently about 3·5 per cent. low, suggesting that it would be desirable to augment results by this amount. S. G. C.

# Agricultural

**Determination of Hydrocyanic Acid by the Picric Acid Method and the KWSZ Photometer. J. T. Sullivan.** (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 781–784.)—The picric acid test for hydrocyanic acid (Guignard, *Compt. rend.*, 1906, **142**, 545) is commonly used for qualitative purposes and has recently been applied to the quantitative determination of hydrocyanic acid in plant products (Rogers and Frykholm, *J. Agr. Res.*, 1937, **55**, 533; Boyd *et al.*, *J. Amer. Soc. Agron.*, 1938, **30**, 569; Doak, *New Zealand J. Sci. Tech.*, 1938, **10**, 163). The procedure here described is an adaptation of Boyd's method to the determination of hydrocyanic acid in individual white clover plants. Owing to the limited amount of material available a determination of less than 0·05 mg. of hydrocyanic acid was often necessary. Such small quantities could be more accurately determined by the KWSZ photometer than by visual comparison with standards. Fresh white clover leaves (10 g.) were allowed to stand with 5 ml. of toluene for several days at room temperature in a rubber-stoppered 500-ml. short-necked Kjeldahl flask. The mixture was steam-distilled from the same flask into 5 ml. of 2 per cent. potassium hydroxide solution until 80 to 90 ml. of distillate had been collected. The distillate was diluted to 100 ml. with water, the supernatant toluene was removed, and 20 ml. or less were treated with alkaline picrate solution (25 g. of anhydrous sodium carbonate and 5 g. of dry picric acid in 1 litre) in a test-tube, and if less than 20 ml. of the original solution had been taken the volume was made up to 30 ml. with water. The test-tube, loosely plugged with cotton wool, was heated in boiling water for exactly 5 minutes. A control tube containing water and alkaline picrate solution was heated simultaneously in the same manner. The contents of the sample tube were placed in one cell of the photometer and the control liquid in the other. A solution of 10 g. of crystalline copper sulphate and 1 drop of conc. sulphuric acid in 1 litre of water was used as the light filter, and the transmission of the sample was compared with that of the control liquid. A transmission curve for the instrument was constructed by means of a standard solution of potassium cyanide containing 0·4 mg. of hydrocyanic acid per ml. From a ten-fold dilution of this solution a series of standards was made by diluting to 100 ml. portions ranging from 1·25 to 25·0 ml. These standard solutions (20 ml.) were used to construct the calibration curve of the instrument. It was found inadvisable to use solutions containing more than 0·2 mg. of hydrocyanic acid. The conditions under which hydrocyanic acid is liberated and distilled from its particular glycoside needs further study especially if this method is to be applied to plants other than white clover. In most instances the period of autolysis before distillation caused the liberation of more hydrocyanic acid than the amount liberated by immediate distillation. Omission of the preservative in the

autolysis, or freezing and thawing followed by distillation with or without a preservative, led to variable results. Immediate heating of the distillate with alkaline picrate solution is necessary, but the examination in the photometer may be delayed for a day or two. In order to compare results obtained by this process with those of the alkaline titration method (*J. Assoc. Off. Agr. Chem.*, 1936, **19**, 94) it was necessary to take larger samples and to use large dilutions for the picric acid test. Under these conditions the picric acid method gave results 8 per cent. higher on an average than those obtained by the alkaline titration method.

A. O. J.

**Determination of Boron in Soils and Plants by means of Quinalizarin. K. C. Berger and E. Truog.** (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 540–545.)—The colour reaction is most sensitive in a medium of 93 per cent. by weight of sulphuric acid (*cf.* Smith, ANALYST, 1935, **60**, 735). Colour standards are prepared by diluting measured volumes of dilute boric acid solution in boron-free test-tubes to 1 ml. with water, adding 9 ml. of 98·5 per cent. sulphuric acid, cooling, and adding 0·5 ml. of quinalizarin solution (0·01 g. in a mixture of 90 ml. of 98·5 per cent. sulphuric acid with 10 ml. of water); the colour develops fully in 15 minutes and remains permanent in stoppered tubes. The use of standards covering the range 0·001 to 0·01 mg. of boron is suggested. Available boron in soils is determined by extraction of a 20-g. sample with 40 ml. of water by boiling under a reflux condenser for 5 minutes. An aliquot portion of the clear extract is evaporated to dryness with 0·1 g. of potassium carbonate in a platinum dish; the residue is ignited, and, after cooling, triturated with 5 ml. of 0·4 *N* sulphuric acid. To a 1-ml. portion of the solution are added 9 ml. of 98·5 per cent. sulphuric acid, the mixture is cooled, 0·5 ml. of quinalizarine reagent is added, and the colorimetric comparison is made after 15 minutes. Total boron in soils may be determined by fusing a 0·5 g. sample with 3 g. of sodium carbonate in a platinum crucible. The melt is dissolved in water and acidified with sulphuric acid to a *p*H value of 5·5 to 6·0; 350 ml. of alcohol are added, and the liquid is diluted to 500 ml. and filtered. A 400-ml. portion of the filtrate is made alkaline with potassium carbonate and evaporated to dryness; the residue is ignited and triturated with 5 ml. of 0·4 *N* sulphuric acid, and the boron is determined as described above. For the determination of the total boron in plants, the plant tissue is ignited to a grey ash, which is extracted with dilute sulphuric acid, and the quinalizarin test is applied to the extract.

S. G. C.

# Organic

**Volumetric Determination of Organic Substances by Chromic Oxidation: Nitro-chromic Solutions. M. H. Cordebard.** (*J. Pharm. Chim.*, 1939, **30**, 263–272.)—The advantages and disadvantages of oxidation by mixtures of potassium dichromate and (*a*) conc. sulphuric acid, (*b*) dilute sulphuric acid (1:1), are discussed. With (*b*) oxidation of ethyl alcohol to acetic acid is not quantitative, as the acid is partly decomposed slowly into carbon dioxide and water. With a mixture of (*b*), potassium dichromate and silver nitrate, it has been shown that the presence of free nitric acid does not interfere with the dichromate titrations

(*cf.* Cordebard, *Bull. Soc. Chim.*, 1928, **43**, 97). The use of "nitro-chromic" solutions (*i.e.* of potassium dichromate in nitric acid) is therefore proposed. Officinal nitric acid dissolves approximately 150 g. of potassium dichromate per litre at room temperature; standard solutions can therefore be prepared without risk of crystallisation of chromic anhydride. Normal and decinormal solutions are remarkably stable (they can be evaporated in air to about a fourth of their initial volume without appreciable loss of strength) and the oxidising power of nitro-chromic solutions, though not equal to that attainable with (*a*), is superior to that of sulphuric-chromic solutions of the same temperature and acidity. Most substances completely oxidisable to carbon dioxide and water with (*b*) are similarly oxidisable with nitro-chromic solutions, *e.g.* methyl alcohol, formaldehyde, formic acid, glycerol in the cold; tartaric, oxalic and citric acids, sugars (in a few minutes on the boiling water-bath); most organic compounds containing oxygen (at 122° C., the b.p. of the mixture, after different periods). Acetic acid is not partly oxidised to carbon dioxide as it is with (*b*); hence alcohol can be determined by oxidation to acetic acid, with nitro-chromic solution and subsequent iodimetric determination of the excess of dichromate. Alcohol in aqueous solution is first diluted to (*a*) 1 per cent. at the maximum or (*b*) less than 0·2 per cent. Ten ml. of $N/10$ nitro-chromic solution are shaken in a stoppered flask with either 1 ml. of (*a*) for 2 minutes or 5 ml. of (*b*) for 5 minutes, 40 ml. of water are added, and the mixture is transferred to a vessel containing 100 ml. of 1 per cent. potassium iodide solution and titrated, after 1 minute, with $N/10$ sodium thiosulphate solution. The greatest care in diluting the alcoholic solution is essential. The following determinations of alcohol in the presence of non-oxidisable substances are described:—(*a*) *Anaesthetic chloroform* (containing little alcohol):—Ten ml. of $N/10$ nitro-chromic solution are shaken vigorously with 8 ml. of the chloroform for 5 minutes to form a temporary emulsion, 50 ml. of water and 100 ml. of 1 per cent. potassium iodide are added, and the mixture is titrated, after 2 minutes, with $N/10$ sodium thiosulphate solution until the aqueous layer is blue. (*b*) *Camphorated alcohol or camphorated brandy* (containing about 95 per cent. of alcohol):—Exact preliminary measurement is important; it is made by pipetting 10 ml. of the alcohol into a 1-litre graduated flask and adding water, drop by drop at first, and then more quickly, until the vessel is full. The liquid is filtered or decanted, and the alcohol is determined as before on 1 ml. When other oxidisable substances are present a preliminary separation of the alcohol must be made before oxidation. E. B. D.

***m*-Nitrobenzazide as a Reagent for the Identification of Phenols. P. P. T. Sah and T. F. Woo.** (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 1013–1017.)—In boiling ligroin solution *m*-nitrobenzazide decomposes into gaseous nitrogen and *m*-nitrophenyl isocyanate, the latter reacting with phenols to form crystalline *m*-nitrophenyl urethanes which can be used for the identification of the phenols. The following procedure is recommended:—A mixture of the azide (0·5 g.), or an equivalent quantity of the isocyanate (prepared by refluxing the benzazide in anhydrous toluene solution in absence of moisture, removing the solvent by vacuum distillation and crystallising the residue from ligroin), and a molecular

equivalent of the phenol is heated under reflux for 4 hours with 5 ml. of anhydrous ligroin and allowed to stand overnight. If necessary, the solution is then concentrated to a small volume, and the crystals of urethane are filtered off with the aid of suction and examined under the microscope. The yield is weighed and the m.p. is determined before the product is purified by recrystallisation from a suitable solvent. The author tabulates the m.p., crystalline form, solvent used for recrystallisation, formulae, and nitrogen-contents of the urethanes prepared from 33 phenols. E. M. P.

**3.5-Dinitro-4-methylbenzazide as a Reagent for the Identification of Amines. P. P. T. Sah.** (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 1008–1012.)—Refluxing amines with 3.5-dinitro-4-methylbenzazide in toluene solution leads to the formation of crystalline 3.5-dinitro-4-methylphenyl ureas which can be used for the identification of the amines. Of the amines examined, the primary amines gave the best results; the secondary amines yielded products which were relatively more soluble in benzene or toluene but which could be isolated by concentrating the solution or by using ligroin as the solvent. The amides also reacted, but the yields were much less. The procedure adopted was as follows:—A mixture of the azide (0·25 g.) and a molecular equivalent of the amine was dissolved in 5 to 10 ml. of anhydrous toluene, and the solution was heated under reflux on the sand-bath for 4 hours. After standing overnight in the cold the crystalline precipitate was filtered off and weighed. The melting-point was determined and the crystalline form examined under the microscope, after which the product was purified by recrystallisation from a suitable solvent (acetone, ethyl acetate, benzene, ligroin, 95 per cent. ethyl alcohol, methyl-ethyl ketone, or a mixed solvent). The author tabulates the m.p., the crystalline form, the solvent used for recrystallisation, the formula and the nitrogen-content of the 3.5-dinitro-4-methylphenyl ureas prepared from 50 amines. E. M. P.

**Phthalisation in the Presence of Pyridine. S. Sabetay.** (*Ann. Chim. anal.*, 1939, **21**, 289–290.)—The method previously described (*Ann. Chim. anal.*, 1937, **19**, 285; Abst., ANALYST, 1938, **63**, 61) for the determination of primary and certain secondary alcohols by phthalisation, *i.e.*, heating with phthalic anhydride in the presence of pyridine and subsequent conversion of the excess of phthalic anhydride into phthalic acid which is determined by titration, does not give concordant results unless there is rigorous adherence to the specified conditions. The instability of the acid phthalic esters renders this necessary, especially as both aqueous pyridine and phthalic acid exert a saponifying action on them. In an investigation of the phthalisation of benzyl alcohol, the effect of prolonging the duration of heating and of varying the amount of water added for hydration was studied. Both these variations were found to affect the process adversely, and it is recommended that the following procedure should be followed minutely. A quantity of the sample (*e.g.* essential oil) equivalent to 0·5 to 1·0 g. of alcohol is treated in an acetylation apparatus, fitted with accurately ground-in glass joints, with 10 ml. of the phthalic anhydride and pyridine mixture (*loc. cit.*). The amount of sample to be taken is such that it represents about four times the amount of phthalic anhydride theoretically necessary for the reaction. A control

experiment is made simultaneously. Both acetylation flasks are heated in boiling water, and at the end of one hour exactly 50 ml. of water are added to each. Within one minute the flasks are removed from the bath and cooled rapidly, and their contents are titrated with alcoholic $N/2$ potassium hydroxide solution in presence of phenolphthalein. The subsequent procedure is as previously described (*loc. cit.*).

A. O. J.

**Glasses: Organic and Inorganic. H. Moore.** (*Chem. and Ind.*, 1939, **58**, 1027–1037.)—At the International Congress on Glass in London, 1936, Eitel and Weyl proposed the following classification of glasses:—(1) Inorganic glasses: derived from silicates, borates, etc. (2) Organic glasses: yielded by undercooled organic substances and showing reversible softening behaviour. (3) Transparent, glass-clear synthetic products obtained not by the undercooling of fusions, but by the condensation or polymerisation of simple constituents. Organic substances with claims to be considered as potential glass substitutes may be grouped as follows:—Group A.—Cast phenol formaldehyde resin, moulded transparent phenol formaldehyde resin, moulded transparent urea-formaldehyde resin, moulded colourless alkyd resin. Group B.—Polystyrene, polymethylmethacrylate and other methacrylic esters, polymethylacrylate, polymethacrylic nitrile, polyvinylmethyl ketone, polyvinylphenyl ketone, polyisopropenyl methyl ketone, polyvinyl acetate, polyvinyl chloride, polyvinyl acetals and co-polymers of many of these substances. Group C.—Cross-linked polymers. Group D.—Regenerated cellulose, cellulose acetate, cellulose nitrate, cellulose acetobutyrate, ethyl and benzyl cellulose, chlorinated deproteinised rubber. The structure and properties of the different organic glasses are discussed, and a description is given of their physical properties as compared with those of inorganic glasses. The following table, largely compiled from published data, summarises some of the physical properties of transparent resins compared with those of glass:

| | Cellulose acetate | Cellulose nitrate | Polymethyl methacrylate | Polystyrene | Polyiso-propenyl methyl ketone |
|---|---|---|---|---|---|
| Sp.gr. | 1·27–1·37 | 1·35–1·60 | 1·18 | 1·05–1·07 | 1·11–1·15 |
| Spec. heat (cal. per °C. per g.) | 0·31–0·39 | 0·34–0·38 | 0·45 | 0·324 | — |
| Softening pt. (°C.) | 60–71 | 71–91 | 77–113 | 104–116 | 60–80 |
| Tensile strength (lb. per sq. in.) | 4000–9100 | 5000–10,000 | 4000–6000 | 5000–5500 | — |
| Volume resistivity (ohm per cm.) | $(4·2–6·2) \times 10^{12}$ | $(2–30) \times 10^{10}$ | $10^{15}$ | $10^{17}$–$10^{18}$ | — |
| Modulus of elasticity (lb. per sq. in. $\times 10^5$) | 2·0–3·5 | 2·0–4·0 | 6·0 | 4·0–6·0 | — |
| Refr. index, $n_D$ | 1·47–1·50 | 1·50 | 1·50–1·52 | 1·60–1·67 | 1·52 |
| Water absorption, per cent. | 2·6–3·1 (48 hours) | 1·0–3·0 (24 hours) | 0·5 (168 hours) | 0·05 (318 hours) | 0·3 (24 hours) |
| Brinell hardness | 8·6–12·2 | 8–11 | 18–20 | 20–30 | 20 |
| Power factor ($10^6$ cycles) | 0·035–0·06 | 0·07–0·10 | 0·02 | less than 0·0002 | — |
| Thermal conductivity ($10^{-4}$ cal. per sec. per sq. cm. per 1° C. per cm.) | 4·5–7·6 | 3·1–5·1 | 4·3–6·8 | 1·9 | — |
| Dielectric constant ($10^6$ cycles) | 4·0–5·0 | 6·15 | 2·8 | 2·6 | — |
| Thermal expansion ($10^{-5}$ per ° C.) | 14–16 | 12–16 | 7–9 | 6·5–7·5 | — |

| | Polyvinyl chloride acetate | Ethyl cellulose | Urea-formal-dehyde | Moulded transparent phenol formal-dehyde | Cast transparent phenol formal-dehyde |
|---|---|---|---|---|---|
| Sp.gr. | 1·34–1·36 | 1·14 | 1·48 | 1·28 | 1·27–1·32 |
| Spec. heat (cal. per °C. per g.) | 0·24 | 0·25–0·40 | — | — | 0·3–0·4 |
| Softening pt. (°C.) | 55–72 | 99–130 | none | none | none |
| Tensile strength (lb. per sq. in.) | 8000–10,000 | 7000–9000 | 4000–6000 | 6000–8500 | 5000–12,000 |
| Volume resistivity (ohm per cm.) | over $10^{14}$ | $10^{15}$ | $(2–2·8) \times 10^{13}$ | $7·5 \times 10^{8}$ | $10^{9}–10^{14}$ |
| Modulus of elasticity (lb. per sq. in. $\times 10^5$) | 3·5–4·1 | 2·0–4·0 | 16 | 7–10 | 5–15 |
| Refr. index, $n_D$ | 1·53 | 1·47 | 1·54–1·6 | — | 1·5–1·7 |
| Water absorption, per cent. | 0·05–0·15 (24 hours) | 1·25 (48 hours) | 1·0–2·0 (24 hours) | 0·1 (48 hours) | 0·01–0·5 (24 hours) |
| Brinell hardness | 15–25 | 10 | 48–54 | — | 30–45 |
| Power factor ($10^6$ cycles) | 0·018 | 0·007–0·03 | 0·01–0·03 | 0·019 | 0·01–0·045 |
| Thermal conductivity ($10^{-4}$ cal. per sec. per sq. cm. per 1° C. per cm.) | 4·0 | 5·6 | 7·1 | — | 3·5 |
| Dielectric constant ($10^6$ cycles) | 4·0 | 2·0–3·0 | 6·0 | 4·5 | 5–7 |
| Thermal expansion ($10^{-5}$ per °C.) | 6·9 | 10–14 | 1·5 | — | 2·8 |

| | Sheet window glass | Soft soda glass | Lead flint glass | Boro-silicate glass (Pyrex) | Fused silica (Vitreosil) |
|---|---|---|---|---|---|
| Sp.gr. | 2·50 | 2·45 | 4·0 | 2·25 | 2·21 |
| Spec. heat (cal. per °C. per g.) | — | — | 0·12 | 0·20 | 0·20 |
| Softening pt. (° C.) | 600 | 570 | 400 | 600 | 1300 |
| Tensile strength (lb. per sq. in.) | 7000 | — | 7000–17,000 | 7000–14,000 | 4000 |
| Volume resistivity (ohm per cm.) | $20 \times 10^{12}$ | $5 \times 10^{11}$ | — | $10^{14}$ | $5 \times 10^{18}$ |
| Modules of elasticity (lb. per sq. in. $\times 10^5$) | 110 | 82 | — | — | 101 |
| Refr. index, $n_D$ | 1·51 | 1·48 | 1·8 | 1·47 | 1·45 |
| Water absorption, per cent. | — | — | — | — | — |
| Brinell hardness | 380 | — | 160–350 | — | 405 |
| Power factor ($10^6$ cycles) | — | — | — | 0·0028 | less than 0·001 |
| Thermal conductivity ($10^{-4}$ cal. per sec. per sq. cm. per 1° C. per cm.) | — | — | — | — | 25 |
| Dielectric constant ($10^6$ cycles) | 6–7 | — | 7–10 | 4·48 | 3·7–3·8 |
| Thermal expansion ($10^{-5}$ per °C.) | 0·93 | 1·2 | 0·9 | 0·32 | 0·054 |

**Determination of Catechin and Catechin-Tans in Gambir. C. J. van Hulssen and D. R. Koolhaas.** (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 831–838.)—About 1 g. of gambir is dissolved in about 200 ml. of hot water and the insoluble residue is filtered off on a 1 G 4 Jena glass crucible, washed with water, dried at 104° C. and weighed as the "impurity"-content of the sample. The filtrate and wash water are combined and made up to 250 ml. Twenty-five ml. of the filtrate are treated with 25 ml. of Stiasny's formalin-hydrochloric acid reagent (100 ml of 35 per cent. hydrochloric acid, 50 ml. of water and 200 ml. of 30 per cent. formalin) and, after shaking, are allowed to stand for 24 hours at room temperature. The precipitate is separated on a 1 G 4 Jena crucible, washed with 100 ml. of

water, dried at 104° C. and weighed. It consists of a combination of the formalin compounds of catechin and of the tanning agents. A further 25 ml. of the filtrate is treated with 25 ml. of gelatin and sodium chloride solution (25 g. of gelatin dissolved in 875 ml. of water, then saturated with sodium chloride, and filtered), and afterwards with 50 ml. of acid sodium chloride solution (saturated sodium chloride solution containing 25 ml. of conc. sulphuric acid per litre), with shaking. After some time 1 g. of kaolin is added, and the mixture is well shaken and filtered. Twenty-five ml. of formalin and hydrochloric acid reagent are added to 50 ml. of the filtrate, and the weight of the precipitate, which is the formalin compound of catechin, is determined. The conversion factors for tanning agents and for catechin were found to be 0·96 and 0·94 respectively, and the results are calculated as follows:—

Weight of (catechin + tanning agent) formalin compound from 25 ml. of extract $= a$ g.
$\therefore$ weight in total extract $= 10a$ g.
Weight of catechin-formalin compound (after treatment with gelatin) in 50 ml. $= b$ g.
$\therefore$ weight in 250 ml. $= 2 \times 10 \times b$ $= 20b$ g.
$\therefore$ weight of tanning agent $= (10a - 20b) \times 0{\cdot}96$ g.
and weight of catechin $= 20b \times 0{\cdot}94$ g.

E. M. P.

**Analysis of Synthetic Resins containing Maleic Acid. E. Sadolin.** (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 608–610.)—The chemical analysis of maleic acid (anhydride) resins is new, and the method put forward is based on the typical solubility of maleic-abietic acid in faintly acid aqueous solution as contrasted with the constituents of rosin and phenol-formaldehyde resins. Phthalic acid from phthalic resins may be removed in advance. The resin (0·2 g.) is dissolved in 5 ml. of benzene and saponified with 2 ml. of *N* potassium hydroxide in 90 per cent. ethyl alcohol for one hour followed by heating for 30 minutes without a condenser in a steam-bath. To the residue are added 50 ml. of water, and the flask is again heated on the steam-bath for 30 minutes, after which water is added to bring the volume to 200 ml. With methyl red as indicator 6 to 7 ml. of 4 *N* acetic acid are added until the colour approaches red, but the precipitate must settle before the colour is observed. The *p*H is about 4·5. After filtering, washing twice and boiling for 10 minutes (to remove any hydrogen sulphide), precipitation is carried out with 5 ml. of a 1 in 10 lead acetate solution. The flocculated colloidal precipitate is cooled and collected on a Jena glass filtering crucible (10 G 4), the operation taking about 2 hours. The precipitate is dried for 45 minutes at 80° to 90° C. and weighed. The factor for the maleic acid and lead precipitate is approximately 0·30, it being assumed that 60 per cent. of the maleic acid used in the resin is found by this method. On heating the precipitate with dilute hydrochloric acid the maleic-abietic acid separates as a resinous lump, whilst phthalic and similar acids will dissolve. Great care is necessary with the various operations, *e.g.* a double sample of resin precipitated in half the solvent produces a precipitate of about one-third the volume of that described above, and the strength of the

potassium hydroxide solution, time of saponification and of evaporation, etc., profoundly affect results. With the procedure described neither colophony nor the phenol formaldehyde resins give lead precipitates, but phthalic acid resins form an easily distinguishable precipitate. The method gives a quantitative determination of maleic-abietic acid and duplicate tests agree to within 2 per cent. The quantity of the acid diminishes during the production of resin from approximately 100 per cent. to an average of 60 to 70 per cent. It is thus possible to control the process of resin production and to form an idea as to the quantity of maleic acid entering into an unknown resin, and so to aid in its identification. D. G. H.

# Inorganic

**Determination of Bismuth by Precipitation as Quinaldine Iodobismuthite. J. R. Hayes and G. C. Chandlee.** (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 531–532.)—To the solution of bismuth as sulphate in dilute sulphuric acid (acidity about 1 *N*; volume 200 ml.) are added 15 ml. of 10 per cent. sodium sulphite solution, and the bismuth is precipitated by the addition, drop by drop, with stirring, of 20 ml. of reagent solution (150 ml. of quinaldine, 50 ml. of conc. sulphuric acid and 75 g. of potassium iodide per litre). The precipitate of quinaldine iodobismuthite is allowed to settle out for about 15 minutes, filtered off on a sintered glass filter, and washed, first with 40 to 50 ml. of a solution of 35 ml. of quinaldine, 15 ml. of conc. sulphuric acid and 0·8 g. of potassium iodide per litre, then with 30 ml. of a 90:10 mixture of dibutyl ether and acetone (water, which decomposes the precipitate, should not be used for washing). The precipitate is decomposed by digestion in boiling 5 per cent. sodium hydroxide solution for 20 minutes. After cooling, the liquid is acidified and the iodide-content of the solution is determined volumetrically by iodate titration as in Lang's iodine-cyanide method; 1 ml. of 0·1 *N* (0·025 *M*) potassium iodate solution is equivalent to 0·002612 g. of bismuth. In test experiments good results were obtained with 0·03 g. of bismuth in presence of amounts of a similar order of the following metals: antimony, lead, cadmium, copper, iron, tin (stannous and stannic), arsenite, arsenate, nickel, chromium, cobalt, manganese, calcium, beryllium, uranyl, aluminium, titanium and barium. Slightly modified precipitation conditions were employed in presence of some ions, thus: antimony, addition of 4 g. of ammonium tartrate before precipitation of bismuth; lead, prior precipitation and filtration of lead sulphate; cadmium, addition of 5 ml. of pyridine to the test solution; phosphate, acidity adjusted to 4 *N* to prevent precipitation of bismuth phosphate. Low results were obtained when appreciable amounts of chloride were present. Silver and mercury interfered. As little as 0·0003 g. of bismuth was determined accurately with the use of 0·01 *N* potassium iodate solution for the titration by Andrews' iodine chloride method. S. G. C.

**Permanent Artificial Standards for the Nephelometric Determination of Arsenic with Bougault's Reagent. J. Thuret.** (*Ann. Falsif.*, 1939, **32**, 328–330.)—The dark coloured turbidity of elemental arsenic given by Bougault's reagent (hypophosphorous acid) slowly subsides in spite of the presence of stabilisers

such as gum arabic. A liquid is proposed which simulates the characteristics of the arsenic turbidity but remains permanent. It is prepared by heating together 150 ml. of water containing 2·5 g. of borax with 1 g. of powdered rosin (colophony) for 15 to 20 minutes, and allowing the emulsion to cool, with continuous shaking throughout. The standards are prepared by matching suitably diluted portions of the emulsion against freshly prepared suspensions of arsenic precipitated by hypophosphorous acid. The standards remained unchanged for 1 month.

S. G. C.

**Elimination of Iron by Cupferron Prior to Colorimetric Determination of Lead with Dithizone. L. Panouse-Digeaud and H. Cheftel.** (*Ann. Falsif.*, 1939, **32**, 296–301.)—Appreciable amounts of iron interfere with the dithizone colorimetric determination of lead, even in presence of potassium cyanide. The authors add to the test solution, rendered distinctly acid with hydrochloric acid, sufficient cupferron to precipitate the iron. The iron-cupferron precipitate is then removed by chloroform, the aqueous portion is evaporated to white fuming with sulphuric and nitric acids in order to destroy the excess of cupferron, and the lead in solution is then determined by the dithizone method in the usual manner.

S. G. C.

**Direct Determination of Alumina in Silicates. E. W. Koenig.** (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 532–534.)—Among silicates considered were felspar, lepidolite, china clay, beryl, cyanite, glass sand, spodumene and a burnt refractory. The aluminium is ultimately precipitated with hydroxyquinoline, residual iron being kept in solution as the ferrous complex with $\alpha\alpha'$-dipyridyl or *o*-phenanthroline. A sample-weight of the finely ground material sufficient to yield 10 to 30 mg. of alumina is fused with sodium hydroxide in a nickel vessel. The melt is extracted with water, the liquid is boiled, and nickel and ferric hydroxides are filtered off and discarded. To the filtrate containing the aluminium 15 ml. of 8-hydroxyquinoline solution (2·5 per cent., in dilute acetic acid) are added, and hydrochloric acid is introduced with stirring until the precipitate which first forms dissolves completely and the solution is distinctly acid. A greenish colour appearing during this process indicates the presence of ferric iron. Sufficient hydroxylamine hydrochloride to reduce the iron is added, and the solution is heated to 80° to 90° C. An excess of $\alpha\alpha'$-dipyridyl or of *o*-phenanthroline is added, and the aluminium is precipitated by the hydroxyquinoline present by the addition of ammonium acetate solution (3 per cent. concentration). The suspended hydroxyquinoline complex is caused to coagulate by stirring (not by boiling), and is filtered off and washed with cold water. The precipitate is dissolved in hot dilute hydrochloric acid and the aluminium is determined by bromate-bromide titration of the hydroxyquinoline in the usual way.

S. G. C.

**Stability of Calcium Hypochlorites. A. Guillaume and Y. Nicolas.** (*Ann. chim. anal.*, 1939, **21**, 261–266.)—Ordinary bleaching powder has been compared with French proprietary hypochlorite powders having a considerably higher content of available chlorine, such as Chlorfix, Jav, Perchlorfix and Perfix.

The keeping properties of ordinary bleaching powder were inferior, particularly when the substances were stored in wooden barrels exposed to damp and varying temperature. The stability of the proprietary materials was satisfactory when diluted with other substances; sand, talc and coke cinder were the best for this purpose. Ready-prepared mixtures of *e.g.* Perfix with sand can be kept in metal drums or stoneware vessels for several months without marked deterioration, a point of importance in connection with the use of hypochlorite for decontamination from war gases. S. G. C.

**Composition of Lithium and Potassium Salts Precipitated by Uranyl Acetate Reagents for Sodium. E. R. Caley and W. O. Baker.** (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 604–607.)—Certain uranyl acetate reagents for sodium also precipitate lithium from concentrated solutions, and the present investigation shows that the lithium precipitates are always triple acetates, analogous to the triple acetates precipitated from sodium solutions by the same reagents. The water-content of these salts when isolated is slightly variable; approximately 6 mols. of water of hydration are present when the salts are dried to constant weight at 100–105° C. The experimental cadmium, mercury and copper uranyl acetate reagents tried gave no precipitates with concentrated lithium solutions. From concentrated solutions potassium also may be precipitated by uranyl acetate reagents for sodium, always as $KUO_2(C_2H_3O_2)_3$. The copper uranyl acetate reagent used appears to be the most nearly specific qualitative reagent for sodium, since it is moderately sensitive to sodium, yet forms no precipitate with lithium solutions. D. G. H.

**Colorimetric Estimation of Silica and its Use in the Metallurgy of Aluminium. P. Urech.** (*Helv. Chim. Acta*, 1939, **22**, 1023–1036.)—The formation of a greenish-yellow colour by the interaction of silicates and ammonium molybdate has been applied to the determination of silicon in crude aluminium and recast metal, of silicon in refined aluminium, of silicic acid in clays, and of silica in fluorides. The following methods are recommended:

*Silicon in crude aluminium and recast metal.*—Sodium hydroxide (2·5 g.) or 15 per cent. sodium hydroxide solution (16·7 g.) is added to 20 ml. of water in a nickel dish of 10 cm. diameter (the sodium hydroxide solution must be stored in a pure nickel flask). One g. of metal filings is added, and the mixture is heated in the dish, which is covered with a pure nickel cover, until reaction begins. After the metal has dissolved the liquid is heated for a short time, cooled, and poured into a 300-ml. beaker containing 50 ml. of 6 *N* nitric acid. The solution is heated until clear, transferred to a 500-ml. graduated flask, diluted to about 450 ml. with hot water (the temperature of the solution should be 70–75° C.), treated with 10 ml. of 10 per cent. ammonium molybdate solution, cooled under running water, and made up to volume. The intensity of colour is measured in a Pulfrich photometer, a 50-mm. layer of solution and an S43 filter being used. The silicon-content of the aluminium is read from a standard curve prepared by applying the same technique to a solution of 0·01 g. of 99 per cent. silicon in 100 ml. of sodium hydroxide solution.

*Silicon in refined aluminium.*—The method of R. Gadeau (*Ann. Chim. anal.*, 1937, **3**, 64) is modified by using hydrochloric acid instead of nitric acid and omitting the heating to 70° C. Standard curves are prepared as follows:—A 15 per cent. solution of sodium hydroxide (33·3 g.) or solid sodium hydroxide (5 g.) and 20 ml. of water are heated to boiling in a nickel dish of 10 cm. diameter, cooled, and poured into a 300-ml. Jena glass flask containing about 80 ml. of water. The solution is treated with 27 ml. of 6 *N* hydrochloric acid, transferred to a 300-ml. graduated flask, cooled to room temperature, treated with 10 ml. of 10 per cent. ammonium molybdate solution, and made up to volume. The flask is shaken and left for 10 minutes, and the colour of the liquid is matched with that of a standard picric acid solution. The colour may also be measured in a Pulfrich photometer. The figure obtained is the zero point of the curve, corresponding with absence of silicon. Other values are obtained by the use of measured quantities of a standard sodium silicate solution, and a curve is drawn.

*Determination of silicic acid in clays.*—One g. of clay and 5 g. of a 3:1 mixture of anhydrous sodium carbonate and anhydrous borax are mixed with a platinum wire in a platinum crucible, which is covered and heated first over an ordinary burner and then over a blow-lamp until no more carbon dioxide is evolved. The crucible and the melt are heated with water in a nickel dish of about 500-ml. capacity until the melt is completely dissolved, the solution is cooled and filtered, and the filtrate and washings are made up to 500 ml. and returned to the nickel dish. For the colorimetric estimation, 50 ml. of the above solution are treated with 8·4 ml. of 2 *N* nitric acid in a 150-ml. beaker, diluted to about 100 ml., treated with 2 ml. of ammonium molybdate solution, and allowed to stand for 10 minutes. An equal volume of water is titrated in a beaker of the same dimensions with a standard picric acid solution until the colours of the two liquids are the same, and the silicon-content is then read from standard curves. Alternatively, the colour may be measured in a Pulfrich photometer. For the preparation of the standard curves 5 g. of the sodium carbonate and borax mixture is melted in a platinum crucible, which is then heated with water in a nickel dish. The solution is cooled, made up to 500 ml. in a volumetric flask, shaken, and returned to the dish. A solution of 37·2 g. of pure potassium alum per litre is also made up. Twenty-five ml. of the alum solution are added to 25 ml. of the carbonate-borax solution in a 150-ml. beaker, and the solution is treated first with 8·4 ml. of 2 *N* nitric acid and then with 2 ml. of 10 per cent. ammonium molybdate solution, diluted to 100 ml., shaken, and allowed to stand for 10 minutes. Titration of this solution gives the zero point of the curves, and the procedure is repeated with quantities of standard sodium silicate solution corresponding to 0·02, 0·035, 0·05, 0·065, 0·08, 0·10, and 0·11 per cent. of silica. It is important not to grind the sample in an agate mortar, to avoid prolonged contact of the alkaline solution with glass, to use fresh ammonium molybdate solutions (not more than one week old), to have absolutely clear solutions, and to use the correct quantity of nitric acid (50 ml. of the solution containing no silicon is titrated with 2 *N* nitric acid in the presence of methyl red; the volume of acid used plus 4 ml. is the correct volume for 100 ml.). The method has also been adapted to the determination of silica in fluorides. E. M. P.

**Analysis of Chrome Green and Similarly-prepared Pigments. J. H. Van Der Meulen.** (*Chem. Weekblad*, 1939, **36**, 855–859.)—Commercial chrome green is a mixture of chrome yellow and Prussian blue. It sometimes contains lead sulphate also, and in the procedure now described (which is a modification of that suggested by Kappelmeier, *Rec. Trav. Chim. Pays-Bas*, 1931, **50**, 711) the presence of this salt is assumed; it is also assumed, for the purposes of calculation, that Prussian blue has the composition $Fe_4(FeCy_6)_3$. Eight g. of an intimate mixture of 2·5 g. of the sample and 7·5 g. of pure anhydrous sodium carbonate are treated with 50 ml. of hot water, and the suspension is boiled until a yellow-brown precipitate in a yellow solution is produced. In this way the lead chromate gives lead carbonate and sodium chromate; the lead sulphate gives lead carbonate and sodium sulphate; and the Prussian blue gives sodium ferrocyanide and ferric hydroxide, carbon dioxide being evolved. The mixture is diluted to 100 ml. with hot water and stirred for 15 minutes, and then placed on the water-bath for 10 minutes. Any organic matter is removed by the addition of 10 ml. of a 0·1 *N* solution of potassium permanganate, followed by 15 ml. of 0·1 *N* hydrogen peroxide, which reduces any ferricyanide to ferrocyanide (if the peroxide contains sulphate, 250 mg. of sodium perborate may be used). When the precipitate has settled the solution is filtered, and the residue is washed with hot water. To the combined filtrates are added 5 g. of sodium carbonate and the volume is made up to 500 ml. To 100 ml. of this are added 10 ml. of *N* potassium iodide solution, 25 ml. of 5 *N* hydrochloric acid, and after 1 minute, 5 ml. of a 0·5 *M* solution of zinc sulphate and 100 ml. of water. The iodine liberated is titrated with 0·1 *N* sodium thiosulphate solution with starch as indicator (1 ml. = 10·7743 mg. of lead chromate). The Prussian blue is determined in terms of the sodium ferrocyanide present in the filtrate, the principle of the method being as follows:—In presence of acid part of the chromic acid produced in the filtrate oxidises the ferrocyanide to ferricyanide. If, however, a known quantity (and an excess) of ferrocyanide is added, the chromic acid is reduced quantitatively and the excess of ferrocyanide may be back-titrated with a permanganate solution. Consequently to 100 ml. of the filtrate are added 100 ml. of water, 10 ml. of 10 *N* sulphuric acid, and 25 ml. of a 0·1 *N* solution of potassium ferrocyanide, and the mixture is then titrated with a 0·1 *N* solution of potassium permanganate with erioglaucin-A as indicator. Then the difference between the total volume of oxidising agents present (*i.e.* chromate plus permagnanate) and the volume of ferrocyanide added (in ml. of 0·1 *N* solutions) gives the volume of 0·1 *N* ferrocyanide formed from the Prussian blue. Alternatively, 100 ml. of the filtrate are acidified with 10 ml. of 10 *N* sulphuric acid, and a slight excess of 0·1 *N* hydrogen peroxide is added and subsequently removed by means of a 0·1 *N* potassium permanganate solution (with 3 drops of a 0·1 per cent. solution of erioglaucin-A as indicator). The iodine liberated on the addition of 5 to 10 ml. of *N* potassium iodide solution and 5 ml. of a 0·5 *M* solution of zinc sulphate is then titrated with 0·1 *N* sodium thiosulphate solution in the usual way. The lead sulphate is determined by acidifying 100 ml. of the original filtrate with 20 ml. of 5 *N* hydrochloric acid, and adding 5 ml. of *N* (sulphate-free) hydrogen peroxide or 400 mg. of sodium perborate, and 3 ml. of *N* sodium nitrite solution. The sulphate may then be

precipitated from the boiling solution by means of 50 ml. of a 0·05 *M* solution of barium chloride, and determined in the usual way. The total lead-content is determined gravimetrically as lead chromate, 2 g. of the dry mixture of pigment and sodium carbonate being boiled with 25 ml. of water until particles of lead chromate are no longer visible; 10 ml. of 5 *N* potassium hydroxide solution are then added, and boiling is continued until the brown ferric hydroxide is produced, after which 50 ml. of hot water are added. The mixture is warmed and filtered, and the residue is well washed with hot water; it may be retained for a determination of the iron in the usual way. The filtrate is added, with stirring, to a hot mixture of 100 ml. of *N* acetic acid, 10 ml. of *N* potassium dichromate solution and 50 ml. of water, care being taken to avoid loss due to the carbon dioxide evolved. The solution is boiled until the yellow precipitate becomes orange and is then allowed to stand for 2 hours, after which it is filtered, and the residue is washed well with 0·1 *N* acetic acid and then with water and dried at 100° C. until constant in weight. J. G.

# Microchemical

**Micro-electrolytic Determinations in Small Volumes. J. Donau.** (*Mikrochem.*, 1939, **27**, 14–20.)—Two procedures are described, one for very small volumes down to a single drop, the other for larger volumes of the order of a few ml. In the first method the electrolysis is carried out directly in the shallow cup-shaped cathode, made out of platinum foil (0·1 mm. thick), with a handle of 0·5 mm. platinum wire. The dimensions of the electrode are determined by the volume of liquid to be electrolysed. The anode consists of platinum wire coiled horizontally at the tip, the coiled portion being immersed in the liquid. The anode and cathode terminals are fixed to the arms of a U-shaped vulcanite holder. The liquid to be analysed is either measured or weighed into the cathode. In the latter instance the cathode must be covered with a well-fitting lid during weighing. Electrolysis is carried out by passing a current of 2-3 milliamps; at this low current the loss by bubbling is negligible. If necessary, heat may be applied, but drops of water must be added to replace any loss by evaporation. Electrolysis is usually complete in 10 to 20 minutes. The vulcanite holder is rotated through 45° and washing is carried out without interruption of the current. When the ammeter shows no more current passing, washing is complete. The cathode may then be removed, dried on filter-paper and finally on an aluminium block heated to 110° C. After cooling, the cathode is weighed in the usual manner. Both a Kuhlmann balance and the author's modification of the Nernst torsion balance were used (Donau, *Mikrochem.*, **1933**, **13**, 155; Abst., ANALYST, 1934, **59**, 136). If necessary the metal may be dissolved and the electrolysis repeated. When working with larger volumes an apparatus similar to that used by Pregl is preferable. The container is, however, provided with a tap, thus allowing the electrodes to be rinsed without interrupting the passage of the current. Excellent analytical results were obtained by both methods. J. W. M.

**1.2-Diaminoanthraquinone-3-sulphonic Acid as a Reagent for Copper. H. E. Ballaban.** (*Mikrochem.*, 1939, **27**, 57–63.)—The reagent is extremely selective for copper in alkaline solution. When the test is made on the spot-plate,

a drop of the neutral or acid test solution is mixed with a drop of the reagent solution (0·05 g. of 1.2-diaminoanthraquinone-3-sulphonic acid in 100 ml. of water; the solution is stable). When the liquid is made alkaline with sodium hydroxide the colour changes from red-violet to cornflower blue. For very small amounts a blank test is advisable. *Limit of identification*: 0·02$\gamma$ of Cu; *concentration limit*: 1 : 2,500,000. The test may also be carried out on impregnated paper. In presence of cobalt and nickel, which interfere, the copper salt is first converted into the insoluble thiocyanate on filter-paper. The cobalt and nickel salts are then washed out of the paper, and when the paper is dry the test may be carried out successfully. The method has been applied to the detection of copper in minerals and alloys, and a number of examples are given. Ammonium salts interfere and should be removed prior to the test. J. W. M.

**Detection of Ammonia, Calcium and Strontium with Organic Nitro Compounds. R. Fischer.** (*Mikrochem.*, 1939, **27**, 67–75.)—Organic nitro-compounds may be employed as reagents for ammonia; picric and styphnic acids are especially suitable, the acids being soluble in chloroform, whilst the ammonium salts are insoluble, and may therefore be readily separated from the reagent. Ammonium picrate and ammonium styphnate are identified by means of micro sublimation and micro-determination of melting-points; the former compound sublimes readily at 170–188° C., the latter at 170–190° C. *in vacuo*; the melting-point of the sublimate is determined; 0·1$\gamma$ of ammonia may be detected. Picrolinic acid forms very characteristic calcium and strontium salts. The crystals obtained after cautious evaporation on a microscope slide are washed with chloroform and water. The calcium salt melts at 250–270° C., but not sharply; the strontium salt does not melt up to 350° C. As little as 0·2$\gamma$ of calcium or strontium may be detected by this method; four photomicrographs are given. J. W. M.

**Micro-determination of Ethyl Alcohol in Pharmaceutical Products: Determination of the Chromic Index. A. Ionesco-Matiu, C. Popesco and O. Constantinesco.** (*J. Pharm. Chim.*, 1939, **30**, 252–263.)—The authors have made a micro-determination of alcohol in pharmaceutical preparations by a modification of the Nicloux method (*cf. Bull. Soc. Chim. biol.*, 1931, **13**, 859). The method is very satisfactory for preparations containing 0·1 to 0·3 per cent. of alcohol; preparations rich in alcohol are diluted, 1000-fold if necessary, before analysis. One ml. of the dilute solution and 1·5 ml. of conc. sulphuric acid are shaken well in a test-tube and titrated on the boiling water-bath with standard potassium dichromate solution at the rate of 1 drop per minute, a micro-burette being used. One drop of methylene blue leuco-base solution, used as external indicator, gives a sharp end-point with a small drop of the solution titrated. The indicator is prepared as follows:—To 1 ml. of a solution of methylene blue (0·05 g. in 25 ml. of glycerin and 75 ml. of water), 3 drops of 10 per cent. sodium thiosulphate solution and 10 drops of 1 per cent. sulphuric acid are added, and the mixture is shaken well and allowed to stand until completely decolorised (about 1 hour). In the dark it can be kept for a few days. One ml. of the standard dichromate solution is equivalent to 1 mg. of alcohol.

Chromic indices of oxidation have been found for (*a*) the original preparation, (*b*) the distillate from it, (*c*) the distillate from acid and alkaline solutions successively. They are known respectively as the total, partial and alcoholic chromic indices of oxidation. The total index is the number of ml. of the standard potassium dichromate solution consumed by 1 mg. of the preparation itself; it is a measure of all the substances oxidisable with chromic acid. The partial index is a measure of the alcohol and volatile material, and the alcoholic index (unless the preparation contains a substance which is retained neither by acid nor alkali on distillation) is a measure of the alcohol only. As each index is a constant for any standard pharmaceutical product, determination of the three constants serves as a test of the quality of a sample. A table of these constants for twenty-eight medicaments is given; determinations of alcohol by the Westphal–Mohr balance, pycnometer, and original Nicloux method are also included. For the analysis, approximately 1 ml. of the product itself is sufficient. E. B. D.

# Physical Methods, Apparatus, etc.

**Separation of the Components of a Mixture by Fractional Centrifuging. A. Gourevitch.** (*Ann. Chim. anal.*, 1939, **21**, 291.)—Separation of a chemical substance from a mixture is often difficult when its chemical properties are imperfectly known. Preliminary experiments were made to determine if separation can be effected by means of a determinable physical property of the body. If, for example, a mixture of salts in solution is evaporated to dryness, the residue, as a rule, will be a mass, more or less homogeneous in appearance, but consisting of crystals, sometimes of microscopic dimensions. If it were found possible to separate the various kinds of crystals occurring in the residue by means of a characteristic physical property (*e.g.* density), a separation of the components of the mass into pure chemical substances would be possible. To investigate the practical application of this principle, it was applied to the residue obtained by the evaporation of an aqueous solution of potassium chloride and potassium dichromate. The residue was placed in a flask with about nine times its weight of thymol and some glass beads, and the flask was shaken in a rotary agitator for three or four days. Microscopical examination of the yellow, compact mass showed it to consist of the débris of the crystals of the two salts suspended in the thymol. If the pieces are sufficiently small, each will consist of one salt or the other. A portion of the ground mass was mixed with a relatively large amount of a mixture of bromoform and nonane, which dissolves the thymol but not the salts. The calculated proportions of bromoform and nonane were such that the density of the liquid after solution of the thymol was 2·20 to 2·40, *i.e.* between that of potassium chloride (1·99) and that of potassium dichromate (2·69). The mixture was then centrifuged at low speed. It was found that the potassium chloride floated on the surface of the liquid and the potassium dichromate formed a sediment at the bottom. A satisfactory separation of the two salts was thus effected, and the practical application of the principle appears to be realisable. A. O. J.

**Immersion Liquids for Determination of Refractive Index of Non-opaque Minerals. E. P. Kaiser and W. Parrish.** (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 560–562.)—The total range covered is $n_D$ 1·411 to 1·785, and the following mixtures are suggested for intermediate ranges:—(1) $n_D$ 1·411 to 1·465: *n*-decane and "medium government oil" mixtures, giving a straight-line curve of *n*/composition. A similar series in which kerosene fractions were used instead of "medium government oil" has been employed by Butler (*Amer. Mineral.*, **1933, 18**, 386). (2) $n_D$ 1·470 to 1·630: "medium government oil"—α-chloronaphthalene, straight-line mixing curves. (3) $n_D$ 1·635 to 1·735: α-chloronaphthalene and methylene iodide; mixing curve is not a straight line and should be determined by experiment (the curve is reproduced in the original paper). (4) $n_D$ 1·740 to 1·785: methylene iodide and solution of sulphur in methylene iodide; straight-line mixing curve. The values of $n_D$ are at 22° C. S. G. C.

# Reviews

CHEMICAL SPECTROSCOPY. By WALLACE R. BRODE. Pp. xi + 494. London: Chapman & Hall, Ltd. 1939. Price 36s.

The lack of available material in English has led to the publication of Professor Brode's book, which is apparently based upon the author's experience of courses in chemical spectroscopy at Ohio State University. It gives directions for setting up a laboratory for spectroscopic work and includes a chapter on laboratory experiments in applied spectroscopy. There can be little doubt that if this course of experiments is followed intelligently a considerable knowledge of the practice of spectroscopy for chemical purposes will be obtained. Chapter II gives a very short and condensed account of the theory and nomenclature of atomic and molecular spectra. Without considerable amplification of this chapter it seems unlikely that a beginner could understand and use the outline of the subject presented here. As, however, the reader has his attention called to such works as that of Candler on "Atomic Spectra," it is possible that the chapter may be considered enough for introductory purpose. The chapters dealing with apparatus and methods, and directions for calibration, identification of lines and choice of standard methods are full and adequate, as are those dealing with absorption spectra and the methods of determining them. Chapters VI and VII give an indication of the results of modern theory. For the chemist who desires to use spectroscopic methods in general work this theoretical discussion may be regarded as sufficient. The table of persistent lines, of principal lines in order of wave-length, and of the lines of the elements under different modes of excitation will be found most useful. A valuable set of charts shows the lines of the iron spectrum. A feature of these charts is the inclusion of the principal lines of other elements; this will save a large amount of work in identifying an unknown element. To use these charts to the best advantage it would appear desirable, in practice, to enlarge negatives containing the standard iron lines and the unknown spectrum to the size of the reproductions given in the charts.

The author has realised that the fields of interest of workers may be different, and he indicates at the outset those parts of the book which various workers may

find useful. In the reviewer's opinion, Chapters III to XI should be read by all chemists who are taking up the subject of spectroscopy. So far as can be seen there are few errors, although the "Paschen-Back" effect is here given as "Paschen Bach." The illustrations are in general well done, but some of the reproductions of line spectra are by no means clear, for example, Figure 4·2, 8·15 and 8·50. The index is good and there is an adequate bibliography, most of the chapters having a smaller bibliography on the relevant subject matter. There are "Inserts" containing coloured cellophane sheets for exercise, and two excellent film negatives of samples examined.

It will be remembered that this Society held a discussion on Spectrum Analysis in 1935, and from the wide interest shown on that occasion it was evident that some guide was needed for laboratory use on the method in general. The volume before us may be considered to fill this need for an authoritative statement by a well-known worker in spectroscopy, who knows the difficulties that have to be met and can from his own experience guide the reader. J. J. Fox

A Text-book of Quantitative Chemical Analysis. By A. C. Cumming and S. A. Kay. Pp. xv + 496. Seventh Edition. Revised by F. C. Guthrie and J. T. Nance. London: Gurney & Jackson. 1939. Price 15s.

The revision of the new edition of "Cumming and Kay" has consisted, for the most part, in bringing the work into line with modern practice by the introduction of new matter, for which space has been provided by deleting the section on organic analysis; the new edition contains fourteen pages more than the sixth. Methods for the determination of lithium, molybdenum, platinum, tungsten and vanadium have been added. Among the more recently introduced methods of procedure now included may be mentioned the use of diphenylamine as internal indicator in the dichromate titration of iron, of ceric sulphate as a volumetric standard solution, and of sodium rhodizonate as indicator in the volumetric determination of sulphate, the determination of fluoride with thorium nitrate, the determination of tungsten by precipitation with benzidine, the determination of titanium with tannin and phenazone and of hardness in water with potassium palmitate. The section on electrometric methods has been extended to include oxidation-reduction systems.

Two useful determinations that were mentioned as missing by the reviewer of the sixth edition (Analyst, 1935, **60**, 503) have now been included—the colorimetric determination of bismuth and the direct determination of sodium by means of zinc uranyl acetate. In the former method no provision has been made for the usual precaution against possible interference by free iodine.

The work of revision has been carried out with thoroughness, leaving but little room for criticism of the present text. There is an ambiguity on page 344, where the statement that "tungstic acid can also be precipitated from alkali tungstate solutions obtained after fusion with alkali hydroxide or carbonate" might be read as meaning that the precipitation is sufficiently complete to form the basis of a method for determination; no such method is, of course, described. The method given for the reduction of stannic chloride by means of metallic antimony, as a preliminary to titration by iodine, has been abandoned by most routine workers as unreliable, probably on account of after-reduction or to action of iodine on the

remaining antimony powder. Among metallic reducing agents for tin, the most favoured at the present time would appear to be aluminium, with nickel, iron and lead for special purposes. The description of the colorimetric determination of titanium contains no mention of suppression by means of phosphoric acid of the colour due to ferric chloride—a modification that sometimes has its uses. The bibliography in the appendix appears to have been overlooked in revision. Thus the authors appear to be unaware that THE ANALYST changed its publishers in 1922.

The book is intended for use at the bench, and therefore contains no general theoretical matter. It is written in an easy style and is practically free from typographical error. The pagination, type and binding constitute an excellent example of the art of book-making. F. L. OKELL

THE BRITISH ENCYCLOPAEDIA OF MEDICAL PRACTICE. Vol. 12. Butterworth & Co. (Publishers), Ltd. 1939. Price 35s.

(1) TOXICOLOGY. I. HOMICIDAL, SUICIDAL AND ACCIDENTAL POISONING, by G. ROCHE LYNCH and D. M. PRYCE. II. INDUSTRIAL POISONING, by DONALD HUNTER.

(2) URINE EXAMINATION, by J. DOUGLAS ROBERTSON.

(3) VITAMINS, by LESLIE J. HARRIS.

An encyclopaedia of medical practice is compiled, primarily, for the general practitioner and not for the expert in any particular branch. It should provide a ready means of finding such known information as may be necessary for the proper understanding and treatment of any medical problem arising in daily routine. The authors must find it difficult to decide how much to include or, possibly with some subjects, how much to omit. The three articles under review have been written by recognised experts and every confidence may be placed in their selections.

(1) These two monographs deal with two different and distinct branches of Toxicology. One is of rare immediate interest to most practitioners, but when a case arises it is usually a matter of life or death; the other is the concern of many.

Drs. Roche Lynch and Pryce begin with four pages of introduction, being general advice to the physician. The importance of samples, either for diagnoses during life or to establish the cause of death, is stressed, and general instructions are given for taking them. It was to be expected that the experience of the authors would place this matter first. Points to be borne in mind during diagnosis are next enumerated; the account is short so that it can be quickly read and to the point so that it can be easily remembered. The remaining 60 pages deal with about 40 substances or groups of substances classified as follows:—(1) Gases (carbon monoxide and a cross reference to war gases). (2) Corrosive acids and alkalis. (3) Synthetic organic substances (other than alkaloids). (4) Alkaloids. (5) Cantharides. (6) Inorganic and metallic poisons. (7) Fungi. (8) Abortifacients. (9) Powdered glass.

The general plan is to treat under each poison the physical properties, fatal dose, morbid anatomy, symptoms and treatment. All the commoner poisons which have caused death in recent years are included, except iodine, chloroform and cinchophen. The omission is probably intentional, since iodine and chloroform are readily recognised, and cinchophen, being now a Fourth Schedule poison, can

be obtained only on medical prescription. In addition these poisons are dealt with specifically in other monographs, such as those covering anaesthetics, toxic jaundice, etc.

The language is clear, and the general use of short, pithy sentences devoid of superfluities and jargon seems to accentuate the facts. Under carbon monoxide there is a liability to confusion in certain instances as to whether percentage refers to blood saturation or to the gas breathed. It would be interesting to know the indicator, a sort of universal "toxicator," suggested by the sentence, "If it is thought that the medicine is being tampered with, the prescription may be modified so that the addition of poison will be betrayed by a change of taste or of colour."

Dr. Hunter opens with notes on the prevention of disease in industry and on legal notification and compensation. This gives much valuable information, particularly useful for the practitioner who is confronted but rarely with industrial illnesses. Then follow particular sub-monographs on arsenic, mercury, silver, manganese, toxic gases, benzene and homologues, nitro and amino derivatives, chlorinated hydrocarbons, other organic compounds (carbon disulphide, acetone and dioxan), injuries from X-rays and injuries from radio-active substances.

It would appear that in each instance there is a good and concise account both as regards the clinical picture and preventive treatment.

Industrial poisoning may be regarded as an important but minor part of industrial diseases and the present article must be considered in conjunction with those on Occupational Diseases, certain Skin Diseases and Lead Poisoning appearing elsewhere in the encyclopaedia.

(2) Dr. Robertson's article gives details of the tests which may be applied in the routine examination of urine. These comprise colour (pigments and drugs), quantity, specific gravity, reaction, albumin and blood, casts, chemical constituents (oxalates, chlorides, sulphates, urea, uric acid, bile, ketone bodies, alcohol and sugar) and tests for renal function.

(3) Dr. Harris first sketches the general historical background relating to vitamins and classifies them broadly on their solubility. He then deals with the more important ones individually or as complexes, discussing history, chemical nature and properties, distribution in food, methods of assay, physiological action, incidence and clinical picture of deficiency diseases, diagnosis, prophylaxis and curative treatment, dosage, daily requirements and special needs. At the end are short notes on dietetics and applications. In the short space of 29 pages a comprehensive survey of vitamins has been attempted and has been achieved.

J. R. NICHOLLS

THE SOCIAL FUNCTION OF SCIENCE. By J. D. BERNAL, F.R.S. Pp. xvi + 482, with 3 charts. London: Routledge. 1939. Price 12s. 6d. net.

In this book Professor Bernal has set out the results of his attempts to discover to what extent science is practised in this country, to what extent that practice is organised and by whom, and to what extent the results of its practice, whether co-ordinated or not, find expression in the machinery of our social and daily life. This has involved him in a survey of a kind never before undertaken, to the best of my knowledge; at any rate, the results of such a survey have never before been published.

After some general observations (Part I: What Science Does) of an introductory and historical nature, the author proceeds to examine the existing organisation of scientific research in this country and then the part played by science in education. Next he discusses the efficiency of scientific research and the application of science, with a separate chapter on its application to war purposes. This part of the book concludes with a chapter on International Science.

The second part of the book (Part II: What Science Can Do) is of a more controversial nature. It ranges over the whole of the matters discussed in Part I and more beside. It discusses such details as revising the scientific curriculum in schools, colleges and universities; the function of scientific publications and the facilitating of travel for scientists; science in relation to the economic organisation of industry and finance; science in relation to individual human needs, such as food, clothing, housing and so on; science in relation to industries producing goods or services; and science and culture.

No review can do justice to the scope and detail of Professor Bernal's book and to the amount of investigation that its preparation must have involved. Indeed, it has involved more than that, for the information, collected from a widely scattered mass of heterogenous sources, has needed the integrative powers of a singularly acute mind—coloured maybe by certain clearly envisaged political principles or preconceptions!—to work the whole of the material into a picture that can be apprehended, if not comprehended.

Chemists will perhaps be a little surprised at Professor Bernal's remarks (page 43) about the National Chemical Laboratory to which he attributes the function of "assisting the Board of Trade in standardising products from the chemical point of view." From the fact that there is no mention anywhere in the book of the Government Laboratory, it seems that he has here, for once, made a slip over his facts and confused the Teddington institution, important but small, with its much larger and more utilitarian elder brother at Clement's Inn. Moreover, the large amount of research carried out at the older laboratory also must be included in any comprehensive survey of official, or officially organised, science in this country.

This curious confusion is the only error of fact that I have been able to discover; this does not mean that there are not others, and it is to be hoped that readers who discover them will inform Professor Bernal, who will be the first to recognise that the value of his work must be enhanced by every further step taken towards correct presentation of the facts.

When allowance is made for any small errors of fact or minor errors in logic, should there be any, the reader of this book will find himself faced then with some major problems, whose nature cannot possibly be affected by the accuracy or inaccuracy of a statistically insignificant number of minor facts. Is the picture that Professor Bernal draws of organisation, or its lack, in British science, a correct one? Are the alterations that he advocates desirable from the point of view of both science and society? Are the steps he proposes for such re-organisation themselves practicable within the present social structure? If not, are the kind of alterations to that structure envisaged, and sometimes depicted, by Professor Bernal possible and desirable methods of obtaining the object in view? Some of

those who are politically minded will agree with Professor Bernal in all his answers to these questions. Some will agree with some of his answers and not with others. Some may agree with none of his answers and on them will be the onus of supplying alternatives. But to those who hold the view, in the teeth of Professor Bernal's evidence, that the interests of science and scientists can be considered apart from politics in general, and from party politics in particular, there will still be open a course that should commend itself, and that is to use this book as a source of facts and information, marshalled with great industry and skill, and to take its author's opinions as red!

A. L. BACHARACH

THE MINERAL WATER TRADE YEAR BOOK. Published by the National Union of Mineral Water Manufacturers, Ltd., Great Charles Street, Birmingham. Pp. 194. 1939.

Early in the present century the mineral water industry received an unpleasant shock when it was found that a large proportion of the soda water sold in London was bacteriologically very impure. This discovery led to far-reaching hygienic changes in mineral water factories and had much to do with putting an end to the rule-of-thumb methods that had for so long been in use. To-day the industry, following the lead of the brewers and food manufacturers, has organised itself into an association which is concerned not solely with material benefits for its members, but also with supplying products of unquestionable purity to the public. For example, a scheme for taking steps towards formulating standards for mineral waters has recently been sanctioned by the National Union.

This is one of the questions discussed in the first edition of the *Trade Year Book*, which appears to have omitted nothing of essential importance to the industry and is thoroughly practical in its outlook. Factory law is dealt with in a useful section which summarises the changes brought about by the Factories Act, 1937. Then come sections on Workmen's Compensation, Electricity Regulations, Road Traffic, Shop Legislation, Table Water Duties, Trade Marks and the Merchandise Marks Act. On the more technical side there are sections on Bottle and Stopper Cleaning, Carbonation and Bottling, Recipes for the Syrup Room, Water Purification and the Use of Saccharin. Lastly, there are miscellaneous sections on such subjects as Cost of Living, National Insurance, First Aid Hints and so forth.

Among the special articles is one contributed by a Scottish lawyer, Mr. T. Young, on the liability of the manufacturer to the consumer. This is a legal discussion on the bearing of the case of *Donaghue* v. *Stevenson*, which arose out of a snail that had introduced itself into a bottle of ginger beer, and finally, after the case had reached the House of Lords, determined the question of the liability of a manufacturer to a member of the public with whom he had had no contact.

Another article of practical value is by an engineer, Mr. Scott Hall, who discusses the factors for the efficient management of motor transport. From this brief outline of its contents it will be seen that this Year Book will become a *vade mecum* for all mineral water manufacturerers, while the chemists whom they employ or consult will also be able to turn to it for help in some of their difficulties.

EDITOR