OCTOBER, 1947 VOL. 72, No. 859

# THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS
AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held on Wednesday, October 1st, 1947, at 6 p.m., in the Chemical Society's Rooms, Burlington House, W.1. The President, Mr. Lewis Eynon, was in the Chair. The following papers were presented and discussed—"The Determination of Small Amounts of Hexachlorocyclohexane (Benzene Hexachloride)," by Bernard H. Howard; "Iodimetric Methods of Estimating Peroxide Oxygen," by J. H. Skellon and E. D. Wills; "A Study of the Cobalt-Ferricyanide Reaction with relation to the Determination of Cobalt in Steel," by B. Bagshaw and J. D. Hobson.

NEW MEMBERS

Allan Adair, B.A., B.Sc., D.Phil. (Oxon.); Thomas Ralph Andrew, B.Sc., A.R.I.C.; Kenneth Vincent Bloomfield, B.Sc. (Lond.), F.R.I.C.; Frederick Percy Handisyde; Rupert Eardley Robinson, F.R.I.C., A.M.C.T.; Percy Smith, A.R.T.C.

DEATHS

We regret to have to record the deaths of

Frederick Alfred Mason.
Alfred Sherlock.
Herbert Procter Smith.

## Polarographic Determination of Lead in Foodstuffs

By F. R. JONES and (MISS) D. M. BRASHER

A polarographic method has been developed for the determination of lead in foodstuffs. It is simple and convenient and does not require preliminary separation of the lead; the conditions of electrolysis are made such that trace metals (Fe, Sn, Zn, As, Cu) do not interfere with the lead wave. The method could be used as an alternative to chemical analysis in routine work.

Few references in the literature relate to the polarographic estimation of lead in organic materials. Yosida[1] devised a method based on the preliminary separation of lead electrolytically as $PbO_2$; Teisinger[2] estimated lead in blood by adding hydrochloric acid and recording the current - voltage curve directly; Forche[3] improved the accuracy of this method by first decomposing the organic matter with sulphuric, nitric and perchloric acids, evaporating the resulting solution to dryness and submitting a solution of the residue in alkaline tartrate to polarographic analysis.

These methods suffer from disadvantages, the first because of the necessity for preliminary separation of lead, the second through interference of tin, and the third through interference of both tin and iron. A further difficulty is that a satisfactory lead wave is not normally obtained from the electrolysis, in the polarographic cell, of the sulphuric acid solution resulting from the wet destruction of foodstuff; this is because of interference by residual organic matter.

As an outcome of the work herein reported, the difficulties can be overcome as follows:—

(*a*) *Interference of residual organic matter*—Complete destruction of organic matter has been found essential to the production of a horizontal current - voltage curve in the absence of trace metals. This is accomplished by the use of perchloric acid.

(*b*) *Interference of ferric iron*—This produces a wave at a potential more positive than that of lead, and in samples containing a relatively large quantity of iron the pronounced

oscillations that follow the iron wave, and the accompanying maxima, make it difficult or impossible to measure the lead wave. Iron, therefore, is first reduced with hydroxylamine hydrochloride.[4] Investigation has shown that reduction is incomplete in solutions of acid normality greater than 2·5, but is effective, up to 2000 p.p.m. of iron in the sample taken, if the normality is suitably adjusted. The resulting ferrous ion is reduced at the dropping mercury electrode at about −1·2 volt, and therefore does not interfere with the lead wave, which occurs at −0·5 volt.

(*c*) *Interference of tin*—In the stannous state (after treatment with hydroxylamine hydrochloride) in sulphuric acid solution of concentration approaching 2·5 *N*, tin produces a wave at − 0·45 volt, that is, at a potential almost identical with that of lead. Investigation has shown, however, that, even with a concentration of 300 p.p.m. of tin in the sample taken, the tin wave can be eliminated without effect on the lead wave, by adjustment of the *p*H to a value between 2·5 and 3·0 by addition of sodium hydroxide. At values much above 3·0, for example at *p*H 5·5, the height of the lead wave is considerably reduced. The control of *p*H is very simply effected with the aid of two indicators which also act as maximum suppressors.

Other trace elements likely to be present in foodstuffs do not interfere with the lead wave. Zinc and arsenic are reduced at −0·7 and −1·1 volt respectively, and copper is reduced at zero potential in presence of hydroxylamine hydrochloride, which provides sufficient chloride ions to stabilise the potential of the anode (a pool of mercury in the reaction cell) at that of a calomel half-cell.

With these precautions, a satisfactory lead wave can be obtained from the sulphuric acid solution resulting from the wet destruction of the material, but the value of the diffusion current is affected by the viscosity of the electrolyte. It has been shown[5] that, in solutions of sulphuric acid and of sodium sulphate, the diffusion current of lead, and of other ions, is inversely proportional to the square root of the viscosity of the electrolyte. The electrolyte, prepared as indicated above, consists mainly of a solution of sodium sulphate, of which the concentration—and hence also the viscosity—may vary largely depending upon the quantity of sulphuric acid remaining after destruction of the sample and upon its subsequent dilution.

The diffusion current is very simply corrected for viscosity with the aid of the curve given in Fig. 2, and the corrected value is referred to a calibration curve, Fig. 3, to obtain the concentration of lead in the solution electrolysed.

The amount of lead that can be determined by this procedure is limited by its solubility in sulphuric acid, but with a 5-g. sample containing up to 40 p.p.m. no loss of lead has been experienced.

## METHOD

### APPARATUS—

The Heyrovský cell used for electrolysis is shown, in position under the dropping mercury electrode, in Fig. 1. The water-bath in which it stands is capable of being lowered from this position and the bung carrying the electrode is fitted with a short glass tube which, by dipping into the water when the bath is raised, isolates the contents of the cell from the atmosphere. A second glass inlet (2) is fitted through the bung.

In the analyses reported below, hydrogen, used for removing air from the cell and its contents, was generated electrolytically. Polarograms were recorded with a Heyrovský Micro-Polarograph (Nejedly, Prague) modified by incorporation of a circuit for compensation of residual current. The photographic paper used in the recording drum had a grid printed photographically upon it so that the current - voltage curve and the grid both appeared on development. Readings of current and potential were made directly.

### PROCEDURE—

(1) *Preparation of the solution for electrolysis*—Destroy 5 g. of the sample in a Kjeldahl flask in the usual way with sulphuric and nitric acids. Note the volume of sulphuric acid used; it should not exceed 2 ml.* When destruction is apparently complete, add about 50 ml. of water and boil until fumes are evolved. Add 3 drops of perchloric acid, heat and add more perchloric acid if a bright yellow colour is not developed in about 1 minute; add

* The concentration of lead in the solution electrolysed may be too small for the accurate measurement of the lead wave if more than 2 ml. of sulphuric acid are used with a sample of low lead content. Destruction of some foods can be accomplished with less than this quantity of acid if the sample is first allowed to stand overnight in contact with nitric acid.

about 50 ml. of water and boil until fumes are evolved. The residual acid should now be clear and colourless. Transfer to a measuring cylinder with the aid of two or three small quantities of water, each boiled in the flask, and bring the diluted acid to a volume, V ml., which must be near to, but not greater than, 15 times the volume of sulphuric acid used for the destruction of the sample. Determine its normality, S, by titration of a small portion with 0·5 *N* sodium hydroxide; it should be less than 2·5 (≡ 1·25 *M*).

Transfer 10 ml. of the acid solution to the polarographic cell, add about 0·1 g. of hydroxylamine hydrochloride, connect the side-tube (Fig. 1 (1) ) to the hydrogen supply, place the cell over a bunsen and boil the solution, very gently to minimise loss by evaporation. After 5 minutes, bubble hydrogen through the solution and place the cell in the water bath in the lowered position under the dropping mercury electrode. Add 3 drops each of bromophenol blue and thymol blue indicators, B.D.H., followed by 5 *N* sodium hydroxide from a 10-ml. graduated pipette until the colour of the solution is just violet; add 2·5 *N* sulphuric acid from a 1-ml. graduated pipette until the colour is just yellow. Note the combined volume

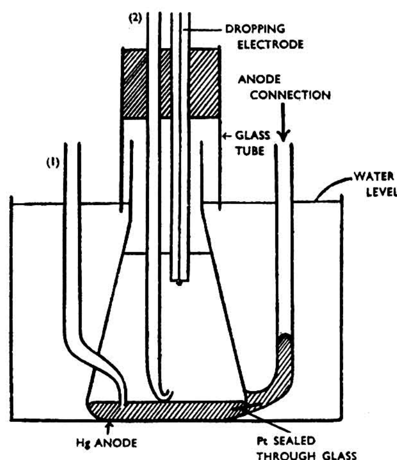
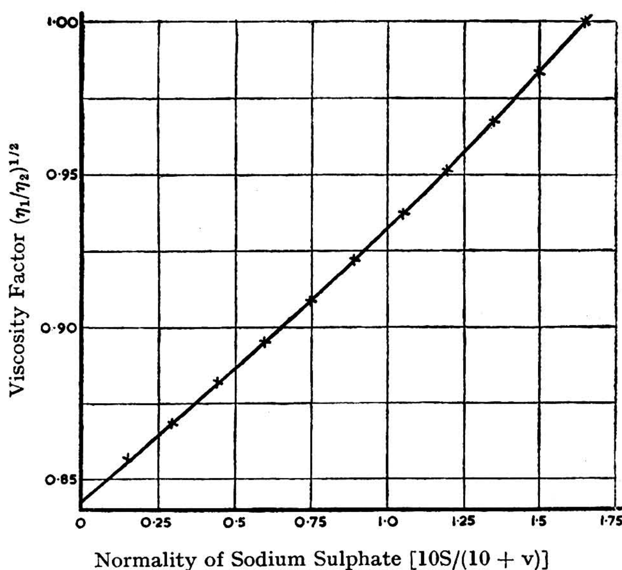



Fig. 1. Electrolytic Cell for Determination of Lead




Normality of Sodium Sulphate [10S/(10 + v)]

Fig. 2. Viscosity Factor.

of alkali and acid added (v ml.). The volume of indicators added can be neglected as it approximates to that of the water lost by evaporation. The volume of the solution electrolysed is thus (10 + v) ml.

Raise the water-bath and cell to the position shown in Fig. 1, transfer the hydrogen supply to tube (2) and introduce sufficient mercury through tube (1) to cover the tip of this tube and the platinum anode. Adjust the level of water in the bath so that the end of the glass tube is immersed. Continue the passage of hydrogen for a further 10 minutes, and meanwhile adjust the temperature of the bath. Record the polarogram under standardised conditions of rate of flow of mercury and rate of change of applied potential. It is only necessary to record between —0·2 and —0·7 volt.

(2) *Correction for viscosity*—The graph of the viscosity factor, Fig. 2, was constructed from experimentally determined viscosities (relative to water) of solutions of sodium sulphate; $\eta_2$ is the viscosity of the 1·67 *N* solution which results from the neutralisation to *p*H 3·0 of 2·5 *N* sulphuric acid with 5 *N* sodium hydroxide and which was used for the construction of the calibration curve, Fig. 3; $\eta_1$ is the viscosity of a solution of sodium sulphate of given normality. The values of $(\eta_1/\eta_2)^{\frac{1}{2}}$ lie on a smooth curve which is not quite linear.

To correct the diffusion current as obtained from the polarogram for the variation of the viscosity of the electrolyte from the standard value, $\eta_2$, calculate the normality of sodium sulphate in the solution electrolysed:

$$\text{Normality} = 10\,\text{S}/(10 + \text{v})$$

where S = normality of the dilute acid solution as found by titration, and v = volume of reagents added to 10 ml. of this acid solution, and refer the value found to Fig. 2. Multiply the diffusion current measured at the half-wave potential of lead, *viz.*, — 0·5 volt, by the value of $(\eta_1/\eta_2)^{\frac{1}{2}}$ corresponding to the normality of the sodium sulphate. In determining the diffusion current from the polarogram no correction for variation of drop time is necessary; the drop time is sufficiently constant under standardised conditions.

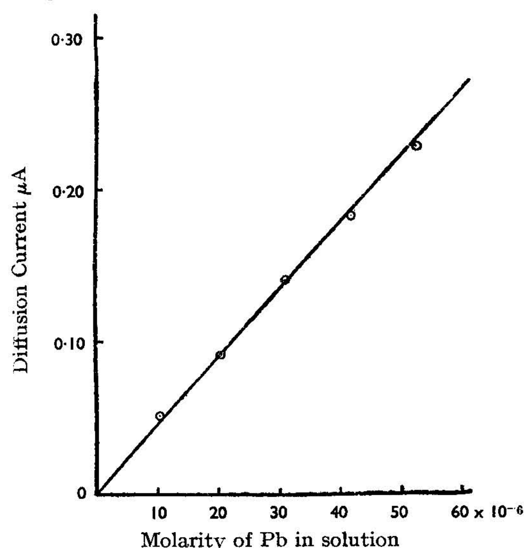



Fig. 3. Calibration Curve of Pb in $Na_2SO_4$ solution (16·7 *N*) at *p*H 3.

(3) *Calculation of lead content*—The calibration curve, Fig. 3, was constructed from polarograms of solutions of known lead content; for each determination 10 ml. of a solution of lead in 2·5 *N* sulphuric acid was treated with hydroxylamine hydrochloride and neutralised exactly as described above. The normality of the solution of sodium sulphate electrolysed was 1·67 (≡ molarity 0·835); its molar concentration of lead was calculated from the known amount of lead in the acid solution. The points on the curve in Fig. 3 should lie on a straight line passing through the origin.

To calculate the lead content of the sample analysed, refer the diffusion current, corrected for viscosity, to the calibration curve to obtain the molarity of lead in the solution electrolysed. If M be this molarity, the weight of lead in grams is:

0·207 M (10 + v) in the solution electrolysed,

and 0·0207 MV (10 + v) in the sample,

where V = the volume in ml. to which the sulphuric acid resulting from the destruction of the sample was diluted.

If 5 g. of material was destroyed the lead content is:

4140 MV (10 + v) p.p.m.

## Results

The accompanying table shows results obtained by this method on samples of canned meat and fish, the lead contents of which were first determined by chemical analysis with an accuracy of ±0·5 p.p.m. Known quantities of tin and lead were added and the table shows the quantity of tin added to, and the total lead present in the sample taken for analysis. The last column shows the molarity of lead in the solution electrolysed.

The standardised conditions of electrolysis were:

| | |
|---|---|
| Temperature of water in bath .. .. .. | 25° C. |
| Height of mercury column above tip of capillary .. | 60·0 cm. |
| Rate of flow of mercury .. .. .. .. | 1·56 mg. sec.$^{-1}$ |
| Sensitivity .. .. .. .. .. .. | 1/1 |
| Potential applied to drum .. .. .. .. | 2·0 volt |
| Rate of change of applied potential .. .. | 0·2 volt min.$^{-1}$ |
| Counter residual current .. .. .. .. | set as required |

The results, which show that the method is not affected by the presence of tin up to 115 p.p.m., are considered to be sufficiently accurate for all normal requirements. Kolthoff and Lingane[6] state that the accuracy of polarographic analysis under ordinary conditions is of the order of ±2 per cent. in the concentration range $10^{-2}$ to $10^{-4}$ molar (16,000 to 160 p.p.m. lead) and ±5 per cent. in the range $10^{-4}$ to $10^{-5}$ molar (160 to 16 p.p.m. lead).

The table shows that the molarities are in the range $10^{-5}$ to $10^{-6}$, these low values being due to the high atomic weight of lead; larger relative errors are to be expected with molarities

of the order of $10^{-6}$, for the wave heights are very small, *e.g.*, about 3 mm. in the first result quoted.

TABLE

| Tin added p.p.m. | Lead content (total) p.p.m. | Lead determined by polarograph p.p.m. | Error p.p.m. | Error per cent. | Molarity of lead in solution electrolysed |
|---|---|---|---|---|---|
| 0 | 5 | 5 | 0 | 0 | $4.0 \times 10^{-6}$ |
| 35 | 5 | 7 | +2·0 | +40·0 | $4.7 \times 10^{-6}$ |
| 35 | 8 | 10 | +2·0 | +25·0 | $6.2 \times 10^{-6}$ |
| 80 | 12 | 13 | +1·0 | +8·3 | $9.5 \times 10^{-6}$ |
| 35 | 18 | 18·5 | +0·5 | +2·8 | $1.1 \times 10^{-5}$ |
| 35 | 20 | 21·5 | +1·5 | +7·5 | $1.1 \times 10^{-5}$ |
| 0 | 23 | 23 | 0 | 0 | $1.5 \times 10^{-5}$ |
| 35 | 29 | 26·5 | −2·5 | −8·6 | $1.7 \times 10^{-5}$ |
| 35 | 32 | 32 | 0 | 0 | $1.8 \times 10^{-5}$ |
| 35 | 32 | 35 | +3·0 | +9·4 | $1.9 \times 10^{-5}$ |
| 80 | 32 | 27·5 | −4·5 | −14·1 | $1.7 \times 10^{-5}$ |
| 115 | 41 | 41·5 | +0·5 | +1·2 | $2.9 \times 10^{-5}$ |

The authors wish to thank Messrs. J. Lyons & Co., Ltd., in whose laboratories the work was conducted, for permission to publish this paper.

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*June*, 1947

# The Determination of Small Amounts of Hexachlorocyclohexane (Benzene Hexachloride)

BY BERNARD H. HOWARD

(*Read at the Meeting of the Society on Wednesday, October* 1*st*, 1947)

## INTRODUCTION

HEXACHLOROCYCLOHEXANE, benzene hexachloride, is a mixture of isomers of which the γ-isomer ("Gammexane") is strongly insecticidal. The normal commercial product contains about 13 per cent. of this isomer, to which almost the whole of the insecticidal activity is due. The toxicity towards mammals is also mainly associated with the gamma isomer.[1] Although biological, *i.e.*, insecticidal, methods of assay are known,[2] chemical methods were required. Such a method should, as far as possible,

(1) be readily applicable to grain and other foodstuffs and to dust and spray deposits on surfaces or fabrics,
(2) be applicable to the routine testing of numerous samples in a chemical laboratory of modest equipment,
(3) be sensitive to a few micrograms of benzene hexachloride,
(4) be specific for benzene hexachloride, especially to distinguish it from other insecticides such as DDT, and
(5) distinguish between the gamma and other isomers present.

The method here described complies with conditions (1), (2) and (3). Point (4), which requires a closer examination of the properties of the substances concerned, has not been fully covered at this stage and is undergoing further investigation. With regard to (5), there appears to be no chemical method available for distinguishing the isomers.

A knowledge of the proportion of gamma isomer in the original preparation is necessary to estimate the insecticidal activity of the amount of benzene hexachloride revealed by chemical methods.

### Preliminary experiments

A. A method involving the separation of trichlorobenzenes with alkali, followed by their intensive nitration, has been described.[2] The nitro-chloro compound decomposes, when boiled with alkali, to give a brightly yellow-coloured nitro-phenol. In the absence of a photo-electric absorptiometer, which was employed by the authors of the above-mentioned method, the possibility of using simple comparisons with Nessler glasses was tested. However, the colour did not appear strong enough to show less than about 0·1 mg. The method was not proceeded with as it was not considered to satisfy the above general conditions (2) and (3).

B. Although a method of determining total chlorine, such as that of Carius, might seem potentially more sensitive than the method removing only half the total chlorine, later to be described, this advantage was considered to be outweighed by the difficulties and hazards of the Carius technique. Furthermore, in presence of much foreign matter a large amount of nitric acid would be required: this is to be avoided because A.R. nitric acid contains up to 1 mg. of chloride per litre.

C. Rough experiments suggested that benzene hexachloride is inert to ammonia, silver nitrite and potassium cyanide, the chlorine atoms appearing not to undergo readily any replacement reactions.

D. Previous reports that benzene hexachloride reacts readily with alkalis to yield trichlorobenzenes and alkali chlorides were confirmed and, since this reaction readily lends itself to compliance with requirements (1) and (2) above, it was examined further.

Van den Linden[3] reported that with alcoholic potash the reaction

$$C_6H_6Cl_6 + 3OH' = C_6H_3Cl_3 + 3Cl' + 3H_2O$$

is quantitative. This was confirmed, but in practice alcoholic alkali was found to have two serious disadvantages—(*a*) Caustic potash, even of A.R. quality, contains up to 0·01 per cent. of chloride. Two ml. of 10 per cent. solution, the amount of alkali used in the preliminary experiments, would therefore contain chloride equivalent to approximately 50 $\mu$g. of benzene hexachloride. Even this high blank figure tended to increase when the solution was stored in the laboratory atmosphere. (*b*) In the determination of benzene hexachloride in foods, the final extract for reacting with alkali consisted of a solution of the insecticide in vegetable fat. Enough alkali had to be added to decompose all this fat: sometimes 5 ml. or even more of the 10 per cent. solution. In some instances the chloride in the reagents was much greater than that derived from the benzene hexachloride The use of alkali was therefore abandoned.

E. Organic bases, that might be freed from chloride by distillation, were next tried as dehydrochlorinating agents. Pyridine appeared to be without effect, but monoethanolamine was satisfactory. After distillation from alkali, the chloride content of this reagent was less than 5 $\mu$g. per ml., corresponding to about 15 $\mu$g. of benzene hexachloride per ml. It was also found that, under the conditions used, this reagent is without effect on fats. The presence of fats, therefore, does not necessitate the use of a large amount of reagent. Enough must be added, of course, to neautralise any free acid in the fat. To test the reaction, various amounts of benzene hexachloride were decomposed by various amounts of monoethanolamine in stoppered tubes immersed in a boiling water bath and the liberated chloride was titrated by Volhard's method.

To investigate the applicability of the method to all forms in which benzene hexachloride might be met in practice, decomposition tests were performed on (*a*) the substance alone, as would be found in dusts or smoke deposits, (*b*) solutions in mineral oils, as would be found in spray deposits, (*c*) solutions in vegetable oils, as would be obtained when foodstuffs are extracted to isolate the benzene hexachloride. Shell oil P.31, a non-volatile paraffin oil, was the mineral oil used. Three samples of arachis oil were available and it was assumed that the reaction in other vegetable oils would be similar. The benzene hexachloride used was recrytstallised material containing 95 per cent. of the gamma isomer. The mixture of isomers met in practice behaves very similarly with dehydrochlorinating reagents. The larger quantities were weighed direct into the reaction tubes; the smaller quantities were obtained by evaporating the appropriate volumes of a 0·100 per cent. solution of the substance in ether.

Each result shown in the table is the mean of at least three tests.

### Decomposition of benzene hexachloride by monoethanolamine

In tests 7 and 8 the monoethanolamine was added as a 1 per cent. aqueous solution; in tests 10, 11, 12, 20, 27 and 28 as a 10 per cent. solution in chloride-free glycerol. The

glycerol was used merely as a solvent, as experiments suggested that when several milligrams of solid benzene hexachloride were used the reaction with the small volume of monoethanolamine did not always proceed to completion, because of insufficient mixing. Of the vegetable oils, (1) and (3) had low acid values, about 0·3, whilst (2) had a very high acid value, about 40.

| Test No. | Benzene hexachloride taken mg. | Monoethanolamine used ml. | Added matter | Time in water bath min. | Decomposition per cent. |
|---|---|---|---|---|---|
| 1 | 100 | 2 | — | 15 | 98 |
| 2 | 100 | 2 | — | 30 | 98 |
| 3 | 100 | 2 | — | 60 | 102 |
| 4 | 100 | 2 | — | 180 | 103 |
| 5 | 100 | 0·1 | — | 60 | 80 |
| 6 | 1·0 | 0·1 | — | 60 | 99 |
| 7 | 5·0 | 0·1 in 10 ml. water | — | 60 | 74 |
| 8 | 5·0 | 0·05 in 5 ml. water + 3 ml. alcohol | — | 60 | 62 |
| 9 | 100 | 0·1 in 2 ml. alcohol | | 30 | 87 |
| 10 | 100 | 0·1 in 1 ml. glycerol + 2 ml. alcohol | | 60 | 90 |
| 11 | 5·0 | 0·1 in 1 ml. glycerol + 2 ml. alcohol | | 60 | 100 |
| 12 | 1·0 | 0·1 in 1 ml. glycerol | | 60 | 100 |
| 13 | 100 | 1 | P.31 oil 5 ml. | 30 | 87 |
| 14 | 100 | 1 | " 5 " | 60 | 101 |
| 15 | 100 | 0·5 | " 5 " | 60 | 92 |
| 16 | 100 | 0·1 | " 5 " | 60 | 43 |
| 17 | 5·0 | 0·1 | " 5 " | 30 | 74 |
| 18 | 5·0 | 0·1 | " 5 " | 60 | 94 |
| 19 | 5·0 | 0·1 | " 0·5 " | 60 | 104 |
| 20 | 1·0 | 0·1 in 1 ml. glycerol | " 0·5 " | 60 | 102 |
| 21 | 100 | 0·5 | Arachis oil (1) 5 ml. | 30 | 100 |
| 22 | 100 | 0·1 | " (2) 5 " | 60 | 20 |
| 23 | 5·0 | 0·1 | " (3) 2 " | 60 | 76 |
| 24 | 5·0 | 0·2 | " (3) 2 " | 60 | 104 |
| 25 | 1·0 | 0·1 | " (3) 0·5 " | 60 | 102 |
| 26 | 1·0 | 0·2 | " (3) 2 " | 60 | 101 |
| 27 | 1·0 | 0·1 in 1 ml. glycerol | " (3) 0·5 " | 60 | 41 |
| 28 | 1·0 | 0·2 in 2 ml. glycerol | " (3) 2 " | 30 | 17 |
| 29 | 300 mg. DDT. | 2 | — | 30 | 97 |

These results show—(i) That amounts of benzene hexachloride from 1 to 100 mg. can be determined accurately either alone or dissolved in mineral or vegetable oils, by decomposing with small amounts of monoethanolamine. In tests 5, 9 and 10, 80 to 90 per cent. decomposition was produced by 1·6 times the amounts of monoethanolamine required by calculation. Where small quantities are being determined, it is obviously advantageous to use very small amounts of the reagents. (ii) The presence of oils necessitates the use of more reagent (*cf.* tests 5, 16; 18, 23). (iii) The aqueous solution of monoethanolamine gives low results, and the glycerol solution does not seem to be necessary for complete reaction of the smaller amounts of benzene hexachloride (test 6). (iv) The low results obtained from arachis oil solutions with the glycerol solution of the reagent are surprising (tests 27, 28). The addition of glycerol renders the mixture of oil and monoethanolamine homogeneous, and a quicker reaction was expected on this account. (v) Under similar conditions the benzene hexachloride is more rapidly decomposed when dissolved in arachis oil than in mineral oil. (vi) The highly acid arachis oil No. 2 prevented the decomposition of the benzene hexachloride dissolved in it (test 22). That decomposition occurred at all is remarkable, as enough acid was present in the oil to neutralise all the monoethanolamine added. (vii) It is known that DDT is dehydrochlorinated by means of alkali under the same conditions as is benzene hexachloride. The test with DDT, No. 29, indicates that its behaviour with monoethanolamine also is similar to that of benzene hexachloride. The decomposition of DDT by organic bases has already been noted.[7]

For smaller amounts of benzene hexachloride, 20 to 200 $\mu$g., both alone and dissolved in the oils (except the very acid arachis oil), and with quantities of monoethanolamine similar to those shown in the above table, the decomposition was still sufficiently close to the theoretical for practical use. The chloride was determined turbidimetrically in these experiments.

F. In practice it is essential to be able to determine benzene hexachloride when inorganic chlorides may be present, *e.g.*, in foodstuffs. Extraction with ether gives a material free from inorganic chloride, as the following tests prove. (i) Two g. of sodium chloride and ammonium chloride were each shaken with 50 ml. of ether. After filtering and evaporating, no turbidity was detectable on addition of silver nitrate. (ii) 100-g. samples of several foodstuffs not contaminated with benzene hexachloride were treated with ether, and the extracts tested in the manner described below. In no case did the final solution show an appreciable turbidity with silver nitrate solution. The materials thus shown to give negligible blanks were maize, barley, wheat, ground nuts, flour, dried yeast, fish meals, meat and bone meal, bitter almonds, dried apricots and milk.

The method finally adopted is as follows.

## METHOD

REAGENTS—

(1) *Distilled water:* chloride-free. (2) *Ether.* (3) *Monoethanolamine:* re-distilled from caustic soda. (4) *Nitric acid:* 10 per cent. of A.R. concentrated acid in water. (5) *Sodium chloride solutions:* a 0·06 per cent. solution is diluted tenfold before use, to give a standard solution for turbidimetric determination of chloride; 1 ml. of the diluted solution contains as much chloride as is liberated from 0·1 mg. of benzene hexachloride by dehydrochlorination. (6) *Silver nitrate solution:* about 0·1 *N*, in a dropping bottle. (7) *Silver nitrate solution, standard:* 0·01 *N*. (8) *Ammonium thiocyanate*, and *ferric alum solutions*, for determination of chloride by Volhard's method; or solution of *dichlorofluorescein* for determination of chloride by Fajans' method.

PROCEDURE—

(i) For foodstuffs. Extract 50 to 100 g. of the sample with ether. The tenacity with which the benzene hexachloride is held varies with the conditions of application. From grain, for example, benzene hexachloride added as a dust may be removed almost completely by two simple washes with ether, but when it has been added as an oil spray more thorough extraction is necessary. For all foodstuffs, therefore, Soxhlet extraction, until all fat is removed, is recommended.

(ii) For deposits. Wash the object well with a jet of ether. If there is any doubt as to absorption of benzene hexachloride by the object, the Soxhlet method should be adopted if possible.

Filter the ethereal solution resulting from these procedures into a boiling tube fitted with a ground-glass stopper. Evaporate the ether in a stream of air while the tube is gently warmed. Add 0·1 ml. of monoethanolamine, or, if oil is present, 0·1 ml. for every ml. of oil. (This is because the figures given in the table demonstrate that about one-tenth as much reagent as oil will react satisfactorily.)

Stopper the tube and immerse in boiling water to a depth of about 2 in. for 1 hour, with frequent shaking. A wire basket to hold about ten tubes was found convenient for holding the tubes in a can of boiling water.

Remove from the water bath after an hour and add 5 ml. of the 10 per cent. nitric acid, or, if more than 0·5 ml. of monoethanolamine has been used, add 10 ml. of acid for every 1 ml. of reagent. Add next from 15 to 20 ml. of water and, when cool, 20 ml. of ether, and shake. After settling, blow off the ethereal layer through a Werner - Schmid tube. If the aqueous layer is still cloudy repeat the ether extraction.

The oils, trichlorobenzenes, etc. having been removed by this ether extraction, the aqueous solution is in a suitable state for estimation of chloride. With 0·01 *N* reagents it was found possible to determine down to 0·2 mg. of benzene hexachloride by Volhard's method. For smaller quantities, down to 20 $\mu$g., the chloride can be determined turbidimetrically. Any faint cloudiness in the solution can be removed by filtration. Bring the volume up to the 50-ml. mark of the Nessler glass. In other glasses prepare standards containing different amounts of the diluted salt solution, and the same volumes of monoethanolamine and nitric acid as were used on the sample under test, in a volume of 50 ml. Add three drops of the silver nitrate solution to the sample and standards, stir, and compare against a dark ground after about 2 minutes.

*Sensitivity*—In 50 ml. of solution in a Nessler glass the eye can detect a turbidity due to 5 $\mu$g. of chloride ion, equivalent to 14 $\mu$g. of benzene hexachloride. In field experiments involving dust and spray deposits the density of the deposit has been found by collecting

samples on 3 in. × 1 in. microscope slides, having an area of 19·4 sq. cm. By this method the minimum surface density detectable is 0·7 μg. per sq. cm. In tests on foodstuffs, where a sample of 100 g. might be used, this is equivalent to a concentration of 0·14 p.p.m. The method is sufficiently sensitive to measure very slight contamination of foodstuffs.

*Selectivity*—Many organic chlorine compounds lose chlorine in treatment with alkali, but none of these occurs naturally. Production of a positive result in the test described above, when applied to foodstuffs, is therefore evidence of contamination by organic chlorine compounds. The most likely such substance with which benzene hexachloride might be confused is DDT, and a test to distinguish the two is necessary where doubt is possible. Of the numerous colour reactions of DDT the pyridine - xanthydrol reaction[4] is simple. It is very sensitive to DDT and its analogues but gives no colour with benzene hexachloride. This could be used on a small portion of a sample to distinguish the two insecticides.

Test 29 suggests that the treatment with monoethanolamine as described in this paper would be applicable to the determination of DDT, but this has not been investigated in further detail. However, a much smaller amount of chloride is removed from DDT than from benzene hexachloride, 1 g. of the former giving 100 mg. of chloride ion and 1 g. of the latter 366 mg. The method would therefore be only about one-third as sensitive if it were applied to DDT.

## SOME APPLICATIONS OF THE METHOD

(1) To grain—Wheat, contained in a beaker, had been exposed to a smoke of benzene hexachloride produced from a Gammexane Smoke Generator. It remained toxic to adult *Calandra granaria*, even after two sievings. The extract from 100 g. of the wheat was found to contain 0·5 mg. of benzene hexachloride, corresponding to 5 p.p.m. in the wheat.

(2) To dust deposits—(*a*) In an experimental chamber of 260 cu. ft. capacity 3 in. × 1 in. microscope slides were placed on the floor and on shelves, and other slides were fixed to the walls by pellets of modelling clay. A 0·5-oz. portion of a Gammexane Smoke Generator was ignited, and after 3 hours the slides were picked up by forceps and placed in the stoppered boiling tubes for removal to the laboratory. The densities of the deposit on the floor and shelves at different heights were very similar, average 20 μg. per sq. cm. The deposit on walls or ceiling was less, about 4 μg. per sq. cm.

(*b*) A ship's hold was treated with smoke generators, and samples were collected on microscope slides. The deposit on horizontal surfaces was heavy, from 20 to 220 μg. of benzene hexachloride per sq. cm.

(3) Recent investigations into the behaviour of these insecticides in the animal body, *e.g.*, the determination of DDT in the milk of cows whose diet contains the substance,[5,6] suggest further applications of the method here described, which is likely to obviate certain difficulties, due to the presence of milk fat, previously encountered in this field. The method might also be adapted to the determination of the insecticides in the blood.

## SUMMARY

A method for the analysis of insecticidal deposits, or of residues in foods, without the use of elaborate equipment was required. After examination of alternatives, a method depending upon extraction with ether followed by dehydrochlorination with monoethanolamine, and subsequent determination of the separated chloride, was developed. The scope and limitations of the method are discussed.

The author wishes to thank Imperial Chemical Industries for the gift of the "Gammexane" used in these experiments, Dr. E. E. Turtle for help in preparing this paper and W. McAuley Gracie, Esq., Director of Infestation Control, for permission to publish.

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*July*, 1947

## Discussion

The PRESIDENT said the author had remarked that commercial Gammexane usually contained about 13 per cent. of the gamma isomer. Was this proportion sufficiently constant to enable a reasonably reliable estimate of insecticidal potency to be based on determinations of total benzene hexachlorides?

Mr. J. H. HIGH asked if it was possible to take advantage of physical properties of the isomers to effect, not necessarily a complete, but at least a partial, separation, and to estimate the relative amounts of the isomers from differences in the physical properties before and after the separation. He also asked if the reproducibility of the results obtained with alkali was good; if it was, the presence of a constant proportion of chloride might not be a fatal disadvantage.

Mr. F. C. HYMAS asked if any control experiments had been made to determine "blanks" on prepared foods. It was to be expected that blank determinations on grains and on inorganic chlorides would yield negative results, but there was some reason to think that blanks on prepared foods containing added halides might be appreciable.

Mr. HOWARD, in reply to the President, said that although the proportion of active isomers in commercial benzene hexachloride varied with the conditions of manufacture, it was likely to be fairly constant under the same conditions. But he understood that the material was now being marketed with higher proportions of the active constituents. In reply to Mr. High, he said that the different isomers did not differ much in physical properties. He had heard that work had been done in America on discrimination between the isomers by means of chromatography and infra-red spectrography. The blank figure resulting from the use of alkali had been found to be somewhat variable, and this had led to uncertainty in the true figure. The author said that he had not made determinations of the kind mentioned by Mr. Hymas, on prepared foods.

# The Determination of Nitromethane in Air

BY H. N. WILSON AND W. HUTCHINSON

IN the manufacture of nitromethane it is necessary to ensure that the atmosphere contains only minute quantities of the nitro-body, which has toxic properties. A method was therefore required to determine nitromethane concentrations of the order of 1 or 2 mg. per litre in the atmosphere where work on nitroparaffins was in progress.

Preliminary work showed that nitromethane could be determined in 0·2 *N* sulphuric acid by the polarograph, giving a well defined step with a half-wave potential of —0·7 to —0·8 volt against the saturated calomel electrode. Suitable solutions were made up and polarographed with a Cambridge instrument at a sensitivity of 1/700. Fig. 1 shows the step height against concentration at this sensitivity. It was found that one division of step height ≡ 16·8 mg. of nitromethane per litre of 0·2 *N* sulphuric acid.

Recovery of nitromethane in air by passage through gas absorption bottles containing 0·2 *N* sulphuric acid was unsatisfactory and was abandoned in favour of a technique using an

| Experiment | Nitromethane added mg. | Concentration in atmosphere at 20° C. and 760 mm. | | Nitromethane found mg. | Percentage recovery at 20° C. |
|---|---|---|---|---|---|
| | | mg./litre | % by volume | | |
| 1 | 36·2 | 13·7 | 0·475 | 34·4 | 95·0 |
| 2 | 24·8 | 9·4 | 0·320 | 23·6 | 95·2 |
| 3 | 18·5 | 7·0 | 0·238 | 17·6 | 95·1 |
| 4 | 11·0 | 4·2 | 0·143 | 10·5 | 95·5 |
| 5 | 6·20 | 2·3 | 0·079 | 5·9 | 95·2 |
| 6 | 4·762 | 1·8 | 0·061 | 4·514 | 94·8 |
| 7 | 3·824 | 1·45 | 0·050 | 3·606 | 94·3 |
| 8 | 3·018 | 1·13 | 0·038 | 2·852 | 94·5 |
| 9 | 1·268 | 0·478 | 0·016 | 1·192 | 94·0 |
| 10 | 0·621 | 0·224 | 0·008 | 0·578 | 93·0 |

evacuated winchester. This employs a winchester fitted with a two-holed rubber bung carrying a 50-ml. tap funnel and a right-angled glass tube with tap for connection to a good water pump. To test this method, known amounts of nitromethane contained in sealed glass bulbs were introduced into the winchester, the volume of which was known. The air was removed by the water pump, the pressure being measured by a mercury manometer. The glass tap to the pump was then closed, the pump disconnected and the bulb inside the winchester broken. The winchester was allowed to stand under reduced pressure for 24 hours to ensure complete vaporisation of the nitromethane. Air was then admitted until atmospheric pressure was reached, the tap closed and the winchester allowed to stand a further

2 hours to ensure thorough mixing of the air with the nitromethane. Fifty ml. of 0·2 *N* sulphuric acid were introduced by cooling the winchester slightly and allowing the acid to be drawn in *via* the tap funnel. The winchester was well shaken and allowed to stand 20 minutes and the 0·2 *N* sulphuric acid containing the nitromethane polarographed without de-oxygenating.

The data on p. 432 indicate the recovery of nitromethane from air, in concentrations varying from about 0·5 to 0·01 per cent. by volume.

It thus appears that under these conditions the dilute sulphuric acid in equilibrium with the atmosphere at 1 atmosphere pressure absorbs 95 per cent. of the nitromethane present and this figure must be taken into account in the analysis of samples of air.

PROCEDURE—Evacuate a winchester of known volume to about 30 mm. of mercury pressure, measuring the pressure with a manometer. Then open it in the atmosphere to be tested, taking the temperature at the same time. Introduce 50 ml. of 0·2 *N* sulphuric acid by cooling the winchester slightly and allowing the acid to be drawn in. Shake well and allow to stand for 30 minutes. Polarograph the sulphuric acid solution, without de-oxygenating, at a suitable sensitivity, *e.g.*, 1/700 or 1/70, over the voltage range —0·3 to —1·3 volt against the saturated calomel electrode.

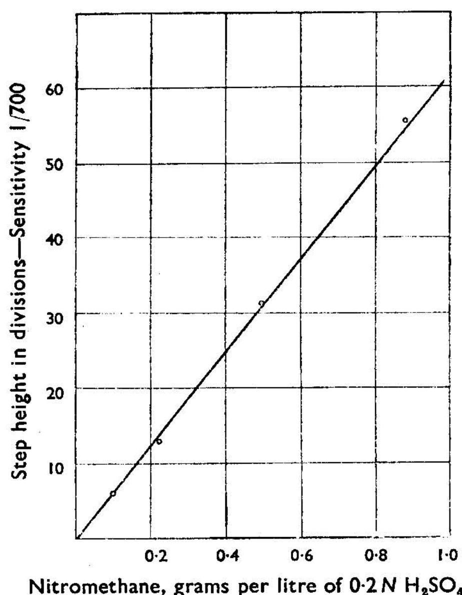


Fig. 1

Prepare a graph similar to Fig. 1 by dissolving known weights of pure nitromethane in a known volume of 0·2 *N* sulphuric acid and polarographing the solutions under the same conditions. Plot grams or milligrams of nitromethane per litre of 0·2 *N* sulphuric acid against the step height. From the graph, the volume of 0·2 *N* $H_2SO_4$ used and the volume of the air sample taken, calculate the proportion of nitromethane in the atmosphere, allowing also for the 95 per cent. recovery.

*Note*—Other nitroparaffins present will react similarly to nitromethane. If some other nitro-body is expected to predominate, a new graph must be prepared.

## SUMMARY

A method for the determination of small quantities of nitromethane in air has been described. The nitromethane is absorbed in 0·2 *N* sulphuric acid and the concentration in this determined with a polarograph.

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*December*, 1946

# The Estimation of the Volatile Matter Content of Propellant Explosives

## Part 3.* The Estimation of Acetone

BY T. G. BONNER

ACETONE is widely employed in the manufacture of various types of cordite (*i.e.*, propellants, containing both nitrocellulose and nitroglycerine). The acetone is used in optimum admixture with water to facilitate the formation of a homogeneous solution of the constituents of the cordite, which is necessary to ensure uniformity of product. The presence of the solvent in the final product is, of course, undesirable, and the last stage of manufacture is designed to remove as much of it as possible by "stoving" at an elevated temperature. This removal is never complete and in order to assess the effect of the residual acetone on ballistic properties, particularly in relation to variations in the acetone content with changing temperature and humidity, an accurate method of estimation is of paramount importance.

Various workers[1,2,3] have reported attempts to determine the residual acetone content, but no evidence is advanced that the methods give absolute figures and in general the results are quite arbitrary. Friedmann[4] recommended reducing the sample to shavings, introducing 2 to 5 g. into a U-tube immersed in a bath at 75° C., drawing a stream of carbon dioxide or nitrogen through the U-tube into either 23 per cent. potassium hydroxide solution or water, and determining the absorbed acetone by Messinger's method[5] by conversion to iodoform with excess of iodine in presence of sodium hydroxide and back-titration with sodium thiosulphate. Although this method has useful features, no evidence is adduced to prove that heating at 75° C. removes the whole of the acetone from the sample, a point which is emphasised by Kostevitch[6] in a criticism of the method used by Benesch,[7] and later by Graulich,[8] of heating samples of propellants to release the volatile matter for estimations. It is well known that solvent matter is tenaciously held by nitrocellulose and its quantitative removal by heat alone is only conceivable with ground material or very small grain or flake samples, and the reduction of larger sizes of cordite to such a state of subdivision introduces the difficulty of avoiding loss of solvent during the process.

These methods were not considered reliable either for routine analysis or for special investigations, and an improved technique was sought. Two possibilities were considered for the quantitative removal of the acetone from a propellant; first, dissolution of the cordite in a suitable medium followed by volatilisation and absorption, and secondly, extraction of the acetone from the cordite by an organic solvent. Since the amount of acetone present in cordites rarely exceeds 0·6 per cent. and also a method suitable for 2- to 3-g. samples was considered necessary, the quantity of acetone to be estimated was of the order of a few mg. Methods applicable to the estimation of small quantities of acetone include Messinger's method,[5] which has been investigated in detail by Goodwin[9]; the hydroxylamine hydrochloride method,[10] in which the hydrochloric acid liberated by the formation of acetone oxime is titrated with standard alkali solution; the formation of double salts of acetone with mercuric salts first employed by Dénigès[11]; colorimetric determination based on the condensation of ace tone with such compounds as *o*-nitrobenzaldehyde[12,13]; and a micro-diffusion method based on the bisulphite reaction described by Winnick.[14] A very useful critical review of methods of estimating small quantities of acetone in air has been given by Komar,[15] who preferred a modification of Messinger's method. An examination of all the above methods indicated that the first two were the most satisfactory. Further, for a given amount of acetone, the equivalent volume of standard iodine solution required in Messinger's method is nearly four times the volume of standard alkali solution of the same normality required in the hydroxylamine hydrochloride method, and this fact was considered to justify a preference for the former method, which later became a necessity on grounds of compatibility of reagents with other constituents of the propellant present during the estimation. With this method of estimating the recovered acetone, the two procedures outlined above for the quantitative removal of the acetone from cordite were investigated.

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* For Parts 1 and 2, see ANALYST, 1946, 71, 483; 1947, 72, 47.

## The quantitative removal of acetone from cordite by entrainment with air and absorption

The removal of the residual organic solvent matter in a propellant by passing a stream of air through a solution of the sample in nitrobenzene at 100° C. has already been described in the method of estimating ethyl alcohol and ether in nitrocellulose powders, in Part 2 of this series.[16] Cordites dissolve even more readily than nitrocellulose powders in nitrobenzene and this method was therefore adopted for cordites. To absorb the acetone carried over by the air stream, various solvents were investigated; it was found that absorption was incomplete in saturated sodium bisulphite solution, water and dilute sulphuric acid, and concentrated sodium hydroxide solution was not wholly satisfactory. Complete absorption was effected, however, in a 1 : 1 by volume mixture of concentrated sulphuric acid and water. An apparatus was used identical with that described in the method for nitrocellulose powders (see Part 2) except that only one absorption tube was employed in place of the three required in that method. The procedure used in carrying out the separation of the acetone in this way and its subsequent titration was as follows.

### Absorption method

About 10 ml. of the sulphuric acid was introduced into the absorption tube, while 2 g. of the cordite sample, cut up into ¼-in. lengths, were added to about 25 ml. of pure nitrobenzene in the 250-ml. three-necked flask. The flask was heated in a boiling water bath and a stream of air bubbled through the nitrobenzene solution to carry the acetone vapour into the sulphuric acid in the absorption tube. After 5 hours, the flow of air was stopped and the sulphuric acid run out and carefully neutralised with 30 per cent. sodium hydroxide solution; 1 drop of phenolphthalein was used as indicator and the solution was cooled during neutralisation. Forty ml. of $N$ sodium hydroxide solution were added and, after cooling in ice for 10 minutes, 10 ml. of 0·1 $N$ iodine were slowly run in, the flask being shaken during the addition. After the flask had been replaced in ice for 10 minutes, the iodine that had not reacted was liberated by addition of a slight excess of 2 $N$ sulphuric acid and titrated with 0·05 $N$ sodium thiosulphate, with starch solution as indicator. A blank determination was carried out on 10 ml. of the original diluted sulphuric acid (1 + 1) and the amount of acetone present in the sample calculated. One ml. of 0·1 $N$ iodine $\equiv$ 0·0009675 g. of acetone.

The accuracy of the method was tested by introducing a solution of acetone in nitrobenzene of known concentration into the flask, adding the other ordinary constituents of cordite, *viz.*, nitrocellulose, nitroglycerine, nitroguanidine and diethyldiphenylurea, and carrying out an estimation as described above. No interference by these constituents was observed and the results obtained for various solutions of acetone in nitrobenzene given in Table I indicate an accuracy of 3 to 4 per cent. with a maximum error of 5 per cent. for

Table I

Absorption method—weighed amounts of acetone in nitrobenzene solution removed at 100° C. and absorbed in sulphuric acid

| Weight of acetone taken mg. | Weight of acetone found mg. | Error per cent. |
|---|---|---|
| 5·31 | 5·08 | −4·3 |
| 2·85 | 2·95 | +3·5 |
| 2·62 | 2·49 | −5·0 |
| 1·88 | 1·89 | +0·5 |
| 1·45 | 1·50 | +3·0 |

quantities of acetone of the order of 1·5 to 5 mg. No difficulties were encountered in applying the method to the analysis of cordites. Confirmation of the reliability of the method was obtained by applying it to a sample of solventless cordite; no acetone or other organic solvent is used in the manufacture of this type of cordite and an analysis for its acetone content gave a figure of 0·00 per cent. The only unsatisfactory feature of this method is that it is impracticable for dealing with the large numbers of samples encountered in routine analysis. For this reason the possibility of quantitative extraction of the acetone with an organic solvent was investigated.

THE QUANTITATIVE EXTRACTION OF ACETONE FROM CORDITE WITH AN ORGANIC SOLVENT

The quantitative extraction of moisture from cordite by means of dioxan has already been described in Part 1 of this series.[17] Of possible solvents for the present purpose, dioxan was unsuitable in that it consumed appreciable traces of iodine, and methyl alcohol had to be rejected owing to its dissolving some nitroglycerine, which by its interaction with sodium hydroxide gave rise to decomposition products interfering in the iodine titration. In point of fact, no single organic solvent was found to be suitable for the quantitative extraction of acetone from cordite; eventually, it was found that a mixed solvent consisting of 3 volumes of nitrobenzene and 2 volumes of chloroform satisfied requirements. Trials were made with

TABLE II

ESTIMATION OF ACETONE IN NITROBENZENE - CHLOROFORM SOLUTION

| Weight of acetone taken mg. | Volume of organic solvent ml. | Volume of water ml. | Volume of *N* NaOH ml. | Time of reaction min. | Weight of acetone found mg. | Error per cent. |
|---|---|---|---|---|---|---|
| 6·36 | 20 | 25 | 15 | 20 | 5·05 | −20 |
| 6·36 | 20 | 25 | 15 | 40 | 6·19 | −3·0 |
| 6·36 | 20 | 25 | 15 | 40 | 6·19 | −3·0 |
| 3·34 | 15 | 25 | 15 | 20 | 3·23 | −3·3 |
| 5·30 | 15 | 25 | 15 | 10 | 5·10 | −3·9 |
| 4·16 | 15 | 25 | 15 | 20 | 4·26 | +2·4 |
| 6·36 | 15 | 25 | 15 | 25 | 6·31 | −0·9 |
| 6·81 | 15 | 25 | 15 | 25 | 6·63 | −2·9 |
| 4·24 | 15 | 25 | 15 | 25 | 4·11 | −3·1 |
| 7·42 | 15 | 25 | 15 | 30 | 7·15 | −3·6 |
| 5·30 | 15 | 25 | 15 | 35 | 5·30 | 0 |
| 5·40 | 10 | 50 | 15 | 15 | 5·20 | −3·7 |
| 5·40 | 10 | 50 | 15 | 20 | 5·22 | −3·3 |
| 5·40 | 10 | 50 | 15 | 27 | 5·26 | −2·6 |
| 5·40 | 10 | 50 | 15 | 30 | 5·24 | −3·0 |
| 5·40 | 10 | 50 | 10 | 15 | 5·07 | −6·1 |
| 5·40 | 10 | 50 | 10 | 20 | 5·26 | −2·6 |
| 4·32 | 10 | 50 | 10 | 20 | 4·28 | −0·9 |
| 7·56 | 10 | 50 | 10 | 20 | 7·35 | −2·8 |
| 5·40 | 10 | 50 | 10 | 25 | 5·27 | −2·4 |
| 5·40 | 10 | 50 | 10 | 25 | 5·27 | −2·4 |
| 5·40 | 10 | 50 | 10 | 25 | 5·28 | −2·2 |
| 4·32 | 10 | 50 | 10 | 25 | 4·21 | −2·5 |
| 7·56 | 10 | 50 | 10 | 30 | 7·41 | −2·0 |
| 7·56 | 10 | 50 | 10 | 40 | 7·49 | −0·9 |

solutions of acetone of known strength in this mixed solvent, the estimations being carried out directly by Messinger's method; the acetone solution was vigorously stirred with the aqueous sodium hydroxide and standard iodine solution during the time allowed for the acetone and iodine to react. All solutions except the iodine solution were maintained at 0° C. before being mixed in the reaction vessel, which was kept during the estimation in a Dewar flask containing ice. The measured volume of iodine was added slowly from a burette over a period of 5 minutes. In a series of determinations the factors that were varied were the relative volumes of the mixed organic solvent and the aqueous solution, the strength of the sodium hydroxide solution and the length of time allowed for reaction between the iodine and acetone. From the results given in Table II it can be concluded that (*a*) an increase in the volume of organic solvent relative to the volume of aqueous solution necessitates a longer period of time for completion of the reaction, (*b*) a decrease in the strength of sodium hydroxide solution must be compensated by an increase in the time allowed for reaction, (*c*) quantities of acetone of the order of 5 mg. dissolved in this mixed solvent can be estimated with an accuracy of 2 to 3 per cent. under the optimum conditions. It was ascertained that neither nitrocellulose nor diethyldiphenylurea interfered in the estimation and nitroguanidine is practically insoluble in nitrobenzene and chloroform. A further series of determinations were carried out with nitroglycerine added to the synthetic solutions of acetone. The variation of factors influencing the estimation was modified in relation to the knowledge gained from the first series of determinations and from the results given in Table III it is evident that the extent of interference by nitroglycerine increases with an increase in either the amount of nitroglycerine present or the strength of the sodium hydroxide solution or

the length of time allowed for the estimation. As the conditions are approached under which no interference at the end-point occurs, the interval of time between the stage at which the end-point is reached and the return of the blue colour of the starch - iodine complex increases until it is of the same order as that occurring when no nitroglycerine is present, *i.e.*, when the gradual reappearance of the blue colour can be attributed solely to the effect of atmospheric oxygen. The last two results in Table III indicate the optimum conditions;

TABLE III

EFFECT OF NITROGLYCERINE ON METHOD OF TABLE II

| Volume of nitro-glycerine added ml. | Weight of acetone taken mg. | Volume of organic solvent ml. | Volume of water ml. | Volume of *N* NaOH ml. | Time of reaction min. | Weight of acetone found mg. | Error per cent. |
|---|---|---|---|---|---|---|---|
| 0·30 | 5·84 | 15 | 50 | 10 | 20 | 5·22 | −11·0 |
| 0·10 | 5·84 | 15 | 25 | 15 | 20 | 5·35 | −9·0 |
| 0·10 | 5·84 | 15 | 50 | 10 | 40 | 5·55 | −5·0 |
| 0·10 | 5·84 | 10 | 50 | 10 | 25 | 5·70* | −2·4 |
| 0·15 | 3·34 | 10 | 50 | 10 | 20 | 3·25* | −2·7 |

* No interference at end-point of titration.

full experimental details based on these conditions are given below. Using this procedure, a sample of solventless cordite which contained no acetone was analysed. This type of cordite has a higher nitroglycerine content than normal cordites, and the amount of nitroglycerine extracted from it by the nitrobenzene - chloroform solvent was obviously much higher than that extracted from ordinary cordites. On two separate samples of this cordite, analyses showed apparent acetone contents of 0·005 and 0·004 per cent. which are negligible. No difficulty was experienced with the end-point and it is clear therefore that the method is quite satisfactory in presence of nitroglycerine. In Table IV is given a comparison of

TABLE IV

DETERMINATION OF ACETONE IN CORDITE—COMPARISON OF EXTRACTION AND ABSORPTION METHODS

| Sample | Acetone per cent. Absorption method | Acetone per cent. Extraction method |
|---|---|---|
| Cordite W 124, lot BS 87 .. .. | 0·09; 0·09 | 0·10; 0·10 |
| Cordite WM 130, lot WAC 1724 .. | 0·33; 0·31 | 0·34; 0·33 |
| Cordite MD St., lot WA 791 .. | 0·32; 0·30 | 0·30; 0·29 |

results obtained on some cordites by this method and by the method of entrainment by air from solution in nitrobenzene at 100° C. described above; excellent agreement is evident.

Final confirmation of the accuracy and reliability of the method was provided by the following experiment. Three g. of a sample of a W.M. cordite containing mineral jelly and diethyldiphenylurea was allowed to stand in contact with 20 ml. of the nitrobenzene - chloroform solvent overnight. Exactly 5 ml. of the supernatant solvent was then removed and replaced by 5 ml. of a synthetic solution of acetone in the same solvent, and this was again allowed to stand overnight. The acetone contents of both this final solution and of the 5 ml. aliquot portion originally removed were estimated. The estimation of the acetone content of the 5 ml. aliquot portion enabled the acetone content of the residual 15 ml. to be calculated; to this figure was added the known amount of acetone present in the added 5 ml. of synthetic solution, and this was compared with the result of the direct analysis of the final solution. As the results of the duplicate determination given in Table V show, these figures differ by about 2 per cent. This experiment establishes that complete extraction of the acetone occurs on standing overnight, for no increase in the acetone content of the supernatant solvent is detected after allowing to stand for a second time overnight.

For most purposes this procedure of allowing the sample of propellant to stand in contact with the solvent overnight was convenient, but if results are required more quickly, the time of standing can be reduced to a few hours by increasing the amount of nitrobenzene relative

to the chloroform in the mixed solvent. When this modification was used, however, it was found that for each particular type of cordite the altered conditions of the estimation varied slightly. Therefore, before this more rapid method is employed, it is necessary to investigate the optimum ratio of nitrobenzene and chloroform and the time to be allowed for extraction for the type of cordite under analysis.

TABLE V

RECOVERY OF ACETONE ADDED TO AN EXTRACTED CORDITE SAMPLE
3 g. of sample in 20 ml. of nitrobenzene - chloroform solvent

| | | (a) mg. | (b) mg. |
|---|---|---|---|
| (1) | Weight of acetone found in 5 ml. of supernatant solvent | 2·31 | 2·48 |
| (2) | Weight of acetone in residual 15 ml. of solvent from (1) | 6·93 | 7·44 |
| (3) | Weight of acetone added to residual 15 ml. of solvent | 5·40 | 5·40 |
| (4) | Total weight of acetone present in final solution, *i.e.*, (2) + (3) | 12·33 | 12·84 |
| (5) | Total weight of acetone found in final solution | 12·6 | 12·6 |
| | Error | +2·1% | −1·9% |

(*a*) and (*b*) are duplicate estimations.

The method is applicable in the presence of ethyl alcohol and has been used without modification for the estimation of acetone in cordites manufactured with a mixed ethyl alcohol - acetone solvent. Details of the method are given below.

## EXTRACTION METHOD

Make up the solvent as required by mixing 3 volumes of AnalaR nitrobenzene and 2 volumes of B.P. chloroform. Cut up the sample of cordite into ¼-in. lengths, and add a weighed 3-g. portion to 20 ml. of the solvent in a 25-ml. cylinder fitted with a ground-glass stopper. Stopper the cylinder and allow to stand overnight. After shaking and allowing to settle, transfer 5 ml. of the supernatant solution to a 200-ml. pear-shaped flask and add 5 ml. of the nitrobenzene - chloroform solvent and 50 ml. of water. After stoppering, place the flask in an ice bath, in which is also maintained a *N*-solution of sodium hydroxide. After 15 minutes in the ice bath remove the flask to a Dewar flask containing ice and clamp it vertically with the lower portion immersed in the ice. Remove the stopper and add 10 ml. of the *N* sodium hydroxide. Introduce a motor driven stirrer into the flask and add 10 ml. of 0·1 *N* iodine dropwise over a period of 5 minutes from a 10-ml. burette, keeping the solution efficiently stirred during the addition. Continue the stirring for a further 20 minutes and then remove the flask and add a slight excess of *N* sulphuric acid immediately. Titrate the liberated iodine without delay, with 0·05 *N* sodium thiosulphate. Near the end-point vigorous shaking is necessary to remove the last traces of iodine dissolved in the nitrobenzene - chloroform layer to the aqueous layer. Carry out a blank determination on 10 ml. of the nitrobenzene - chloroform solvent and, after correcting for the very slight consumption of iodine in this "blank" (usually equivalent to 0·05 or 0·10 mg. of acetone per 10 ml. of solvent), calculate the amount of acetone present from the relationship between the iodine solution and acetone given above (p. 435).

## SUMMARY

Existing methods of estimating the residual acetone content of cordite are critically reviewed, particularly from the viewpoint of ensuring quantitative removal of the acetone from the cordite prior to its estimation. A new method is described in which the acetone is extracted with a mixed nitrobenzene - chloroform solvent and estimated by Messinger's method with an accuracy of 2 to 3 per cent. Interference by nitroglycerine has been studied in detail and the conditions established for its complete elimination.

In conclusion, I should like to thank Mr. G. L. Hutchison, of the Armament Research Department for his helpful advice, and the Director-General of Scientific Research (Defence), Ministry of Supply, for permission to publish this material.

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*March*, 1947

# Spot-tests for the Detection of Alloying Elements in Tin-Base Alloys*

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Tin is extensively used as the basis material for the manufacture of bearing metals and solders. The composition of bearing metals varies considerably according to the particular work required of them. The alloying elements are usually some or all of the following: lead, antimony, zinc, copper and aluminium in varying proportions. Tests have been worked out for lead, copper, arsenic, antimony, zinc and aluminium.

*Apparatus*—In addition to the droppers, stirrers and capillary tubes already described in former papers[4] the following are needed: (*a*) white porcelain spot-plate, and (*b*) apparatus used for the detection of arsenic (*vide* (III) Arsenic, and this Vol., p. 108).

*Cleaning the specimen*—The surface of the sample is thoroughly cleaned by rubbing it with emery paper—Grade "F" (Buff), or similar—prior to addition of the attacking reagent.

*The tests*—Of the tests described, those for lead, copper and arsenic are completed on the surface of the sample; the tests for antimony, zinc and aluminium require for completion the removal of the reaction drops from the specimen at some intermediate stage. The test described for lead is the only one of this series that is new to spot-testing. The tests for the remaining elements are either identical with or modifications of tests published earlier, *e.g.*, antimony and arsenic: "Lead-base Alloys"[1]; aluminium: "Steels"[2] and "Zinc-base Alloys"[3]; copper and zinc: "Aluminium- and Magnesium-base Alloys."[4] Iron is seldom added to tin-base alloys, but is usually found as an impurity varying in amounts from 0·02 to 0·05 per cent. The only specification[5] in which iron is a constituent gives a figure of 0·10 per cent. Fe, and since no spot-test could be expected to differentiate between an alloying content of 0·1 per cent. and an impurity of 0·02 to 0·05 per cent., a test for it has not been included.

## (I) Lead

*Reagents*—(*a*) Nitric acid (sp.gr. 1·42).
(*b*) Distilled water.
(*c*) Urea (solid).
(*d*) Potassium iodide solution (4 per cent.).

*Method*—Place 2 drops of (*a*) on the thoroughly cleaned surface and leave them to react until a solid crust has formed or, for less reactive alloys, until the reaction appears to be complete. Add 2 drops of (*b*) and stir; then add a small quantity of (*c*), sufficient to form a small heap on the end of a pen-knife blade and again stir until the crystals are well mixed with the drop. Add 2 or 3 drops of (*d*) and stir thoroughly. In presence of much lead, say above 10

* Communication from the Armament Research Department (formerly the Research Department, Woolwich).

per cent., a very heavy bright yellow precipitate, and down to about 1 per cent. a heavy yellow precipitate, is formed; with about 0·5 per cent. of lead a slight yellow precipitate only is produced. In absence of lead the composite drop on the specimen is water-white. The precipitate of lead iodide may be transferred to a filter-paper, dried and retained for future reference.

Tried on: Samples Nos. 10, 7, 12, 11, 22, 15, 8, 6, 4, 3, 14, 5, 9, 13, 1, 23, 21—Lead present and all gave positive results.
Nos. 2, 16, 24, 25, 26—Lead absent and all results negative.

(II) Copper

*Reagents*—(*a*) Nitric acid (sp.gr. 1·42).
(*b*) Diluted ammonia (1 + 1).
(*c*) Mixture of α-benzoin-monoxime (saturated solution in alcohol), 10 vols.; diluted ammonia (1 + 1), 20 vols.; citric acid solution (50 per cent.), 5 vols.

*Method*—Place 2 drops of (*a*) on the thoroughly cleaned surface and leave to react until the attack is complete, add 2 drops of (*b*), stir well (the drop should now be alkaline), then add 4 to 6 drops of (*c*), again stir well and leave for 5 to 10 minutes. In presence of copper a dirty green complex separates out slowly, whilst in absence of copper the drop remains water-white. The deep blue coloration produced on addition of the 2 drops of (*b*) when copper is present is quite unmistakable and could be used as a quick test for copper.

Tried on: Samples Nos. 6, 21, 22, 1, 16, 5, 13—Copper present and all results positive.
Nos. 14, 15, 2, 3, 4, 7, 8, 9, 10, 11, 12, 24, 25—Copper below 0·05 per cent. and all results negative.

(III) Arsenic

*Reagents*—(*a*) Diluted hydrochloric acid (1 + 1) saturated with bromine.
(*b*) Hydrochloric acid (concentrated).
(*c*) Arsenic-free zinc.
(*d*) Mercuric chloride test paper.
(*e*) Ferrous sulphate (small crystals).

*Apparatus*—(*g*) A glass tube 1 in. by $\frac{5}{8}$ in., ground flat at both ends, (*h*) a glass tube $2\frac{3}{4}$ in. by $\frac{3}{8}$ in. fitted at one end with a half-inch length of rubber tubing so arranged that a little of the tubing overlaps the end of the glass tube, forming a slightly tapered end which serves as a stopper; this tube with its rubber end should fit snugly into tube (*g*), (*j*) rubberised vaseline such as is used for stop-cock lubricants, and (*k*) cotton-wool.

To prepare the tube (*h*) for the test, insert a tightly packed plug of cotton-wool into the tube so that its lower end is about $\frac{1}{2}$ in. from the bottom of the tube, the plug being about $\frac{1}{8}$ in. deep. To the rubber-tubing end of the cotton-wool plug add fine crystals of (*e*) until a layer about $\frac{1}{4}$-in. thick has been formed, insert a second plug of cotton-wool to prevent the ferrous sulphate from falling out when the tube is in position for the test. Cut a strip of paper (*d*) about $\frac{1}{4}$ in. by $1\frac{1}{4}$ in., insert it in the glass tube and then plug the free end of the tube loosely with cotton-wool; the tube is now ready for the test.

*Method*—Thoroughly clean the surface of the specimen with emery paper. Dip the end of the glass tube (*g*) into the hot sealing grease (*j*), then withdraw it and, after making sure that there is no film of grease across the end, press it firmly on the specimen and allow the grease to set. Add 4 drops of (*a*) inside the wide tube and leave to react for 5 minutes. Add 15 drops of (*b*). Drop a small granule of (*c*) into the wide tube and allow the reaction to proceed for a few seconds; then, before the bromine has been destroyed, insert the rubber-stoppered end of the prepared tube (*h*) and leave for 15 minutes. Detach the top tube, (*h*), remove the top plug and shake out the test strip. A yellowish-brown stain on the strip indicates the presence of arsenic. Four samples gave a slight yellow coloration of the bottom $\frac{1}{8}$ in. of the strip, and subsequent chemical analysis has shown that these samples contained 0·014, 0·011, 0·020 and 0·027 per cent. of arsenic respectively. In absence of arsenic the paper remains quite white; this is in sharp contrast to the same test as applied to lead-base alloys, where heavy greyish-black stains were produced by high antimony contents.

Tried on: Samples Nos. 13, 2, 3, 4, 14—Arsenic present and all results positive.
Nos. 1, 5, 6, 7, 8, 9, 10, 11, 12, 15, 16, 21, 22, 23, 24, 25—Arsenic absent and all results negative.

### (IV) ANTIMONY

*Reagents*—(*a*) Nitric acid (sp.gr. 1·42).
(*b*) Hydrochloric acid (concentrated).
(*c*) Potassium nitrite (solid).
(*d*) Rhodamine "B"[6] (0·01 per cent. solution in water).

*Method*—Place 2 drops of (*a*) on the thoroughly cleaned surface and leave to react until a solid crust has formed, or, for the less reactive alloys, until the reaction appears to be complete. Add 3 drops of (*b*) and transfer quickly, by means of a capillary tube, to a well of a white porcelain spot plate. Add a further 2 drops of (*b*) and then a few small crystals of (*c*) and leave to react for about half a minute. In another well of the spot-plate place 4 drops of (*d*) and add to them 2 or 3 drops of the solution from the first well; stir, add 2 more drops of (*b*), stir again, then leave. In presence of much antimony an immediate heavy purple precipitate or coloration is produced; 0·12 per cent. of antimony gives a purplish coloration to the drop. In absence of antimony the reagent drop has a dirty reddish-pink colour. A positive reaction was given by three samples to which antimony had not originally been added, but chemical analysis has shown that the samples contained 0·26, 0·22 and 0·15 per cent. respectively. While removing the reaction solutions to filter-paper for future reference it was noticed that samples that gave a dirty reddish-pink colour on the spot-plate (regarded as having no antimony present) now gave slight purplish precipitates when washed once or twice with water. All samples not supposed to contain antimony were tested on filter-paper and it was found that down to about 0·06 per cent. of antimony could be detected in this way. AnalaR tin, spectrographic tin and the reagents alone did not give a purple precipitate. When dry, the purplish precipitates became mauvish in colour. It is recommended that removal of the drop to a filter-disc should not be used as part of the test.

Tried on: Samples Nos. 15, 21, 1, 11, 6, 22, 10, 7, 12, 13, 4, 2, 5, 16—Antimony present and all results positive.
Nos. 3, 9, 14, 24, 8, 26, 27—Antimony below 0·09 per cent. and all results negative.

The antimony in samples Nos. 3, 9, 14, 24, and 8 was first detected by removal of the reaction drop to a filter-disc and subsequently confirmed by chemical analysis of another portion of each alloy.

### (V) ZINC

*Reagents*—(*a*) Nitric acid (sp.gr. 1·42).
(*b*) Urea (solid).
(*c*) Diluted ammonia (1 + 1), 1 vol.; ammonium acetate* solution, 2 vols.; potassium cobalticyanide solution (10 per cent.), 2 vols.
(*d*) Diphenylcarbazone (1·5 per cent. solution in alcohol).
(*e*) Acetone.
(*f*) *Iso*propyl alcohol.

*Method*—Place 1 drop of (*a*) on the thoroughly cleaned surface and leave until the reaction appears to be complete; add a small heap of (*b*), sufficient to cover the point of a pen-knife blade, follow with 5 drops of mixture (*c*) and stir thoroughly. Add 5 drops of (*d*), stir, and after a few seconds transfer, by means of a capillary tube, to the centre of a disc of close-grained filter-paper supported on the open mouth of a beaker; the transfer should be made 3 or 4 drops at a time in order to spread out the spot for subsequent acetone washing. Allow to spread completely, then wash three times with 3 drops of (*e*), and continue with three or four 3-drop washings of (*c*). Zinc, lead and copper all give precipitates under the conditions existing before treatment of the transferred drop; copper slowly destroys the reagent colour, the decolorisation being greatly accelerated by acetone. The acetone wash also dissolves, decolorises and washes out the lead precipitate, whilst the deep blackish-purple precipitate due to zinc is dissolved and spread out over a limited area as a deep permanganate-coloured patch. Washing with *iso*propyl alcohol (*f*) removes any incidental reagent colours but leaves the zinc patch in its original position. In presence of zinc an intense blackish-purple spot at the centre of the paper, surrounded by a permanganate-coloured patch about 1½ to

* Preparation of ammonium acetate solution: add, to 1140 ml. of distilled water in a 3-litre porcelain beaker placed in a cooling bath, 500 ml. of 0·880 ammonia solution followed by 570 ml. of glacial acetic acid, the solution being stirred continuously. Allow to cool; the solution should be neutral.

2 in. in diameter, is obtained. In absence of zinc the paper has a clear centre (sometimes a slight light brown or pink smudge due to traces of copper or lead precipitates not completely washed out) and a narrow ring about 2½ in. in diameter, which varies in colour from light brown to maroon. Zinc down to 0·47 per cent. gives a fair reaction. Where the presence of zinc is doubtful it is best to wait 5 minutes after the last addition of (*f*) before deciding whether the centre contains a precipitate or a colour which *does not* fade.

Tried on: Samples Nos. 5, 13, 14, 3, 16, 2, 4, 19, 20, 18, 17, 15—Zinc present and all results positive.
Nos. 1, 6, 7, 8, 9, 10, 11, 12, 21, 22, 23, 24, 25—Zinc absent and all results negative.

### (VI) Aluminium

*Reagents*—(*a*) Concentrated hydrochloric acid saturated with bromine.
(*b*) Mixture of sodium hydroxide solution (20 per cent.), 3 vols.; potassium cyanide solution (10 per cent.), 1 vol.
(*c*) Ammonium aurintricarboxylate (0·01 per cent. solution in alcohol).
(*d*) Mixture of ammonium chloride solution (20 per cent.), 1 vol.; ammonium phosphate solution (10 per cent.), 1 vol.
(*e*) Ammonium chloride solution (20 per cent.).

*Method*—Place 2 drops of (*a*) on the thoroughly cleaned surface and allow them to react until the bromine colour is all but dispelled, then add 4 or 5 drops of (*b*) stir well, and if the

Table I

Specimens of alloys used in the tests. Constituents per cent.

| No. | Mark | Pb | Sb | As | Cu | Zn | Al | Fe |
|---|---|---|---|---|---|---|---|---|
| 1 | DOF .. .. | 0·05 | 9·75 | — | 3·60 | — | — | — |
| 2 | EX 14 .. .. | — | 0·22* | 0·014* | — | 7·60 | 3·87 | — |
| 3 | EX 15 .. .. | 3·41 | 0·09* | 0·011* | — | 11·41 | — | — |
| 4 | EX 16 .. .. | 4·38 | 0·26* | 0·020* | — | 6·10 | — | — |
| 5 | EX 7 .. .. | 1·10 | 0·15* | — | 2·67 | 40·9 | — | — |
| 6 | EX 46 .. .. | 8·37 | 7·0 | — | 9·35 | — | — | — |
| 7 | EX 47† .. .. | 39 | 3 | — | — | — | — | — |
| 8 | EX 48† .. .. | 20 | 0·06* | — | — | — | — | — |
| 9 | EX 49† .. .. | 1·0 | 0·09* | — | — | — | — | — |
| 10 | EX 50 .. .. | 46·95 | 3·11 | — | — | — | — | — |
| 11 | EX 51 .. .. | 23·25 | 9·57 | — | — | — | — | — |
| 12 | EX 52 .. .. | 38·65 | 2·24 | — | — | — | — | — |
| 13 | EX 53 .. .. | 0·84 | 1·20 | 0·40 | 1·63 | 25·34 | 0·03 | 0·10 |
| 14 | EX 54 .. .. | 1·31 | 0·09* | 0·027* | 0·03 | 19·16 | 0·26 | — |
| 15 | EX 55 .. .. | 19·45 | 11·12 | — | 0·04 | 0·36 | — | — |
| 16 | EX 56 .. .. | — | 0·12 | — | 3·44 | 9·27 | — | — |
| 17 | EX 78 .. .. | 0·56 | — | — | — | 0·46 | — | — |
| 18 | EX 79 .. .. | 30·24 | — | — | — | 0·50 | — | — |
| 19 | EX 80 .. .. | 0·68 | — | — | — | 1·33 | — | — |
| 20 | EX 81 .. .. | 30·63 | — | — | — | 1·11 | — | — |
| 21 | BCN .. .. | 0·37 | 9·89 | — | 3·91 | — | 0·02 | — |
| 22 | BCM .. .. | 21·94 | 5·63 | — | 3·81 | — | 0·01 | — |
| 23 | USA .. .. | 0·49 | — | — | — | — | — | — |
| 24 | "Pure" Tin .. | — | 0·08* | — | — | — | — | — |
| 25 | "Chempure" Tin | — | — | — | — | — | — | — |
| 26 | "Spectro" Tin .. | — | — | — | — | — | — | — |
| 27 | A/R Tin.. .. | 0·01 | 0·03 | — | — | — | — | — |

* Found first by spot-test and later confirmed by chemical analysis.
† Samples not analysed chemically.

heavy white gelatinous precipitate has not dissolved add a further drop of (*b*). Treat a circle of close-grained filter-paper with 1 ml. of reagent (*c*), causing it to spread evenly and finally drying over a source of hot air. Place the paper on the open mouth of a beaker and add the reaction solution, which is removed from the sample by means of a capillary tube, to the centre of the paper, in a dropwise manner. When the last drop has been added and the liquid

has finished spreading, remove the filter paper from the beaker, place it flat on a clean porcelain tile and cover it with a 7-cm. filter-paper thoroughly wetted with mixture (*d*); press the latter paper on to the reaction filter-paper, to ensure good contact at all points and after a few seconds strip it off and reject it. Return the original paper to its beaker, leave it for 5 minutes, then wash it twice with 3 or 4 drops of (*e*) and finally dry it. In presence of aluminium the paper shows a sharp pinkish-crimson irregular ring about 1½ in. in diameter outside which is a broad band of colour, similar to that of the ring but less intense; the ground both inside and outside the ring should be white while wet. In absence of aluminium the paper should be completely white after 5 minutes standing. With 0·26 per cent. of aluminium, instead of the characteristic markings of the high aluminium contents there is a single light pinkish irregular band of the same diameter.

Tried on: Samples Nos. 2, 14—Aluminium present and both give positive results.
Nos. 1, 3, 4, 5, 6, 7, 10, 11, 12, 13, 15, 16, 21, 22, 23, 24—Aluminium below 0·05 per cent. and all results negative.

SUMMARY

Tests are described for the detection of alloying elements in tin-base alloys. The alloying elements so detected are lead, copper, arsenic, antimony, zinc, and aluminium. With the alloys available the tests are specific and unambiguous. No test has been included for iron since the margin between impurity and alloying constituents is too small.

Thanks are due to the Chief Scientist, Ministry of Supply, for permission to publish this paper.

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*May*, 1947

# A System of Qualitative Analysis for the Common Metals in Presence of Phosphates, using Ammonium Benzoate

BY G. J. AUSTIN

THE benzoate iron group separation[1] has been proposed[2,3] for group analysis, instead of the more common separation by ammonia. It gives much better separations than other methods and can be used in presence of phosphate. However, some of the phosphate passes into the filtrate and when ammonia is added phosphates of the bivalent metals may precipitate, thus interfering with the rest of the analysis. This is overcome in the system now proposed by using some of the principles employed in my phosphate method[4,5] in which the solution remains acid until all the metals except magnesium and alkali metals have been separated.

This system of analysis can be applied regardless of the presence of phosphate and, except when 0·20 g. or more of phosphate ($P_2O_5$) is present, it will usually give much better separations than my phosphate or other methods. However, when phosphate is present the iron group precipitate is unsuitable for direct ignition and weighing, as a mixture of oxides and phosphates is obtained. The phosphate method[4,5] can be used in such instances.

An important advantage of the benzoate method of separating iron group metals, which is used in this system, is that it can be used when chromium is the only iron group metal present. Under these conditions chromium cannot be precipitated as basic acetate, formate or succinate. Uranium, beryllium, and tervalent cerium are only partially precipitated in the benzoate separation unless sufficient phosphate is present to precipitate these metals as phosphates, but these metals and also chromium can be precipitated in my phosphate method.

When this system is used for ordinary qualitative analysis it is sufficient to wash the

precipitates with water. Until the 5 g. of ammonium acetate is added, the solution is apt to deposit benzoic acid on cooling, but this will redissolve on warming.

## A SYSTEM OF ANALYSIS SUITABLE FOR PHOSPHATES

Remove Groups I and II as usual. (Chromates and Fe''' are best reduced with HI—see ref. 4.) To a solution of 0·5 g. in 20 ml. add dilute ammonia until a slight ppt. persists. Add 1 ml. of 5 *N* HCl. Heat to incipient boiling, add 2 ml. of 10% $(NH_4)_2SO_4$ solution and if there is a ppt. add another 2 ml. of $(NH_4)_2SO_4$ solution and heat in boiling water for 15 to 30 min. Filter and wash with 0·05 *N* $H_2SO_4$.

| *Ppt.* | *Solution.* |
|---|---|
| **$SrSO_4$ $BaSO_4$**<br>Try flame test and/or boil with 50 ml. of *N* $Na_2CO_3$. Decant through filter. Repeat process. Dissolve the carbonates in acetic acid. Add $K_2CrO_4$: ppt. = $BaCrO_4$. To solution add $H_2SO_4$: ppt. = $SrSO_4$. | Add sat'd. bromine solution and boil off excess. To the cold solution add dilute ammonia until a slight ppt. persists. Add 1 ml. of glacial acetic acid and 2 g. of $NH_4Cl$, dilute to 100 to 150 ml. Heat and add 20 ml. of 10% ammonium benzoate solution. Boil. (*p*H is now 3·8 to 4·0.) Filter hot and wash with hot benzoate wash solution or with 2% ammonium nitrate solution. |

| *Ppt.* | *Solution.* |
|---|---|
| **Fe, Al, and Cr as phosphates and/or basic benzoates**<br>Suspend in water, add $H_2O_2$ and NaOH solution. Boil, dilute and filter; $Fe(OH)_3$ remains. To solution add ammonium phosphate solution and excess of acetic acid; $AlPO_4$ is pptd. If the solution is yellow, Cr is present. To confirm Cr add diphenyl carbazide—gives red colour. | Add 5 g. of ammonium acetate. (*p*H is now 4·6 to 5·0.) Heat to boiling and pass $H_2S$ through the hot solution for 5 to 10 min. Boil for a few seconds and filter. Wash with 0·1 *N* acetic acid. |

| *Ppt.* | *Solution.* |
|---|---|
| **ZnS, CoS, NiS.**<br>If Zn is present white ZnS pptes. before the black CoS or NiS. Dissolve the sulphides in 1:1 $HNO_3$ and test parts for Ni, Co and Zn. | Boil off $H_2S$. To the gently boiling solution add 5-ml. portions of the periodate reagent until a positive spot test for periodate with the starch iodide solution is obtained. Filter and wash with a little water and then with hot 0·1 *N* $HNO_3$. |

| *Ppt.* | *Solution.* |
|---|---|
| **$MnO_2.H_2O$.**<br>To confirm Mn, extract the ppt. with $KHC_2O_4$ solution; a deep red colour proves Mn. | To the hot solution add 5 ml. of *M* citric acid and 25 ml. of sat'd. ammonium oxalate solution. Allow to stand at least 5 min., filter and wash. |

| *Ppt.* | *Solution.* |
|---|---|
| **$CaC_2O_4.H_2O$.** | Concentrate to about 150 ml. Add 5 ml. of *M* ammonium phosphate and to the hot solution add 20 ml. of conc. $NH_3$. Stand overnight. Filter and wash with 2% $NH_3$. |

| *Ppt.* | *Solution.* |
|---|---|
| **$MgNH_4PO_4.6H_2O$** | Reject. |

The 20 ml. of ammonium benzoate solution are sufficient for 0·10 g. of aluminium or 0·20 g. of iron or chromium. For larger amounts of these metals, add the ammonium benzoate solution until the solution has *p*H 3·5 to 4 as indicated by a blue spot test with bromophenol blue indicator. At *p*H 3·0, after 5 minutes boiling, 0·2 mg. of iron or aluminium is left in solution, while at *p*H 3·5 to 4·0 less than 0·1 mg. remains dissolved. When present alone, chromium requires longer boiling than iron or aluminium; after 20 minutes boiling 3 mg. of chromium remained dissolved at *p*H 3·0 and 1 mg. at *p*H 3·5. However, when iron or aluminium was also present then usually not more than 0·1 mg. of chromium remained dissolved after 5 minutes boiling at *p*H 3·5 to 4·0. For ordinary qualitative analysis it is usually sufficient to boil for about one minute before filtering off the basic benzoates.

Table I compares adsorption or co-precipitation of bivalent metals by precipitates of the iron group obtained by various methods. The tests by the ammonia method[3] were with phosphate absent and at *p*H 6·7 to 7·3. The tests by my phosphate method were with 0·355 g. of $P_2O_5$ present. It is evident that as a general method the benzoate method is best. It may be noted that by ignoring any phosphate present and using the benzoate method as in this system of analysis, the adsorption of zinc, nickel, and cobalt is considerably less than if the phosphate is first removed and then the ammonia method used.

Adsorption losses in the system now described, other than in the iron group, are very small; some examples are given in Table II.

TABLE I

ADSORPTION OF BIVALENT METALS IN THE IRON GROUP

The figures represent the amounts of the various bivalent metals co-precipitated, expressed as percentages of the amounts taken

| Weight of metals taken | | Adsorption by benzoate method | | | | | |
|---|---|---|---|---|---|---|---|
| | | phosphate absent | 0·072 g. $P_2O_5$ present | 0·21 g. $P_2O_5$ present | Adsorption by phosphate method[4] | Adsorption by ammonia method[3] | Adsorption by acetate method[4] |
| g. | g. | % | % | % | % | % | % |
| 0·055 Al | 0·127 Zn | 1·4 | 4·9*a* | 14 | 8 | 19 | 15 |
| " | 0·116 Mn | 0·20 | 0·8 | 2·4 | 1·2 | 0·10 | 0·5 |
| " | 0·120 Co | 0·33 | 0·8 | 1·5 | 1·0 | 6·2 | — |
| " | 0·120 Ni | 0·8 | 2·2 | 0·8 | 0·5 | 71 | 1·3 |
| " | 0·097 Ca | < 0·2 | < 0·2 | 0·6 | < 0·2 | — | — |
| " | 0·069 Mg | < 0·2 | < 0·2 | < 0·2 | < 0·2 | — | — |
| 0·093 Fe | 0·127 Zn | 0·2 | 3·0*b* | 11 | 10 | 12 | 13·5 |
| " | 0·116 Mn | 0·1 | 0·35 | 3·2 | 3·0 | 2·7 | 4·5 |
| " | 0·120 Co | 0·1 | 0·8 | 2·6 | 0·7 | 6·0 | 4·0 |
| " | 0·120 Ni | 0·1 | 0·5 | 1·7 | 0·3 | 6·8 | 6·0 |
| " | 0·097 Ca | < 0·2 | < 0·2 | 0·6 | < 0·2 | — | — |
| " | 0·069 Mg | < 0·2 | < 0·2 | < 0·2 | < 0·2 | — | — |
| " | 0·171 Ba | < 0·1* | < 0·1**c* | 30* | 30* | 0·2 | 14 |
| 0·088 Cr | 0·127 Zn | 4·5 | 15 | 29 | 26 | 90 | — |
| " | 0·116 Mn | 0·4 | 3·8 | 10 | 8 | 3·2 | — |
| " | 0·120 Co | 0·8 | 4·5 | 4·5 | 5·5 | 75 | — |
| " | 0·120 Ni | 1·6 | 4·3*d* | 4·5 | 3·5 | 90 | — |
| " | 0·097 Ca | 0·2 | 0·7 | 7·0 | 5·0 | 0·8 | — |
| " | 0·069 Mg | < 0·2 | 0·5 | 1·5 | 1·5 | 1·5 | — |
| " | 0·171 Ba | < 0·1* | 6·0* | 37* | 52* | 0·8 | — |
| 0·022 Al, 0·037 Fe, 0·035 Cr | 0·080 Zn | 1·5 | 2·9 | 25 | 14 | 33 | 20 |
| 0·046 Fe, 0·044 Cr | 0·116 Mn | 0·3 | 1·0 | 5·6 | 7 | — | — |
| 0·028 Al, 0·044 Cr | 0·116 Mn | 0·20 | 1·0 | 5·8 | 3·4 | — | — |

* The adsorption of barium and strontium is avoided by prior removal of these metals as sulphates

*a* 52% of the $P_2O_5$ taken was in the filtrate.
*b* 8% " " " " "
*c* 2·3% " " " " "
*d* 30% " " " " "

TABLE II

TESTS ON ADSORPTION ELSEWHERE THAN IN THE IRON GROUP

| Taken (g.) | Result |
|---|---|
| Zn ≡ 0·2000 of ZnS<br>Mn ≡ 0·2000 of MnS<br>0·142 of $P_2O_5$ | The ZnS, weighed as sulphate, gave Zn ≡ 0·2012 g. of ZnS and contained 0·55% of the Mn taken.<br>The $MnO_2$ was ignited at 1000° C. and weighed as $Mn_3O_4$. Obtained Mn ≡ 0·1992 g. of MnS. |
| Ni ≡ 0·200 of NiS<br>Mn ≡ 0·200 of MnS<br>0·142 of $P_2O_5$ | Less than 0·1% of the Mn taken was present in the nickel sulphide. |
| Co ≡ 0·200 of CoS<br>Mn ≡ 0·200 of MnS<br>0·142 of $P_2O_5$ | Less than 0·1% of the Mn taken was present in the cobalt sulphide. |
| Ca ≡ 0·1500 of CaO<br>Mg ≡ 0·1500 of MgO<br>0·142 of $P_2O_5$ | 1·3% of the magnesium was carried down by the calcium oxalate.<br>Obtained $CaCO_3$ ≡ 0·1511 g. of CaO.<br>" $Mg_2P_2O_7$ ≡ 0·1483 g. of MgO. |
| Fe ≡ 0·1000 of $Fe_2O_3$<br>Mn ≡ 0·1000 of MnO<br>Ca ≡ 0·1037 of CaO<br>Mg ≡ 0·0963 of MgO | Iron ppt. ignited gave 0·1000 g. of $Fe_2O_3$<br>Mn in $MnO_2$ estimated as $Mn_2P O_7$ 0·1005 g. of MnO<br>Calcium was re-pptd. Ignition gave $CaCO_3$ ≡ 0·1043 g. of CaO<br>Mg ppt. ignited gave $Mg_2P_2O_7$ ≡ 0·0966 g. of MgO |

REAGENTS USED—

*Sodium periodate solution*—Dissolve 4·0 g. of the salt ($Na_2H_3IO_6$) by warming in about 190 ml. of water containing 1·5 ml. of glacial acetic acid. Dilute to 200 ml. and filter.

*Starch iodide*—Prepare 1 per cent. starch solution and in 100 ml. dissolve 10 g. of sodium bicarbonate and 1 g. of potassium iodide.

*Benzoate wash solution*—This contains 1 g. of ammonium benzoate and 2 ml. of glacial acetic acid per 100 ml.

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# ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

## Food and Drugs

**Colorimetric Determination of Iron and Manganese in Foods. L. C. E. Kniphorst** (*Chem. Weekblad*, 1946, **42**, 311–316, 328–334)—An investigation was made of the determination of iron in foods, after wet combustion, by means of sulphosalicylic acid. In the determination of iron alone, phosphates, up to a proportion of 4000 parts of phosphorus pentoxide to 1 of iron, do not interfere. The sulphosalicylic acid has a solvent action on iron phosphate. Large quantities of ammonium sulphate are without influence on the colour. In presence of calcium and magnesium salts, large quantities of ammonium salts are necessary to prevent the precipitation of calcium phosphate or of magnesium hydroxide. Manganese gives a brownish-yellow colour with the reagent, but does not interfere if the ratio of manganese to iron does not exceed 10 to 1, and the colour is matched within one hour. The method for iron and manganese together is applied to a solution, obtained by wet combustion, containing less than 10 mg. of calcium oxide, 10 mg. of magnesium oxide, 60 mg. of phosphorus pentoxide, and 1 mg. of iron. If the amount of manganese found is more than 0·1 mg., the determination should be repeated with less material.

*Procedure*—Carry out a wet combustion with sulphuric and nitric acids, completing with hydrogen peroxide in order to obtain a solution as free from colour as possible. Add 10 ml. of water, boil for 3 min., and cool. Add to the liquid a piece of Congo Red paper and a piece of litmus paper, and neutralise with aqueous ammonia so that the Congo Red paper is red and the litmus paper pale red. Then add 5 ml. of a suspension of zinc hydroxide containing 160 mg. of zinc hydroxide. This precipitates the iron. Filter the mixture and wash the precipitate with a small quantity of water. Add to the filtrate 0·1 ml. of copper sulphate solution (containing 0·01 mg. of copper), 0·4 ml. of formaldoxime reagent, and 2 ml. of 25 per cent. aqueous ammonia solution (traces of copper accelerate the colour development). After allowing the solution to stand for one hour, make the volume up to 100 ml., and compare the colour with that of standard manganese solutions. The standard contains 0·1 mg. of manganese, and is prepared with sulphuric acid in the same way as the solution to be tested. A control test, containing 0·1 mg. of iron and 0·1 mg. of manganese, is also prepared. The difference between the control and the standard gives the correction to be applied for manganese in the reagents. Dissolve the zinc hydroxide, containing the iron, in 20 ml. of hot, 4 *N* sulphuric acid, and wash the filter three times with small portions of water. Treat part of the solution, containing about 0·1 mg. of iron, with 2 ml. of 20 per cent. sulphosalicylic acid solution, approximately neutralise with aqueous ammonia, and add a few drops in excess. Sufficient aqueous ammonia must be added to remove any turbidity due to precipitated zinc phosphate. Compare the colour with a standard solution containing 0·1 mg. of iron, and also carry out a blank test on the reagents. Results obtained on a number of foodstuffs are as follows:

| Material | Iron | Manganese |
|---|---|---|
| | mg. per 100 g. | |
| Green peas | 7·5; 7·6 | 0·99; 1·18 |
| Household syrup | 30·5 | 0·73; 0·80 |
| Cooking syrup | 26·9 | 0·94 |
| Potato starch | 3·5; 3·2 | 0·53; 0·43 |
| Wheat germ | 10·8; 10·5 | 17·0; 16·9 |

G. M.

**Haemoglobin in Meat Scraps and Tankage. R. Reiser** (*Anal. Chem.*, 1947, **19**, 114–118)—According to the definition of the Association of American Feed Control Officials Inc. (Offic. Publ., 1946), meat scrap differs from tankage in that blood is excluded from the former but not from the latter. Presence of more than "such traces of blood as might occur unavoidably in good factory practice" thus constitutes adulteration.

There is evidence also that the biological value of blood meal protein for growth is low and that its biological value, palatability, and digestibility decrease with increasing temperature of preparation (Morris, *et al.*, *J. Dairy Res.*, 1936, **7**, 97; Winter, *Ohio Agr. Expt. Sta. Bull.*, 1929, 436). There is need, therefore, for a method to determine blood meal in meat scraps and tankage and for a means of determining the degree of heat treatment to which a sample of blood meal has been subjected.

A method for the determination of blood in packing-house by-products has been reported (Reiser *et al.*, *Ind. Eng. Chem.*, *Anal. Ed.*, 1942, **14**, 851; *cf.* ANALYST, 1942, **67**, 302). The sample, after extraction with ether, was boiled in 1 per cent. sodium hydroxide solution, the mixture was added to pyridine, made up to a definite volume with water, and filtered. An aliquot of the filtrate was reduced with sodium hyposulphite ($Na_2S_2O_4$) and the increase in optical density at 550 mμ. was determined in a spectrophotometer by comparing it with that of the unreduced solution.

It has been found that dried blood dissolves more readily in an alcoholic solvent, that a greater colour intensity per unit of haemoglobin is produced, that no loss of colour occurs during boiling, and that preliminary extraction with ether is then unnecessary. Variations in the optical density of the haemochromogens of blood are so great that the customary standards cannot be used, and it thus became necessary to develop a new method for the determination of the extinction coefficient of the haemoglobin in blood meal.

The effects of conditions such as the alcoholic concentration, alkalinity, pyridine concentration, and particle size of the sample on the intensity and stability of the resulting haemochromogen were studied exhaustively. Alcoholic solutions produced more colour than aqueous solutions with no change in the colour intensity in the alcoholic concentration range of 20 ml. to 60 ml. per 100 ml. of solution. Maximum solubility of the blood meal occurred when the alcoholic concentration was 50, 55, or 60 ml. per 100 ml. Complete solution in 5 per cent. sodium hydroxide was obtained in 10 min. with blood meal and in 20 min. with tankage. Visual observations showed that boiling for 20, 10, and 7 min. was necessary to attain complete solution of blood meal samples ground to pass through 20-, 40-, and 60-mesh sieves, respectively. Samples should therefore be ground to pass a 40-mesh sieve. Pyridine aids solution and should therefore be added as part of the solvent.

To determine the extinction coefficient of haemochromogen in blood meal 19 samples were obtained from 13 sources with, in many instances, details of the drying process used. Iron was determined in each sample by digesting 50 mg. in a 100-ml. flask with 4 ml. of sulphuric acid and completing the digestion with 30 per cent. hydrogen peroxide. About 50 ml. of water and 2 ml. of 10 per cent. iron-free hydroxylamine hydrochloride solution were then added, followed by 1 ml. of 1·5 per cent. alcoholic *o*-phenanthroline solution. Aqueous ammonia was added until the liquid changed the colour of Congo Red paper and the resulting colour was read in a photo-electric colorimeter with a 440 mμ. filter. The iron content multiplied by 100 divided by 0·335, the iron content of haemoglobin, gave the haemoglobin content. The optical density of the haemochromogen of each sample of blood meal was then determined by boiling 100 mg. for 30 min. in 100 ml. of a solution containing 55 ml. of 95 per cent. alcohol, 5 g. of sodium hydroxide, 5 ml. of pyridine, and water to 100 ml. A 10- or 20-ml. aliquot was then reduced with a few mg. of sodium hyposulphite ($Na_2S_2O_4$) and the increase in optical density of the reduced solution over that of the unreduced solution at 553 mμ. was determined. The extinction coefficient of the haemoglobin was then calculated from the haemoglobin content by use of the relation $e = D/CL$, where $e$ is the extinction coefficient, $D$ the optical density of the haemochromogen, $C$ is the percentage of haemoglobin in the solution, and $L$ is the depth of the solution in centimetres. It was found that the extinction coefficient of blood that had been heated for less than 7 hr. in steam-jacketed dryers at less than 55 lb. pressure was 5·4, whereas with blood that had been heated for over 7 hr. at over 55 lb. pressure the corresponding coefficient was 3·6. An investigation of the coefficient of extinction of fresh beef blood that had been submitted to varying degrees of heat for varying periods showed that, according to the heat-treatment applied, the extinction coefficient reached a minimum value of 5·4 and, with more drastic treatment, a minimum value of 3·3, these being in close agreement with the corresponding values found for blood meal.

*Procedure*—To 1 g. of finely ground meat scraps or 0·5 g. of tankage in a 300-ml., ground-glass-jointed Erlenmeyer flask add 100 ml. of a solution containing 55 ml. of 95 per cent. alcohol, 5 ml. of pyridine, 5 g. of sodium hydroxide, and water to volume. Heat under refluxing conditions for 30 min., cool, and centrifuge. To 10 or 20 ml. of the clear supernatant liquid add a few mg. of sodium hyposulphite ($Na_2S_2O_4$) and determine the increase in the optical density at 553 mμ. of the reduced solution over that of the unreduced solution. Calculate the haemoglobin content from the relation $Hb = 100DV/100eLS$, where $Hb$ is the percentage of haemoglobin in the sample, $e$ is the extinction coefficient, $D$ is the increase of optical density, $L$ is the depth of solution in cm., $S$ is the weight of the sample in g., and $V$ is the volume of the solution. Extinction coefficients for this calculation fall into two groups, depending upon the time and

temperature of drying. If the blood meal has been heated for over 7 hr. in steam-jacketed dryers at over 55 lb. pressure the extinction coefficient 3·6 should be used; if the product has been heated for less than 7 hr. at less than 55-lb. pressure or if the treatment is unknown, the coefficient 5·4 should be used. The result thus obtained represents the minimum amount of haemoglobin in the sample; the correct value may be 50 per cent. higher. When blood meal of known haemoglobin content was added to meat and bone scraps also of known haemoglobin content the recovery of haemoglobin ranged from 93 to 104 per cent., with an average recovery of 98·3 ± 2·3 per cent.

The amount of blood in a sample may be estimated as blood meal instead of as haemoglobin from the average haemoglobin content of blood meal, *viz.*, 76 per cent., but this procedure can provide only an approximate figure. The amount of haemoglobin in meat scrap "as might occur unavoidably in good factory practice" remains to be determined. More data are necessary, but the results of this investigation suggest that 1·0 or 1·5 per cent. may be the limit. Values of 2 per cent. or more must be due to careless separation of the blood or to actual adulteration to raise the protein content. The two values for the extinction coefficient of the haemoglobin in blood meal may be used as measures of the heat treatment that any given sample of blood meal has received, and, if it is true that blood meal prepared at high temperatures has a decreased biological value, the extinction coefficient is a measure of the biological value of a given sample.

A. O. J.

**Fatty Acids of Corn (Maize) Oil. F. J. Baur, jun. and J. B. Brown** (*J. Amer. Chem. Soc.*, **1945, 67,** 1899–1900)—Corn oil fatty acids were methylated, without previous separation into saturated and unsaturated fatty acids, and the esters were fractionated. The composition of the several fractions was calculated from iodine values, molecular weights, and thiocyanometric equations. From these results the percentage composition of the acids was calculated as: myristic, 0·1; palmitic, 8·1; stearic, 2·5; hexadecenoic, 1·2; oleic, 30·1; linoleic, 56·3; above $C_{18}$, 1·7. The linoleic acid content is considerably higher than that obtained by Baughman and Jamieson (*Ibid.*, 1921, **43,** 2696, ANALYST, 1922, **47,** 171), whose calculations of percentage of fatty acids gave: palmitic, 7·8; stearic, 3·6; arachidic, 0·4; lignoceric, 0·2; oleic, 46·3; linoleic, 41·7. These workers separated the saturated and unsaturated acids of corn oil by the lead salt - ether method and based their calculations on iodine and saponification values and on the bromine derivatives of the unsaturated acids. Similarly, Longenecker (*J. Biol. Chem.*, 1939, 9, 13), who separated the saturated and unsaturated acids by a modified Twitchell method and fractionated the methyl esters from each group, obtained only 34·0 per cent. of linoleic acid; the other fatty acid percentages obtained were: myristic, 1·7; palmitic, 11·0; stearic, 2·9; hexadecenoic, 1·6; and oleic, 48·8.

E. B. D.

**Microscopical Differentiation of Some Common Mustard Seeds with Polarised Light. G. L. Keenan** (*J. Assoc. Off. Agric. Chem.*, **1946, 29,** 173–175)—The common commercial mustard seeds resemble each other structurally in transverse section, especially in the epidermal layer of mucilage cells. This mucilage is particularly noticeable when surface sections are mounted in 50 per cent. glycerol, and examined between crossed Nicols. In some species the mucilage is arranged round a central core in the cell, as in white mustard (*Brassica alba*), in Montana brown and Montana oriental mustard (*B. juncea*), and in charlock (*B. arvensis*). In sarepta or brown mustard (*B. besseriana*) the core is not so noticeable and it appears to be absent from black mustard (*B. nigra*).

The polarisation crosses are much larger, sharper, more refractive, and more numerous in white mustard than in the other species, and the arms of the cross measure about 48 $\mu$. Montana brown and Montana oriental mustards show less numerous, less sharply delineated, smaller crosses with arms measuring about 30 $\mu$. In sarepta or brown mustard the crosses are infrequent and not as large as those of white mustard. No crosses are shown by the mucilage cells of black mustard. In charlock the crosses are infrequent and the arms measure about 30 $\mu$. In this species the contents of the cells of the palisade layer are coloured red by acidified chloral hydrate solution.

A. O. J.

**Determination of Sulphathiazole and other Sulpha Drugs in Honey. C. E. Shepard and H. J. Fisher** (*J. Assoc. Off. Agric. Chem.*, 1946, **29,** 175–177)—Sulphathiazole has recently been introduced for the treatment of bees in hives affected with foul brood, the drug being administered in a 50 per cent. sugar solution containing 0·5 g. per gallon. Some of the thiazole appears in the honey and as the amount is of the order of a few parts per million, the colorimetric method of Bratton and Marshall (*J. Biol. Chem.*, 1939, **128,** 537; ANALYST, 1939, **64,** 524) as modified by Gordon and Dunn (*Biochem. J.*, 1941, **35,** 1231) for determination of sulpha compounds in urine was adapted to their determination in honey.

*Procedure*—Mix 10 g. of the honey with 50 ml. of water and 5 ml. of 4 *N* hydrochloric acid and dilute to 100 ml. In 10 matched test tubes place 1, 2, 3, . . . 10 ml., respectively, of the standard sulphathiazole solution (*infra*) and dilute the contents of each tube to 10 ml. with a solution

prepared by diluting 18 ml. of 15 per cent. trichloroacetic acid to 100 ml. For a blank determination place 10 ml. of the diluted trichloroacetic acid solution in another tube. These 11 tubes then contain 0, 3, 6, 9, . . . 30 µg. of sulphathiazole, respectively. In another tube place 10 ml. of the honey solution (≡1 g. of honey) and develop the colour in the sample and standard tubes at the same time by the following procedure.

Add 1 ml. of freshly prepared, 0·1 per cent. sodium nitrite solution and, after 3 min., add 1 ml. of 0·5 per cent. ammonium sulphamate solution and, after a further 3 min., add 1 ml. of 0·1 per cent. *N*-(1-naphthyl)-ethylenediamine solution. By comparing the sample tube with the standard tubes estimate the amount of sulphathiazole present to the nearest µg.

The red colour develops immediately, is relatively intense, and is stable for several hours. The method could probably be developed as a spectrophotometric method, but this might require filtration of the honey solution. With the honeys used, visual comparison with the series of standard solutions was simpler, filtration was unnecessary, and no interference from the colour of the honey itself was noted at the dilution used. Should other sulpha drugs be used it would be necessary only to substitute these for sulphathiazole in the standard solutions. In honeys from eight hives in which sulphathiazole had been fed to the bees the amount in the honey ranged from 1 to 20 p.p.m. In samples from six hives not subjected to this treatment no sulphathiazole was found in five, and the trace of red colour given by the sixth corresponded to a sulphathiazole content of less than 0·1 p.p.m.

The stock standard solution contains 200 mg. of sulphathiazole in 1 litre of water. To prepare the working standard solution dilute 5 ml. of the stock solution to 100 ml., mix 30 ml. of this solution with 18 ml. of 15 per cent. trichloroacetic acid solution, and dilute to 100 ml. Each millilitre of this solution contains 3 µg. of sulphathiazole. A. O. J.

**Microchemical Detection of Vanillin and Bourbonal. A. M. G. Rutten** (*Chem. Weekblad*, 1946, **42**, 95, 119)—Most of the microchemical reactions for vanillin and bourbonal are unsatisfactory, especially in presence of other aromatic aldehydes. The following method is claimed to give a sensitive and trustworthy test for the two compounds.

*Procedure*—Add one drop of the solution to be tested to a drop of 0·05 per cent. aqueous solution of sulphanilic acid on a microscope slide, and allow the liquid to dry in air. Bourbonal gives yellow starry rosettes and "wheatsheaf" bundles; vanillin forms thin branching crystals. Esters, aldehydes, phenols, and colouring matter do not interfere. For essences containing glycerol, or vanilla sugar, extract the material with a small amount of light petroleum, add a drop of sulphanilic acid solution and a few drops of 96 per cent. alcohol, and allow to evaporate on a watch glass. The reaction occurs between two molecules of sulphanilic acid and one of the aldehydic compound. The coloration disappears, reversibly, above 80° C. Photographs of the crystalline forms are given. G. M.

**Effect of the Anaesthetic and the Rate of Injection of Digitalis upon its Lethal Dose in Cats. H. G. O. Holck, K. K. Kimura, and B. Bartels** (*J. Amer. Pharm. Assoc., Sci. Ed.*, 1946, **35**, 366–370)—It has been reported that different anaesthetics employed in the biological assay of digitalis by the cat method influence the minimum lethal dose of this substance. The fatal dose is reported to be 19 to 20 per cent. higher after urethane than after ether (Edmunds, Moyer, and Shaw, *Ibid.*, 1937, **26**, 290; Holck, Smith, and Shuler, *Ibid.*, 1945, **34**, 90), but conflicting statements exist that the two anaesthetics do not differ in effect in this application (David and Rajamanickam, *Quart. J. Pharm.*, 1934, **7**, 36).

Cats were used anaesthetised with urethane or ether, and were injected with different concentrations of digitalis in parallel experiments.

The dilutions were 1·60, 2·26, 3·20, 4·53, 6·40, and 9·05 per cent. of U.S.P. Digitalis Reference Standard (1942) Tincture, 24 cats being used at each concentration. The results were expressed as the lethal doses per kilogram of cat. The hearts were weighed in addition, but the gain in accuracy did not compensate for the extra work involved.

The two curves relating the logarithms of the median lethal doses (mg. per kg.) to the concentrations of the corresponding digitalis solutions, after either urethane or ether anaesthesia, were parallel.

The less concentrated digitalis preparations gave smaller values for the median lethal dose uniformly throughout the concentration range studied. At equal concentrations of the injection material the lethal dose of digitalis was 6·5 per cent. greater with urethane than with ether anaesthesia. The difference was statistically significant.

The concentration of digitalis with which the lethal dose in cats was smallest was 1·76 per cent. of the standard tincture. When weaker or stronger concentrations were used, larger doses were needed to cause cardiac arrest.

The data presented are statistically analysed and show the errors to be of the same magnitude using either urethane or ether anaesthesia. R. H. T.

**Erratum**: July issue of **1947**, p. **310**: In the heading of the first abstract the name of the third author should be, not "J. Warren," but "J. W. Sackett."

## Biochemical

**Estimation of Ethyl Alcohol in Blood. J. Rochat** (*Helv. Chim. Acta*, 1946, **29**, 819–830)—The original method, introduced by Nicloux, gives results that may be in error by as much as 10 per cent. Subsequently, Nicloux published a modified method (*Bull. Soc. Chim. biol.*, 1931, **13**, 857), designed for use in research work demanding greater accuracy, but the older method has nevertheless continued in use for medico-legal work, mainly because the newer method proved to be more complicated. A modification has now been devised that is simple to operate and gives more accurate results than the original method.

*Procedure*—Put 5 to 15 g. of the fresh blood into a 300-ml. flask, and add 6·5 volumes of a saturated solution of picric acid. If the blood is clotted, break up the clot with a spatula or scissors and add it to the flask. Close the flask with a rubber bung, shake carefully, and leave overnight. Attach the flask to a distillation apparatus of the type described by Nicloux (*loc. cit.*), with a tin condenser to which is attached a glass tube dipping into a few ml. of water contained in a 50-ml. graduated cylinder. Distil at ordinary pressure until two-fifths of the contents of the flask have collected in the graduated cylinder. Stopper the cylinder, mix the contents, and note the volume, V ml. Pipette 5 ml. of a solution (approximately 0·02 *N*) of Mohr's salt (dissolve 7·8 g. of the solid ferrous ammonium sulphate crystals in 1 litre of water containing 20 ml. of concentrated sulphuric acid) into a conical flask, add 40 to 50 ml. of water, and a few drops of concentrated sulphuric acid, and then add from a micro-burette 0·1 *N* potassium permanganate until a permanent pink tinge is produced. Record the volume *a*. Into another flask, pipette 5 ml. of the solution of Mohr's salt, add 0·50 ml. of potassium dichromate solution (8·475 g. per litre) from a micro-burette, followed by water and sulphuric acid as before, and titrate the excess of Mohr's salt with 0·1 *N* potassium permanganate solution. Record the volume *b*. Each titration should be carried out at least twice, and the average used in the calculations. Then 0·50 ml. of potassium dichromate solution is equivalent to $(a - b)$ ml. of 0·1 *N* potassium permanganate solution.

Carry out a preliminary titration of the distillate. Pipette 5 ml. into a 150-ml. beaker, add 6 to 7 ml. of concentrated sulphuric acid and then run in rapidly, from a micro-burette, potassium dichromate solution until a distinct yellowish colour persists. Note the volume. Repeat the oxidation on another 5-ml. portion of the distillate, adding first a volume of potassium dichromate solution equal to that found in the preliminary experiment, and then a volume of concentrated sulphuric acid equal to that of the combined volumes of the test and dichromate solutions plus 1·5 ml. The acid is added down the side of the beaker and mixed by a rapid rotatory movement. Leave for 25 to 30 sec., dilute with about 50 ml. of water, and pipette 5 ml. of the solution of Mohr's salt to reduce the excess of potassium dichromate, and titrate back with 0·1 *N* potassium permanganate. If *c* and *d* are the volumes of potassium dichromate and potassium permanganate solutions, then the volume (*u*) of potassium dichromate solution used to oxidise the alcohol plus oxidisable impurities is equivalent to

$$c - [(a - d)/2(a - b)]$$

Repeat the distillation using water instead of the sample of blood, and oxidise 5 ml. of the distillate as described above. If *r* is the volume of potassium dichromate solution used, then the volume used to oxidise the alcohol only is $(u - r)$ and the concentration of alcohol in the blood (ml. per kg.) $= \frac{u - r}{2} \times \frac{V}{\text{wt. of blood}} \times F$, where *F* is an empirical factor which, for aqueous solutions, is 0·97; for fluorinated blood, 0·98; and for coagulated blood, 0·99. The method gives results with an error of only 1 to 2 per cent. Qualitative tests for acetone, aldehydes, etc. may be carried out on portions of the distillate. If acetone is present, satisfactory determinations of alcohol can be made by a modification of the method described, in which the time allowed for the reaction and the excess of dichromate used are reduced.

The method can also be used, with modifications, for the estimation of alcohol in only 1 g. of blood. Transfer the sample, with the aid of 4 ml. of water and 10 ml. of saturated picric acid solution, to a 50- or 100-ml. distillation flask. Distil 4 to 5 ml. through a micro-condenser of tin, the end of which dips into a small volume of water. Distil another 4 to 5 ml., interrupting the heating 2 or 3 times to allow the distillate to be sucked up into the condenser; on resuming the heating, the liquid is forced back into the receiver, thus rinsing out the condenser. Measure the volume of distillate, and to a 2-ml. portion add the requisite volume of potassium dichromate solution (3·39 g. per litre), followed by a volume of concentrated sulphuric acid equal to the combined volumes of the dichromate and test solutions plus 1 ml. Add a solution of Mohr's salt (0·01 *N*) and titrate the excess with 0·02 *N* potassium permanganate. Carry out a blank determination and calculate the result as described above. F. A. R.

**Chromatographic Adsorption of Amino-Acids on Organic Exchange-Resins. C. S. Cleaver, R. A. Hardy, and H. G. Cassidy** (*J. Amer. Chem. Soc.*, 1945, **67**, 1343–1352)—Several attempts have been made to separate amino-acids by adsorption on organic exchange resins, generally with the solution of a specific problem in

mind. In the present paper, an examination is made of the fundamental problems of the exchange process with the object of clarifying the mode of operation of the organic exchange resins in their application to the amino-acids. Two resins were used, a cation exchanger, Amberlite IR-100, and an acid-binding resin, Amberlite IR-4. The former was conditioned by being washed successively with water, 5 per cent. hydrochloric acid solution until the effluent was acid, water, 5 per cent. sodium carbonate solution or aqueous ammonia until the effluent was basic, and then water; this cycle was repeated two to four times until no coloured material was given off at any time during the last cycle. Amberlite IR-4 was conditioned in a similar way with water, 5 per cent. hydrochloric acid solution, water, 5 per cent. sodium carbonate solution or 2 per cent. sodium hydroxide solution, and then water; five or six cycles were usually necessary. With IR-100 the cycle was stopped at the point that gave the desired resin: ($H^+R^-$), ($NH_4^+R^-$) or ($Na^+R^-$). The Amberlite IR-4 was left at the point where it was activated by sodium carbonate or hydroxide, symbolised thus: IR-4 (*$Na_2CO_3$), and IR-4 (*NaOH).

The hydrogen resin, IR-100 ($H^+R^-$), produced an equilibrium *p*H of 1·9 to 2·9 whatever the *p*H of the amino-acid solution, whilst the sodium resin, IR-100 ($Na^+R^-$), had less effect on *p*H. At lower equilibrium concentrations the hydrogen resin adsorbed more, and at high equilibrium concentrations less, amino-acid than did the sodium resin. The smaller is the amount of resin used, the greater is the specific adsorption, a result that is inconsistent with simple adsorption and is presumably associated with the exchange. The resin ($H^+R^-$) appeared to behave like a strong, but very insoluble, acid.

The behaviour of the resins when amino-acid solutions percolated downwards through columns of the resins in a glass tube was studied. Two or more amino-acids were used, one not adsorbed and the other adsorbed. The one that was not adsorbed was used to estimate the amount of liquid initially in the column, whilst the other indicated the exchange capacity of the resin. The two together showed whether the resin would be suitable for separating the mixture. The most convenient particle size was from 60- to 80-mesh. No advantage resulted from the use of a long, narrow column, as compared with a shorter, wider column containing the same weight of resin. The higher is the flow rate, the earlier is the break-through of amino-acid, but the concentration of the amino-acid solution could be varied over a ten-fold range without affecting its behaviour on the column.

The adsorption of histidine in presence of other amino-acids was studied in detail. When alanine was present, histidine was not quantitatively retained on the ammonium resin, ven in the first 10 ml. of percolate. The reason for this is that the ammonium resin tends to yield a nearly neutral solution when it acts as an exchanger, and under this relatively low hydrogen ion concentration the histidine is not maintained wholly in the cationic form and therefore not in a state to be completely adsorbed by the ammonium ion. In presence of glutamic acid, however, histidine was retained more strongly by the resin, since the *p*H of the solution is lower than with alanine. A similar difference in behaviour was observed with the sodium resin. When ternary mixtures were investigated, it was found that both histidine and arginine were well adsorbed on ammonium resin in presence of glutamic acid; the histidine leaked through slightly, but both amino-acids broke through at the same point.

Following these preliminary experiments, an attempt was made to separate a mixture of a basic, an acidic, and a neutral amino-acid. A solution (200 ml.) of arginine hydrochloride (1·0 g.), glutamic acid (0·6 g.), and glycine (0·34 g.) was passed through 10 g. of IR-100 ($Na^+R^-$) at the rate of 2 ml. per min. The column was washed with three, 10-ml. portions of water and the entire percolate was collected. The *p*H of this solution was adjusted to 3, and the solution made up to 250 ml. Of this solution, 200 ml. were passed through 6 g. of IR-4 (*NaOH) at the rate of 2 ml. per min. and the column was washed with three, 10-ml. portions of water and the percolate made up to 200 ml. The IR-100 retained virtually all the arginine and held back practically none of the other two amino-acids. The second column retained 60 per cent. of the glutamic acid and no glycine. An attempt to separate glutamic and aspartic acids on IR-4 was not successful. F. A. R.

**Separation and Determination of Primary, Secondary, and Tertiary Alkaryl Amines (Ring-methylated and Nitrogen-methylated Homologues of Aniline). W. Seaman, A. R. Norton, J. T. Woods, and H. N. Bank** (*J. Amer. Chem. Soc.*, 1945, **67**, 1571–1578)—The method of Hinsberg (*Ber.*, 1890, **23**, 2962) was found to be unsatisfactory for the separation of aniline and its homologues, and an improved method was developed in which the toluenesulphonamides of the primary and secondary amines are formed and separated from unreacted tertiary amines. The tertiary amines are estimated by extraction from a chlorobenzene solution by means of hydrochloric acid, whilst the sulphonamides of the primary and secondary amines are hydrolysed separately, and the liberated amines are titrated potentiometrically in acid solution by means of standard alkali.

*Procedure—Reaction with* p-*toluene sulphonyl chloride*—To 6 to 7 g. of the sample in a dry, 250-ml.

flask, add 50 ml. of benzene. Cool in ice, and rapidly add 20·0 g. of *p*-toluene sulphonyl chloride in 25 ml. of dry pyridine. Leave for 30 min. in a stoppered flask in the ice-bath, and then remove the stopper, rinse it with benzene, and attach a reflux condenser to the flask. Pour 10 ml. of water in small portions at a time down the condenser, while cooling the flask in ice. Leave for 30 min. in the ice-bath.

*Separation of tertiary from primary and secondary amines*—Transfer the reaction mixture quantitatively by means of water and benzene to a 2-litre flask and add 100 ml. of 5 *N* sodium hydroxide. Steam-distil, collecting the distillate under 30 ml. of concentrated hydrochloric acid until 500 ml. have collected. Test the last runnings for amine, to ensure that distillation is complete, by making alkaline and observing whether the solution becomes turbid. Transfer the distillate to a separating funnel, add concentrated hydrochloric acid until acid to Congo red paper and remove the lower aqueous layer. Wash the benzene layer with two, 50-ml. portions of *N* hydrochloric acid and add the washings to the aqueous layer (Solution A). Save the benzene layer for subsequent use (Solution B).

*Separation of sulphonamides*—Leave the alkaline residue from the steam-distillation in the flask until the oil has settled, and decant the aqueous liquid through a filter paper; if the filtrate is turbid, repeat the filtration. Heat the oil nearly to boiling with *N* sodium hydroxide with shaking, and cool in ice. Filter through the same filter paper as before and repeat the procedure with 200 ml. of *N* sodium hydroxide and several 100-ml. portions of water until a 25-ml. portion of the filtrate does not become turbid or opalescent on acidification. Wash any oil from the filter paper into the flask with hot water and save the filter paper.

*Estimation of sulphonamides of primary amines*—Transfer the combined alkaline filtrates and washings to a separating funnel and acidify to Congo red paper with concentrated hydrochloric acid. Extract the liberated sulphonamides once with 100 ml., and twice with 50 ml. of benzene. Dry the extracts over anhydrous calcium sulphate and transfer quantitatively through a filter into a tared, 250-ml., glass-stoppered flask containing boiling-chips. Distil off the benzene and dry the residue at 110° C. to constant weight. This gives the weight of sulphonamides of primary amines ($W_p$).

*Estimation of sulphonamides of secondary amines*—Transfer the oil by means of Solution B to a 500-ml. separating funnel. Rinse the flask several times with benzene and water, and macerate the filter paper with two or three 50-ml. portions of benzene. Add the rinsings to the separating-funnel, shake, and remove the aqueous layer. Wash the latter with 35 ml. of benzene and add the washing to the main benzene layer. Dry over anhydrous calcium sulphate, filter into a tared, 250-ml. flask, and evaporate and weigh as described above. This gives the weight of sulphonamides of secondary amines ($W_s$).

*Regeneration of primary and secondary amines*—To the flasks containing the sulphonamides, add 5 ml. of diluted hydrochloric acid (1 + 1) per g. of sulphonamide, and heat under reflux until the oily layers dissolve or become crystalline (75 to 100 hr.). Test for completeness of hydrolysis by diluting a 1-ml. portion with 10 ml. of water; a turbidity indicates that hydrolysis is incomplete. Dilute the reaction mixture with 10 to 15 volumes of water, transfer with the aid of water and benzene to a separating funnel and, if necessary, extract with two, 100-ml. portions of benzene to dissolve unsaponified sulphonamide. Extract the combined benzene extracts with two, 35-ml. portions of *N* hydrochloric acid and add the acid extracts to the main solution. Dry the benzene solution over anhydrous calcium sulphate, dry, and weigh as before. This gives the weights of unhydrolysed sulphonamides of primary amines ($W_{pu}$) and secondary amines ($W_{su}$). Treat the combined acid solution with 5 *N* sodium hydroxide until only slightly acid, cool in an ice-bath, transfer to a 500-ml. separating-funnel, and make strongly alkaline with 5 *N* sodium hydroxide. Extract the amines with three, 100-ml. portions of benzene, excluding any insoluble material. Extract the combined benzene extracts with three 100-ml. portions of *N* hydrochloric acid, again excluding insoluble matter as far as possible. Transfer the acid extracts to a beaker and add 5 *N* sodium hydroxide until the *p*H is 1·0. Boil gently for 5 min. to expel carbon dioxide, cool to room temperature, and saturate with a small excess of sodium chloride. Titrate the solution with *N* sodium hydroxide to *p*H 1·8 and then take *p*H readings after the successive addition of 0·2-ml. portions of alkali until a *p*H of 3·5 is reached. Now add *N* sodium hydroxide to *p*H 6·0 and again take readings after addition of 0·2 ml. portions of alkali to *p*H 10. One inflection ($J$) occurs at about *p*H 2·5 and a second ($K$) at about *p*H 7. Record the mg.-equivalents of alkali ($J_p$ and $K_p$) consumed at the first and second inflection points, respectively, for the primary amines and the corresponding values ($J_s$ and $K_s$) for the secondary amines. Then the number of mg.-equivalents of regenerated primary and secondary amines equals, respectively, $L_p = K_p - J_p$ and $L_s = K_s - J_s$. From these values and the weight of sulphonamides, the percentage weight of amines can be calculated. A correction must, however, be applied for the unhydrolysed sulphonamide and, for this, the nature of the unhydrolysed sulphonamide must be known. In the present work, the unhydrolysed

sulphonamide of the primary amine was mainly *p*-toluene sulphonmesidide and that of the secondary amine *p*-toluene sulphonmonomethyl-*p*-toluidide, with molecular weights of 289·4 and 275·4, respectively. The corrections in terms of mg.-equivalents are therefore $K_p = 1000W_{pu}/289{\cdot}4$ and $K_s = 1000W_{su}/275{\cdot}4$, respectively, and

Percentage of primary amines =

$$\frac{100W_p - 15{\cdot}42\ [L_p + (1000W_{pu}/289{\cdot}4)]}{\text{Wt. of sample in grams}}$$

Percentage of secondary amines =

$$\frac{100W_s - 15{\cdot}42\ [L_s + (1000W_{su}/275{\cdot}4)]}{\text{Wt. of sample in grams}}$$

*Estimation of tertiary amines*—Transfer Solution A, after cooling, to a separating-funnel, make alkaline with 5 *N* sodium hydroxide and, extract once with 150 ml., once with 75 ml., and three times with 50-ml. portions of ether. Dry the combined ethereal extracts over anhydrous calcium sulphate, filter, and transfer to a tared flask containing boiling-chips. Distil off the ether, add 75 ml. of pure chlorobenzene, and distil the mixture carefully through an efficient fractionating column until the b.p. of chlorobenzene (132° C.) has been reached and an additional 10 to 15 ml. of distillate have collected. Weigh the flask to obtain the weight ($W_C$) of the chlorobenzene solution of the tertiary amine (Solution C). Prepare an apparatus consisting of a glass bulb of convenient size joined by means of a glass tube with a graduated scale to a second larger bulb, through the top of which liquid can be introduced by means of a small funnel. Calibrate the scale in terms of weight of chlorobenzene by putting into the apparatus known weights of chlorobenzene, adding 1 ml. of *N* hydrochloric acid, extracting as in the estimation of tertiary amines and noting the scale reading. Fit the dry, calibrated apparatus with a cork stopper, and weigh. Put sufficient of Solution C into the apparatus to come to the top of the scale and weigh the apparatus again to obtain the weight of Solution C taken ($W_Q$). Now add 15 ml. of *N* hydrochloric acid, shake for about 5 min., and centrifuge. Immerse in a thermostat at 25·0 ± 0·2° C. for 30 min., and record the scale reading corresponding to the interface. Repeat the extraction with fresh 15-ml. portions of *N* hydrochloric acid until constant differences are observed in successive scale readings; 3 or 4 extractions are generally necessary. This constant difference is caused by the slight solubility of chlorobenzene in *N* hydrochloric acid. Let $f$ be the correction factor for this solubility, $n$ be the number of 15-ml. portions of hydrochloric acid used, and $h$ be the first scale reading at which constant differences are obtained, then $h$ (corr.) $= h + (f \times n)$. From the calibration constants of the apparatus, calculate the weight of chlorobenzene ($W_B$) corresponding to the scale reading $h$ (corr.). Then $W_Q - W_B$ is the weight of tertiary amine in the weight $W_Q$ of the chlorobenzene solution, and percentage of tertiary amines =

$$\frac{W_C\ (W_Q - W_B)}{W_Q \times \text{wt. of sample in grams}} \times 100$$

Where the method was used for the estimation of known amounts of primary, secondary, and tertiary amines in six different mixtures, the error exceeded ± 2·3 per cent. in only 2 analyses out of 18.

F. A. R.

# Organic

**Quantitative Method for Aconitic Acid and Aconitates. E. J. Roberts and J. A. Ambler** (*Anal. Chem.*, 1947, **19**, 118–119)—Balch, Broeg, and Ambler (*Sugar*, 1945, **40**, 32; 1946, **41**, 46) found that dilute, aqueous solutions of aconitic acid evolve carbon dioxide during evaporation by heat at normal temperatures and pressures, but the decarboxylation proceeds too slowly for analytical purposes. It was observed that, although aconitic acid is stable in hot, glacial acetic acid, some aconitates evolve carbon dioxide when boiled in this medium, the decarboxylation being very rapid with the soluble alkali aconitates, slow with the slightly soluble cadmium, calcium, and calcium-magnesium salts and extremely slow with the very insoluble lead salt. When, however, an excess of potassium acetate is added to suspensions of the more insoluble aconitates in acetic acid, and the mixtures are heated to boiling point, decarboxylation proceeds rapidly and is complete in from 30 to 40 min., each molecule of aconitic acid (or each aconitate radicle in an aconitate) yielding 1 molecule of carbon dioxide according to the reaction $C_6H_6O_6 \rightarrow CO_2 + C_5H_6O_4$. This principle can be applied to the determination of aconitic acid and aconitates.

The apparatus consists of a 250-ml. Erlenmeyer flask heated by an electric plate and connected with a tube through which a stream of carbon-dioxide-free air is introduced into the flask above the level of the liquid and with a short reflux condenser, the top of which is connected with a wash-bottle containing water for removing acetic vapour from the gas and air mixture. The wash bottle, in turn, is connected with a suitable carbon dioxide absorption train.

*Procedure for dry solids.*—To 1 to 2 g. of aconitic acid or 2 to 5 g. of aconitate in the flask add 75 to 100 ml. of "empyreuma free" glacial acetic acid, some carborundum chips, and 5 or 10 g. of potassium acetate, using the larger amount for insoluble aconitates. Connect the flask with the air inlet tube and with the condenser, attach the wash-bottle, and pass a slow stream of carbon-dioxide-free air through the system for 15 to 20 min. Start

heating the flask and attach the carbon dioxide absorption train and maintain the passage of the slow stream of air while the reaction mixture is heated under reflux for 1 hr. Then disconnect the absorption train and determine the carbon dioxide absorbed.

*Procedure for aqueous solutions*—Dilute an amount of solution containing from 0·5 to 2·0 g. of organic acid, calculated as aconitic acid, to about 200 ml. with carbon-dioxide-free water, adjust the *p*H of the solution to 6·0 to 6·2 with either acetic acid or sodium hydroxide solution and add, with stirring, 50 ml. of saturated, neutral lead acetate solution. Collect the precipitate on a strong filter paper fluted to fit a Hirsch or a small Buchner funnel and pre-coated with a thin layer of finely divided asbestos. Wash the paper and precipitate once with water and drain completely by suction. Discontinue the suction and fill the paper with acetone, carefully manipulating the precipitate so that the acetone penetrates it thoroughly. Drain off the acetone and repeat the extraction. Finally, drain the acetone through by suction and maintain the suction until the paper is dry. Dry the precipitate and paper at 100° to 105° C. for 0·5 hr. Place the paper and precipitate in the decarboxylation flask, add 100 ml. of acetic acid, 10 g. of potassium acetate, and some carborundum chips and proceed as directed for dry solids.

The carbon dioxide may be absorbed and determined by any standard method. In the work reported it was determined volumetrically by precipitation of the carbonate with barium chloride solution and titration of the residual alkalinity according to Reid and Weihe's modification (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 271) of Winkler's method. For this and similar volumetric methods 1 ml. of *N* sodium hydroxide ≡ 0·087 g. of aconitic acid; for gravimetric methods, 1 mg. of carbon dioxide ≡ 3·954 mg. of aconitic acid.

If carbonates or bicarbonates are present, acidify the solution strongly with acetic acid and remove carbon dioxide by aeration at room temperature. Neutralise the solution and proceed with the precipitation and decarboxylation of the lead salt as already described. When solid aconitates are contaminated with carbonates, two determinations of carbon dioxide are necessary. For total carbon dioxide, set up the apparatus with a separating funnel delivering into the decarboxylation flask. Proceed as already described, but at the end of the decarboxylation period allow the reaction mixture to cool until refluxing stops, keeping the absorption train attached and maintaining the current of air at such a rate as to prevent backward suction. Add 100 ml. of carbon-dioxide-free water through the funnel and heat the diluted mixture under refluxing conditions for a further 30 min. to ensure complete decomposition of the carbonates. Determine the total carbon dioxide evolved and calculate it as per cent. of aconitic acid. Determine the carbon dioxide from the carbonates by dissolving a second portion in hydrochloric acid and aerating at room temperature for 1 hr. (MacIntire and Willis, *J. Ind. Eng. Chem.*, 1915, **7**, 227; ANALYST, 1915, **40**, 251), calculating the carbon dioxide obtained as per cent. of aconitic acid. For the actual aconitic acid in the sample deduct this value from the value obtained from the modified decarboxylation procedure.

Water retards the reaction and with alcohol low results are obtained, probably owing to esterification of some of the aconitic acid. Malonic acid and acetonedicarboxylic acid are rapidly decarboxylated, the latter acid yielding two molecular proportions of carbon dioxide. The presence of acids of these two types has not been reported in sorgo or sugar cane. Galacturonic acid yields 53 per cent. of its carbon dioxide in 1 hr. Since uronic acids are normal constituents of plants and have been reported in sugar cane, the extent of this interference will receive further investigation. Oxalic, succinic, maleic, fumaric, itaconic, citraconic, mesaconic, malic, lactic, tartaric, tricarballylic, glutamic, aspartic, aminoacetic, and phthalic acids do not interfere. Citric acid and some citrates yield small amounts of carbon dioxide under certain conditions, and the extent of their interference will be investigated. Cystine gives no carbon dioxide, but the solution darkens and evolves hydrogen sulphide. Carbohydrates do not yield carbon dioxide in the procedure. Salts of easily volatile inorganic acids (chlorides, nitrates, and carbonates) yield acid vapours which pass into the absorption train. Hydrogen chloride from chlorides can be trapped effectively by washing the gas with silver nitrate or sulphate solutions. Nitrates, even in small amounts, interfere both by evolving acidic oxides of nitrogen and by oxidising the aconitic acid and the decarboxylated residue with evolution of some carbon dioxide. Hence the method is not applicable in presence of nitrates. Copper aconitate when tested by the method gives excessive and variable results, and cuprous oxide appears in the reaction mixture. For this reason the method is not applicable to material containing cupric, silver, mercuric, or other oxidising compounds that are soluble in the hot acetic acid and acetate mixture.

The method gives results of satisfactory accuracy in the assay of laboratory preparations of aconitic acid and aconitates. A. O. J.

**Micro-determination of Tetra-ethyl Lead in Gasoline. B. E. Gordon and R. A. Burdett** (*Anal. Chem.*, 1947, **19**, 137–140)—The method is based upon the decomposition of the tetra-ethyl lead with iodine, removal of the volatile constituents by evaporation, destruction of the organic residue

with mixed sulphuric, nitric, and perchloric acids, and subsequent volumetric micro-determination of precipitated lead chromate. The entire analysis is conducted without transfer of the sample from one flask and thus serious errors are eliminated.

Into a clean, 125-ml. Erlenmeyer flask containing 1 ml. of a saturated solution of iodine in carbon tetrachloride pipette 1 ml. of the sample of gasoline and, at the same time, observe its temperature. If the tetra-ethyl lead content of the gasoline is 1 ml. or less per gallon, use 5 ml. of the sample. Swirl the mixture and evaporate the volatile constituents by gentle heating over a hot-plate, assisting the removal of iodine by tilting the flask and pouring out the heavy vapour. Add 9 ml. of a digestion mixture prepared by mixing 300 ml. of concentrated sulphuric acid, 500 ml. of concentrated nitric acid, and 100 ml. of 72 per cent. perchloric acid, insert a glass bead, and fit the anti-spatter device (*infra*) into the neck of the flask. Boil the contents of the flask on a hot-plate with occasional swirling until the sulphuric acid condenses near the neck of the flask. Remove the flask from the plate, cool slightly, and add 0·5 ml. of perchloric acid through the anti-spatter device. Repeat the boiling until the sulphuric acid condenses near the neck of the flask and continue until the solution is colourless. Allow the flask to cool and, after a short time, accelerate the cooling by immersing the flask in a shallow water-bath. Cautiously add 10 ml. of water through the anti-spatter device and, if the liquid now shows a yellow colour due to residual iodine or chlorine, the boiling must be repeated.

Remove the anti-spatter device, rinsing it with 15 ml. of water, and slowly add down the side of the flask 7 ml. of concentrated aqueous ammonia and 2 drops of 0·5 per cent., aqueous *p*-nitrophenol solution. Cautiously add concentrated aqueous ammonia until 1 drop changes the colour of the liquid to deep yellow, guarding against the appearance of a false end-point. Add diluted acetic acid (1 + 3) until 1 drop removes the strong yellow colour, and then add an excess of 4 drops. Add 3 ml. of 10 per cent. ammonium acetate solution, boil gently on a hot-plate, and, if lead sulphate is evident as a white precipitate, continue boiling until this has dissolved. Add 2 drops of the diluted acetic acid followed by 5 ml. of 5 per cent. potassium dichromate solution, boil for 10 min., and allow to cool for 15 min.

Remove the supernatant liquid by reverse filtration through a Munroe platinum filter-stick connected with a filter flask and suction pump. Wash the precipitate and flask with 5-ml. portions of 1 per cent. ammonium acetate solution, removing the liquid through the filter-stick after each addition. Disconnect the filter-stick and attach it by means of a short length of small-bore pressure tubing to a micro-funnel that has been inserted through one hole of a two-holed stopper. Insert this stopper with the filter-stick attached into the neck of the flask and apply suction through the second hole in the stopper. Draw 2 ml. of water through the funnel and filter-stick into the flask and then, drop by drop, 4 ml. of diluted hydrochloric acid (1 + 3) followed by five, 1-ml. portions of water, and finally remove the stopper without interrupting the suction and rinse the outside of the filter-stick into the flask with water. To the contents of the flask add 1 ml. of the diluted hydrochloric acid and enough water to make the volume 30 ml. To the solution of lead chromate in hydrochloric acid add 0·5 g. of potassium iodide and swirl gently until solution is complete. Titrate the liberated iodine to a light yellow colour with 0·0018 $N$ sodium thiosulphate, add 1 ml. of 1 per cent. starch solution, and complete the titration. Effective swirling of the liquid is necessary as the end-point is approached. The tetra-ethyl lead content in ml. per gallon (uncorrected) is given by $(M \times N \times 0{\cdot}1077 \times 2296)/S$, where $M$ is the number of millilitres of sodium thiosulphate solution of normality $N$ used in the titration, 0·1077 is the mg.-equivalent weight of lead chromate, 2296 is the factor for converting lead chromate to ml. of tetra-ethyl lead per gallon, and $S$ is the number of millilitres of sample used. If $U$ is the uncorrected tetra-ethyl lead content found by this calculation, the corresponding figure (ml. per gallon) corrected to 15·5° C. is $0{\cdot}001U(T - 15{\cdot}5) + U$, where $T$ is the observed temperature of the sample taken and 0·001 is the mean cubical coefficient of expansion of gasoline.

It was found that the use of 0·0018 $N$ (0·00171 $N$ to 0·00191 $N$) sodium thiosulphate rather than 0·002 $N$ resulted in greater sensitivity without reduction of precision. Since A.S.T.M. specifications demand a precision of ±0·03 ml. of tetra-ethyl lead per gallon, the method requires rigorous attention to detail throughout: the sodium thiosulphate must be accurately standardised, the semimicro-burettes should be of 10-ml. capacity graduated to 0·05 ml. and readable to 0·01 ml.

The anti-spatter device consists of a wide glass tube ground in to fit the neck of the flask. The walls of the tube have been made to collapse inwards at three points to form three internal nipples one above the other and arranged at points 120° apart on the circumference of the tube so that passage of droplets through the tube is impeded by one or other of the nipples. A. O. J.

# Inorganic

**Colorimetric Determination of Molybdenum as the Thiocyanate Complex. N. A. Tananaev and A. P. Lochvitzkaja** (*Zavod. Lab.*, 1945, **11**, 6–10) —The red coloration obtained with thiocyanates

and molybdenum is due to quinquevalent molybdenum, probably in the form $H_2MoO(SCN)_5$, and not to molybdenum in still lower valency states as is usually supposed. This is shown by reducing $Mo^{VI}$ (ammonium molybdate) in diluted sulphuric acid (1 + 3) with zinc amalgam to $Mo^{III}$, estimating in one aliquot the volume of standard permanganate solution necessary for complete oxidation, and then testing (i) an unoxidised aliquot, (ii) an aliquot oxidised with one-third of the permanganate required for full oxidation, and (iii) an aliquot oxidised with two-thirds of the amount. With potassium thiocyanate in diluted sulphuric acid (1 + 5), aliquot (iii) gives the familiar orange or red colour, aliquot (ii) does not give any colour at first, but air oxidation causes the red colour to appear in time, and after several days $Mo^{IV}$ is completely oxidised to $Mo^{V}$, and aliquot (i), originally bluish-green, does not assume an orange or red tint until after a much longer time. Bismuth amalgam reduces $Mo^{VI}$ quantitatively to $Mo^{V}$, which with thiocyanate gives a stable compound not oxidisable by air.

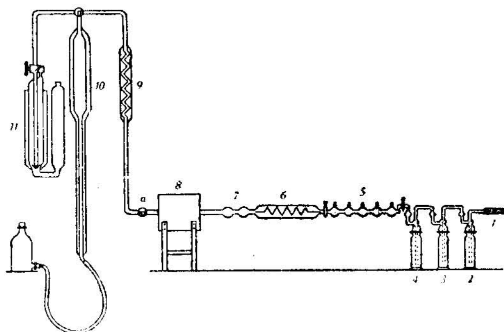
Thiocyanate alone (*i.e.*, without stannous chloride or other reducing agent) reduces $Mo^{VI}$ to $Mo^{V}$, slowly in the cold, but fairly rapidly in hot solutions, and the reaction may be used for the detection of molybdenum in absence of iron, thus: (i) to the diluted hydrochloric or sulphuric acid solution (1 + 5 to 1 + 7 in either case), heated to boiling, add, after removal from the source of heat, 1 to 3 drops of saturated potassium thiocyanate solution; a coloration, developing after 20 to 30 sec., reaches a maximum after 2 to 3 min., (ii) place a drop of the solution to be tested on a filter paper, add a drop of diluted hydrochloric acid (1 + 1), and then a drop of saturated potassium thiocyanate solution. The development of a yellow, orange, or red colour is proof of the presence of molybdenum if iron is absent. In neutral or weakly acid solution, molybdenum gives no colour with thiocyanate, hence the presence of iron may be detected under these conditions by the formation of the normal ferric thiocyanate colour.

The colour forms in nitric acid solutions, free from nitrous acid, as well as in hydrochloric and sulphuric acid solutions. The test must be carried out in the cold, but stannous chloride should then be added. It is found that the colour is stable at least for one hour; other workers have made contrary statements.

The sensitivity of the reaction when stannous chloride is used is 2 $\mu$g. of molybdenum per ml. under the following conditions: to 3 ml. of diluted (1 + 5 to 1 + 7) hydrochloric or sulphuric acid add 1 drop (about 0·05 ml.) of 0·001 *M* ammonium molybdate, 3 drops of saturated potassium thiocyanate solution, and 1 drop of stannous chloride solution (20 g. of $SnCl_2,2H_2O$ and 1 g. of tin heated to solution of the crystals in 15 ml. of concentrated hydrochloric acid, and the solution diluted to 100 ml.).

*Determination of molybdenum in steel. Procedure*—Dissolve 1 g. in 30 to 40 ml. of diluted sulphuric acid (1 + 5), add concentrated nitric acid until frothing ceases, boil off the reddish-brown fumes, transfer the solution to a 250-ml. graduated flask, cool, add permanganate to give a permanent red colour, dilute to the mark, and mix. Pipette 10 ml. of the solution into a beaker, add 2 ml. of 10 per cent. potassium thiocyanate solution and 4 ml. of 25 per cent. stannous chloride solution, and mix. Compare in a colorimeter with a similarly prepared solution of a standard steel. G. S. S.

**New Method for the Determination of Oxygen in Iron and Steel. N. Vigna** (*Helv. Chim. Acta.*, 1946, 29, 1667–1669)—Existing methods for the determination of oxygen in iron and steel, based on heating the sample in hydrogen, are considered to be difficult and unreliable. The proposed method is a modification of the Ströhlein method for carbon. The sample is heated in a current of pure nitrogen and the oxygen is converted to carbon monoxide; the volume of this is determined by absorption in ammoniacal cuprous chloride solution.



*Apparatus*—Commercial nitrogen is passed over hot copper oxide (1), through alkaline pyrogallol solution (2 and 3), through sulphuric acid (4), and over phosphorus pentoxide (5). To remove any remaining trace of oxygen it is then passed over hot reduced copper (6) and through a glass-wool filter (7) to the combustion tube (8). From the outlet from the combustion tube the gas may be vented to the atmosphere or directed through a cooler (9) to a measuring burette (10), which may be connected to the absorption vessel (11) containing cuprous chloride solution. As the volume of carbon monoxide is small the part of the burette in which the contraction is measured is of 5 mm. bore. The confining liquid in the burette is a saturated solution of potassium chloride, coloured with methylene blue, and saturated with pure nitrogen.

*Method*—The sample is prepared in such a way that oxidation is avoided. This may be achieved by clamping the specimen in a recessed steel block and putting a piece of solid carbon dioxide in the recess during the machining operation. The sample, in a boat, is introduced into the combustion tube and the apparatus is swept with nitrogen. The boat is then heated at 350° C. in a stream of nitrogen to remove occluded air. The sample is finally heated to 1200° C., the gas is collected in the burette and the measurement of the carbon monoxide volume finally made. With some steels it is desirable to mix a small amount of pure carbon with the sample.

The average error of the method is about ±0·01 per cent. L. A. D.

**Determination of Hydrogen in Liquid Steel. J. E. Wells and K. C. Barraclough** (*J. Iron and Steel Inst.*, 1947, **155**, 27–32)—The paper reviews five methods of sampling a liquid steel bath. The determination is made by heating the sample in a vacuum at 600° C. as described by Newell (*Ibid.*, 1940, No. I, p. 243P). The apparatus for handling small samples has been modified so that the specimens are introduced and removed through a mercury seal without admitting air.

The sampling methods are:—

(*a*) The balloon-tube method of Hatfield and Newell (*Ibid.*, 1943, No. II, p. 407P).

(*b*) The notched-pencil method, also of Hatfield and Newell (*loc. cit.*).

(*c*) The water-chilled mould method.

(*d*) The cast iron chill mould method.

(*e*) The ingot sample.

In the first four methods, a sample spoon is "slagged" and a spoonful of metal withdrawn from the furnace. Any slag is skimmed off, the steel is "killed" with aluminium and the sample prepared. In the fifth method, a 5-cwt. ingot is cast with the other ingots from the heat and sectioned to yield two samples 2¾ in. in diameter and 3 in. long. The machining and analysis must be conducted without delay to avoid loss of hydrogen from the samples.

All the methods give satisfactory results for the hydrogen content, a modification of method (*b*) being considered simplest. The mould is filled and as soon as the metal solidifies it is removed from the mould and quenched in water. If any interval must elapse before analysis the samples are kept in solid carbon dioxide. L. A. D.

**Determination of Gallium in Silicate Rocks. E. B. Sandell** (*Anal. Chem.*, 1947, **19**, 63–65)—The method for the determination of traces of gallium in silicate minerals and rocks is based on the fluorescence given by gallium with 8-hydroxyquinoline (*Idem.*, *Ind. Eng. Chem.*, *Anal. Ed.*, 1941, **13**, 844). The gallium hydroxyquinolinate is extracted with chloroform from an aqueous solution at *p*H 2·6 to 3·0. The only other metal hydroxyquinolinates that impart a fluorescence to the chloroform in this *p*H range are indium and scandium. At *p*H 3, the fluorescence given by indium is 1/500 that of an equal weight of gallium, and that of scandium 1/40,000 as strong. Coloured hydroxyquinolinates that dissolve in chloroform are formed by ferric iron, quinquevalent vanadium, cupric copper, and sexavalent molybdenum. Iron and vanadium do not interfere when reduced by hydroxylamine hydrochloride. Interference by several of the elements mentioned is avoided by extracting the gallium as its chloride with ether before applying the fluorescence reaction. As the presence of much iron in the ether extract makes the subsequent treatment of the extract more difficult, ferric iron is reduced by finely divided silver before the ether extraction. Traces of copper and vanadium may be extracted by the ether, but the amounts of these metals present in igneous rocks are such as to cause no error. Molybdenum, if present in quantity, would be extracted by the ether and would give a yellow colour to the chloroform.

*Reagents*—Prepare the silver powder by reducing silver nitrate with metallic copper. Wash well with dilute sulphuric acid and water, and dry. To prepare the silver column place a plug of glass-wool at the bottom of the stem of a funnel, stem diameter 8 mm., and fill the stem loosely to a depth of 15 mm. with powdered silver. After use, rinse the column with diluted hydrochloric acid (1 + 1) and water, and dry.

Use analytical grade ether treated daily as follows. Shake 65 ml. in a separating-funnel with 25 ml. of diluted hydrochloric acid (1 + 1) containing 0·05 g. of sodium hydrogen sulphite. Separate the phases. Do not wash the ether phase, but rinse the stem of the funnel by pouring a small quantity of the diluted hydrochloric acid into the funnel and running it off.

8-Hydroxyquinoline solution. Dissolve 0·1 g. in a small quantity of water containing 0·6 ml. of 6 *N* acetic acid and dilute to 100 ml.

Standard gallium solution. A suitable concentration is 0·0005 per cent. of gallium. The solution should be 0·05 *N* with respect to hydrochloric acid.

*Procedure*—To 0·25 g. of the 100-mesh rock powder in a platinum dish add 2 ml. of 6 *N* sulphuric acid and 3 ml. of hydrofluoric acid. Evaporate to dryness and fume off the excess of sulphuric acid. Take up the residue in 0·5 ml. of 6 *N* sulphuric acid and 1 to 2 ml. of water, evaporate to dryness, and fume off the sulphuric acid. Warm the residue, stirring at intervals, in a covered dish with 10 ml. of diluted hydrochloric acid (1 + 1) until all soluble material has dissolved, filter off any calcium sulphate, and wash with 5 ml. of water containing

a few drops of hydrochloric acid. Collect the filtrate and washings in a 25-ml. graduated flask. The residue from some minerals will require further treatment according to its nature. Add 0·5 g. of silver powder to the contents of the flask and swirl until most of the ferric iron has been reduced; add 8 ml. of concentrated hydrochloric acid and dilute to 25 ml. After mixing for 1 min., run the solution through the silver column and transfer 10 ml. of the effluent to a small separating-funnel previously washed with the diluted hydrochloric acid. Add 8 ml. of ether and shake for 20 to 30 sec. Drain the aqueous phase into another separating-funnel and shake it with 5 ml. of ether. Discard the acid layer and combine the second ether extract with the first, rinsing the funnel with 1 ml. of ether. Shake the combined ether extracts vigorously for 10 sec. with 1 ml. of diluted hydrochloric acid (1 + 1), drain off the aqueous layer and shake again with 1 ml. of the hydrochloric acid. Discard the acid layer. To rinse out the stem, add a few drops of acid to the funnel and draw it off without shaking.

Run the washed ether extract into a 50-ml. beaker containing 0·5 ml. of 10 per cent. sodium chloride solution, and rinse the funnel with 1 to 2 ml. of ether. Evaporate the ether at a low temperature from the covered beaker, remove the watch glass, and allow the water to evaporate. Dissolve the cold residue in 2 ml. of 0·2 *N* hydrochloric acid and transfer the solution to a flat-bottomed, glass-stoppered bottle, 1·8 cm. by 15 cm., of 25-ml. capacity, washing the beaker and cover glass with about 3 ml. of water. Add 1 ml. of 20 per cent. hydroxylamine hydrochloride solution, mix, add 6 ml. of potassium hydrogen phthalate solution (40·82 g. per litre), and allow to stand for 20 min. Prepare a comparison solution of the same composition.

To the sample and comparison solutions add 0·25 ml. of the 8-hydroxyquinoline solution, mix by inversion, and add 2 ml. of analytical grade chloroform. Shake the sample tube vigorously for at least 30 sec. and allow the chloroform to settle. Add portions of the standard gallium solution from a micro-burette to the comparison tube, shaking for 30 sec. after each addition. Compare the fluorescence of the two chloroform layers by holding the two tubes vertically above an ultra-violet lamp in a dark room. When the intensities of fluorescence are nearly the same shake the sample tube for up to 1 min. and then shake both tubes for 30 sec. after each further addition of gallium to the comparison tube. When the intensities are the same, shake both tubes for 1 min. to ensure that distribution equilibrium has been reached. Run a blank determination through the whole procedure.

The procedure was tested on a series of rocks containing from 0·5 to 19 p.p.m. of gallium, further quantities of gallium equivalent to up to 50 p.p.m. being added to some of the samples. The results present indicate that several per cent. of the gallium escape extraction. Application of a correction factor of +10 per cent. is believed to be justified. With this correction, all the results but one are within 10 per cent. of the theoretical results. The blank was equivalent of 0·1 $\mu$g. of gallium. B. A.

## Agricultural

**Determination of the Pyrethrins in Pyrethrum Concentrates in Mineral Oil. J. T. Martin and S. T. P. Brightwell** (*J. Soc. Chem. Ind.*, 1946, **65**, 379–384)—For the determination of pyrethrins in extracts of pyrethrum flowers in heavy mineral oil, such as are used for the control of insects that attack stored products, the Wilcoxon-Holaday method (*Assoc. Off. Agric. Chem., Methods of Analysis*, 1940, 67) is modified (*a*) by removing uncombined acids before analysis, by extracting a chloroform solution of the concentrate with dilute baryta, (*b*) by fractionating the saponified concentrate between water and light petroleum to remove oil, (*c*) by extracting the chrysanthemum monocarboxylic acid in the presence of the barium sulphate precipitate, to avoid losses by adsorption of the acid on this precipitate, and (*d*) by twice washing the light petroleum solution with 2·5 ml. of water instead of once with 5 ml. in the recovery of the monocarboxylic acid before treatment with Dénigès' reagent, thus obtaining a clear separation of the aqueous and the light petroleum layers.

Determination of pyrethrin I. *Reagents. Dénigès' reagent*—Mix 5 g. of yellow mercuric oxide with 40 ml. of water, and, while stirring vigorously, slowly add 20 ml. of concentrated sulphuric acid and then 40 ml. of water. Continue to stir until all the oxide has dissolved, cool, and filter. *Iodine monochloride reagent*—Dissolve 10 g. of potassium iodide and 6·44 g. of potassium iodate in 75 ml. of water in a glass-stoppered bottle. Add 75 ml. of concentrated hydrochloric acid and then 5 ml. of chloroform. Shake well and add solutions of potassium iodide or iodate until the chloroform layer is just pink. Keep in the dark and adjust periodically. *Potassium iodate* (0·01 *M*)—Dry potassium iodate at 105° C. Dissolve 2·14 g. in water and dilute to 1 litre. N *alcoholic* (95 *per cent.*) *sodium hydroxide*—Dissolve 40 g. of caustic soda in 1 litre of 95 per cent. alcohol distilled from *m*-phenylenediamine; or, purify the alcohol by means of silver oxide (Griffin, *Technical Methods of Analysis*).

*Preparation of sample*—Mix the sample well by shaking, allow to settle until clear, and use the clear solution for analysis. If necessary, remove suspended particles by centrifuging. Take for

analysis a sample containing sufficient pyrethrin I to give a titration of the order of 12 to 15 ml. of potassium iodate solution. When this is greatly exceeded, make up to a definite volume the filtrate from the barium chloride precipitation and continue the assay with aliquot portions. Approximate volumes required are 20 ml. of a preparation said to contain 0·8 per cent. of total pyrethrins, or 4 ml. of a preparation said to contain 4·0 per cent. of total pyrethrins.

*Procedure*—Weigh the sample into a 100-ml. beaker, dissolve in 50 ml. of chloroform, and wash into a 500-ml., pear-shaped separating funnel, using 50 ml. of chloroform. Add 75 ml. of water, 1 drop of 1 per cent. phenolphthalein, and 5 ml. of 0·1 *N* baryta. Agitate the funnel for a minute or two, adding more baryta if the aqueous layer does not remain alkaline. Add 10 ml. of saturated salt solution and 10 ml. of 10 per cent. barium chloride solution, rotate, and allow the chloroform layer to separate. Run the chloroform layer into a second separating funnel containing 25 ml. of water and a few ml. of saturated salt solution, and swirl. Run the chloroform layer into a 250-ml. round-bottomed flask. Wash the aqueous layers successively with four 20-ml. portions of chloroform, shaking vigorously for the third and fourth washings to break any emulsion in the aqueous layers. Wash for a fifth time with 10 ml. of chloroform if the colour of the chloroform separating or the persistence of an emulsion in the aqueous layer indicates that this is necessary. Add the washings to the main chloroform solution. (At this stage, the estimation may be left overnight.) Retain the aqueous layers for the determination of free chrysanthemum monocarboxylic acid when this is required. Distil the chloroform to low bulk from boiling water and remove as completely as possible under moderate vacuum at 35° to 40° C., rotating the flask and using an anti-splash device. Add 20 ml. of *N* alcoholic (95 per cent.) sodium hydroxide, washing out the anti-splash device, saponify for 2 hours, and cool. Add 80 ml. of water, swirl to dissolve the soaps, add 50 ml. of light petroleum, and wash into a 500-ml. pear-shaped separating funnel, using 50 ml. of water and then a few millilitres of light petroleum. Swirl, but do not shake. Run the aqueous layer into 50 ml. of light petroleum in a second separating funnel and again swirl. Draw off the aqueous layer into a 600-ml. beaker with a mark at 150 ml., and wash the light petroleum layers successively with two portions of 25 ml. each of water; if material insoluble in water and light petroleum causes troublesome emulsification at the junction of the two layers, strain the emulsion through a loose plug of cotton wool to break it up. Add the washings to the main aqueous layer. Boil the aqueous layer down to 150 ml., gently at first to avoid frothing. Cool, add a little Celite filter aid and 10 ml. of 10 per cent. barium chloride solution, stir, and allow to stand for at least 10 min. (At this stage the estimation may be left overnight.)

Filter into a 500-ml. separating funnel through a fluted, 12-cm., No. 1 Whatman paper, testing the filtrate with a little barium chloride solution to ensure that precipitation is complete. Wash the beaker and precipitate thoroughly with successive portions, 50 ml. in all, of water. Add 5 ml. of diluted sulphuric acid (1+4) to the filtrate, mix, and test to see that the solution is acid to litmus. Add a few ml. of saturated salt solution and shake vigorously for at least 1 min. with 50 ml. of light petroleum (b.p. below 40° C.). Allow the layers to separate. Draw off the precipitate and aqueous layer into a beaker and run the light petroleum extract through a loose plug of cotton wool into a separating funnel. Repeat the extraction of the aqueous layer with 50-ml. and 25-ml. portions of light petroleum, adding these through the wool to the first extract. Draw off any water that separates and wash the light petroleum solution with 3 portions of 10 ml. each of water, allowing adequate drainage. Retain the aqueous layer and each of the washings (separately) for the determination of pyrethrin II. Extract the light petroleum solution by vigorous shaking with 5 ml. of 0·1 *N* aqueous caustic soda for at least 1 min. Allow the alkaline layer to separate as completely as possible and run it into a 100-ml., lipped conical flask with a ground-glass stopper. Wash the light petroleum solution with two portions of 2·5 ml. of water and add these to the first extract, allowing each to drain as completely as possible. (At this stage the estimation may be left overnight.) Add 10 ml. of Denigès' reagent to the alkaline extract and set aside for 1 hour at room temperature (approximately 20° C.). Add 20 ml. of acetone and 3 ml. of saturated salt solution, stir, heat just to boiling and, after the precipitate has settled, decant through a 7-cm., No. 1 Whatman paper. Wash the precipitate by decantation with 10 ml. of hot acetone, and two portions of 10 ml. each of hot chloroform. Place the drained paper in the flask used for the precipitation, add 30 ml. of concentrated hydrochloric acid and 20 ml. of water, and cool. Add 6 ml. of chloroform and 1 ml. of iodine monochloride solution and titrate, with vigorous shaking, with 0·01 *M* iodate solution until the chloroform has no pink colour. The pink colour will return slowly. If over-titrated, add a definite volume of 0·02 *M* potassium iodide solution and titrate back. Then 1 ml. of 0·01 *M* iodate ≡ 5·7 mg. of pyrethrin I (taking the Graham and LaForge factor for pyrethrin I, *Soap*, 1943, **19**, No. 11, 111).

DETERMINATION OF PYRETHRIN II. Use the aqueous layers retained above. Allow the precipitate in the main layer to settle, decant the solution

into a second beaker, boil down to 50 ml., and cool. Filter the solution on a Gooch crucible containing filter paper and a little asbestos, finally washing the precipitate in. Wash the beaker and filter with the three 10-ml. portions of washings retained above. Make the clear filtrate alkaline with sodium bicarbonate, wash into a separating funnel, and extract twice with 25-ml. portions of chloroform. Wash the chloroform extracts successively with two portions of water and combine all the aqueous layers. Discard the chloroform extracts. Acidify the aqueous layer with hydrochloric acid and saturate with sodium chloride, avoiding loss by frothing. Extract thoroughly in a separating funnel with two 50-ml. and two 25-ml. portions of ether (distilled from caustic soda). Combine the ether extracts in a second separating funnel, allow to drain, and wash with two portions of 10 ml. of water, allowing careful drainage each time. Run the ether solution into a 350-ml. conical flask and remove the ether on the water-bath. Allow the flask to dry at 100° C. for 10 min. and remove any hydrochloric acid fumes with an air stream. Dissolve the dicarboxylic acid in 2 ml. of neutral, 95 per cent. alcohol, add 20 ml. of water, and warm to complete solution. Titrate, with phenolphthalein as indicator, with 0·02 *N* aqueous sodium hydroxide. One ml. of 0·02 *N* sodium hydroxide ≡ 3·74 mg. of pyrethrin II. Carry out blank determinations on the reagents. These should not exceed 0·1 ml. of 0·01 *M* iodate and 0·25 ml. of 0·02 *N* sodium hydroxide.

DETERMINATION OF UNCOMBINED ACIDS (IF REQUIRED). Filter into a 500-ml. separating funnel the baryta extract containing the salts of the free acids, acidify with 5 ml. of dilute sulphuric acid, extract with light petroleum and continue the analysis as described above.

Application of the method to the determination of pyrethrins in light petroleum, ethylene dichloride, and acetone extracts of pyrethrum flowers gave comparable values for pyrethrin I in the extract with all three solvents, but the values for pyrethrin II in the acetone extract were high. Further tests showed that the method is applicable to the determination of pyrethrin I in oil solutions made from light petroleum, ethylene dichloride, or acetone extracts of the flowers. Determinations by two observers of the pyrethrin I content of commercial samples of pyrethrum extract in light and heavy mineral oils, and of the apparent pyrethrin I present in the form of uncombined acid, showed good agreement; the removal of uncombined acid before analysis is particularly important with solutions of high pyrethrin content. In a further series of experiments, values of the pyrethrin I content of oil solutions by the mercury-reduction method were slightly higher than those obtained by the steam-distillation method. E. M. P.

# Water Analysis

**Colorimetric Method of Determining the Hardness of Water. S. M. Dratschev** (*Zavod. Lab.*, 1945, **11**, 46–48)—Tropaeolin OO, which gives difficultly-soluble, coloured compounds with magnesium and calcium salts, may be used for the colorimetric determination of water-hardness. Variation of *p*H within the range 6·5 to 8·7 does not affect the results. The method is sensitive to 0·5° of hardness and is accurate to 1 to 1·5°.

*Preparation of standards for the scale of hardness*—Mix at 20° C. equal volumes of (*a*) 1·23 g. of $MgSO_4.7H_2O$ dissolved in one litre of water, giving 28° of hardness, and (*b*) 0·369 g. of $CaSO_4.2H_2O$ dissolved in one litre of water, giving 12° of hardness, and dilute 10-, 20-, 30-, 40-, and 50-ml. portions of the mixture to 100 ml., thus obtaining solutions of hardness 2°, 4°, 6°, 8°, and 10°, respectively. In separate tubes place 1 ml. of distilled water and 1 ml. of each of the solutions, and to each add 0·5 ml. of tropaeolin OO solution (0·4 g. mixed with 50 ml. of alcohol until nearly dissolved and made up to 100 ml. with distilled water). This gives the lower part of the scale of hardness, *viz.*, 0°, 2°, 4°, 6°, 8°, and 10°. For the upper part of the scale, dilute 50-, 60-, 70-, 80-, 90-, and 100-ml. portions of the mixture above to 100 ml., to give solutions of hardness, 10°, 12°, 14°, 16°, 18°, and 20°, but take 1 ml. of each solution with 1 ml. of the tropaeolin OO solution.

*Procedure*—Pipette 1 ml. of the water to be tested into a tube similar to those used for the hardness scale, add 0·5 ml. of the indicator solution, mix, and compare the coloration with the lower set of standards. If the hardness exceeds 10°, add a further 0·5 ml. of indicator and compare with the upper scale. Wide variations in the ratio of magnesium and calcium salts in the water tested appear to have no effect on the results. G. S. S.

[The degrees of hardness in this abstract are in terms of CaO.]

# Physical Methods, Apparatus, etc.

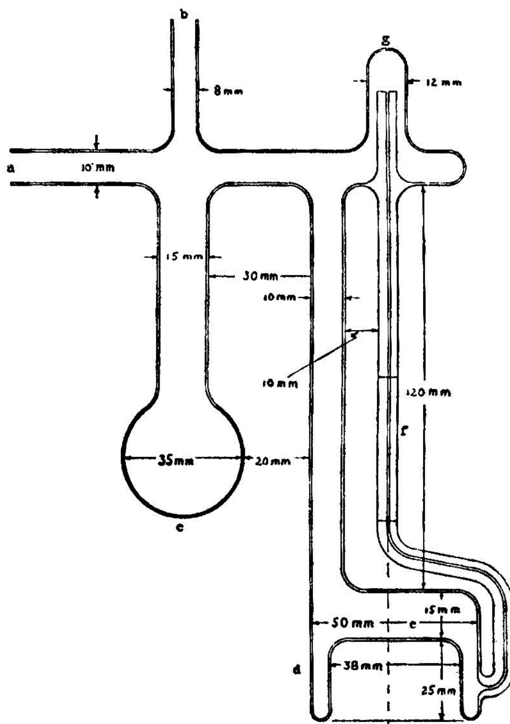
**New Type of Precision Capillarimeter. J. J. Jasper and K. D. Herrington** (*J. Amer. Chem. Soc.*, 1946, **68**, 2142–2144)—The device described was designed for the accurate measurement of the surface tension of pure compounds prepared in a vacuum system and available in amounts of approximately 10 ml. Details of the instrument are shown in the figure. A horizontal arm *a* carries the liquid receiver *c*, the capillary chamber *d*, and the capillary tube *f*. Tube *b* is connected to the vacuum system and tube *a* is sealed. The capillary tube extends into the housing *g* to prevent liquid from flowing into it from above. The re-entrant bottom *e* of the

capillary chamber reduces the quantity of liquid required to give a flat liquid surface and hastens the establishment of thermal equilibrium. As the axis of the capillary *f* coincides with that of the chamber *d* there is no need to revolve the cathetometer telescope when measuring the capillary rise.

Choose the capillary tube and the larger cylindrical tube for the liquid reservoir with great care. Prepare the capillary and determine the radius and constancy of its bore by the procedure of Harkins and Brown (*Ibid.*, 1919, **41**, 499). Test the walls of the chamber for distortion by viewing through the chamber, along its diameter, a scale placed beyond.

*Procedure*—Transfer the liquid from the vacuum system to *c* by immersing the latter in a freezing-bath. Seal off the arm *b* and transfer the liquid to *d* by tipping the instrument.

Values for the surface tension of several pure liquids were determined and were found to agree closely with the values given in the "International Critical Tables." B. A.




# Reviews

F. Pregl, Quantitative Organische Mikroanalyse. Fünfte Auflage. Nach dem gegenwärtigen Stand der Forschung und Praxis bearbeitet von H. Roth. Pp. xii + 317. Vienna: Springer-Verlag. 1947. Price 32 Swiss francs.

The various editions of this work were outlined about eighteen months ago (Analyst, 1946, **71**, 199) on the occasion of the appearance of Dr. Grant's new English version. To this series must now be added another German edition written by Dr. Roth, the publication of which supplies information concerning war-time developments on the continent hitherto unavailable in this country. Former reviews of the recent German texts have complained of the neglect of non-German progress; because of the history of the last few years the time is inopportune to complain that the omission has not been rectified in the book now under review.

The current English and German editions are similar in that the methods described in detail are usually those originated by Pregl, while alternative procedures are mentioned only briefly. It is, however, interesting that the Parnas and Wagner distillation apparatus favoured by Pregl for Kjeldahl determinations is retained in the English book, but has been displaced in the German by a simpler assembly. Also, the Meixner and Kröcker method for the determination of mercury is replaced by an improvement due to Boëtius. It is curious that ebullioscopic molecular weight determinations, including that devised by Pregl, are omitted by Dr. Roth as being of no practical importance: these methods are to be found in the English text, which also has a brief review of general physical methods. It is not proposed to note all the differences in detail between the two versions of Pregl's book now available, but the following items appear only in the German edition. Oxygen is determined directly by a combustion method due to Unterzaucher, in which the organic material is "cracked" and the hot gasses passed over carbon to form carbon monoxide; the latter is oxidised by iodine pentoxide and the iodine liberated is titrated. Nitrogen is determined by Lacourt's hydrogenation method, which uses nickel and thoria as a catalyst; ammonia is formed and is determined acidimetrically. Zimmermann's method for sulphur determination consists of fusion of the material with potassium in a sealed tube, followed by evolution of hydrogen sulphide which is absorbed in cadmium acetate and determined iodometrically. Brief

reviews are given of methods for the determination of selenium and antimony. An additional procedure for phosphorus depends upon the formation of the blue molybdenum complex. Descriptions are given of Furter, Bürger, and Baláž alkoxyl determinations. The section on melting-points is expanded to include mixtures and mixed melting-points; it is illustrated with photomicrographs. A useful list of solvents for cryoscopic molecular weight determinations is given, together with their uses and molecular melting-point depressions.

In spite of the differences noted above, Dr. Grant and Dr. Roth have produced very similar texts and it is probable that only specialists will wish to incur the expense of buying both. Neither of the books retains the highly personal and entertaining writing of Pregl, and the reviewer wonders whether the time has arrived when this pioneer's monopoly of organic micro-analysis has passed and future editions should describe in detail the more modern alternative procedures.

G. H. WYATT

MODERN CEREAL CHEMISTRY. By D. W. KENT-JONES, Ph.D., B.Sc., F.R.I.C. and A. J. AMOS, Ph.D., B.Sc., F.R.I.C. Fourth Edition. Pp. vii + 651. Liverpool: The Northern Publishing Co. Ltd. 1947. Price 50s. net.

The first edition of this book was published in 1924 as a modest little volume of 324 pages. The then reviewer (ANALYST, 1924, **49**, 609) accepted the "Modern" part of the title but regarded "Cereal Chemistry" as being rather too wide. The second edition of 1927 contained 446 pages and was little more than an expanded reprint of the first; but the third edition of 1939, with 720 pages, was a real justification of the title. It became the standard work on flour and bread, and quotations from it were accepted as authoritative. Owing to the loss of unsold copies by enemy action, this edition was soon unobtainable and second-hand copies were at a premium.

Now an enlarged edition, the fourth, has appeared under joint authorship with Dr. Amos, the increase in material amounting to approximately 50 per cent. A change in set-up—a credit to the publishers and a delight to the reader—has resulted in fewer pages, achieved by about one-third more words per line and one-fifth more lines per page. The principal increases are in Wheats of the World, Other Cereals, Nutritive Value of Cereals, Rations for Livestock and Analytical Procedure. The only significant reduction is in Conditioning and the Effect of Heat on Wheat and Flour.

The arrangement follows previous issues—for which old and familiar users will be glad—and is particularly appropriate to the subject. Since the index of authors refers to paragraphs it would be helpful if each page quoted the paragraph number.

The material is really comprehensive and cannot be found collectively elsewhere. The wealth of data, the critical review and the summing-up of evidence are the principal features that characterise the volume and assure for it a prominent place in and out of the bookshelves of all concerned with cereal chemistry or with the production of food and food products from cereals. Apart from the mechanical testing of flour and dough, analytical procedures occupy nearly one-quarter of the space and special attention is given to vitamin assays including microbiological methods, to which the authors have materially contributed.

Knowing the authors, interest is naturally aroused in their approach to certain controversial matters. The reviewer of the first edition described it as "a plea for white flour and for the bleaching and 'improving' of white flour" and stated that "many of the views expressed and quoted will have to be revised." Such revision was made in subsequent editions and has been continued, through a more descriminating selection from the vast knowledge now available on nutrition, and the special pleading has become more of a judicial survey. The authors' views on giving the public what it wants have not changed; and although they may appear "bleached" and, indeed, "improved" by the narrowing down of the controversy from white flour *v.* wholemeal flour to enriched white flour *v.* near-white flour, the calories remain the same.

J. R. NICHOLLS