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# THE ANALYST

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

## Graphites and other Pencil Pigments.

By C. AINSWORTH MITCHELL, M.A., F.I.C.

(*Read at the Meeting, May* 3, 1922.)

In the course of a paper which I read before the Society of Chemical Industry (*J. Soc. Chem. Ind.*, 1919, **38**, 381T) I called attention to the previously unnoted differences in the markings made by various graphites upon paper, and showed how those microscopical differences could be used as a rapid method of judging as to the purity and characteristics of a sample of graphite.

The method depends upon the fact that when a vertical line, made with the graphite upon paper, is examined under the microscope with a magnification of 20 to 25 diameters, and with a side illumination, the silicious impurities in the material are shown up as fine or coarse striations irregularly distributed across the masses of black or brownish pigment. Where, however, as in the case of the best Borrowdale graphite, the carbon appears to be present in a more amorphous form, or possibly in a form of loose combination with the non-carbon constituents, the striations may be entirely absent, even when a considerable proportion of silica is present. This affords an explanation why the old Cumberland graphite was more highly esteemed as a pencil pigment than other graphites, even though these might contain a much higher percentage of carbon.

I have now used this method in the examination of various other types of graphite, and, as before, have compared the microscopical appearances of the markings on paper with the results of the chemical analysis of the graphites.

I am indebted to the Curator of the Geological Museum for the first three specimens of the old exhibits in that Museum, and to Mr. Brodie, Secretary of the Fitzpark Trust, Keswick, for the specimens of old Borrowdale graphite.

| | Moisture Per Cent. | Ash Per Cent. | Carbon Per Cent. | Silicates (insol. in HCl) Per Cent. | Aluminium Per Cent. | Iron Per Cent. |
|---|---|---|---|---|---|---|
| 1. Grampound, Cornwall (No. 30) | 1·2 | 1·30 | 97·50 | 0·62 | — | 0·24 |
| 2. Huasco, Chili (No. 7630) | — | 26·26 | 73·74 | 4·89 | 2·82 | 0·16 |
| 3. Upper California (No. 45) | 1·37 | 45·15 | 53·48 | 35·64 | 0·55 | 1·37 |
| 4. Seathwaite Mine, Borrowdale | 2·20 | 37·93 | 59·87 | 25·26 | 2·30 | 5·00 |
| 5. Borrowdale | 4·76 | 21·42 | 73·82 | 11·08 | 2·19 | 1·86 |
| 6. Ancient Egyptian | 1·20 | 59·37 | 39·43 | 47·64 | 13·45 | |
| 7. Compressed Graphite, Keswick | 4·06 | 43·40 | 51·94 | 33·64 | 1·07 | 2·42 |
| 8. Aquadag (Air-dried) | 32·79 | 5·25 | 61·96 | 2·04 | 0·22 | 2·11 |
| 9. Compressed Acheson Graphite | — | 0.39 | 99·61 | — | — | 0·14 |

The Cornish graphite yielded brilliant scales, which were very difficult to burn. The markings made by it showed under the microscope, rich black lines with hardly any trace of striations, but with brilliant high lights where pigment was deposited on the fibres of the paper (See Fig. 1).

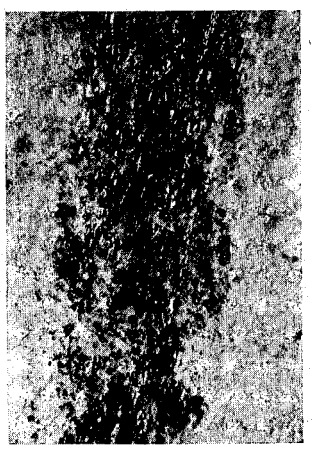

FIG. 1.
Marking with Cornish Graphite.

The Chilian specimen (No. 2) showed numerous broad and narrow striations, irregularly distributed, whilst the tone of the pigment anged from sepia to a poor black.

In the case of the Californian graphite (No. 3), the black pigment appeared irregularly distributed, and showed brilliant silvery striations in broad and narrow bands, which were not continuous.

The two Borrowdale samples are of interest, since they show the composition of the mineral at the time when the mines were nearing their end. They contain much less carbon than did the Borrowdale graphite at its best, as, for example, the specimen of 1850 exhibited in the Geological Museum, which contains nearly 91 per cent. (*cf. J. Soc. Chem. Ind., loc. cit.*). The lines made by them show isolated bands of striations.

GRAPHITE FROM EGYPT. The Egyptian graphite (No. 6) is particularly interesting, for it is unquestionably the oldest known specimen of the mineral in existence. It was kindly given to me by Professor Flinders Petrie, whose attention had been drawn to the statement in my paper in *Nature* (1920, **105**, 12) that graphite was discovered about the year 1560 A.D. This graphite was found by Professor Petrie in a tomb of the 18th Dynasty age at Ghorub, at the mouth of the Fazum, and would therefore probably date back to between 1500 and 1200 B.C.

It is the only discovery of graphite that has been made in Egypt, and the lump might conceivably have been brought there from Syria or Persia, with which countries Egypt traded as far back as 5000 B.C.

Since there is no evidence that graphite was ever used as a pigment by the ancient Egyptians, it is possible that this particular specimen was imported as a curiosity or as a sample.

The microscopical appearance of the markings on paper confirmed the chemical analysis. The pigment deposit was of a fairly rich tone, but showed many striations, in some places in the form of very fine lines and, in others, forming interrupted irregular masses (See Fig. 2). Parts could be selected which closely resembled the markings made by a modern coarse, composite pencil.

COMPRESSED GRAPHITES. When the supply of Cumberland lead showed signs of exhaustion, numerous attempts were made to utilise the dust from the works by compressing it into solid blocks which were then sawn up in the same way as the original material. In one of these processes, patented by Brockedon in 1843, the dust was subjected to the simultaneous action of pressure and exhaustion of air, whilst in other processes pressure alone was used. I have to thank Mr. Brodie for the compressed graphite, No. 7 in the table, which as will be seen, is not rich in carbon.

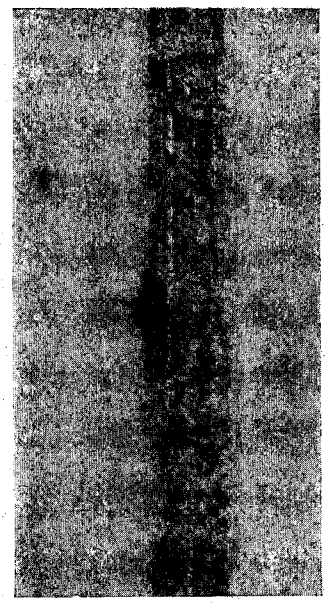

FIG. 2.
Marking with Egyptian Graphite.

Like the specimens of Brockedon's compressed graphite in the Geological Museum, this preparation produced markings which, under the microscope, showed regular, finely-distributed black particles with very few striations visible, whilst the field appeared covered with a series of uniform light dashes. The effect of fine division and compression was to dispose of the irregularity of the scanty striations in the natural Borrowdale graphite. An illustration of a marking with Brockedon's graphite will be found in *Nature* (*loc. cit.*).

Acheson's "Aquadag," when air-dried, produces analogous, but more brilliant markings, which are free from striations.

The ordinary Acheson's compressed graphite usually contains a considerable amount of non-carbon constituents derived from the iron mould, and so sometimes produces striations, but the Acheson Company have very kindly prepared for me rods of pure compressed graphite, and these, as will be seen by the analysis, consist of nearly pure carbon. The markings made with these rods show no indications of striations. In the heavier strokes some of the fibres of the paper reflect the light brilliantly, whilst other fibres show the black pigment distributed in fine dots. The microscopical appearance differs considerably from that of lines produced by pure Cumberland graphite.

METALLIC PENCIL MARKINGS. In view of the proof that graphite was known long before its reputed discovery in 1560, I decided to examine further specimens.

of early pencil markings available in this country. Owing to the kindness of Bodley's Librarian and of Dr. Craster, I have been able to examine various specimens of early pencil markings in the Bodleian Library and have given some account of my results in a recent communication to *Nature* (**1922, 109**, 516). I have also studied the markings made with various alloys of lead with antimony and other metals, and have found that there is no difficulty in distinguishing between metallic markings and ordinary graphite markings. In the case of the former the lines show disconnected patches of pigment which reflect the light strongly and show uniform striations. Photography of lead markings, however, is difficult, owing to the extreme brilliance of the particles, and I have to thank Mr. T. J. Ward for the trouble he has taken to obtain characteristic photomicrographs (See Fig. 3).

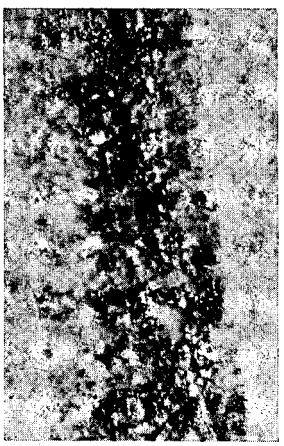

FIG. 3.
Marking with Metallic Lead.

It was customary in early vellum MSS. to rule lines with a stylus beneath the written lines and vertically at their edges, and these are the markings to which Schönemann refers when he mentions the occurrence of lines in black lead in documents of the 11th and 12th century (*Versuch eines Systems der Diplomatik*, Leipzig 1818, Vol. I, 515; Vol. II, 108).

The earliest MS. in the Bodleian Library known to contain pencil markings is a discourse on the Book of Job (Auct. D. III, 14) of the 12th century, and the ruled lines in this are undoubtedly in a metallic pigment. Similar markings appear in Hatton MSS. of the 13th and 14th centuries.

The first occurrence of writing in graphite noted was in an inscription of Anthony Wood in a collection of poems of 1688, which was of about the same date as the earliest instances of graphite writing discovered in the British Museum (*cf. J. Soc. Chem. Ind., loc. cit.*).

The earliest example of writing in metallic pigment, as distinct from ruled lines, which I have been able to discover is in a book printed in 1472 at Venice: "*Quæstiones Dignissimæ d'Anima a St. Thom. Aquinas*"; and, here again, I have to thank Professor Flinders Petrie for bringing this writing to my notice. The notes in pencil at the sides of the paragraph, which there is reason to believe were contemporaneous, have the characteristics of metallic pigment, whilst annotations of a later date are written in a rich black graphite.

COMPOSITE PENCIL PIGMENTS. I have already published analyses of the pigments in early specimens of 18th century composite pencils in South Kensington Museum (*J. Soc. Chem. Ind., loc. cit.*). These contained a large proportion of sulphur, which was one of the substances used at an early date at Faber's works in Nüremberg. From 30 to 40 per cent. of sulphur was melted and incorporated with the blacklead, but the method was subsequently abandoned, as it was found to make the pencils too brittle; while, at best, the pigments gave only faint markings on paper.

A mixture of the blacklead with fused antimony was also tried, but proved very unsatisfactory as a pigment, and all such mixtures were ultimately displaced by the mixtures of purified graphite and kaolin or other clay, which together with wax form the main ingredients of modern pencils.

These early composite pigments can be distinguished from pure graphite in writing by their greyish tint and by the uniform distribution of the fine striations in the lines.

COMPOSITION OF PIGMENTS IN BLACKLEAD PENCILS. The following analyses of pencil pigments are given to supplement those published in my former paper (*loc. cit.*):

| Pencil | Moisture, Wax, etc., Per Cent. | Carbon Per Cent. | Ash Per Cent. | Silicates. (insol. in HCl) Per Cent. | Ether Extract Per Cent. | Iron Per Cent. | Aluminium Per Cent. |
|---|---|---|---|---|---|---|---|
| 1. George Rookin, Keswick. | — | 34·27 | 62·30 | 18·84 | 3·43 | 24·40 | 12.91 |
| 2. Gilbert & Cie H. (Belgium) | 17·45 | 46·16 | 36·39 | 27·21 | — | 1·25 | 2·54 |
| 3. Gilbert & Cie HHH. (Belgium) | 3·14 | 43·41 | 53·45 | 31·44 | — | 6·23 | 5·22 |
| 4. Conté, Drawing Crayon (No. 2) | — | 26·53 | 73·47 | 67·66 | — | 2·49 | 2·72 |

The Keswick pencil (No. 1), which Mr. Brodie kindly sent to me, is typical of those being manufactured shortly before the Cumberland mines became exhausted about 1869. At that time pencils were being made in numerous small shops in Keswick, the leads being merely sawn out of the "sops" as found in the mine, and George Rookin was one of these small makers. The analysis shows the poor character of the graphite, which contains only 34 per cent. of carbon, and the microscope confirms this, for the lines made with the pencil show pigment deposited in irregular masses, with fine interrupted silvery striations.

This pigment was also characterised by its high proportion of iron, which caused the writing done with this pencil to give a pronounced reaction with ferrocyanide and acetic acid.

As in the case of many old graphite pencils, ether extracted from the pigment a small amount of a wax-like substance, probably cedrol, derived from the cedar oil in the wood, which had been gradually absorbed by the graphite (*cf. J. Soc. Chem. Ind., loc. cit.*). The markings made with an 18th century graphite pencil are shown in Fig. 4. The striations, due to impurities, are interrupted and irregularly distributed.

FIG. 4.
Line made with 18th Century Pencil.

The Belgian pencils are typical of those made in that country, and the composition of the pigments calls for little comment. The markings show the usual fine beaded striations produced by composite pencils.

The Conté drawing crayon is typical of the compressed charcoal pigments manufactured in Paris. The black pigment appears to consist of lampblack, and it is not difficult to distinguish the lines under the microscope from those made by soft blacklead pencils containing lampblack.

DIFFERENTIATION OF BLACKLEAD PIGMENTS. I have already given an outline of the general methods of distinguishing between blacklead pencil pigments in writing (*loc. cit.*).

Briefly, the points of distinction are the colour-tone and arrangement of the pigment, the quantity and appearance of silver striations, and various chemical differences, of which the most important are the reactions for iron after treatment of the writing with a weak and with a strong acid. The tests are applied by means of a capillary pipette and the course of the reactions is followed under a magnifying glass.

It has been shown by Lunt (*Annals Cape Observatory*, 1913, **10**, Part IV.) that the spectroscope affords a means of differentiating between graphites and pencil pigments. In those researches graphite cores from lead pencils were used to replace the iron terminals of the apparatus, and the sparks examined spectroscopically.

It was found that the pigments from the pencils of the principal manufacturers varied chiefly in their proportion of alkaline earth metals, whilst there were slighter variations in the intensity of the spectroscopic lines of titanium, vanadium and chromium. In the case of natural graphites three specimens from Ceylon showed only traces of iron and calcium. Bavarian graphite contained traces of chromium and vanadium, and South African graphite gave only a faint titanium line.

Under ordinary conditions spectroscopic examination would be too delicate a test for distinguishing between the pigments in pencil writing, and, although titanium is a common constituent of graphites, it is only rarely that it is present in sufficient quantity to be detected in markings on paper by means of a chemical reaction. In one case only have I obtained a distinct reaction for titanium by treating the writing with hydrochloric acid and hydrogen peroxide.

PIGMENTS IN COLOURED PENCILS. Cases where it is necessary to determine, if possible, whether writing done with a coloured pencil is in the same pigment as that of a particular pencil, or in another specimen of writing, are of fairly frequent occurrence, and I have already given an outline of some of them involving the differentiation of the pigments of copying-ink pencils (ANALYST, 1917, **42**, 3). Since that time I have extended the study so as to include red and blue pencils, and, in order to obtain the necessary data, have examined the pigments in typical commercial specimens.

The results are given in the following table, which also includes the analysis of a Japanese violet copying-ink pencil, and, for comparison, the analyses of two specimens of blue copying-ink pencils given in the former table (ANALYST, *loc. cit.*):

PIGMENTS IN COLOURED PENCILS.

| | | Moisture loss at 100° Per Cent. | Residue insol. in alcohol Per Cent. | Dye-stuffs Per Cent. | Loss on ignition, (graphite, wax, etc.) Per Cent. | Insol. in Acid (Silicates, etc.) Per Cent. | Ash (Kaolin, etc.) Per Cent. | Iron Per Cent. | Aluminium Per Cent. |
|---|---|---|---|---|---|---|---|---|---|
| | *Violet.* | | | | | | | | |
| 1. | Copying-ink pencil, "Dufferin" Japan | 2·81 | 77·84 | 22·16 | 61·83 | — | 13·20 | — | — |
| | *Blue.* | | | | | | | | |
| 2. | Duplex Copying, American Pencil Co. | 2·35 | 76·45 | 21·20 | 27·09 | — | 47·36 | 10·18 | — |
| 3. | Faber, Copying, 2251, Bavaria | 1·82 | 58·68 | 39·50 | 29·34 | — | 29·34 | large amount | — |
| 4. | Levis Creta (1840) S. Kensington Museum | 2·45 | — | nil | 27·25 | 35·27 | 71·54 | — | 8·90 |
| 5. | Blue, 1750. American Pencil Co. | 1·94 | — | — | 14·74 | 53·11 | 83·20 | 0·18 | 0·57 |
| 6. | Blue, A. Johnson & Co. | 2·72 | — | — | 25·46 | 35·69 | 71·82 | 13·04 | 4·92 |
| 7. | Blue, Rowney & Co. | 2·15 | — | — | 46·64 | 43·90 | 51·21 | 6·81 | 1·29 |
| | *Red.* | | | | | | | | |
| 8. | Swan Pencil Co., Bavaria | 2·68 | — | — | 52·52 | 14·07 | 44·80 | — | — |
| 9. | Cohen, London | 2·84 | — | — | 19·05 | 22·34 | 78·11 | 1·13 | — |

DIFFERENTIATION OF THE PIGMENTS IN WRITING. The Japanese violet copying-ink pencil can be classified with the Kurz pencil (No. 15) in the table of analyses in my former paper, since the amount of graphite is greatly in excess of the proportion of clay. The pigment could be distinguished from those in other violet copying-ink pencils by the methods previously described.

The blue Duplex pencil (No. 2) contained an aniline dyestuff soluble in water, whilst in the case of Faber's pencil (No. 3) methyl violet was the soluble constituent and Prussian blue the blue pigment.

I am indebted to Mr. T. H. Court for the specimen of Wolff's *Levis Creta* of 1840 (No. 4) in the South Kensington Museum. The pigment of this crayon consisted of ultramarine incorporated with wax. It could readily be distinguished from the pigments of other blue pencils in writing by being bleached on treatment with hydrochloric acid.

The pigments in Nos. 5, 6 and 7 consisted mainly of smalt, and in the case of No. 5 the amount of cobalt separated was 1·81 per cent. These pigments only dissolve very sparingly in hydrochloric acid, and the residues given in the table were those left after treatment of the material with *aqua regia*. The blue pigments could, however, be decomposed by treatment with strong potassium hydroxide solution. Although the smalt pigments contain varying proportions of iron, it is difficult to utilise this characteristic for their differentiation, since the blue colour produced in the reaction is masked by the original blue colour of the pigment.

The only chemical method of differentiation which I have devised depends upon the fact that some of the pigments are more readily bleached than others by the action of *N*-potassium hydroxide solution.

In a recent case I had to determine whether the blue lines on a letter which purported to be registered were in the same pigment as that of a pencil handed to me. Chemical tests were not permissible, but I was able to prove, by the use of Osborn's comparison microscope that the two pigments were different in shade, and also differed distinctly in their mode of arrangement on the paper.

Analogous difficulties of differentiation present themselves in the case of the red pencil pigments, which, in the case of those included in the table, consisted mainly of red lead, and contained only small proportions of iron.

Here again, slight differences may be noted in the colour and disposal of the original pigment on paper. For instance, some pencils give markings of a distinctly yellow tint, which can be readily distinguished from those produced by other red pencils, when examined with the aid of a comparison microscope.

Again, the pigments frequently differ in their behaviour on treatment with hydrochloric acid. For example, the pigment in Cohen's pencil becomes magenta, whereas that of the "Swan" pencil remains relatively unaffected. As in the case of the pigments of the other pencils, differences may also be noted in the reactions given by them for iron: and in this case the colour of the red pigment does not interfere with the test to the same extent as the pigments of the blue pencils.

In the case of blacklead pencil pigments, it is frequently possible to determine which of two intersecting lines was written first, since the sequence of the silver striations clearly shows which line is uppermost.

In the case of most coloured pencil pigments, however, this test is not applicable, for the striations are so masked by the coloured deposit that their course cannot be followed. It is only by removing the soluble part of the pigment by means of ether that it becomes possible to trace the striations in the residual mineral matter. Even then, a definite conclusion can only be drawn when the colour of the pigment is derived entirely from a soluble dye, as in the case of most copying ink pencils, and obviously this method cannot be applied to coloured pigments such as smalt or red lead.

## Discussion.

Mr. C. C. Roberts asked whether a pencil of pure silver and a specially prepared paper were not sometimes used.

Mr. E. R. Bolton enquired what the differences were in the composition of the graphite between pencils labelled H, HB, BBB, etc.

Dr. H. P. Stevens said that the use of a silver point was well-known in a method employed by artists.

Dr. Dyer enquired whether the pressure employed in drawing or writing did not affect the microscopical appearance of the pencil mark on paper.

Mr. W. Partridge enquired whether in the case of pencil-written letters which were no longer legible owing to immersion in water (*e.g.* letters found on drowned persons), there was any means of rendering the writing more legible than was possible by drying the paper.

Mr. MITCHELL, replying, said that silver pencils had certainly been used in association with specially prepared papers, and that Casaubon's note book in the Bodleian Library appeared to be an instance of the kind. The markings on pencils (H, HB, BB, F, etc.) indicated varying degrees of hardness, blackness and fineness, and the differences were obtained by varying the proportions of graphite, clay and wax in the pigment. The grades produced by one manufacturer did not agree with those produced by another. With regard to the point raised by Dr. Dyer, it was possible, by moistening the point of the pencil or pressing hard upon the paper, to produce marks which varied in their microscopical appearance, and it was therefore necessary to select markings of similar intensity for a comparison. The problem of deciphering erased pencil writing, to which Mr. Partridge had alluded, was a very difficult one. The best methods were to photograph the paper with different lightings and to expose the erased writing to iodine vapour; this would sometimes reveal the indentations in the paper made by the point of the pencil.

# The Estimation of Meconic Acid in Opium.

BY H. E. ANNETT, D.SC., F.I.C., AND M. N. BOSE, M.A.

(*Read at the Meeting, June* 7, 1922.)

IN work which we are carrying out on the opium poppy, it became necessary for us to have a method for estimating meconic acid with a fair degree of accuracy. The methods referred to in the literature have not given us satisfaction. Reference is made in *Allen's Comm. Org. Analysis* (Vol. VI., p. 411), to most of these.

The method we have adopted gives very satisfactory results in our hands and may probably be of use to other workers on opium. We proceed as follows :— Five grms. of opium are rubbed up carefully with water in a mortar and transferred to a stoppered flask, 50 c.c. of water in all being used. The flask is well shaken and allowed to stand overnight. The liquid is then filtered, and a measured quantity, *e.g.* 40 or 45 c.c., of the filtrate, is taken for the estimation of the meconic acid. Six c.c. of 50 per cent. calcium chloride solution are added, and the liquid shaken and allowed to stand for 24 hours. Any attempt partially to neutralise the opium solution before addition of the calcium chloride always results in the meconic acid being contaminated with colouring matters. The precipitate is filtered off in a Hirsch funnel and washed with water till the washings are colourless, and then consists almost entirely of calcium meconate and calcium sulphate, and is almost perfectly white. It is transferred to a small beaker, with the aid of 15 c.c. of 1·25 *N* hydrochloric acid, the filter paper being removed, and the beaker heated on the water bath until the precipitate has completely dissolved. The liquid is now allowed to stand in a cool place for 24 hours, when the meconic acid will have separated in white crystalline scales in a highly pure condition. It is filtered off in a Hirsch funnel, being removed completely from the beaker by means of the mother liquor, and then

washed twice with 0·5 c.c. of distilled water, dried between filter paper, and then in a desiccator over sulphuric acid for 3 hours, and weighed as $C_7H_4O_7 \cdot 3H_2O$.

The amounts of water used for the extraction of the opium, and of hydrochloric acid used for the decomposition of the calcium meconate precipitate, were decided on after a series of experiments with pure meconic acid.

In the calculations it is necessary to make corrections for the amount of meconic acid not precipitated by calcium chloride and for the meconic acid remaining in solution on decomposing the calcium meconate precipitate with hydrochloric acid. We have made numerous tests to determine the magnitude of these corrections.

CORRECTION FOR SOLUBILITY OF MECONIC ACID IN 1·25 *N* HCl.—A quantity of 0·40 grm. pure crystallised meconic acid was heated on the water bath with 15 c.c. of 1·25 *N* hydrochloric acid. After it had passed into solution, it was allowed to stand at about 23° C. for 24 hours. It was then filtered, dried over sulphuric acid in a desiccator for 3 hours, and weighed. The weight was 0·3785 grm. Therefore the amount of meconic acid remaining in solution was 0·0215 grm. The experiment was repeated with 0·2 grm. of meconic acid, when 0·1788 grm. of meconic acid was recovered, showing that 0·0212 grm. of meconic acid remained in solution. (Average = 0·0213 grm.).

CORRECTIONS FOR MECONIC ACID NOT PRECIPITATED BY CALCIUM CHLORIDE.—We have arrived at this figure by dissolving amounts of pure meconic acid in 50 c.c. water, treating* 45 c.c. of the solution with 6 c.c. of 50 per cent. calcium chloride solution, washing the precipitate with water and then decomposing it with 15 c.c. of 1·25 *N* hydrochloric acid, as above described. By adding the correction figure found above for the solubility of meconic acid in the 15 c.c. of 1·25 *N* hydrochloric acid solution, *viz.*: 0·0213 grm., and deducting the result from the amount of meconic acid originally taken, we arrive at the correction figure for the amount of meconic acid not precipitated by the calcium chloride. The experiments were carried out at the temperature of the room (23° C.).

The results obtained are shown in the following table:—

| Meconic acid taken in 50 c.c. of solution | Meconic acid 45 recovered in c.c. of solution | Weight corrected for solubility in HCl (*viz.*: 0·0213 grm.) | Figures in previous column corrected for 50 c.c. original solution, *i.e.* $\times \frac{50}{45}$ | Meconic acid not precipitated by $CaCl_2$ (difference fourth and first col.) | Meconic acid recovered (after correcting for solubility in HCl) |
|---|---|---|---|---|---|
| Grm. | Grm. | Grm. | Grm. | Grm. | Per Cent. |
| 0·1000 | 0·0574 | 0·0787 | 0·0874 | 0·0126 | 87·4 |
| 0·1500 | 0·1044 | 0·1257 | 0·1397 | 0·0103 | 93·1 |
| 0·2000 | 0·1433 | 0·1646 | 0·1807 | 0·0193 | 90·3 |
| 0·2500 | 0·1864 | 0·2077 | 0·2308 | 0·0192 | 92·2 |
| 0·3000 | 0·2304 | 0·2517 | 0·2797 | 0·0203 | 93·2 |
| 0·3500 | 0·2644 | 0·2857 | 0·3174 | 0·0326 | 90·7 |
| 0·4000 | 0·3051 | 0·3264 | 0·3627 | 0·0373 | 90·7 |
| 0·4500 | 0·3294 | 0·3507 | 0·3897 | 0·0603 | 86·6 |
| 0·5000 | 0·3646 | 0·3859 | 0·4289 | 0·0711 | 85·8 |

* In the estimation of meconic acid in opium we take 50 c.c. of water and usually obtain about 45 c.c. of filtrate for analysis. Hence, we took 45 c.c. only of the solution in these experiments, in order to have the conditions similar to those we use in the analysis of opium for meconic acid.

It will be seen from the foregoing table that, after adding the correction for solubility of meconic acid in 15 c.c. of 1·25 *N* hydrochloric acid, we recover about 90 per cent. of the meconic acid taken.

In estimating the amount of meconic acid in opium we therefore proceed as described, but correct the weight of meconic acid actually obtained as follows :—

We first add 0·0213 grm. to the weight, to correct for the solubility of meconic acid in 15 c.c. of 1·25 *N* hydrochloric acid. We then multiply the figure obtained, by a factor depending on the amount of the aliquot portion of the opium solution taken for analysis. If this were 45 c.c., we multiply by 50/45. We then multiply the product by 10/9 since the above table shows that, roughly, about 10 per cent. of the meconic acid is unprecipitated by the calcium chloride. The following example illustrates the method of calculation :—In a certain analysis we extracted 5 grms. of opium with 50 c.c. of water. We took 44 c.c. of the filtrate for treatment with calcium chloride and obtained 0·2744 grm. of meconic acid. The calculation is as follows :—$(0{\cdot}2744 + 0{\cdot}0213) \times \frac{50}{44} \times \frac{10}{9}$ = corrected weight of meconic acid from 50 c.c. of solution or 5 grms. opium.

Hence, in 100 grms. of opium we get $(0{\cdot}2744 + 0{\cdot}0213) \times \frac{50}{44} \times \frac{10}{9} \times \frac{100}{5}$, equivalent to 7·47 per cent. of meconic acid in opium.

The method of calculation may, perhaps, be made somewhat more accurate by a slight modification. After correcting for the solubility in hydrochloric acid by adding 0·0213 grm., and then multiplying by the factor to correct the weight for the amount present in 50 c.c. of solution, the result can be obtained by utilising columns 1 and 4 of the above table. Thus, in the example just given we should calculate as follows :—$(0{\cdot}2744 + 0{\cdot}0213) \times \frac{50}{44} = 0{\cdot}3359$ grm.

By interpolation in column 4 of this table, it will be seen that this figure corresponds to 0·3625 grm. of meconic acid taken, *i.e.* in 5 grms. opium.

Hence, the percentage of meconic acid obtained is 7·25, which shows a very close agreement with the result given by the first method of calculation.

TESTS OF THE METHOD ON OPIUM, WITH AND WITHOUT KNOWN ADDED AMOUNTS OF MECONIC ACID.—An aqueous extract was prepared by shaking 30 grms. of opium with 300 c.c. of water for half an hour. Six portions, each of 44 c.c., of the filtrate were then measured off. To each of 2 portions 0·1 grm. of meconic acid was added, and to each of 2 other portions 0·2 grm. of meconic acid. The meconic acid was then estimated in all six samples, with the following results:—

| | Substance taken | Wt. cryst. meconic acid obtained | Average of duplicates previous column | Previous column 0·0213 and × by $\frac{10}{9}$ |
|---|---|---|---|---|
| | | Grm. | Grm. | Grm. |
| 1 | 44 c.c. opium solution | 0·3104 | 0·3107 | 0·369 |
| 2 | .....do..... | 0·3111 | | |
| 3 | 44 c.c. opium sol. + 0·1 grm. meconic acid | 0·3945 | 0·3939 | 0·461 |
| 4 | .....do..... | 0·3933 | | |
| 5 | 44 c.c. opium sol. + 0·2 grm. meconic acid | 0·5091 | 0·5074 | 0·587 |
| 6 | .....do..... | 0·5057 | | |

In the last column of the table the amount of meconic acid recovered has been corrected by adding 0·0213 grm. as a correction for the solubility of meconic acid in 15 c.c. of 1·25 *N* hydrochloric acid, and the figure obtained has then been multiplied by 10/9 to allow for meconic acid unprecipitated by calcium chloride, as previously explained. Assuming 0·369 grm. to represent the correct amount of meconic acid in 44 c.c. of opium solution, the other figures in this last column should theoretically be 0·469 and 0·569 grm., instead of 0·464 and 0·590 grm. actually obtained. This is a sufficiently satisfactory agreement. Moreover, in all three cases the duplicate determinations agreed very well with one another.

Methods depending on the use of a correction factor are not usually satisfactory, but we know of no other method which will give such accurate results as ours for meconic acid estimation in opium. The amount of the acid present is usually large, varying from 2 to 10 per cent. in our experience. The method will certainly give results which will enable us to determine any large variation in meconic acid content in a series of samples of opium, and it is easy of manipulation. Moreover, the meconic acid we recover is in a high degree of purity. This is borne out by analyses carried out on the substance as recovered by us in the ordinary course of analysis from opium.

WATER OF CRYSTALLISATION.—0·2172 grm. kept in a vacuum desiccator over concentrated sulphuric acid, gave 0·1735 grm. of anhydrous acid, corresponding to 20·12 per cent. of water of crystallisation. Theory for $C_7H_4O_7 . 3H_2O = 21·26$ per cent.

TITRATION WITH SODIUM HYDROXIDE SOLUTION.—0·3 grm. required 23·60 c.c. of 0·1 *N* sodium hydroxide solution for neutralisation to phenolphthalein, which corresponds to a purity of 99·90 per cent.

SILVER SALT.—This was prepared direct from the acid, and on ignition yielded 49·92 per cent. of silver. $C_7H_2O_7.Ag_2.H_2O$ requires 50·00 per cent. Ag.

We recommend our procedure as a simple method of preparing pure meconic acid from opium. The methods described in the literature on the subject (See *Allen's Comm. Org. Anal., loc. cit.*) always yield meconic acid highly contaminated with colouring matter.

In conclusion, we would add that we have had considerable experience of the above-described method. It has worked admirably, and by its use we have been able to show that the alkaloids in the opium poppy latex occur entirely as meconates. An account of this work is being published as No. 3 of our Memoirs on Indian Opium by the Imperial Department of Agriculture in India.

## DISCUSSION.

Mr. A. CHASTON CHAPMAN wondered whether it would not be possible to find some more insoluble salt than calcium meconate; methods involving considerable corrections for solubility were seldom satisfactory. He thought that possibly one or other of the organic bases might be used.

Mr. W. PARTRIDGE thought that the divergence in the results obtained with calcium meconate by people working under the same conditions might be slight;

but that numbers of different people working in different parts of the country might obtain results showing much greater differences.

Dr. HENRY replied that the authors in their paper did not say that they had tried experiments with other bases, but he thought a lead salt would probably be unsuitable. With regard to the corrections to be applied for the solubility of meconic acid in hydrochloric acid and for meconic acid not precipitated as calcium meconate, the authors realised that methods involving such corrections were open to criticism. They had worked out this process as being the best solution of the difficulty, and had found that more accurate results could be obtained by it than by previously-recorded methods. The precipitated calcium meconate was washed until it was perfectly white; how much washing that amounted to was not shown.

# Notes from the Reports of Public Analysts.

*The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.*

## METROPOLITAN BOROUGH OF STEPNEY.

### ANNUAL REPORT OF THE BOROUGH ANALYST FOR 1921.

DURING the year 1427 samples were submitted for analysis, 1402 of which were taken under the Food and Drugs Acts (935 formally and 467 informally). Of the 1402 samples 86 (6·1 per cent.) were adulterated.

MILK.—The number of samples analysed was 824, of which 37 (4·5 per cent.) were adulterated. The average composition of all the samples was: Fat, 3·60, and solids-not-fat, 8·70 per cent.

BUTTER.—Three of 125 samples analysed were adulterated. Boric acid was present in 80 of these samples, but only in 3 cases did the amount reach 0·5 per cent. Since 78 per cent. of the samples contained not more than 0·25 per cent., it is suggested that the permissible amount of boric acid might well be reduced to that proportion.

MARGARINE.—Of the 187 samples examined 173 contained boric acid, the average amount being 0·23 per cent. No sample contained more than 0·5 per cent.

SPIRITS.—Six of 17 samples of spirits were adulterated. The position of spirits with regard to the Food and Drugs Acts is very unsatisfactory. For example, two samples of gin were purchased at a bar where a notice was shown stating that spirits were "below 43° u.p." The samples were 55° u.p. and 56° u.p. No ordinary purchaser would be likely to think that the notice was intended to cover such a high degree of dilution. It is advisable that there should be a statutory form of notice, stating the dilution of the spirits sold in words that the general public can understand. Notices are commonly met with stating that "to meet the requirements of the Food and Drugs Acts all spirits are sold as diluted spirits." Such notices are intended to evade the Acts and should be required to make this clear.

DRUGS.—Ninety samples were analysed, ten of which were adulterated. The adulterated samples included four sold as pure borax, two of which contained 100 and two 200 parts per million of arsenic. A circular letter was sent to all pharmacists in the Borough, cautioning them as to the liability of borax to contain arsenic, and advising them to take suitable precautions to see that their supplies were pure, as proceedings would be taken on subsequent occasions.

H. HAWLEY.

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## DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

### FOOD INVESTIGATION BOARD.

### THE PRESERVATION OF FOOD BY FREEZING, WITH SPECIAL REFERENCE TO FISH AND MEAT*.

IN this report the problems connected with processes involved in the method of cold storage are considered. For the method to be successful the condition of the material after the three processes—(1) freezing, (2) storage in frozen condition, and (3) thawing or defrosting—should be similar to its original condition. Each food substance presents its special problems.

The physics and chemistry of the freezing process are first discussed, and from a survey of the factors which influence the rate of cooling and freezing of a body it is made clear that these rates are to a great extent under the control of the investigator.

INFLUENCE OF LOW TEMPERATURES ON ENZYMES.—The general conclusion to be drawn from the investigations of Hepburn (*Biochem. Bull.*, 1915, **4**, 136) and others is that enzymes survive exposure to low temperatures, and are again able to act as catalysts when the temperature is raised. The activity of lipase towards esters is increased during storage in the frozen condition, a result attributed by Pennington and Hepburn to the conversion of a zymase into a more active form.

INFLUENCE OF LOW TEMPERATURES ON VITAMINS.—Experiments made by Harden for the Food Investigation Board have proved that the vitamin content of butter is not diminished by cold storage.

THE FREEZING OF COLLOIDAL SYSTEMS.—An outline is given of the reasons which justify the conclusion that in living and dead animal and plant tissues we have to do with colloidal systems comprising both hydrosols and hydrogels.

The observations made by Fuld and Wohlgemuth (*Biochem. Zeitsch.*, 1907, **5**, 118) on the causes leading to the irreversibility of the changes produced in human milk on freezing can probably be explained as follows :—In the rapid freezing of the milk by means of liquid air a more or less homogeneous glass is produced, which, on thawing, gives the original system, whereas, by the much slower methods of ordinary freezing, formation of ice crystals takes place, so that the protein particles are pressed together into greater aggregates, with the result that, on thawing, a much coarser-grained system results.

FREEZING OF LIVING CELLS AND TISSUES.—The available information is summarised, and it is shown that it all points to the fact that if the cells and tissues are frozen sufficiently rapidly, the changes in structure resulting from the freezing can be reversed on thawing.

THE DIFFERENT FREEZING METHODS.—The two methods which are of practical importance are (1) freezing in cold air, and (2) freezing in a cold salt solution.

*Air Freezing.*—The chief differences between pure air cooling and pipe cooling lie in the movement of the air and in the humidity of the air at the surface of the

* Special Report No. 7. By W. Stiles, D.Sc., pp. 186. H.M. Stationery Office, 1922, Price 10s. net.

food. In the case of meat loss of water does not take place to any extent, whilst moulds develop without much difficulty; consequently in the freezing of meat pure air cooling is indicated. Fish, on the other hand, suffers much from desiccation, but is not very liable to attack by micro-organisms, and hence a moister atmosphere can be employed with advantage.

The loss of weight by evaporation may be reduced by protecting the object with a covering, such as a glaze or parchment paper, but the time of freezing will necessarily be lengthened, and another operation introduced into the process, thereby increasing the cost.

*Freezing in Salt Solutions.*—An outline is given of the different processes used since the introduction of the method. The principal advantage of freezing in solutions over air freezing is the greater speed, but it is essential that the solution should be kept in a state of active agitation.

*Exchange of Material between the Cooling Medium and the Food Substance.*—When meat or fish is immersed in a solution of sodium chloride osmotically stronger than the cell fluid, water will be withdrawn from the tissue, provided the salt does not penetrate into the muscle cells. But the high concentrations of salt used in the freezing tank lead to the death of the cell, and the complete permeability of the plasma-membrane, so that the entrance of salt into the tissue is only a matter of time.

*The Penetration of Salt.*—Below the freezing-point of the food the entrance of salt takes place in a considerably reduced amount. If, however, before this temperature is reached, salt has penetrated into the outer layers in high concentration, its presence will lower the freezing-point of these outer parts of the tissue, so that the whole will not freeze until a very much lower temperature is reached. The penetration of salt can be minimised or prevented by surrounding the object to be frozen with an impervious covering, if the conditions warrant the cost. The skin of fish and the fat of meat act to some extent in this way. By choosing the lowest concentration which it is possible to obtain at any temperature the entrance of salt can be reduced to a minimum.

*Interaction of the Dissolved Substance with the Food Material.*—For certain foods, as, for example, fish, and perhaps poultry and butter, freezing in sodium chloride brine appears satisfactory from every point of view. On the other hand, whilst large pieces of beef frozen in brine are in some particulars superior to beef frozen in air, a reaction takes place between the sodium chloride and the pigment of the beef, with the result that the meat acquires an unusual appearance, which would greatly prejudice its sale.

COMPARISON OF THE TIME TAKEN TO FREEZE IN AIR AND BRINE.—Data for the comparison and tables for the freezing times of beef and of fish based upon the observations are given.

THE STORAGE OF FOOD SUBSTANCES IN THE FROZEN CONDITION.—The changes which may take place in frozen food material comprise evaporation of water, evaporation of aromatic substances, chemical changes (including hydrolysis of fats), with or without the aid of enzymes, and development of moulds and bacteria. By varying the conditions of the temperature, degree of movement, and humidity in the storage chambers these changes can be lessened to a considerable extent.

EVAPORATION OF WATER.—The following means of reducing evaporation may be employed: (1) Reducing the exposed surface by close packing of the material. (2) Preventing the movement of the air. (3) Increasing the humidity of the storage chamber. (4) Lowering the temperature. (5) Covering the material with a protective layer of a substance, such as ice, parchment paper or specially prepared coverings of paraffin wax or mixtures of waxes with other substances.

EVAPORATION OF AROMATIC SUBSTANCES.—The flavour and aroma of food are best preserved by close packing and by covering the material with a protective coating.

CHEMICAL CHANGES DUE TO AUTOLYSIS.—All the investigations go to show that such changes are practically negligible during storage for many months. In the case of fowls stored for a year in the frozen condition the proteolysis only equalled in amount that which had occurred in fowls after 3 weeks' storage in the chilled condition at about 0° C.

CHANGES DUE TO THE PRESENCE OF WATER AND OXYGEN.—The prevention of access of moisture and oxygen may be achieved by means of protective wrappings. Reduction of the relative humidity of the storage chamber will also reduce the moisture necessary for the rancidity of fats. In the case of lean meat the problem is to prevent the loss of water from the surface, whereas in the case of fat it is condensation of moisture on the surface which has to be prevented.

DEVELOPMENT OF MOULDS AND BACTERIA.—For the prevention of moulds the temperature and the relative humidity must be kept as low as possible. When the mould is confined to the surface it can often be completely washed or brushed off, but if it has penetrated into the interior, it may produce substances which have not only an unpleasant taste and odour, but which may also be poisonous, although there is no known case of this among the moulds.

THAWING OF FROZEN FOOD.—In the case of food materials frozen quickly enough to preserve the original space relations of the colloid, it is immaterial whether the substance is thawed rapidly or slowly, so far as the reproduction of the original structure of the food is concerned. On the other hand, with slow freezing it is possible that the original system will not be re-formed on thawing, however this is carried out.

THE CONDITIONS OF THAWING.—The disadvantages attending the use of air as a thawing medium are those which also obtain in the storage chamber. The chief disadvantage of water is that it may dissolve soluble substances from the food material. The best conditions must therefore be determined according to the nature of the material and its state when withdrawn from storage.

COURSE OF THAWING.—It is shown by means of curves, that, other things being equal, the time of thawing will be longer than the time taken in freezing. Plank's formula for the freezing time will hold equally well for the time taken to thaw, if the correct values are given to the constants in the equation.

PRESERVATION OF FISH BY FREEZING.—The chief advantage of freezing fish in air is the simplicity of the method. Against this are the disadvantages of (1) the comparatively long time required, with consequent changes in structure; (2) loss of water by evaporation; and (3) loss of surface mucilage, which gives a dull appearance and reduces the market value of the fish. The freezing time of fish is, roughly, inversely proportional to the difference in temperature between the cooling medium and the freezing point of the fish. As the latter is about $-1°$ C. in most cases, lowering the temperature from $-10°$ C. to $-19°$ C. would reduce the freezing time about one half.

*Freezing in Solutions.*—In order to obtain as rapid freezing as possible the lowest possible temperature should be used. With sodium chloride this is about $-21°$ C.; with magnesium chloride below $-30°$ C.; and with calcium chloride below $-40°$ C. To prevent penetration of salt the lowest possible concentration should be used It is desirable that the medium should always be kept in active movement relatively to the frozen object. There are no records of experiments in which the minimum concentration of magnesium chloride or calcium chloride solutions has been used.

There is no loss of water during freezing in brine; on the contrary, a gain in weight of 1 to 2 per cent. has been observed in most cases.

In the case of expensive fish the use of a protective coating may be commercially profitable, as it will prevent the penetration of salt. In certain cases a combination of the methods of air cooling and brine cooling may be found useful, whilst pre-cooling the fish in ice-water has the advantage of preventing loss of water.

*Histological Differences.*—The main difference between brine-frozen and air-frozen fish is that in the former the water of the sarcoplasm solidifies inside the muscle-fibres, so that the space relations of the fibres and connective tissue are not disturbed, whereas in the case of air-frozen fish the water, on freezing, passes out from the muscle-fibres into the connective tissue, whereby the connective tissue spaces become enlarged and the muscle-fibres come to be pressed together into irregular-shaped bundles. On thawing, the liquid in the connective tissue easily runs out of the fish, and this results not only in desiccation and shrivelling, but also in the loss of salts and nutritive substances.

STORAGE OF FROZEN FISH.—Loss of water by evaporation is one of the greatest difficulties to be overcome; on the other hand, fish is less liable to the attacks of micro-organisms than other kinds of food. Hence, a relatively high moisture content of the storage chamber is indicated in the case of fish.

THAWING OF FROZEN FISH.—Three methods are in use: (1) Thawing in crushed ice; (2) thawing in water; and (3) thawing in warm air. Comparative tests made by Plank and Ehrenbaum have indicated that the velocity of thawing affects neither the taste nor the keeping properties of the fish. The actual thawing method only influences the fish indirectly, in that in thawing in air less water is taken up by a desiccated fish than in the case of thawing in water or in crushed ice. These conclusions are in accordance with the general opinion of the industry in this country.

PRESERVATION OF MEAT BY FREEZING.—All kinds of meat are frozen in air on a commercial scale, but frozen beef is frequently inferior to the fresh material, owing to the loss of meat juice which occurs on thawing. Hence, wherever possible, beef is transported from abroad in the chilled condition. Since, however, beef can rarely be kept in this state for longer than 3 or 4 weeks, the method of preservation by chilling is inapplicable to the transport of meat from Australia and New Zealand.

The freezing time depends on the dimensions of the body frozen, and on the presence of fat and, if present, on the thickness of the layer of fat. With a temperature in the freezing chamber of $-70°$ C., the average times required to freeze pre-cooled sides of pork and quarters of beef, until the middle of the thickest part reaches a temperature of $-5°$ C. are as follows :—Sides of pork, 3 days; fore-quarters of beef, 5 days; hind-quarters of beef, 7 days.

*Freezing in Solution.*—Experiments have indicated that it may be found possible to prevent the "drip" from frozen beef by sufficiently rapid freezing. With a fat layer 1 cm. thick surrounding the hind quarter, the freezing time in brine is less than half the freezing time in air at the same temperature.

The reaction between the salt and the tissues, whereby the bright red colour is changed to dull brown or reddish-brown, takes place only at the surface of the meat, and does not extend into the interior more than 1 cm. The change is due to the conversion of the hæmoglobin of the blood into methæmoglobin. By exposing the discoloured meat to moist air the original colour is restored, apparently by bacterial action, but the method cannot be used in practice.

The presence of $0{\cdot}1\,N$ alkalinity inhibits the development of the brown discoloration on a small scale, and $0.1\,N$ ammonia is still more effective. The method has failed, however, on a large scale.

The use of other salts giving lower temperatures may solve the problem. Mutton has been frozen in calcium chloride solution at −28° C., and, when thawed and cooked, has shown not the slightest sign of unpleasant flavour due to the presence of the salt.

*Bone-taint.*—This is a defect characterised by deep-seated putrefactive changes in the thick muscles in the neighbourhood of the hip and shoulder joints. It shows no external appearances and is most frequently observed in the best conditioned animals.

The opinion in the trade is that pre-cooling above the freezing point is essential to prevent bone-taint, but this view is not supported by experiments made for the Food Investigation Board.

THE STORAGE OF FROZEN MEAT.—On the Continent temperatures of −6° to −8° C. are usual for storage; in this country the average temperature is −8° to −10° C.; whilst in America the temperature is usually −9° C. to −12° C., and in some cases as low as −20° C.

*Freezing of Meat in Relation to Autolysis.*—Experiments on the autolysis of lean beef and mutton have shown that there is a constant difference between the two, the mutton being more acid and containing a higher proportion of nitrogenous compounds of relatively lower molecular weight. Also, the autolysis, which reaches an equilibrium in about 9 days, has then proceeded further in the case of mutton than that of beef. Autolysis is practically negligible when meat is stored in the frozen condition.

The course of autolysis in meat which has been frozen and subsequently thawed varies greatly with the rate of freezing. In the case of beef frozen by the ordinary method in air, the autolysis is resumed after thawing, but equilibrium is not reached, as is the case with fresh meat, and chemical changes are still proceeding 16 days after thawing. If, however, the beef is frozen so rapidly that the "drip" on thawing is avoided, autolysis proceeds to equilibrium in the same way as in fresh unfrozen beef, and to the same extent.

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## MINISTRY OF HEALTH.—FOOD ORDERS IN FORCE.

THE following Orders and Regulations in regard to the inspection and supervision of food are in force. (July, 1922):—

The Dairies, Cowsheds and Milkshops Orders, 1885, 1886, and 1899.
The Sale of Milk Regulations, 1901 and 1912.
The Foreign Meat Regulations, 1908 and 1909.
The Unsound Food Regulations (First Series), 1908.
The Public Health (Milk and Cream) Regulations, 1912 and 1917.
The Public Health (Shell-fish) Regulations, 1915.
The Milk (England and Wales) Order, 1921.
Order amending the Milk (England and Wales) Order, 1921. (S.R.O. No. 1056/1921).
The Sale of Food Order, 1921.
Order amending the Sale of Food Order, 1921. (S.R.O. No. 1883/1921).

CIRCULAR 325 (*England and Wales*).

THE subjoined Circular has been sent by the Minister to the Clerks of the Authorities administering the Food and Drugs Acts in England and Wales:—

MINISTRY OF HEALTH,
Whitehall, S.W.1,
17*th July*, 1922.

SIR,—I am directed by the Minister of Health to state that his attention has been called to a case in which a milk vendor was prosecuted for selling milk deficient in fat, and on the case coming before the Court, it was shown that the vendor had held a good record for a number of years and that during that period constant tests had given uniformly satisfactory results. It was further shown that special circumstances existed to account for the milk being deficient in fat on the occasion of the test on which the prosecution was based. As soon as the local authority became aware of the facts of the case they withdrew the prosecution

The Minister fully appreciates that in order to prevent the systematic selling of milk deficient in fat, local authorities will often be compelled to institute proceedings against vendors who sell milk containing less than the proper amount of fat; but at the same time he feels that local authorities would desire to avoid a course of action calculated to cause irritation to those vendors who are doing their best to secure that the milk they sell is of good quality. He is advised that conditions of a purely temporary character may on occasion cause the milk from cows which normally give milk of the proper fat content, to be below the limit laid down in the Sale of Milk Regulations, and that the results of an isolated test cannot be regarded as conclusive evidence that the milk in question is in general below this limit. The Minister is therefore of opinion that it is extremely undesirable that a prosecution should be based upon the results of an isolated test when other tests of the particular milk supply have proved satisfactory, and I am to suggest for the consideration of the local authority, that in such cases prosecutions should be instituted only where a series of tests have shown repeated default.

I am, Sir, Your obedient Servant,

A. K. MACLACHLAN (*Assistant Secretary*).

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# ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

## Food and Drugs Analysis.

**Estimation of Hydrogen Sulphide evolved by Foods when Cooked at Various Temperatures. E. E. Kohman.** (*J. Ind. Eng. Chem.*, 1922, **14**, 527–529.)—The method described is designed for the estimation of the hydrogen sulphide which is evolved when such foods as green maize are cooked at 100° C., or higher temperature. The sample is placed in a 3-litre flask which is fitted in an autoclave supplied with steam from a boiler; the flask is provided with a wooden stopper, through which pass a delivery tube and a tube extending from just above the stopper to the bottom of the flask. Steam enters the flask through

the latter tube and escapes through the delivery tube (which passes through the cover of the autoclave) to a condenser. The distillate is collected in a receiver containing bromine solution, and the hydrogen sulphide is estimated subsequently as barium sulphate. The delivery tube is provided with a tap, so that the rate of distillation may be regulated; if desired, a double delivery tube may be used, one branch being a wide tapped tube, and the other a capillary of any required diameter. Both branches enter the condenser, and with this arrangement the amount of distillate obtained will vary only with the different temperatures in the autoclave. W. P. S.

**Detection of Soya Bean Albumin in Cow's Milk. K. Nakayasu.** (*J. Pharm. Soc. Japan*, 1921, No. 476, 880–887; *Chem. Abstr.*, 1922, **16**, 1469.)—Soya bean albumin (or bean milk) is made in Japan by soaking the washed beans for 10 hours in water, then grinding them, and boiling and filtering the product. The filtrate of "soya bean albumin" has a sp. gr. of about 1·03, and a sample examined by Suda contained 10·57 per cent. of total solids, 2·27 per cent. of fat, 4·88 per cent. of albumin, 2·72 per cent. of carbohydrates, 0·07 per cent. of fibre, and 0·6 per cent. of ash. Unlike rice milk, the bean carbohydrates cannot be detected in milk by the iodine test. A sensitive test, however, has been based upon the fact that glycinine, the main constituent of soya bean protein, is soluble in alkali solution, and is then readily oxidised on exposure to the air, becoming yellowish-brown in colour, whereas casein and lactalbumin do not become yellow on similar treatment. If, on treating 10 c.c. of milk with 4 or 5 drops of a 28 per cent. solution of potassium hydroxide a yellow coloration is produced, the presence of soya bean protein is indicated.

**Detection of Apple Juice in "Pure Fruit" Preserves. M. C. F. Muttelet.** (*Ann. Falsificat*, 1922, **15**, 196–200.)—One hundred grms. of jam or jelly are mixed with 50 c.c. of water, the mixture being heated and agitated until the jelly is dissolved, when the volume is made up to 300 c.c. After cooling, 150 c.c. of 95 per cent. alcohol are gradually added, and the mixture allowed to stand several hours, after which the fruit and precipitated pectins are removed by filtration. If highly coloured, the filtrate is shaken for 20 minutes with 3 or 4 grms. of purified animal charcoal free from inorganic salts, and again filtered. Twenty c.c. of the filtrate are diluted to approximately 100 c.c. and titrated with 0·1 *N* potassium hydroxide solution, phenolphthalein being used as indicator, and the results are expressed as the number of c.c. of *N* alkali equivalent to 100 grms. of the original material. A volume of the solution equivalent to 5 c.c. of *N* potassium hydroxide solution is diluted with 200 c.c. of 95 per cent. alcohol, and neutralised by the addition of the potassium hydroxide solution, after which 25 to 30 c.c. of 5 per cent. solution of barium bromide in 85 per cent. alcohol are added, and the mixture allowed to stand several hours. The clear supernatant liquid is decanted, and the precipitate is transferred to a filter and washed with 80 per cent. alcohol, after which it is dissolved by heating it for an hour and shaking it with 100 c.c. of water. This aqueous solution is filtered, cooled, diluted to 100 c.c. and treated

gradually with 50 c.c. of 95 per cent. alcohol. After filtration, traces of barium citrate remaining in solution are removed by evaporation of the filtrate to 50 c.c., and the gradual addition of 25 c.c. of 95 per cent. alcohol, with subsequent filtration. The filtrate, containing barium malate, is evaporated to 25 c.c., and the salt precipitated by the gradual addition of 50 c.c. of 95 per cent. alcohol. The resulting precipitate is suspended in water and decomposed by the addition of sulphuric acid, and the precipitate of barium sulphate is washed, dried and weighed. The weight of barium sulphate, multiplied by 0·574, gives the weight of malic acid contained in the volume of original solution taken. Since currants, raspberries and strawberries contain no malic acid, the presence of that substance in preserves made from those fruits indicates the addition of apple or cherry juice, the latter being used for colouring. Further evidence of this adulteration is provided by the reduction in acidity, the addition of 50 per cent. of apple jelly reducing this by 30 to 50 per cent. Quince jelly resembles that of apples in showing a low acidity on titration, in its content of malic acid, and in the absence of citric acid. T. J. W.

**Detection of Thymine in the Presence of Sugar. H. J. Deuel and O. Baudisch.** (*J. Amer. Chem. Soc.*, 1922, **44**, 1581–1584.)—The detection of acetol in the product of the oxidation of thymine is not sufficient for its identification in the presence of sugar, because acetol is also produced by the distillation of the simple carbohydrates with sodium hydrogen carbonate. The thymine is therefore separated from the sugar by precipitation as the mercury salt, and the acetol, pyruvic acid, and urea are identified after its oxidation. To 100 c.c. of the solution are added 10 c.c. of mercuric chloride solution and excess of sodium hydroxide, the precipitate is separated by centrifuging, washed with water and again centrifuged. The washed precipitate is suspended in water and decomposed by means of hydrogen sulphide, the mercuric sulphide is filtered off, and the hydrogen sulphide removed by boiling. The resulting solution of thymine is then oxidised by shaking it with 10 grms. of sodium hydrogen carbonate and 10 grms. of ferrous sulphate for 45 minutes; the ferric hydroxide is now removed by filtration, and the acetol distilled off and identified by Johnson and Baudisch's test with *o*-aminobenzaldehyde. (*Cf.* ANALYST, 1922, 177.) The residue in the flask is centrifuged to remove any remaining iron oxide and divided into two parts. To one part is added *o*-nitrobenzaldehyde and the mixture warmed, the formation of indigo blue indicating pyruvic acid. The other part is considerably diluted and two volumes of glacial acetic acid added, and then excess of an alcoholic solution of xanthydrol; a precipitate of dixanthyl-urea (m. pt. 250-260° C.) forms in the presence of urea, but may not appear for some hours, if the solution is very dilute. The limit of sensitiveness is 10 to 15 mgrms. of thymine in the presence of sugar in daylight or 1 mgrm. if an iron arc is used as illuminant. H. E. C.

**New Test for Carbohydrates. O. Baudisch and H. J. Deuel.** (*J. Amer. Chem. Soc.*, 1922, **44**, 1585–1587.)—It is shown that the following simple carbohydrates yield acetol when distilled with a solution of sodium hydrogen

carbonate : Arabinose, ribose, xylose, dextrose, fructose, mannose, galactose, glucosamine, lactose, sucrose, maltose, dextrin. Starch and glycogen produce no acetol under these conditions. The acetol is readily identified by the *o*-amino-benzaldehyde test, and serves for the qualitative detection of the simpler carbohydrates. (*Cf.* preceding abstract.) H. E. C.

**Oil of Cape Chestnuts.** (*Bull. Imp. Inst.*, 1922, **20**, 5.)—The Cape Chestnut, (*Calodendron capense*, Nat. Ord. *Rutaceæ*), is a large tree producing a white timber, and is found in various parts of South Africa up to an altitude of 4,000 ft. It is said to be one of the few indigenous trees which may prove worth cultivation. The seeds, of average weight of 1·1 grms., are black and angular, and have crinkled woody shells (57 per cent.) enclosing irregular shaped cream coloured kernels (43 per cent.) which are bitter and contain 59·2 per cent. of a liquid lemon yellow oil of faintly bitter taste. The oil gave the following constants :—Specific gravity at 15/15° C., 0·9219 ; acid value 0·4 ; saponification value, 192·6 ; iodine value, 108·7 ; unsaponifiable matter, 0·5 per cent. ; volatile acids : soluble, 0·5, insoluble, 0·2 per cent. ; solidifying point of fatty acids, 26·8° C. ; and $n_D^{40}$, 1·465. These values show a fairly close agreement with those of a sample previously examined at the Institute (*Bull. Imp. Inst.*, 1908, **6**, 364). The suitability of the oil for edible purposes is doubtful, but for soap and other uses it would be very similar to cotton oil. The residual meal was bitter, and though cyanogenetic glucosides were not found, a substance was present which gave reactions similar to those of alkaloids ; and therefore, although rich in protein and low in fibre, the cake cannot be recommended for cattle, and is probably only suitable for manure. The analysis of a meal, calculated to 7 per cent. of fat, showed : Moisture, 7·3 ; crude protein, 40·2 ; carbohydrates (by difference), 37·0 ; and ash 4·6 per cent. Its nutrient ratio was 1 : 1·3 and food units 155. D. G. H.

**Oil from the Seeds of Samuela Carnerosana. O. F. Black and J. W. Kelly.** (*Amer. J. Pharm.*, 1922, **94**, 477–479.)—The tree *Samuela carnerosana*, which is abundant in Mexico, produces soft red or purple fruits, which are eaten by the Indians and Mexicans. The seeds are flattened discs, light yellow when immature, and black when ripe; they constitute about 30 per cent. of the dried fruit. A sample of the dried seeds, extracted with ether, yielded about 20 per cent. of a pale yellow tasteless and odourless oil, with the following characteristics : Sp. gr. at 22° C., 0·9265 ; acid value, 5·1 ; saponification value, 192·8 ; and iodine value, 125·6. On extracting the seeds with alcohol about 10 per cent. of an amorphous white compound was separated. This frothed strongly and gave other tests characteristic of a saponin. Unlike other compounds of this type, it was not highly toxic, and might therefore prove of value as a substitute for commercial saponins. The fruit is rich in pectinous material and might prove a useful adjunct in the manufacture of jams from fruit lacking in pectin.

**Composition of Soya Bean Oil. W. B. Smith.** (*J. Ind. Eng. Chem.*, 1922, **14**, 530–531.) The composition of the mixed fatty acids obtained from

soya bean oil having an iodine value of 134 was as follows :—Linolenic acid, 2 to 3 per cent. ; linolic acid, 55 to 57 per cent. ; oleic acid, 26 to 27 per cent.; and saturated fatty acids, 9 to 10 per cent. W. P. S.

**Perilla Oil. K. H. Bauer.** (*Chem. Zeit.*, 1922, **46**, 538–539.)—The sample of oil examined had: Sp. gr. at 20° C., 0·9280 ; $n_D^{20}$, 1·4830; saponification value, 187·4 ; iodine value (Hanus), 204·3 ; and hexabromide value, 50·8. The fatty acids were separated by the lead method into 12 per cent. of saturated acids (mainly palmitic acid) and 88 per cent. of unsaturated acids, which, on oxidation with permanganate, yielded a tetrahydroxystearic acid (m. pt. 135°–140° C.) and a mixture of hexahydroxystearic acids, including linusic and isolinusic acids, and an acid melting at 165° C. This last acid has not been prepared from linseed oil. Sativic acid, as obtained by the oxidation of the linolic acid in linseed oil, and the dihydroxystearic acid from the oleic acid of linseed oil were not yielded by this perilla oil. T. H. P.

**De-acetification [Dépiquage] of Wines. L. Ferré.** (*Ann. Falsificat.*, 1922, **15**, 139–146.)—Wines in which volatile acids have been developed as a result of bacterial action are sometimes illegally treated with a neutralising agent with the view of masking the effect. When this treatment, termed *dépiquage*, is applied to a wine containing a high proportion of free tartaric acid, combined volatile acids appear only if the quantity of neutralising agent added is large. A smaller addition leads to the formation of either potassium hydrogen tartrate or normal calcium tartrate, which are precipitated and hence do not sensibly modify the constitution of the wine ; in this case the treatment cannot be detected. When, however, the treated wine contains little or no free tartaric acid, as is usually the case, it is possible to detect the treatment and to determine the nature of the substance added. No matter what this may be, a certain proportion of volatile acid in the combined condition is found. If a potassium salt is added, the quantity and alkalinity of the ash, as well as the total potassium and the value of the ratio of potassium to total tartaric acid, are sensibly increased. If calcium carbonate is used, the wine will contain a high proportion of calcium salts and the total tartaric acid present will be diminished, possibly to zero. The estimations necessary to detect such de-acetification are carried out as follows : Ten c.c. of the wine are shaken in a test-tube, 1 cm. wide and 20 cm. long, with four successive quantities of 10 c.c. of ether, the tube being closed with a cork, shaken for three minutes and cooled in water, and the ether siphoned off. The combined ethereal extracts, containing the free volatile acids and some fixed acids, are distilled, with additions of water, until about 50 c.c. of distillate are obtained. This distillate is titrated with 0·1 *N* alkali hydroxide in presence of phenolphthalein and the result multiplied by 1·25, since it is found that only 80 per cent. of the free volatile acids are extracted under the above conditions. The residual wine, left after extraction with ether, is distilled with 0·5 c.c. of 10 per cent. sulphuric acid, with repeated additions of water as before ; the distillate contains the combined volatile acids as well as 20 per cent. of the free volatile acids. T. H. P.

**Hydroferrocyanic and Hydroferricyanic Acids as Reagents for Essential Oils. Van der Wielen.** (*Pharm. Weekblad*, 1922, **59**, 683–685.)—On shaking cajuput oil with an equal quantity of a mixture in equal volumes of dilute sulphuric acid and 10 per cent. potassium ferrocyanide solution a voluminous crystalline white mass is obtained. This reaction, which is due to the presence of cineol, is also given by pinene, caryophyllene and ascaridol. When cineol is shaken with an equal volume of a mixture of dilute sulphuric acid and 10 per cent. potassium ferricyanide solution the crystalline mass is not obtained, but on diluting the liquid with water (10 times the quantity of reagent added) and adding a drop of ferric chloride solution the aqueous layer turns brown, instead of green or blue. The same reaction occurs, although to a less pronounced extent, with pinene, caryophyllene and ascaridol. The following oils, among others, give negative results in the hydroferrocyanic acid test: Peppermint, cinnamon, caraway, bitter almonds, cherry laurel, anise, absinthe, orange, lemon, savin, thyme, origanum, valerian, santal wood, fennel, pepper, mace, pimento, mustard and elemi. The following oils containing pinene give the reaction: Turpentine, juniper and pine. By applying the test to the first 10 c.c. of the distillate it is possible to detect the presence of 5 per cent. of oil of turpentine in oils which, when pure, do not give the reaction. Very slight crystalline deposits are given by bergamot, citronella and geranium oils. The following oils give a brown coloration on treatment with hydroferricyanic acid and ferric chloride: Wintergreen, peppermint, santal-wood and eucalyptus, whilst oil of bergamot gives a green or blue coloration. A very fluid product with hydroferricyanic acid, and a green or blue coloration on adding ferric chloride, is given by citronella, lavender, geranium, anise, clove, and fennel oils, whilst turpentine and cajuput oils yield a larger amount of the compound. Clove oil differs from other oils in forming with hydroferrocyanic acid a compound which is heavier than water.

**Distilled Cherry Laurel Water. H. Pecker.** (*J. Pharm. Chim.*, 1922, vii., **25**, 424–429.)—Distilled cherry laurel water which, in accordance with the French pharmacopœial requirements, contains 1 grm. of hydrocyanic acid per litre, should contain a considerable proportion of benzaldehyde, usually more than 3 grms. per litre. Under such conditions, the proportion of free hydrocyanic acid does not exceed 0·25 grm. per litre, the rest existing in combination with the aldehyde. If the water is not artificial, but is prepared from cherry laurel leaves, it gives (1) a precipitate almost immediately, in the cold, with a reagent obtained by adding 20 drops of sodium sulphite solution (French Codex) to a solution containing 1 c.c. of recrystallised phenylhydrazine and 0·5 c.c. of glacial acetic acid per 100 c.c. (2) a deep blue coloration with a solution containing 2 grms. of ammonium molybdate and 5 c.c. of pure sulphuric acid per 100 c.c.; this coloration varies in depth with the age of the sample, but it is not given by samples prepared artificially from hydrocyanic acid and benzaldehyde. T. H. P.

**Pyrethrum Powder. D. Costa.** (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 251–253.)—The water-soluble extract of pyrethrum flowers may be readily estimated by extracting the coarsely ground flowers in Procter's apparatus for estimating tanning materials. Finely ground commercial insecticide powders are, however, best treated in a cylindrical separating funnel, in which are placed in order layers of cotton wool, powdered pumice, powdered pumice mixed with the insecticide, pumice and cotton wool. Two hundred c.c. of water are poured into the funnel, 100 c.c. of extract being drawn off and replaced by water after 12 hours; after two repetitions of this process the extraction is complete. The percentage of water-soluble extract, calculated on material dried at 100° C., is 22 to 25, 12 to 14, and 9 to 11 for closed flowers, open flowers and stems respectively. (*Cf* ANALYST 1922, **47**, 260.) T. H. P.

# Bacteriological, Physiological, etc.

**Identification and Estimation of Saponins. L. Kofler.** (*Zeitsch. Nahr. Genussm.*, 1922, **43**, 278–287.)—The hæmolytic index, which has been suggested as a means of identfying saponins, varies with the degree of puiity of these compounds and with the method of purification used. The author finds, however, that the ratio of the hæmolytic index to the "frothing power" is a constant for any particular saponin and is independent of the degree of purity. To determine the frothing power a series of test-tubes of equal bore (16 mm.) is charged with 1, 2, 3, . . . . . 10 c.c. of a 0·1 per cent. solution of the saponin in water or physiological salt solution, the volume in each being made up to 10 c.c. with the solvent and the tubes closed with the thumb, shaken for 15 seconds and then left at rest. That tube which after 15 minutes exhibits froth 1 cm. in depth is noted, the frothing power being the corresponding dilution of the saponin.

The hæmolytic index is determined as follows: Fresh defibrinated rats' blood is diluted with 50 times its volume of physiological salt solution and 5 c.c. of the solution mixed with 0, 1, 2, 3, 4 and 5 c.c. of a 0·1 per cent. solution of the saponin in physiological salt solution, the volume in each case being made up to 10 c.c. with the same solution. Each tube is rotated once to mix the contents, and the tubes examined after 12 to 20 hours, partial hæmolysis being indicated by an intense red coloration of the liquid, accompanied by intact blood corpuscles, at the bottom of the tube. The first tube in the series in which this occurs is noted, and the corresponding dilution of the saponin is taken as the hæmolytic index. The values of the quotient, hæmolytic index: frothing power, vary widely for saponins of different origins and allow of the identification of impure saponins isolated from aerated waters. An indication is obtained also of the quantity of the saponin present in any material. From the results, as yet obtained, it would appear that the value of the above quotient should not exceed 0·5 or 1 for saponins to be used in foodstuffs. T. H. P.

**Oxidation Reaction in the Living Cells of Plants. K. Shibata.** (*J. Orient. Sci. Arts*, 1922, **38**, 67–72; *Chem. Abstr.*, 1922, **16**, 1443.)—The oxidising

action of certain complex salts of cobalt, nickel, copper, zinc, etc., on polyphenolic compounds has been applied to living plant cells. For example, on immersing a section of plant tissue in a 0·5 to 1 per cent. solution of purpureo salt the cell sap may be oxidised, and changed from yellow to reddish-brown or dark-brown, and a granular precipitate is sometimes produced. If the cell contains a flavone compound or polyphenol, such as pyrocatechol or pyrogallol, the reaction will be obtained. The toxic action of cobaltammines, such as purpureo salts, is so slight that a filamentous mould fungus can be grown in solutions of these salts, whilst their pronounced penetrating capacity and oxidising power render them particularly suitable reagents for oxidation reactions in living plant cells.

**Influence of Various Antiseptics on the Activity of Lipase. L. S. Palmer.** (*J. Amer. Chem. Soc.*, 1922, **44**, 1527–1538.)—The effect of antiseptics on hydrolysis in a protein-free acacia emulsion containing 4 per cent. of butter fat and having a Sörensen value of 5·0 is as follows: Formaldehyde in concentrations under 0·25 per cent. has no influence on the activity of the lipase; above 1 per cent. it exerts a retarding action. Chloroform in concentrations from 1·5 to 2·5 per cent. retards the activity to the extent of 20 to 60 per cent. Acetone in concentrations from 6 to 12 per cent. retards it from 12 to 20 per cent. A 3 per cent. solution of iodoform in acetone added so as to give a concentration of 0·3 per cent. of iodoform in the liquid retards the activity of the enzyme by 25 to 40 per cent. when fresh, and, after standing a little time, completely inhibits it. It is further shown that iodoform retards lipolysis in direct proportion to its concentration, 0·5 per cent. of iodoform retarding it to the extent of 55 per cent. A similar result is obtained for iodine, which in only 0·045 per cent. solution completely inhibits the lipase. Bromine acts similarly to iodine, but is less powerful, 0·25 per cent. retarding lipolysis to the extent of 94 per cent. H. E. C.

**Influence of Avitaminosis on Lactation. E. Wollman and M. Vagliano.** (*Comptes rend.*, 1922, **174**, 1637–1639.)—The results of experiments with rats confirm the statement of McCollum and Simmonds (1918) that the mother animal cannot effect the synthesis of the vitamins necessary for the growth of the young. If supplied with a vitamin-free diet, the mother furnishes sufficient milk of suitable quality to maintain the development of the young for about eight days, but later the secretion of milk becomes insufficient; no improvement is brought about by addition of vitamins to the diet, so that factors other than vitamins are concerned. The young rats are able from their earliest days to utilise extraneous vitamins, such as those of yeast extract and butter. T. H. P.

**Direct Estimation of Uric Acid in Urine. S. R. Benedict and E. Franke.** (*J. Biol. Chem.*, 1922, **52**, 387–391.)—The urine is diluted 1 in 20 by the addition of water, and 10 c.c. of the dilute solution are transferred to a 50 c.c. graduated flask, together with 5 c.c. of 5 per cent. potassium cyanide solution and 1 c.c. of Benedict's arseno-phosphotungstic acid reagent (*J. Biol. Chem.*, 1922, **51**, 187), and the mixture then gently shaken, allowed to stand 5 minutes and

diluted to 50 c.c. The blue colour produced is compared with that obtained by using 10 c.c. of a standard solution containing 0·2 mgrm. of uric acid. The uric acid solution is prepared by dissolving 0·2 grm. of uric acid in 500 c.c. of a hot solution containing 9 grms. of disodium hydrogen phosphate and 1 grm. of sodium dihydrogen phosphate. When solution is complete, the liquid is cooled, 1·4 c.c. of glacial acetic acid is added, and the whole volume diluted to one litre. Fifty c.c. of this solution are diluted to about 400 c.c., 25 c.c. of 3·5 per cent. hydrochloric acid are added, and the mixture diluted to 500 c.c. A table giving results obtained by this method and by the Benedict-Hitchcock modification of the Folin-Denis method (*loc. cit.*) shows very satisfactory agreements. The results obtained are unaffected by the presence of dextrose, diacetic acid or phenolic substances, but any albumin present should be removed by heating the urine with one drop of acetic acid and filtering it. T. J. W.

*See also:* **Estimation of Magnesium,** p. 409. **New Analytical Applications of Nessler's Reagent,** p. 405.

# Organic Analysis.

**Oxidation by means of Mixtures of Sulphuric Acid and Chromates. L. J. Simon.** (*Comptes rend.*, 1922, **174**, 1706–1708.)—The estimation of carbon in organic compounds by oxidation with sulphuric acid and chromic anhydride and measurement of the carbon dioxide evolved is applicable to all sugars except the methylpentoses and their derivatives, and to most phenols and aromatic acids except those methylated in the nucleus, but acetic acid and its salts remain almost unattacked by this oxidising agent. It is found, however, that if 0·1 grm. of acetic acid or an acetyl derivative is heated with 15 c.c. of concentrated sulphuric acid and 12 grms. of silver chromate, the whole of the carbon present is liberated as carbon dioxide; this method is applicable also to the homologues of acetic acid and to the corresponding primary alcohols. The action of the silver chromate appears to be specific, as the chromates of lead, mercury, nickel and cobalt do not act similarly. T. H. P.

**New Analytical Applications of Nessler's Reagent.—Detection of Ketones; Estimation of Aldehydes. J. Bougault and R. Gros.** (*J. Pharm. Chim.*, 1922, vii, **25**, 5.)—*Detection of Ketones*: Ketones act on Nessler's reagent, rapidly producing, in the cold, a yellowish-white compound of mercury, nearly the same colour for all ketones examined. On acidification or addition of alkaline cyanides, this precipitate dissolves and the ketone is liberated. A crystallising dish of 100–200 c.c. containing the liquid to be examined is placed on a glass plate and supports a glass triangle on which rests a small capsule containing 10 c.c. of Nessler's reagent. The whole is covered by a bell jar and left to stand. If the liquid contains up to 1 mgrm. of ketone a cloudiness, followed by the yellowish-white precipitate, is obtained in 1 to 2 hours. The reaction is still definite with 0·1 mgrm., but only after 24 hours. Normal urine was found to contain either no

free ketones or less than 1 mgrm. per litre; acidification of the urine is recommended before testing, in order to prevent, as far as possible, the liberation of free ammonia. *Estimation of Aldehydes:* The estimation is based on the reaction $—R.CHO+H_2O+2I=2HI+R.COOH$. : An aqueous solution of the aldehyde to be estimated (corresponding to 1 to 5 cgrms. of aldehyde according to the molecular weight) is placed in a lipped flask, excess of Nessler's reagent added (about 30 c.c.) and 10 c.c. of sodium hydroxide solution. After a varying interval, never less than a quarter of an hour, the alkali is treated, in the cold, with a slight excess of hydrochloric acid (1:3), and excess of 0·1 *N* iodine solution added. The mercurous compounds and deposited mercury take up the amount of iodine necessary to convert them into the mercuric state, *i.e.* the amount of iodine which measures the degree of reduction. The excess of iodine is then titrated with 0·1 *N* thiosulphate solution. Certain necessary precautions are detailed; *e.g.* a blank test must be made with the sodium hydroxide used.

The following aldehydes have been quantitatively determined with very good results:—Formaldehyde, furfural, benzaldehyde and piperonal, but others, and in particular vanillin and acrolein, are not so satisfactorily dealt with. The conclusion is drawn that each aldehyde must be studied individually, and all possible interactions taken into account. Alcohols, with the exception of methyl alcohol, are probably sufficiently reduced to spoil the estimation. Possible further developments are pointed out, particularly for the identification of aldehydes. D. G. H.

**Wood Turpentine. C. A. Lambert.** (*J. Ind. Eng. Chem.*, 1922, **14**, 491.)—Wood turpentine is obtained from stumps, sawmill slabs, etc., by destructive distillation or by steam distillation; the crude product is redistilled over soda-ash, and, when thus refined, can scarcely be distinguished from spirits of turpentine, the volatile portion of the oleo-resin exuded from the living tree. Refined wood turpentine has the following characteristics: Sp. gr. at 15° C., 0·863; $n_D^{20}$, 1·468; initial boiling point, 153° C.; distillation range, 91 per cent. below 170° C.; acidity, trace. About 70 per cent. distils below 160° C., and this portion has been identified as $\alpha$-pinene. W. P. S.

**Estimation of Tar Acids and Tar Bases in Road Drainage and Mud. J. J. Fox and A. J. H. Gauge.** (*J. Soc. Chem. Ind.*, 1922, **41**, 173–176.)—With the colorimetric method previously described for the estimation of tar acids (*J. Soc. Chem. Ind.*, 1920, 260T), the dye produced is sometimes orange or red and cannot then be compared satisfactorily with that given by standard solutions containing only cresols. This difficulty is obviated by means of two additional standards: (1) The fraction of the tar acids from coal tar boiling at 205–230° C. (mainly xylenols), and (2) $\beta$-naphthol, each of these being used in a solution containing 0·00005 grm. of the material per c.c. According to the colour to be matched, the standard solution taken contains either cresols, tar acids or $\beta$-naphthol, or a mixture of any two of these or a mixture of all three, the total weight of phenolic substance per c.c. being the same in all cases. It is necessary to adhere fairly closely to the proportion of alkali previously given (*loc. cit.*).

Aqueous extracts of vegetable substances, such as bracken, leaves, straw, peat, etc., contain phenolic compounds giving a coloration with diazotised sulphanilic acid, but such compounds are not appreciably soluble in chloroform, whereas the coal-tar phenols are readily soluble. The following procedure serves, therefore, for the estimation of tar acids due to coal-tar in solution in water and in mud or silt : The liquid or solid is extracted with a small volume of chloroform, the resulting chloroform solution being extracted with 20 per cent. sodium hydroxide solution ; the diazo-sulphanilic acid test is then applied to an aliquot part of the alkaline extract, the proportion of alkali in the standard being adjusted so that it equals approximately that in the solution under examination. It is advisable to boil muds, silts, or other solid substances with chloroform for 30 minutes under a reflux condenser and then to filter under pressure through asbestos, the extraction being repeated if necessary.

Tar bases may be detected by either of the two following methods: (1) One hundred c.c. of the water or drainage are made alkaline and extracted with chloroform, the chloroform solution being then shaken with a few c.c. of sulphuric acid (sp. gr. 1·27 at 15° C.) and the acid treated with Wagner's reagent (solution of iodine in potassium iodide solution); an opalescence or precipitate indicates the presence of bases. (2) A similar concentration in a small volume of the sulphuric acid is exposed in a 20 mm. quartz cell to the electric spark passing between metal poles; if tar bases are present, a pronounced fluorescence, usually blue or bluish-green, is obtained. These methods indicate roughly the proportion of tar bases present, but the latter may be estimated accurately by the following modification of Flürscheim's method. (*J. Chem. Soc.*, 1910, **97**, 95.)

Five hundred c.c. of the sample are rendered slightly alkaline with sodium hydroxide and extracted three times with chloroform, of which about 100 c.c. are used in all. The chloroform solution is extracted three times with sulphuric acid (sp gr. 1·27 at 15° C.), about 40 c.c. of acid being used altogether. The acid is washed once with a little chloroform and then diluted to about 150 c.c. with water and made slightly alkaline with 50 per cent. sodium hydroxide solution, the mixture being kept cold meanwhile. The alkaline solution is extracted three times with chloroform (about 100 c.c. in all), the chloroform solution being run into a separator with a dry exit-tube, washed once with 10 c.c. of water and transferred to a tared vessel containing a weighed quantity of picric acid which has been previously dried for 2 to 3 hours at 70° C.; none of the wash water should be allowed to enter the vessel. The 10 c.c. of water in the separator are washed twice with 10 c.c. of chloroform, and this added to the main solution, which is yellow in presence of small quantities of tar bases. The chloroform solution is slowly evaporated on a water bath without direct exposure of the vessel to the steam, the last portions of the chloroform being expelled in an oven at 70° C. Usually two weighings, after 60 and 90 minutes respectively, are identical. The weight of picric acid used should be at least ten times the weight of bases expected, 0·1 grm. being a suitable quantity for 500 c.c. of road drainage. The method gives accurate results with quinoline,

isoquinoline, acridine and various fractions of tar bases from refined and dehydrated tars. Bases with lower boiling points, such as pyridine, are not wholly retained by the picric acid, but these are not usually present to an appreciable extent in refined tars used on roads.

The presence of bases giving the tests described above indicates fairly conclusively pollution by the products of distillation of coal or wood, but substances such as sheep dips may account for the occurrence of tar bases in drainage. Samples containing small proportions of tar products in aqueous solution should be examined shortly after collection, as many of the constituents of coal-tar undergo biological change fairly rapidly in non-sterile water. T. H. P.

# Inorganic Analysis.

**Potassium Hydrogen Oxalate and the Standardisation of Alkali Solutions. Y. Osaka and K. Ando.** (*Mem. Coll. Sci. Kyoto*, 1921, **4**, 372.)—A solid acid or acid salt which crystallises without water of crystallisation, and which can be easily purified, is greatly needed for the standardisation of alkali solutions. Potassium hydrogen oxalate crystallises in an anhydrous state above 15° C., but it cannot be purified by simple crystallisation between 25° C. and 30° C., since its solutions are then unequally saturated. From a diagram it is seen that the solution becomes equally saturated at about 40° C. If, however, oxalic acid, potassium oxalate and water are mixed in proportions (obtainable from the authors' curve) to form a saturated solution for a given temperature, the anhydrous potassium hydrogen oxalate will crystallise out from the solution. Four methods for the preparation of the salt are described in detail. In each case the yield of pure product was about 83 per cent., and one method does not require the use of a thermostat. D. G. H.

**Symmetrical Diphenyl-Guanidine as a Standard in Acidimetry and Alkalimetry. C. A. Carlton.** (*J. Amer. Chem. Soc.*, 1922, **44**, 1496–1474.)—Symmetrical diphenyl-guanidine $(C_6H_5NH)_2CNH$, a mono-acid base, readily soluble in dilute acids, fulfils all the requirements of an ideal standard substance, particularly for the direct standardisation of acid solutions. The purification of the commercial product is simply effected by three or four recrystallisations from dry toluene. Solutions of hydrochloric acid standardised against it agree exactly with those standardised against sodium carbonate, than which substance it is much more convenient because it is unalterable in air and evolves no carbon dioxide during titration. It may be used in dilute alcoholic solution, and may be titrated with either aqueous or alcoholic solutions of acids. Bromphenol blue or methyl red are suitable indicators ; a mixture of these two is particularly useful, as the colour change then gives a warning of the approach of the end-point, which is indicated by a sudden change to violet. H. E. C.

**Colorimetric Method for the Estimation of Small Amounts of Magnesium. A. P. Briggs.** (*J. Biol. Chem.*, 1922, **52**, 349–355.)—The following method is a modification of one described by Bell and Doisy (ANALYST, 1921, **46**, 13), for the estimation of phosphorus: A known volume of blood plasma is diluted with three volumes of water and one volume of 20 per cent. trichloracetic acid, the whole being well mixed and filtered. To 15 c.c. of the filtrate 1·5 c.c. of 36 per cent. potassium acetate solution free from calcium and magnesium is added, followed by 2 c.c. of saturated ammonium oxalate solution, and the inside of the tube is rubbed with a rubber-tipped rod until no further precipitation occurs. The tube is heated in a boiling water-bath for 15 minutes and centrifuged, after which the supernatant liquid is poured into a 50 c.c. centrifuge tube, and 1 c.c. of 2 per cent. ammonium phosphate solution is added, followed by 5 c.c. of concentrated ammonia solution, the interior of the tube being rubbed as above. After standing 3 or 4 hours, the mixture is centrifuged, the clear liquid being poured off, and the residue washed twice with ammoniacal alcohol containing 20 per cent. of 95 per cent. alcohol and 5 per cent. of concentrated ammonia. The precipitate is then dissolved in 5 c.c. of *N* sulphuric acid, 1 c.c. of a 5 per cent. solution of ammonium molybdate in *N* sulphuric acid is added, followed by 1 c.c. of 2 per cent. hydroquinone solution, and the mixture is diluted to 20 c.c. The colour produced is compared with that obtained by using about 5 c.c. of a standard solution containing 0·01413 per cent. of magnesium ammonium phosphate dissolved in 0·01 *N* sulphuric acid. Details are given of the development of the method, and comparison with the gravimetric method shows a difference not exceeding 3 per cent. The magnesium content of plasma is fairly constant; in six samples it ranged from 2·20 to 2·50 mgrms. per 100 c.c.

T. J. W.

**Estimation of Small Amounts of Molybdenum in Tungsten. D. Hall.** (*J. Amer. Chem. Soc.*, 1922, **44**, 1462–1465.)—The method consists in the extraction of molybdenum xanthate from a slightly acid solution by means of chloroform. It is not suitable for quantities of molybdenum greater than 5 mgrms, nor should more than 1 grm. of tungsten be taken. The sample is dissolved in acids as usual, and the solution is then neutralised with 0·2 *N* sodium hydroxide solution, and solid potassium xanthate added in quantities of about 0·5 grm. at a time, after which dilute sulphuric acid (1 : 3) is added, drop by drop, until the curdy precipitate of tungstic acid is redissolved. On adding the acid a white turbidity, due to molybdenum xanthate, appears which soon turns red; this red compound is extracted with chloroform, well washed with water, and evaporated to dryness, the residue dissolved in nitric acid, and the molybdenum estimated in the usual way. Attempts to separate molybdenum from iron, nickel, vanadium, and uranium, were unsuccessful, but traces of these elements can be removed during the final separation of the molybdenum. H E. C.

**Electrometric Titration of Uranium with Potassium Permanganate and Potassium Dichromate. D. T. Ewing and E. F. Eldridge.** (*J. Amer.*

*Chem. Soc.*, 1922, **44**, 1484–1489.)—When a solution of uranyl sulphate is reduced with zinc and titrated electrometrically with potassium permanganate (or potassium dichromate for a chloride solution), the change in potential shows two distinct stages, the oxidation of the trivalent uranium to the tetravalent form and the oxidation of the tetravalent to the hexavalent. For the first end-point the concentration of the acid is unimportant, but for the accuracy of the second it is essential that the concentration of the sulphuric acid should not exceed 2 c.c. for each 100 c.c. of solution. From the volume of the permanganate solution required between the two end-points the amount of uranium is calculated, but no hexavalent uranium must be present in the liquid to be titrated. The titration may be conducted in the usual apparatus, fitted with a cover, a current of carbon dioxide being passed meanwhile to prevent oxidation by the air. In the presence of iron there is a third end-point, corresponding with the oxidation of the iron to the ferric state. Colour changes take place just after the end-points indicated electrometrically. H. E. C.

**Glacial Acetic Acid Method for Estimating Uranium in Carnotite. W. W. Scott.** (*J. Ind. Eng. Chem.*, 1922, **14**, 531–532.)—About 0·5 grm. of high-grade carnotite, or a larger quantity of a low-grade ore, is heated with dilute nitric acid until decomposed completely, the mixture then evaporated to dryness, and the residue baked for a few minutes to expel water. Twenty-five c.c. of a mixture of glacial acetic acid and nitric acid (100:5) are added, the mixture is boiled for five minutes, filtered, and the insoluble portion washed with a small quantity of the mixed acids. The filtrate, containing all the uranium, is evaporated to dryness, the residue heated over a flame until it turns black, and the extraction with the mixed acids is repeated. The filtrate thus obtained is evaporated to dryness, the residue ignited to destroy organic matter, and then dissolved in 10 c.c. of nitric acid and 40 c.c. of water, with the aid of heat, if necessary. The solution is nearly neutralised with ammonia, solid ammonium carbonate is added in quantity sufficient to dissolve the uranium carbonate which first precipitates, 3 grms. of ammonium carbonate and 5 c.c. of ammonia solution are added, and the mixture is filtered to separate iron and aluminium. The filtrate is acidified with nitric acid, boiled to expel carbon dioxide, an excess of ammonia is added, and the solution boiled until the precipitation of ammonium uranate is complete, which is indicated by the yellow solution becoming colourless. The precipitate is collected, washed with 2 per cent. ammonium nitrate solution, dried, ignited and weighed as $U_3O_8$.

W. P. S.

**Method for the Estimation of Bisulphites. F. Kühl.** (*J. Soc. Leather Trades Chem.*, 1922, **6**, 199.)—Two grms. of the bisulphite are dissolved, and the solution titrated with *N* sodium hydroxide solution (*a* c.c.). The neutral sulphite thus formed is treated with 10 c.c. of neutral formaldehyde solution (40 per cent.); this results in the formation of the bisulphite-formaldehyde compound and the liberation of sodium hydroxide, which is then titrated with *N* hydrochloric acid

($b$ c.c.). If $a = b$, any impurities are neutral, *e.g.* sodium sulphate. If $a$ is greater than $b$, acid impurities are present, and should be calculated as $NaHSO_4$. If $b$ is greater than $a$, normal sulphite is present, and should be calculated as $Na_2SO_3$. R. F. I.

**Composition of Commercial Phosphoric Acid. W. H. Ross, C. B. Durgin and R. M. Jones.** (*J. Ind. Eng. Chem.*, 1922, **14**, 533–535.)—Analyses are given of ten samples of commercial phosphoric acid prepared from bones and phosphate rock by the sulphuric acid method, and also from phosphate rock by the volatilisation method. In most cases, the acids had been refined or treated for the elimination of certain impurities. The concentration of the acids varied from 27·6 to 79·5 per cent. $H_3PO_4$. In order that the figures may be comparable, the quantities of impurities present are all expressed as percentages of an acid containing 50 per cent. of $H_3PO_4$. The samples prepared from phosphate rock by the sulphuric acid method contained: Sodium, 0·06 to 0·41; potassium, trace to 0·12; calcium, trace to 9·16; iron, 0·18 to 1·0; aluminium, 0·10 to 1·25; manganese, 0·15 to 0·35; total sulphur (as $H_2SO_4$), 0·15 to 0·56; hydrochloric acid, 0·01 to 0·04 per cent. The amounts of impurities present in the acids prepared by the volatilisation method were considerably less than the above. Lead was present to the extent of 4 to 14 parts per million in all the samples, and was probably due to contamination from lead vessels. W. P. S.

# Physical Methods, Apparatus, etc.

**Use of Mercuric Perchlorate in Electrometric Methods of Analysis. I. M. Kolthoff.** *Zeitsch. Anal. Chem.*, 1922, **61**, 332–343.)—When a solution of a mercuric salt is added to one containing certain anions, and the addition followed by conductivity measurements, the first effect is a reduction in the conductivity as a slightly ionised mercury salt is formed; when this stage is complete a further addition increases the conductivity as a mercury complex forms, and the end of this stage is marked by a sudden rapid increase in conductivity. There are therefore two well-marked breaks in the curve, and by taking advantage of this principle it is possible to titrate electrometrically a number of anions, with the use of a standard (0·1 $N$) solution of mercuric perchlorate, which salt is most suitable for such titrations. The halogens can be accurately estimated, even in great dilution, but not when they are mixed, though an iodide can be approximately estimated in the presence of a chloride. Thiocyanate and cyanide can be estimated either together or separately, and the cyanide can be estimated in the presence of a chloride. Ferrocyanide forms with mercury salts compounds of the general formula $KM_3'FeC_6N_6$, (an excess of the reagent producing a normal salt) and can be estimated with an accuracy of about 1 per cent. The following anions also can be directly estimated: Acetate, formate, monochloracetate, lactate, butyrate, benzoate, and salicylate, but not trichloracetate or salts of the polybasic aliphatic acids. H. E. C.

**Analysis of Alloys by means of their Specific Heats. K. Zahlbruckner.** (*Chem. Zeit.*, 1922, **46**, 637–638.)—It is not possible to deduce accurately the composition of alloys from their densities because their volumes are not the sum of the volumes of their component parts. Specific heats are free from such an objection. In the case of a binary alloy the composition can be determined from the specific heat by means of the formula:—

$$\frac{pc_w(\tau - t)}{(c_1 - c_2)(T - \tau)} - \frac{pc_2}{c_1 - c_2} = p_1$$

where $p_1$ and $p_2$ are the weights of the components $A$ and $B$, $p$ the total weight of alloy taken, $c_1$, $c_2$ and $c_w$ the specific heats of the component elements and of water, $t$ and $T$ the initial temperatures of the water and the alloy (100°C. is convenient for the latter), $\tau$ the temperature after mixing, and $P$ the weight of water, including the water equivalent of the calorimeter. If the temperatures are recorded to 0·01°C., accuracy to within 1 per cent. is obtainable when water is used as the calorimetric substance, or a greater accuracy is obtainable by using turpentine ($c_w = 0{\cdot}416$). For ternary alloys having components $A$, $B$ and $C$ of specific heats $c_1$, $c_2$ and $c_3$ and weights $x$, $y$ and $z$ ($x > y > z$) the equations are:—

$$z = p - x - y; \quad \frac{pc_w(\tau - t)}{t - \tau} - pc_3 = (c_1 - c_3)x + (c_2 - c_3)y \ldots\ldots\ldots\text{(i)},$$

which in general must be solved graphically. The following special cases are worked out:

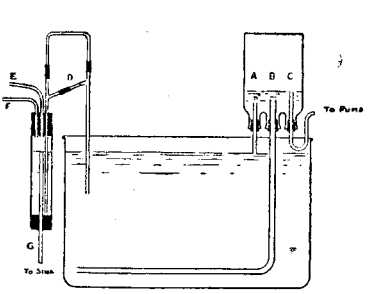
$$\text{Cu—Sn—Pb: (i)}\ldots\ldots\frac{pc_w(\tau - t)}{T - \tau} - 0{\cdot}030p = 0{\cdot}056x + 0{\cdot}025y,$$

and

$$\text{Cu—Zn—Pb: } \frac{pc_w(\tau - t)}{T - \tau} - 0{\cdot}030p = 0{\cdot}056x + 0{\cdot}063y.$$

H. E. C.

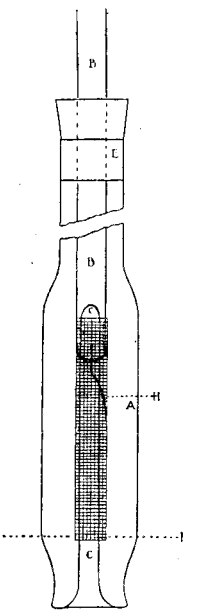
**Apparatus for Stirring Waterbath. C. H. D. Clark and G. T. P. Tatham.** (*Chem. News*, 1922, **125**, 24.)—The device for stirring the water in a thermostat by means of a filter pump is especially useful where electric power is not available. The inverted three-necked bottle (see diagram) being exhausted through C, the water rises in the bottle until the lower end of A is uncovered, when air enters in a stream of bubbles along with water which passes continuously down the tube B. A constant water level is maintained by means of the arrangement shown on the left of the diagram; this comprises a siphon D, the construction of which prevents breaking of the water column, any air bubbles rising into the upper limb from which they are expelled by blowing through E. A slow stream of water enters from the tap through F, and overflows through G. The correct position of G is found by experiment, starting with it below the



position and gradually raising it until the water maintains itself at the level of the upper end of C when equilibrium is attained. A maximum deviation of $\pm 0{\cdot}1$°C. was found in different parts of the tank. W. R. S.

**Direct Estimation of Very Small Quantities of Radium by means of Penetrating Rays. B. Szilard.** (*Comptes rend.*, 1922, **174,** 1695–1698.)—Improvements in the electrometer recently described (*Comptes. rend.*, 1922, **174,** 1618), give it a sensitiveness previously not attained with a portable instrument working without a high tension battery or a projection mirror. If 500 grms. of material containing $10^{-9}$ grm. of radium per grm. are employed, estimation to within 2·5 per cent. is possible.

T. H. P.




**Improved Hydrogen Electrode. C. W. G. Hetterschij.** (*Chem. Weekblad*, 1922, **19,** 293–294.)—A drawback of the tube hydrogen electrode, which is now constantly used for determining the reaction of soil, is the necessity for frequently replatinising the gauze, owing to the action of the sand in the soil. This is obviated in the apparatus shown in the diagram, by surrounding the electrode, H, with a glass mantle, A, the top of which passes through the rubber cover of the electrode vessel, whilst the electrode itself is fixed in the mantle by means of the rubber stopper, E. The mantle, which is open at the bottom, has a slot above at C, whereby communication with the electrode vessel is assured.

# Reviews.

A Text-book of Inorganic Chemistry. By A. F. Hollemann (issued in English in co-operation with Hermon Charles Cooper). Pp. viii.+528. London: Chapman and Hall. 1921. Price 19s. net.

The present volume is the sixth English edition of this well-known book, and is stated to have been thoroughly revised by the author. When it first appeared in 1901, it was, as the American collaborator who writes the preface claims, a pioneer in the presentation of inorganic chemistry from the point of view of physical chemistry. Since that time several other books of this type have been published in English, and the writer must state as his opinion that some of these are better adapted to the needs of the majority of students in this country than the one under review. For the general reader with a knowledge of elementary chemistry who wishes to obtain an idea of how physical chemistry has affected the development of the science, it remains a very useful guide—but again, perhaps not a better one than other books. In fact, the small number of diagrams, miscellaneous in nature and unequal in quality, are a handicap in this respect.

The book contains, interspersed in the text, the usual short sections on reaction, velocity, equilibrium, osmotic pressure, electrolytic dissociation, etc. (an inorganic chemistry on this scale, both assuming and using knowledge of such matters, remains to be written). But the author is not always consistent in his method of treatment—thus the critical constants of oxygen are mentioned early in the book without any previous explanation.

The systematic information given as to the preparation and properties of the compounds selected is generally sound, if not detailed. Thus nickel and its compounds receive two pages only, whilst cadmium is dismissed in about twenty lines. Certain sections to which prominence is given are well done—for example, those on the metal-ammonia compounds, flames, determination of equivalent weights, etc., whilst it is pleasant to see more than the usual perfunctory reference to photochemistry, and to meet with a section on the experimental determination of gaseous equilibria.

An attempt has obviously been made to bring the book up-to-date—thus we have mentioned Mather's work on fluorine, "mustard gas," the Nelson alkali-chlorine cell, solid calcium hypochlorite, Tolman's experiments on centrifugal cells, to take a few examples haphazard. The statements made are not always happy—thus we are told that two of the "most practical processes" for manufacturing hydrogen for filling balloons are the interaction of calcium hydride with water, and the decomposition of acetylene by "induction sparks."

In conclusion, the reviewer must enter a protest against the use of equations of the type

$$KBr+Cl=KCl+Br$$
$$2FeS_2+7O=2SO_2+Fe_2O_3.$$

A. J. ALLMAND.

VITAMINS AND THE CHOICE OF FOOD. By VIOLET G. and R. H. A. PLIMMER. Pp. xii.+164. London: Longmans, Green & Co. 1922. Price 7s. 6d.

General interest in the physiological principles involved in the proper choice of food has recently been aroused in two independent ways. During the war we found ourselves cut off from many of our customary articles of diet, and it became necessary to replace these by others of a different and frequently less agreeable kind, so that the problem forced itself on the individual attention of large numbers of people. Coincident with this came a great and rapid development of the idea of accessory food factors or vitamins, substances present in foods in minute quantities, but absolutely essential for health and well being. The remarkable nature of the experiments upon which this idea was based, the elusive nature of the principles in question and the immediate practical application which it was possible to make of the results gained in the laboratory all combined to arrest the attention of the general public and to create an intense interest in this fascinating subject. In response to the demand for information which naturally ensued a considerable literature has arisen, the latest addition to which is the work now under review. The authors have cast their net fairly widely, and include not only an account of the

three essential vitamins, but also a discussion of the important question of quality of protein. Of special value will be found the chapters on the effect of partial deficiencies in the food and on errors in the selection of food, in which direct application is made of the facts related in the earlier part of the book. Valuable tables of the distribution of the vitamins in foodstuffs and of the foodstuffs which contain the various vitamins are also given, from which it is easy to gain a rough idea of the vitaminic efficiency of a mixed diet. Finally, a valuable series of notes on foodstuffs is appended in which the commoner articles of diet are discussed chiefly with regard to their vitamin content. The book throughout is clearly and well written, although occasionally the desire to include as much information as possible renders the style somewhat encyclopædic.

In face of the discoveries recounted in this book the chemical analyst finds himself somewhat at a loss. He is no longer able, indeed at no time has he ever been able, to found a rational judgment of the efficiency of a diet on his chemical examination of its constituents. Even if he face the difficulty of determining the amino-acid composition of the protein, the vitamins still elude him. Attempts, so far unsuccessful, have however been made to overcome this difficulty. It has been suggested, for example, that the stimulating effect on yeast growth, undoubtedly possessed by many antineuritic preparations, and easily capable of measurement, gives also a measure of the concentration of vitamin B, and this method has been tentatively employed, especially in America. Further experiments have however clearly shown that this particular effect is not due to the same principle as that which promotes growth and cures beri-beri. Similarly, various colour reactions have been proposed as tests for the presence of vitamins, but again without satisfactory proof that it is actually the vitamin which gives the reaction. For the present the only way in which reliable information can be obtained as to the vitamin content of food materials or medicinal preparations is by quantitative feeding experiments. It is not, however, too much to hope that before long some chemical process may be devised by means of which both the estimation and investigation of these important principles will be rendered much more easy.

A. HARDEN.

MODERN MICROSCOPY. By M. I. CROSS and M. J. COLE. Fifth Edition, revised by H. F. ANGUS. Pp. x.+315. 12 plates. London: Baillière Tindall & Cox. 1922. Price 10s. 6d.

The fourth edition of this well-known handbook has previously been reviewed (ANALYST, 1912, **37**, 117), and since that time advances in microscopy have necessitated the rewriting of Part I. dealing with the construction and use of the microscope, and the enlargement and rearrangement of Parts II. and III. in which the applications of the microscope are treated. The various chapters in the last two parts are contributed by different authors, each of whom is an authority on the subject dealt with, thus ensuring accuracy of description and in methods of manipulation. The volume is intended primarily for beginners and students,

but advanced microscopists will find much that is of value and applicable in their own line of work.

The first eleven chapters are devoted to elementary optics, the construction, use and testing of the microscope and its numerous accessories, and conclude with an appendix comprising a glossary of technical terms, official gauges and specifications, and a feature which should prove of great value to amateurs, viz. particulars of the chief microscopical societies in this country. This portion of the book is, on the whole, very satisfactory, although the unscientific amateur will meet with much difficulty in comprehending certain portions, owing to the brevity with which these have been treated. This is particularly noticeable on page 4 in the section on "Diffraction and the Abbé Theory," where several words occur which should be defined in the glossary. The upper limit given for the refractive index of glass on page 2 is somewhat incorrect, since glasses have been produced and used in which this constant reaches a value of 1·96. On turning to Figs. 7, 8 and 9, as indicated on page 3, in order to observe the means by which lenses are corrected, one finds elevations of three objectives, half of each being in section. Without some explanation, this will be of little value to those readers for whom the book was chiefly intended. In Chapter X., dealing with Recording Apparatus, three sections are headed "Size," "Shape" and "Detail," but are indexed under their sub-headings of "Micrometers," "Drawing Apparatus" and "Photomicrographic Apparatus." The illustrations in this part of the book are numerous and clear, but some of them occupy considerably more space than is necessary. For instance, Fig. 18 would have been no less valuable if reduced to one-quarter its present size.

Part II., comprising Chapters XII. to XVIII., provides admirable accounts of the scientific applications of the microscope in medicine and public health work, animal and plant histology, geology, engineering and agriculture. For most readers, even those who have little or no interest in the microscope, many of these pages will provide fascinating reading and give an excellent insight into the enormous progress made in applied science during recent years. On page 131 one small omission may be noted; in the preparation of worms for sections it is advisable to remove the contents of the alimentary canal before treatment, as the small stones present rapidly ruin the edge of the razor or other knife used for section cutting.

The remainder of the book will appeal particularly to the amateur microscopist, since the use of the microscope in natural history is described with the detailed preparation of slides. A general introduction is followed by chapters on pond life, fresh water mites, foraminifera, mosses, and mycetozoa, concluding with one chapter devoted to the mounting of common objects, containing many thoroughly reliable methods of preparation and mounting, the execution of which is well within the powers of the careful beginner. Exception must be taken to the statement on page 220, "Shells of foraminifera . . . form the ooze which is taken from the very greatest depths of the ocean," since these shells are rarely met with below

2500 fathoms, owing to the solvent action of the water. The method given on page 237 for the narcotisation of rotifers, although very efficient, will be difficult of application at the present day, since the operation of the Dangerous Drugs Act renders it practically impossible for an amateur to obtain the necessary cocaine or eucaine. The preservative referred to on page 239 and described as "a 2½ per cent. solution of *formalin*" should obviously read as "a 2½ per cent. solution of *formaldehyde*." It is a little difficult to decide what the author intends when he states on page 253 that "balsam-mounted specimens (of water mites) will have a tendency *to vaporise*." Possibly he refers to the ghostly microscopical appearance produced owing to the high refractive index of the balsam, but this is by no means clear.

The volume is illustrated by twelve plates, in addition to numerous figures in the text, and many of these are excellent examples of photomicrography, particularly beautiful ones being the "Eggs of Spider" × 10 and "Trypanosome Brucei" × 1041 on Plate I. A knowledge of the magnification of any photomicrograph is always useful and may at times be of importance, but this feature is entirely omitted from the photographs on Plates 3, 4, 8, 9, and 10. Three photographs, which by no means reach the high level of the remainder, are shown on Plate III. Of these the "Sewage Fungus" is very disappointing owing to the low magnification used, and without the printed name, it would be impossible to identify the specimen. The same remark also applies to "*Pencillium glaucum*," although here the magnification is quite sufficient. "*Bacillus anthracis*," whilst showing fair detail, is somewhat small, and compares unfavourably with the same organism shown on Plate II.

The index, containing some 600 references, is very complete, and the page numbers are accurate, but the reviewer has been unable to find "Net" and "Radulæ of mollusca," although these occur in the text on pages 225 and 306 respectively under these names, but have been indexed under the headings of "Collecting apparatus" and "Palates." It is usual in a volume of this type to provide an index of the plates, but this convenience does not appear either at the beginning or the end of the book.

It is noticeable that a few appliances which are of much service to the amateur worker are entirely omitted from the volume. Among these are turntables, stage forceps and the old-fashioned Lieberkuhn reflector, which is so useful in the examination of opaque objects and is far more readily manipulated, besides being considerably cheaper, than the modern vertical illuminators.

The volume is well bound, and the type used is of such a size that no discomfort will be experienced during prolonged reading. The subject-matter is sufficiently extensive to provide material for the work of a lifetime, and may be thoroughly commended as a valuable stimulus and guide to all desirous of acquiring familiarity with the microscope and microscopic methods for the purpose of occupying themselves with interesting and useful scientific work, whether as specialists or general workers.

T. J. WARD.

# Publications Received.

A SYSTEMATIC QUALITATIVE ANALYSIS. By G. W. SEARS, Ph.D. Pp. vi.+119. London: Chapman & Hall. 1922. Price 8s. 6d. net.

LABORATORY MANUAL OF COLLOID CHEMISTRY. By H. N. Holmes. Pp. xii.+127. London: Chapman & Hall. 1922. Price 10s. net.

PROTEINS AND THE THEORY OF COLLOIDAL BEHAVIOUR. By J. LOEB. Pp. xi.+292. London: McGraw-Hill Book Co. 1922. Price 15s.

TRATTATO DI CHIMICA ANALYTICA APPLICATA. Vol. II. By G. V. VILLAVECCHIA. Milan: V. Hoepli. 1922. Price 58 lire.

ANALYTISCHE CHEMIE DER ALKALOIDE. By H. BAUER. Pp. 425. Berlin: Gebrüder Borntraeger. 1922. Price 30s.

INFANT MORTALITY. By H. J. ASHBY, M.D. 2nd Edition. Pp. xii.+224. Cambridge: The University Press. 1922. Price 15s net.

Published in the Cambridge Public Health Series. The Chapters on "Milk," on "Flies and their Relation to Disease," and "The Regulations of the Sale of Food and Drugs for Infants," are of especial interest to Public Analysts.

TECHNICAL PAPERS. DEPT. OF THE INTERIOR. BUREAU OF MINES, U.S.A.

No. 268. PREPARATION AND USES OF TAR AND ITS SIMPLE CRUDE DERIVATIVES. By W. W. ODELL. Pp. 84. 1922.

No. 298. METHODS FOR TESTING PETROLEUM. (Adopted by the Inter-Departmental Petroleum Specifications Committee). Pp. 58. 1922.

No. 305. SPECIFICATIONS FOR PETROLEUM PRODUCTS. (Effective Jan. 1922. Amended March 1st, 1922.)

CATALOGUE OF COLLEGE TEXT-BOOKS AND WORKS OF REFERENCE ON SCIENCE AND TECHNOLOGY. H. K. Lewis & Co., London. 1922.

# The Institute of Chemistry of Great Britain and Ireland.

## PASS LIST

### EXAMINATIONS: JULY, 1922.

THE following Associates have passed the Examination for the Fellowship: *In Branch* (*a*) II.: *Metallurgy*: (1 entered and passed, P. D. Oakley, B.Sc. (London). *In Branch* (*e*): *The Chemistry, including Microscopy, of Food and Drugs and Water*: (4 Candidates entered of whom 2 passed): R. E. Essery, B.Sc. (Bris.), J. R. Walmsley, A.M.C.T. The following candidates have passed the examination for the Associateship: *In General Chemistry* (45 candidates entered of whom 28 passed): A. H. Bateman, R. O. G. A. Berchem, W. T. Brow, B.Sc. (Edin.), K. F. Carmichael, H. F. Cooler, A. V. Crawley, W. C. Easterbrook, C. J. Eastland, J. H. C. D. Fairgrieve, J. Fritz, J. Grant, M. M. Haslam, B.Sc. (Lond.), C. W. Herd. L. O. Kekwick, J. T. Luke, J. R. Mathie, A. G. D. Maunder, P. McGregor, B. W. Melhuish, H. F. Miller, R. E. Mitchell, G. H. F. Polglaze, W. R. Richardson, H. W. Rigden, E. J. Schorn, H. V. T. Stokoe, B.Sc. (Lond.), J. M. Tucker, D. O. Wallace (Nat. Sci. Tripos, Cantab.). Under Regulations in force prior to March, 1920. *In Branch* (*a*), *Mineral Chemistry* (4 entered of whom 2 passed): P. H. Cutting, T. E. Laing. *In Branch* (*d*) *Organic Chemistry* (4 entered of whom 3 passed): G. E. Dodds, W. McCartney, A. Renton. *In Branch* (*e*) *The Chemistry, including Microscopy, of Food and Drugs and Water* (3 entered of whom 1 passed): M. Pearson.

By Order of the Council,

RICHARD B. PILCHER, *Registrar and Secretary.*

30, RUSSELL SQUARE, LONDON, W.C. 1.
July 28th, 1922.