# THE ANALYST

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

## Obituary.

### RICHARD BODMER.

WITH deep regret we record the death of one of the senior members of our Society, Richard Bodmer, who died suddenly on July 4.

Bodmer was born, in 1856, of Swiss parents in Switzerland. Coming to England in his early manhood, he went to Sheffield as assistant to A. H. Allen, whose laboratory was even then recognised as one of the best training grounds for the profession of analytical chemistry. Then, at the age of 25, he became assistant to Dr. (afterwards Sir) Thomas Stevenson, Official Analyst to the Home Office, who had his laboratory in Guy's Hospital.

Bodmer's first public appointment, in 1889, was as Public Analyst for the old St. Saviour's Board of Works, and, after the passing of the London Local Government Act, he became Public Analyst for the newly-created Borough of Bermondsey. In 1908 he was appointed Public Analyst for the Borough of Northampton. Both of these appointments he held until his ·death. For many years he was one of the gas examiners of the London County Council, and only retired owing to his having reached the age limit.

His association with Stevenson led to his being engaged in several notorious criminal trials, notably that of Chapman (*alias* Klosowski), who poisoned several women with antimony, and that of Brinkley, who was convicted of poisoning a family with prussic acid.

At one time Bodmer was a regular attendant at the meetings of our Society, and he frequently took part in the discussions. He was associated with Allen in the reading of a paper on the free acids of vinegar (ANALYST, 1878, 3, 268), and he was joint author with A. W. Stokes of a paper on the Determination of Milk Sugar and Cane Sugar (ANALYST, 1885, 10, 62), and with C. G. Moor of one on Copper in Peas (ANALYST, 1897, 22, 141). In 1915 he read a paper on the Detection of $\beta$-Naphthol in Lysol (ANALYST, 1915, 40, 341), and his last communication was a note on desiccated coconut (ANALYST, 1920, 45, 18).

He never lost his love of his Swiss mountains, and until well on in years spent many a holiday in climbing them. Music was another of his relaxations, and for years he was a violinist in the Stock Exchange orchestra.

Bodmer was twice married, and has left a family of two sons and two daughters.

.EDITOR.

# The Detection and Determination of Glycerin in Tobacco.

## By A. CHASTON CHAPMAN, F.R.S., F.I.C.

*(Read at the Meeting, May 18, 1926.)*

OWING to the fact that tobacco containing glycerin or other sweetening material is placed for Inland Revenue purposes in a different category from unsweetened tobacco, the detection and determination of glycerin is frequently a matter of very considerable importance. The problem is one with which I have had to deal on several occasions, and I have been impressed not only with the scantiness of the published information on this point, but also with the unsatisfactory character of the methods which, so far as I have been able to ascertain, are generally employed. I therefore decided, some time ago, to submit this matter to a thorough investigation, in the hope that I might be successful in working out a trustworthy process, and one by which it should be possible to obtain the glycerin present in a condition sufficiently pure to admit of its complete identification.

Several modifications of the lime process were examined in the first place, but these were ultimately rejected, as even moderately good results could only be obtained by the compensation of somewhat considerable errors, and it was rarely, if ever, possible to obtain the glycerin in an even approximately pure condition. Ultimately the following method was devised, and has been found to yield extremely good results:

EXTRACTION WITH ACETONE.—Ten grms. of the finely cut and thoroughly mixed tobacco are weighed out and transferred, together with a few grms. of anhydrous sodium sulphate, to a Soxhlet thimble. The amount of sodium sulphate added should be sufficient to absorb the whole of the moisture present in the tobacco. The thimble and contents are then thoroughly extracted with pure acetone, the extraction being maintained continuously for a whole day, the thimble being allowed to remain full over-night, and the process then continued for several hours on the following day. A Soxhlet apparatus and condenser with all ground-glass joints should, if possible, be used. After the exhaustion of the tobacco, the acetone is distilled off on a water-bath, and the last traces of solvent are rapidly removed by passing a current of air over the contents of the flask.

SEPARATION OF RESINS.—The residue is then dissolved, as far as possible, by adding about 20 c.c. of warm alcohol, and water is gradually added to the alcoholic solution until the precipitation of the resins appears to be complete. Usually about 150 c.c. of water are sufficient for this purpose. The diluted solution is then transferred to a separating funnel and shaken with petroleum spirit (b.pt. 50°–60° C.) to extract the resins. After having been allowed to stand, the aqueous layer is run off, the petroleum spirit and the funnel are washed with a few c.c. of

water, and the main solution and washings gently distilled from a flask, the distillate so obtained being collected. When the volume in the flask is reduced to about 30 c.c. the liquid is cooled, and filtered into a weighed carbonic-acid flask of approximately 150 c.c. capacity. The distillate is evaporated to a small volume (say, 5 to 10 c.c.), and this is added to the main extract, and the whole is then finally evaporated to a syrup at a temperature of about 80° C. in a gentle current of air, the evaporation being stopped when there is a marked odour of nicotine. The resulting crude extract is allowed to cool, and weighed.

DETERMINATION OF GLYCERIN.—A portion of this extract is then weighed out on a small piece of glass which is dropped into a long-necked flask, B, of the type usually employed in Perkin's Modified Zeisel apparatus, from one-fourth to one-third of the whole extract being taken. The apparatus is illustrated in the accompanying sketch.
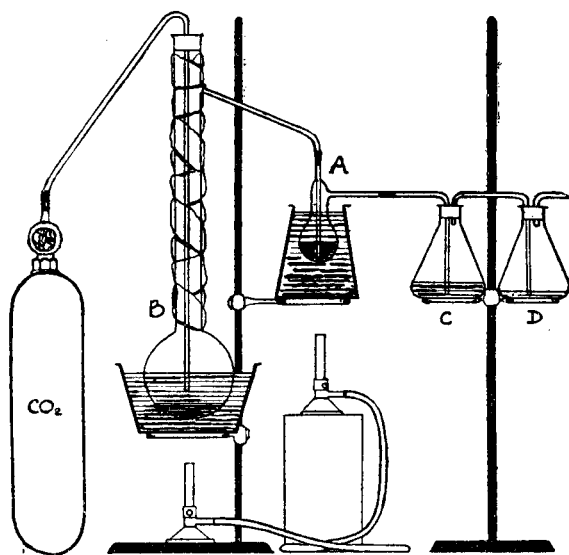


A single small flask, A, containing a suspension of red phosphorus in water is sufficient to retain any iodine liberated, and this can be attached directly to the flask, B, without any condenser being interposed. A conical flask, C, containing alcoholic silver nitrate of the usual strength, and a guard flask, D, satisfactorily absorb the isopropyl iodide formed during the reaction. The flask containing the red phosphorus is immersed to the neck in a water-bath maintained at 60° to 70° C. throughout the experiment. For the determination, 15 c.c. of hydriodic acid (sp. gr. 1·7) are placed in the flask, B, with the weighed amount of crude extract, and the apparatus connected in the usual manner. The decomposition flask, B, is placed in an oil-bath maintained at 135°–140° C., and a slow current of carbon dioxide passed into it. The neck of this flask, which is about 35 cm. long, should be thoroughly lagged with cloth. After about twenty minutes, if an

appreciable amount of glycerin is present, the first precipitation of silver iodide commences, and the experiment is continued until all further formation of silver iodide has ceased. This is determined by detaching the absorption flask and replacing it by a test tube containing some of the silver nitrate solution. After complete precipitation of the silver iodide, the contents of the absorption flasks are washed into a beaker, the alcohol is driven off, and sufficient nitric acid added. After settling, the silver iodide formed is filtered off and weighed in the usual manner. The reaction is, of course, represented by the following skeleton equation

$$
\begin{array}{ccc}
CH_2OH & & CH_3 \\
| & & | \\
CHOH & \longrightarrow & CHI \\
| & & | \\
CH_2OH & & CH_3
\end{array}
$$
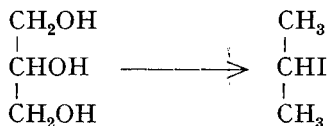
The weight of silver iodide, multiplied by 0·392, gives the equivalent of glycerin.

A number of tests which will be referred to subsequently showed that the above method is entirely trustworthy, and that the formation of silver iodide, beyond the trace which appears to be normally obtained from unsweetened tobacco, may safely be regarded as a sufficient proof of the presence of glycerin. At the same time, it is obviously desirable that a method involving the application of direct and specific tests for the presence of glycerin should be devised, since such a method would be an advantage in cases where the *detection* of glycerin is the important point, and where a determination of the amount is not needed. In disputed cases, and especially in cases involving legal procedure, the specific identification would, moreover, become a necessary addition to the quantitative method described above. For this purpose the following process was ultimately devised.

QUALITATIVE DETECTION OF GLYCERIN.—A sufficient quantity of the tobacco (say 300 grms.) is extracted with boiling acetone for several hours, and the acetone distilled off. The residue obtained is then dissolved in alcohol, and the resins removed, after the addition of water, by means of petroleum spirit, as in the process for the quantitative determination.

The aqueous solution, after separation of the petroleum spirit, is finally evaporated to a small bulk, and transferred to a small Würtz flask. The last traces of water are then removed under reduced pressure (40 mm.), and when frothing has ceased the flask is connected with a small Brühl apparatus, and immersed in an oil-bath. The distillate obtained, using a high vacuum pump, is collected, the temperature of the oil-bath being finally raised to 170° C. The distillate, boiling at 120°–130° C. at 5 mm., is dissolved in water, and the aqueous solution is extracted with ether in a separating funnel to remove the greater part of the nicotine, the remainder of the unextracted base being precipitated from solution by the addition of a slight excess of silico-tungstic acid. The bulky precipitate formed is filtered off, and the filtrate evaporated to a small bulk after neutralisation with soda. The residue is again transferred to the small distillation flask, the water evaporated as before, and the material remaining distilled

under a pressure of 2 to 3 mm. The distillate so obtained could, if necessary, be further purified, but with the single distillation a viscous liquid having a sweet taste, and boiling at approximately 140° C. at 3 mm., is usually obtained. This should be further identified as glycerin by the following tests:—

(1) Heating with potassium bisulphate for production of acrolein;

(2) The production of dihydroxyacetone on warming with bromine water, and its recognition by the application of certain reagents; and

(3) The formation of glycerol α-naphthylurethane.

*Dihydroxyacetone Test.*—The dihydroxyacetone test is carried out as follows:

About 0·1 grm. of the distillate is heated with 10 c.c. of freshly-prepared bromine water for twenty minutes in a water-bath. The excess of bromine is then boiled off, and the resulting solution tested in the following manner:

Half a c.c. is heated for two minutes with 2 c.c. of sulphuric acid, to which is added 0·1 c.c. of a 5 per cent. alcoholic solution of a phenol. The results obtained are as follows:

| Phenol. | | Colour. |
|---|---|---|
| β-Naphthol | .. | Emerald green, the solution possessing a marked fluorescence. |
| Resorcinol | .. | Bright red. |
| Thymol | .. | Purplish red. |

*α-Naphthylurethane Test.*—For the production of the α-naphthylurethane about 0·5 c.c. of the distillate is gently heated with five times its weight of α-naphthylisocyanate in a dry tube until a vigorous reaction occurs. The solidified mass, when cool, is purified by crystallisation from pyridine. The melting point of the urethane, after one recrystallisation, should be 278° to 280° C., although softening usually commences at about 270° C. or even lower.

EXPERIMENTS TO TEST THE ACCURACY OF THE QUANTITATIVE METHOD.— Having devised a process which appeared to be capable of accurately determining glycerin in tobacco, it became necessary to ascertain the behaviour, towards this method, of tobacco known to be free from added glycerin.

For this purpose several samples of tobacco, of which the history was known, and which I had every reason to believe contained no added glycerin, were submitted to the method described above. During the passage of the gas through the silver nitrate solution there was formed slowly and very gradually a *very* small amount of a precipitate. This behaviour was entirely different from the comparatively sudden manner in which the substantial quantities of silver iodide were produced in cases where glycerin was known to be present.

The quantities of silver iodide obtained in these control experiments corresponding with 10 grms. of tobacco amounted to 0·05 to 0·07 grm., and it may be taken, I think, that a deduction of 0·06 grm. from the weight of the silver iodide

corresponding with 10 grms. of glycerined tobacco would be very approximately correct.

Experiments were then made with unsweetened tobacco of different kinds to which known weights of glycerin were added, and it was found that the quantities determined were very close, in all cases, to those known to be present. So far as my experiments have gone, it would appear that when the quantity of glycerin present is in the neighbourhood of 5 per cent. the results may be slightly low, but that when smaller quantities, say 2 or 3 per cent., are present, the inherent experimental error is so small as to be entirely negligible.

I may add, in conclusion, that the results obtained in the case of tobacco to which quantities of glycerin unknown to the operator had been added differed by less than 0·1 per cent. from the amount added. One great advantage of the process described in this communication is that, in the circumstances in which it is employed it is practically specific for glycerin.

I desire to offer my best thanks to my assistants, Mr. F. A. Hatch, A.I.C., and Mr. J. J. Scanlan, A.R.C.Sc.I., A.I.C., for valuable help.

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## DISCUSSION.

The PRESIDENT described the determination of glycerin in tobacco as a difficult operation not hitherto carried out in a very satisfactory manner, and said that he considered the method worked out by the author to be a great advance, and to consist of stages of separation and purification which were fascinating in their ingenuity. Although this method of determination might be regarded as chemically unassailable, the author had also presented to those who might require further evidence, a method for the definite chemical recognition of glycerin. Possibly, the somewhat lengthy time of extraction in a Soxhlet apparatus might be curtailed by the use of a glass extractor of the "flow-through" type.

Mr. CHASTON CHAPMAN, in reply, said that he was obliged to the President for his kind remarks, and thought that quite possibly the use of the type of extracting apparatus to which he had referred might result in a little saving of time. Still, the ordinary syphon Soxhlet answered the purpose perfectly well.

# Further Notes on the Crystalline Bromides of Linseed and some other Drying Oils.

### By HAROLD TOMS, M.Sc. (Lond.), A.I.C.

*(Work done under the Analytical Investigation Scheme.)*

*(Read at the Meeting, May 5, 1926.)*

IN a previous paper (ANALYST, 1924, **49**, 77–82; *Annual Reports*, 1924, 158) I have shown that the "insoluble" bromide of linseed oil consists of at least two substances, and that the more insoluble compound is probably one of the possible linolic-di-linolenic bromoglycerides ($\alpha$-dilinolenin–$\alpha$-linolin). Very shortly, 8 days to be precise, after the reading of the above paper, Eibner and Schmidinger published (*Chem. Umschau*, 1923, **30**, 293; ANALYST, 1924, **49**, 245) identical results, thereby affording excellent confirmation of my work. It should be noted that in both papers the conclusions rest on analytical data only. I have made many attempts to obtain conclusive proof of constitution by actual synthesis, but so far these have proved unsuccessful.

Recently it was pointed out to the author that the product previously described (*loc. cit.*) had been purified by prolonged boiling with ethyl acetate, and that therefore double decomposition might have occurred, with the result that the material investigated might not have been a glyceride at all, but ethyl hexa-bromostearate. This suggestion was regarded as serious enough to require further attention for the following reasons:—

(1) The melting point of ethyl hexa-bromostearate is 152·5° C. (Erdman and Bedford, *Ber.*, 1909, **42**, 1324–1333), and that of the supposed glyceride purified from ethyl acetate is 153° C. (corr.). Eibner and Schmidinger purified their compound from tetralin, and give the melting point as 156° C. (corr.). I have confirmed this.

(2) All attempts to hydrolyse the substance have, so far, produced only one recognisable product, namely, hexabromostearic acid.

(3) The theoretical figures for carbon, hydrogen and bromine in the two compounds are as follows:—

|  | Ethyl hexabromostearate $C_{20}H_{34}O_2Br_6$. | The glyceride $C_{57}H_{94}O_6Br_{18}$. |
|---|---|---|
| C | 30·54 | 31·7 |
| H | 4·33 | 4·36 |
| Br | 61·06 | 59·42 |

Comparison of these figures shows that elementary analysis is not conclusive.

This paper is a record of the work done in order to decide between these two alternatives. It contains also some observations on the bromination products of some other vegetable oils.

<div align="center">EXPERIMENTAL.</div>

LINSEED OIL.

The linseed oil bromide was prepared as previously described (*loc. cit.*), and crystallised twice from ethyl acetate, with the addition of animal charcoal, and finally from a mixture of tetralin and acetone by the method of Eibner and Schmidinger (*loc. cit.*).

In this method the crude product is dissolved in 20 times its volume of tetralin on the boiling water bath, and, after a short period of cooling, acetone is added until a slight deposit is formed. On now again heating the liquid, and allowing it to cool, the bromoglyceride is deposited, relatively pure and white, in very fine crystals. These are washed and dried first with acetone and then with ether, and then melt at 155°–156° C. without colouring. In Eibner and Schmidinger's experiments the melting point of the compound remained constant after four crystallisations.

The compound thus obtained by me was white and microcrystalline, and. melted at 156° C. (corr.).

(*a*) ATTEMPT AT HYDROLYSIS.—Hydrogen chloride in absolute alcohol yielded, even after 2 hours' boiling, only the original substance unchanged. Aqueous potassium hydroxide solution also had no effect.

Hydrobromic acid (48 per cent.) hydrolysed the compound, but the only recognisable product was hexabromostearic acid. No tetrabromostearic acid could be found. In view of this fact, some tetrabromostearic acid was prepared from poppy seed oil and soya bean oil, and, after several crystallisations from petroleum spirit (b.pt. 60°–80° C.), the products from both sources melted, both separately and mixed, at 115° C. (corr.).

Hexabromostearic acid (two mols.) and tetrabromostearic acid (one mol.) were mixed together and boiled for 2 hours with 48 per cent. hydrobromic acid. From the mixture only hexabromostearic acid, in poor yield, could be obtained. The tetrabromostearic acid seemed to have disappeared entirely.

In another experiment pure tetrabromostearic acid was boiled for 2 hours with 48 per cent. hydrobromic acid, after which time it was converted into a sticky substance which was not appreciably soluble in petroleum spirit, acetone or benzene.

Hence the failure to extract this acid from the hydrolysis mixture of the linseed oil bromide must not be taken as evidence of the absence of the tetra-bromostearyl radicle in that compound.

(*b*) PREPARATION OF ETHYL HEXABROMOSTEARATE.—The preparation of this substance involved that of hexabromostearic acid. This was made from linseed oil by saponification and bromination of the mixed fatty acids in ether. The product was crystallised twice from glacial acetic acid and once from benzene, with the addition of animal charcoal each time. The product was well washed with ether after each crystallisation. In this way a white granular substance, melting at 185° C. (corr.), was obtained. (*Cf.* Hazura, *Monatsh.*, 1887, **8**, 260; m.pt. 177° C. Hehner and Mitchell, ANALYST, 1898, **23**, 310; m.pt. 180°–181° C.

Erdmann and Bedford, *Z. physiol. Chem.*, 1910, **69**, 76; m.pt. 179°–180° C.    Coffey, *J. Chem. Soc.*, 1921, T, 1306; m.pt. 185° C.)

This acid was boiled for several hours with 20 to 30 times its volume of thionyl chloride (b.pt. 78° C., prepared from sulphur dioxide and phosphorus penta-chloride).    At the end of this period the excess of thionyl chloride was distilled off, and the last traces were removed by heating the product to 100° C. at 15 m.m. pressure until no further loss in weight occurred.    The substance left was heated for 2 hours under a reflux condenser with alcohol (previously distilled from metallic calcium).    The liquid was filtered hot, and, on cooling, ethyl hexabromostearate crystallised out.    The yield was about 10 per cent.; calculated on the weight of acid used.    The melting point remained the same on recrystallisation, *viz.* 152·5° C. (corr.).

MELTING POINT OF MIXED GLYCERIDE AND ESTER.—The melting points of both the glyceride and the ethyl ester were very sharp, but a mixture of the two was found to melt indefinitely between 146° C. and 150° C., the mixture being completely liquid at this temperature.    The two substances are therefore *not* identical.

## PERILLA OIL.

This oil was unobtainable as such, but the Director of the Imperial Institute very kindly gave a small bag of perilla seeds.    These were crushed, divided into three equal portions and extracted separately in Soxhlet extractors with ether, petroleum spirit (b.pt. 60°–80° C.) and isobutyl chloride.    In each case about the same amount of oil was obtained.    The total yield was less than 10 per cent. of the weight of seed taken.

The oil was dissolved in ether and brominated as usual.    The precipitate came down very slowly, and only after the lapse of some hours was it deemed advisable to remove it.    The crude product was dark in colour, and inclined to cake together.    The yield, calculated on the weight of oil taken, was 33 per cent.; the unpurified bromide melted indefinitely at 140° C.    On purification directly from tetralin and acetone, as described for the linseed oil bromide, it also melted at 156° C. (corr.), and a mixture of it with the linseed oil bromide melted at the same temperature.    The two compounds are therefore identical.

In passing, it may be noted that recently K. H. Bauer (*Chem. Umschau.*, 1924, **31**, 33) isolated from the mixed fatty acids of perilla oil a bromo acid melting at 179°–181° C., which he assumes to be identical with the hexabromostearic acid of linseed oil.    He purified the product by crystallisation from xylene.

## CANDLENUT OIL.

A sample of oil extracted from candlenuts (*Aleurites triloba*) from the Cook Islands, New Zealand, was obtained from the Imperial Institute.    This oil had the following characteristics (*Bull. Imp. Inst.*, 1920, **18**, 25):—Sp. gr. at 15°/15° C., 0·928; $n_D^{40}$, 1·4703; acid value, 1·3; saponification value, 194·8; and iodine value, 158·5.    When brominated, this oil yielded a granular white precipitate which could be easily filtered off, and showed little tendency to cake.    The yield of crude product

(m.pt. 148° C.) was 21 per cent., calculated on the weight of oil taken (cf. Walker and Warburton, ANALYST, 1902, 27, 237, who obtained a yield of 7·3 to 8·2 per cent.). After several crystallisations from ethyl acetate and one from tetralin the product melted at 156° C. (corr.). This substance produced no alteration in the melting points of either the linseed or perilla compounds, and therefore the three substances are identical.

Twenty grms. of the oil were hydrolysed with alcoholic potassium hydroxide solution. The resulting soap was of a red colour. It was acidified with hydrochloric acid, extracted with ether, dried over anhydrous sodium sulphate, filtered and brominated, with stirring and cooling. The precipitated acid was filtered off, washed well with ether and dried. The yield was 5 grms. The crude product was crystallised from benzene, boiled with ether and dried on a porous tile. The substance either alone or with pure hexabromostearic acid melted at 185° C. (corr.). The two substances are therefore identical.

### PARA RUBBER SEED OIL.

This oil is very rare, and, although it has drying properties, it is unlikely to become a commercial product so long as the demand for rubber remains in excess of the supply. In view of its scientific interest, however, Dr. W. W. Myddleton, of the Birkbeck College, London, kindly gave a sample (of unknown age) for this investigation. The oil was covered with a thin elastic film, and in smell resembled linseed oil. There was also a semi-solid deposit which disappeared on warming.

The oil was dissolved in ether and brominated in the usual way. The product was very sticky, but after very liberal washings with ether it melted slowly at 146°–150° C. The yield amounted to only 3 per cent., calculated on the weight of oil taken. After several crystallisations a small amount of substance was obtained, which melted at 153° C. (corr.). As the amount was too small for further purification, it was mixed with the pure compound from linseed oil (m.pt. 156° C., corr.), and the resulting melt was 154·5° C. (corr.). Hence it is concluded that para rubber seed oil contains the same glyceride as the other oils mentioned in this paper.

Twenty grms. of this oil were hydrolysed and treated as described for candle nut oil. After purification 2 grms. of pure product were obtained. This was also found to be identical with hexabromostearic acid.

SUMMARY AND CONCLUSIONS.—From the foregoing experiments it is evident that the crystalline bromide of linseed oil (m.pt. 156° C., corr.) is not decomposed by prolonged boiling with ethyl acetate, and also that this solvent is not so efficient a crystallising agent as the tetralin-acetone mixture.

Attempts at hydrolysing this bromoglyceride have resulted in the isolation of hexabromostearic acid, but no tetra bromostearic acid has been found. It must be noted, however, that the hydrolysing agent used, namely, 48 per cent. hydrobromic acid, has been shown to convert tetrabromostearic acid into a substance insoluble in ether, benzene and petroleum spirit.

The bromination products of perilla, candle nut and para rubber seed oils have been prepared, purified and proved to be identical with that from linseed oil. It appears, also, that the hexabromostearic acids from these sources are also identical.

The author wishes to acknowledge the work done by Mr. J. Pollitt in preparing large quantities of the bromo acids used in this investigation, to thank Dr. F. Barrow, of the Birkbeck College, London, for the interest he has taken in the work; and finally to record his appreciation of the help freely given by Mr. C. Ainsworth Mitchell in preparing the paper for publication.

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## DISCUSSION.

The PRESIDENT, commenting on the paper, said that it represented difficult and tedious work. He hoped that the interesting data the author had produced would be some reward to him for undertaking the research. It was very important that these highly unsaturated bodies, which characterised certain drying oils, should be fully investigated so as to render further assistance in differentiating between oils of this class.

The fact that the author had obtained only some 10 per cent. of oil instead of 35 per cent. from Perilla seeds was probably due to imperfect grinding of the seeds; he raised the question as to the possible effect of operating upon an unrepresentative portion of the oil.

Mr. C. A. MITCHELL congratulated the author on having established the insoluble bromide test on a firm basis. His work had definitely proved that the more insoluble linseed oil bromide was not a hexabromide, but a bromo-glyceride; hence the term "hexabromide test" ought only to be applied to the fatty acids. The lower melting points recorded by Hehner and the speaker, both for the insoluble bromide and for hexabromostearic acid, were due to their products having been purified by extraction and not by crystallisation. The amount of insoluble bromide obtained by Mr. Toms from candlenut oil was about three times as much as had previously been recorded. As there could be no doubt as to the purity of the oil, it seemed probable either that the candlenuts were a special variety or that they gave an abnormal oil. He (Mr. Mitchell) had met with a specimen of linseed oil yielding 42 per cent. of insoluble bromide, as against the usual 25 per cent., and so it seemed possible that candlenut oil might also, exceptionally, give a much higher yield of bromide.

Mr. A. CHASTON CHAPMAN asked whether the molecular weight of the bromoglyceride had been determined.

Mr. TOMS, in his reply, explained that the perilla seeds had been crushed, but by a somewhat crude method, which might have had a serious effect on the quantity of oil produced, but could not have affected the main fact that the insoluble bromo-glyceride of perilla oil was identical with that from linseed oil.

The high yield of insoluble bromide from candlenut oil was very remarkable, and in this connection it was worth while quoting the remark of the Imperial Institute as to the origin of the oil: "The oil was extracted at this Institute from a sample of candlenuts received here from the Cook Islands. The botanical identity of these nuts is not known with certainty, but there is little doubt that they are the product of *Aleurites mollucana* (=*A. triloba*)."

In reply to Mr. Chapman, the author pointed out that no attempt had been made to determine the molecular weight of the oil bromides owing to their insolubility in ordinary solvents.

# The Separation of Iridium from Iron.

### By W. R. SCHOELLER, Ph.D.

THE classical investigations of Deville and Stas for the purpose of establishing the exact composition of the standard metre bars (*Procès-verbaux des Séances de* 1877, *Comité International des Poids et Mesures*) marked an important advance in the analytical chemistry of the platinum metals. Deville and Stas fuse mixtures or alloys of these metals with metallic lead at 1000° C. The resulting button contains platinum, palladium, and rhodium in an acid-soluble form, whereas iridium and ruthenium (osmium) form an alloy insoluble in weak *aqua regia*. This alloy is fused with alkaline oxidising fluxes, and the ruthenium volatilised as tetroxide by distillation of the resulting solution in a current of chlorine. If iron is present in the material submitted to fusion with lead, it passes almost wholly into the insoluble iridium-ruthenium alloy, as it displays a preferential affinity for these metals over lead. After the volatilisation of the ruthenium, the iron and iridium are found in the residual liquor, more or less completely precipitated as hydroxides.

METHOD OF DEVILLE AND STAS.—The procedure elaborated by Deville and Stas for the separation of iridium and iron is rather cumbrous, and not suitable for the requirements of technical and analytical practice. It consists in precipitating the hydroxides by evaporation, and boiling with sodium hydroxide and alcohol; the precipitate is filtered off, submitted to prolonged washing until free from sodium salts, dried, separated from the filter, and ignited. The last operation must be conducted with extreme care so that loss by decrepitation may be avoided. The ignited precipitate is digested with ammonium iodide solution acidified with hydrochloric acid, which dissolves the whole of the iron and a little iridium; the latter is recovered by precipitation of the iron with ammonia, ignition of the precipitate, and subsequent volatilisation of the iron in a current of hydrogen chloride and hydrogen.

THE NITRITE METHOD OF SEPARATION.—The nitrite method for the separation of iron from the platinum metals, advocated by Leidié (*Bull. Soc. Chim.*, 1901, 25, 9), and Leidié and Quennessen (*ibid.*, 1901, 840; 1903, 29, 802), has been criticised by Koukline (*Rev. Mét.*, 1912, 9, 815), who finds that the ferric hydroxide precipitate adsorbs quite considerable quantities of sodium platinum nitrite. The author has observed such adsorption to take place to a marked extent in the separation of iridium from iron by the same process. In Leidié's process the iridium filtrate, after evaporation with hydrochloric acid, must still be freed from the large amount of sodium chloride contained therein by saturation with hydrogen chloride, as the salt has a prejudicial effect on the precipitation of the iridium.

GILCHRIST'S FUSION PROCESS.—In a recent paper on the determination of iridium in platinum alloys by fusion with lead (*J. Amer. Chem. Soc.*, 1923, 46, 2820), Gilchrist proposes testing the final iridium residue for iron by fusing it with

zinc, dissolving the metal in hydrochloric acid, and fusing the residue with bisulphate. The applicability of the process is probably limited to low iridium and still smaller iron percentages; even so, Gilchrist's figures for iridium are rather low. Some years ago the author tried to separate larger quantities of the two metals by bisulphate fusion, but abandoned the method as unreliable, since part of the iron remained insoluble after several fusions.

PRECIPITATION OF IRIDIUM AS AMMONIUM CHLOROIRIDATE.—In studying the determination of iridium in such materials as osmiridium concentrates, alloys, and high-grade residues as a question of daily routine, the author soon discarded the methods just discussed in favour of the precipitation of the iridium as ammonium chloroiridate. This procedure has the merit of speed, accuracy, and comparative simplicity; it effects the separation from iron by precipitation of the iridium in a form suitable for ignition and subsequent weighing. The precipitate is crystalline, and the precipitation, though normally effected in two fractions, is quantitative—an important* consideration in the analytical chemistry of an element distinguished by a number of incomplete precipitation reactions.

OBJECTIONS TO AMMONIUM CHLORIDE AS PRECIPITANT.—The use of ammonium chloride as an analytical reagent for the platinum metals has been criticised by some writers on the ground of adsorption of salts of other metals by the ammonium chloride precipitate. Thus, Koukline (*loc. cit.*) states that, in one of his experiments, 2·0356 grms. of platinum had occluded ("*entraîné*") 0·015 grm. of iron in the form of chloride. He gives no details as to the procedure used, or the platinum and iron concentration of the solution, but the author must express his inability to understand how such a degree of contamination could be achieved. In any case, it is far beyond anything experienced in ordinary analytical practice.

CORRECTION FOR CO-PRECIPITATED IRON.—Co-precipitation of iron, as observed by the author in platinum ore analysis (involving separation of 1 to 2 grms. of platinum from 0·1 to 0·2 grm. of iron) is of the order of 0·001 grm. This can be ascertained and rectified by several methods.

(1) The ignited and weighed metallic sponge is dissolved in *aqua regia*, the acid evaporated, and the nitric acid completely removed by repeated evaporation with hydrochloric acid. The chloride solution is boiled under reflux with formic acid and ammonium acetate. The precipitate is filtered off, and the filtrate tested for iron.

(2) Re-crystallisation of the ammonium chloride precipitate from boiling water acidulated with hydrochloric acid; the solution is evaporated to small bulk and a little ammonium chloride is added. After standing for some time, the precipitate is filtered off, and the iron in the filtrate precipitated with ammonia and determined colorimetrically as thiocyanate.

(3) If the ammonium chloride precipitate is considerable, it may be destroyed by digestion with *aqua regia*. The liquid is freed from nitric acid, and the platinum (iridium) re-precipitated as usual.

(4)   The solution of chloroplatinic acid is treated with a slight excess of sodium chloride and evaporated to dryness.   The sodium chloroplatinate is dissolved in a little water and the solution boiled with disodium phosphate for a few minutes: the platinum remains in solution, whilst iron is precipitated.   This procedure, which precipitates rhodium as well as base metals, is being investigated.

Ammonium chloroiridate is conveniently freed from adsorbed iron, if necessary, by re-crystallisation as outlined under (2) above.   The procedure offers no difficulties with large quantities of iridium, as the chloroiridate can be reduced to the soluble chloroiridite by boiling and cautious addition of oxalic acid or alcohol. The chloroiridate is re-precipitated by oxidation (nitric acid or sodium chlorate) during evaporation with ammonium chloride.

ADSORPTION OF RHODIUM AND PALLADIUM.—More serious than the adsorption of iron by ammonium chloroplatinate in the usual method of platinum ore analysis is the adsorption of rhodium and palladium, because it cannot, apparently, be prevented altogether, and the determination of the adsorbed metals is a lengthy process.   The author found the following quantities of palladium and rhodium in metallic sponges obtained by ignition of the mixed chloroplatinate and chloroiridate precipitate in the analysis of platinum minerals, aliquot volumes of solution equivalent to 1 grm. of mineral being taken in each case:

| Mineral. | Total wt. of sponge. Grm. | Iridium content. Grm. | Adsorbed rhodium. Grm. | Adsorbed palladium. Grm. |
|---|---|---|---|---|
| A | 0·8782 | 0·0094 | 0·0010 | 0·0014 |
| B | 0·8774 | 0·0106 | 0·0018 | 0·0010 |
| C | 0·8769 | 0·0106 | 0·0016 | 0·0015 |
| D | 0·8826 | 0·0104 | 0·0014 | 0·0010 |

The total palladium content of these minerals was 0·5 to 0·6 per cent., the rhodium content being a trifle higher.

ADSORPTION OF PLATINUM METALS BY FERRIC HYDROXIDE.—In the author's experience, the adsorption of iron by ammonium chloroplatinate (chloroiridate) is trifling compared with the adsorptive properties of ferric hydroxide or basic ferric salts towards the platinum metals; hence, to advocate precipitation of the iron by sodium carbonate and nitrite (as do Leidié and Quennessen) instead of precipitation of the platinum (iridium) by ammonium chloride, is to prescribe a remedy that is worse than the trouble.   A much more efficient reagent will have to be discovered before ammonium chloride can be dispensed with as a precipitant for platinum and iridium.

AUTHOR'S PROCESS OF SEPARATING IRIDIUM.—In the following description of the separation of iridium from iron as carried out by the author, it is assumed that the iridium-ruthenium-iron alloy, remaining after the extraction of a lead button, has been fused with sodium peroxide and hydroxide in a nickel crucible, and ruthenium (osmium) volatilised by distillation in a current of chlorine.   From this point onwards the author departs from the other processes in that he boils the

residual suspension of the hydroxides of iridium, iron, and nickel, still contained in the distillation flask, with an excess of several grms. of sodium hydroxide and alcohol for about 10 minutes. The liquid is poured into an 800 c.c. squat beaker, and the distillation flask well rinsed and discarded. The liquid is left to settle, and decanted through a common filter paper; beaker and precipitate are washed twice with hot water, which removes the bulk of the sodium salts. The filtrate has always been found free from iridium: presumably the nickelous hydroxide favours its complete precipitation. The precipitate is returned to the beaker with hot water; the filter is thoroughly rinsed with hot dilute hydrochloric acid, and rejected. The suspension is now evaporated on a water-bath to dryness after addition of 15 c.c. of hydrochloric and 5 c.c. of nitric acid. The dry residue is taken up with hot, dilute hydrochloric acid, and the brown solution filtered through a 9 cm. paper into a 250 c.c. squat beaker; the residue (silica resulting from the action of the alkali on the glass, generally containing a little adsorbed iridium) is collected and washed with hot water, ignited strongly, and treated with hydrofluoric and dilute hydrochloric acids in a platinum (gold) dish; it is then collected on a small filter, washed, and transferred to a tared porcelain crucible (Precipitate $A$).

The iridium filtrate is meanwhile being evaporated on a water-bath, after addition of 5 grms. of ammonium chloride, until the solution over the black, crystalline chloroiridate precipitate is pure green and ammonium chloride begins to crystallise out at its surface. While the liquid is still hot, the crystals are dissolved by addition of a little half-saturated ammonium chloride solution, and the covered beaker is left to stand overnight.

The clear solution is decanted through a 9 cm. filter; the precipitate ($B$) is washed a few times by decantation with half-saturated ammonium chloride solution and a drop of hydrochloric acid. It is then washed on to the filter with the same solution, and the washing completed. The precipitate, wrapped in the wet paper, is transferred to the crucible containing $A$, and gently heated on an asbestos mat. When dry it is heated a little more strongly, until a very slight evolution of ammonium chloride fumes occurs.

The filtrate is meanwhile evaporated on a waterbath, after addition of about one c.c. of nitric acid, till a copious crust of ammonium chloride is obtained; the small quantity of soluble chloroiridate present is thus converted into insoluble chloroiridate. This precipitate ($C$) is collected and washed, like $B$, after standing overnight, added to the other two precipitates, and the whole ignited at the lowest possible temperature until all the volatile matter is driven off. The heat is then raised to redness, and the iridium oxide reduced in the usual manner by means of hydrogen or coal gas.

The metal is still contaminated with a few mgrms. of silica; the iron is usually quite negligible, and largely removed in the subsequent treatment with hydrofluoric and hydrochloric acids. The metal is then filtered off, washed, ignited, reduced, and weighed in the porcelain crucible previously used. This weight gives the amount of iridium in the sample unless ruthenium is also present, in which

case the weighed metal is fused with sodium peroxide in a nickel crucible, and the solution of the melt distilled in a chlorine current. The small quantity of ruthenium thus found is determined, iridium being found by difference.

PROCEDURE WITH SMALL AMOUNTS OF IRIDIUM.—If the quantity of iridium to be determined is very small (as shown by the pale colour of the filtrate from the silica precipitate), it may be preferable to precipitate the second iridium fraction $C$ from a very small bulk of solution. To accomplish this, the filtrate from $B$ is boiled down in a 500 c.c. conical flask with 30 c.c. of strong nitric acid almost to dryness, the ammonium chloride being entirely decomposed. The residual solution is returned to the precipitation beaker, evaporated to dryness, the residue taken up with 10 c.c. of hot dilute hydrochloric and a drop of nitric acid, and the solution once more evaporated to crystals with one grm. of ammonium chloride. The precipitate is then treated as described above.

DETERMINATION OF THE IRON.—The iron is obtained from the filtrate from by the usual methods, most conveniently by double precipitation with ammonia (The very small quantity of iron which may be found in the filtrate from the hydrofluoric acid treatment of the ignited iridium is precipitated by ammonia and added to the bulk.)

Should a minute quantity of iridium have escaped precipitation by ammonium chloride, it will be recovered in the ammonia precipitate. In such a case, and if the amount of iron present is small, the hydrochloric acid solution of the first ammonia precipitate will not be pure yellow, and the ignited ferric oxide will be brown to black, not reddish. The precipitate, after ignition with filter pulp, is dissolved in strong hydrochloric acid, the iridium remaining partly undissolved; the soluble fraction is recovered by another evaporation with ammonium chloride and a drop of nitric acid. Residue and precipitate are collected together on a minute filter, washed with ammonium chloride solution, and ignited. The filtrate containing the iron will now be pure yellow, and the ignited ferric oxide exhibit its characteristic colour.

A small amount of iron is derived from the nickel crucible; a blank determination must therefore be made. The crucible is weighed before and after the peroxide fusion, the loss in weight varying with the conditions of the fusion and the quality of the crucible. Thus, the following losses were ascertained in ten consecutive analyses: 0·795, 0·201, 0·271, 0·954, 0·625, 0·777, 0·802, 0·303, 0·531, and 0·427 grm. The iron content of English nickel crucibles is 0·4 to 0·5 per cent.

In the blank fusion, the same crucible is used as in the assay; it is again weighed before and after fusion. The cold mass is leached with water, the solution acidified with hydrochloric acid, and made ammoniacal. The small precipitate is collected and the iron therein titrated, the quantity of iron to be deducted from the assay being found by a simple proportion.

The blank generally amounts to several mgrms. When the amount of iron to be estimated is of the same order as the blank, recourse must be had to Deville and Stas's procedure (*loc. cit.*) of fusion with potassium hydroxide and nitrate in

a crucible of pure gold.    However, if no gold crucible is available, the fusion may
be effected in a crucible of pure silver, and in this case sodium hydroxide with a
subordinate quantity of sodium peroxide may be used.    The crucible is attacked
in the fusion, and some silver chloride will be obtained in the silica residue after
filtration of the iridium solution.    The washed silica, before being ignited and
treated with hydrofluoric acid, is therefore leached with saturated ammonium
chloride solution, which dissolves the silver chloride.    The small quantity of
dissolved silver chloride that finds its way into the iridium solution does not
interfere with the precipitation of that metal, as it remains dissolved in the
strong ammonium chloride solution.

# The Air Tester.

## By ROBERT C. FREDERICK.

AN apparatus which has been given the above name, has recently been placed on
sale in this country.    It is the invention of Professor Alan W. C. Menzies, of
Princeton University, is manufactured in America, and is protected by British
Patent No. 230617/24.*    It is apparently intended for popular use, but as it
appeared to have a scientific basis, and might be a useful accessory in the in-
vestigation of ventilation conditions, some examination has been made of its
behaviour under varying conditions.    The examination was by no means exhaus-
tive, but sufficient information was obtained to enable an opinion to be formed
regarding the claims made for the apparatus as an indicator of ventilation
conditions.

PRINCIPLE OF THE APPARATUS.—The popular nature of this little apparatus
(it is only 3 inches high) is at once evident from its design.    The essential part is
a glass tube enlarged to a bulb at each end and containing a small quantity of
carbon tetrachloride coloured red.    The larger bulb has to be kept moist, on the
same principle as that of a Mason hygrometer; this is achieved by covering with
absorbent material and allowing the loose ends to dip into water.    The body of
the apparatus is the water container, and the whole is supported on a circular
wooden base.

Except under abnormal conditions, evaporation is continuously proceeding
from the wet bulb, and this causes an unceasing movement of the coloured liquid
up and down the tube.    The reading of the apparatus consists in observing the
number of pulsations or strokes occurring in one minute; the temperature is also
noted.    These figures are compared with those in a table supplied with the

* The London agents for the apparatus are Messrs. John Swain & Son, Ltd., 89, Shoe Lane,
E.C.4.    Price 6s. 6d.

apparatus and reproduced below; satisfactory ventilation is indicated if the observed figures fall within the limits laid down.

TABLE I.

COMFORT ZONE.

Air Tester Strokes.

| Temperature °F. | | | | Min. | | Max. |
|---|---|---|---|---|---|---|
| 65 | .. | .. | .. | 0 | .. | 4 |
| 62 | .. | .. | .. | 4 | .. | 10 |
| 64 | .. | .. | .. | 8 | .. | 18 |
| 66 | .. | .. | .. | 12 | .. | 26 |
| 68 | .. | .. | .. | 16 | .. | 34 |
| 70 | .. | .. | .. | 20 | .. | 42 |
| 72 | .. | .. | .. | 24 | .. | 50 |
| 74 | .. | .. | .. | 30 | .. | 60 |
| 76 | .. | .. | .. | 36 | .. | 70 |
| 78 | .. | .. | .. | 42 | .. | 80 |
| 80 | .. | .. | .. | 50 | .. | 90 |
| 82 | .. | .. | .. | 58 | .. | 100 |

The apparatus, therefore, depends for its manifestations upon the evaporative power of the air in which it is situated, that is the collective influence of temperature, humidity, and air movement. The supreme importance of these factors in the investigation of ventilation conditions has been discussed by the author in a previous communication (ANALYST, 1925, **50**, 213).

EFFECTS OF TEMPERATURE, HUMIDITY AND AIR MOVEMENT.—The results of some experiments on the effects of these factors on the working of the apparatus are summarised below. (D.B. = dry bulb temp. (°F.); W.B. = wet bulb temp. (°F.); R.H. = relative humidity; P = pulsations.)

TABLE II.

EFFECT OF INCREASING TEMPERATURE AND DECREASING RELATIVE HUMIDITY.

| Still Air. | | | | Air moving at a velocity of 12 feet per sec. | | | |
|---|---|---|---|---|---|---|---|
| D.B. | W.B. | R.H. | P. | D.B. | W.B. | R.H. | P. |
| 58·5 | 50·5 | 56·5 | 20 | 58 | 50·0 | 56·0 | 90 |
| 62·5 | 54·0 | 57·0 | 22 | 60 | 51·5 | 55·5 | 86 |
| 65·0 | 56·5 | 59·0 | 38 | 62 | 53·0 | 54·0 | 107 |
| 66·5 | 57·0 | 55·5 | 38 | 64 | 54·5 | 53·0 | 104 |
| 69·0 | 59·0 | 57·0 | 38 | 66 | 56·0 | 53·0 | 102 |
| 71·0 | 62·0 | 60·0 | 40 | 68 | 58·0 | 54·0 | 120 |
| 72·0 | 62·0 | 57·0 | 40 | 70 | 59·0 | 51·0 | 114 |

The primary object of this series of readings was to determine the effect of varying temperature, but the relative humidity varied to some extent, too, in the absence of the very elaborate apparatus which would have been necessary to keep it constant. It is evident that the number of pulsations is influenced by temperature and much more so by air movement, but that there is some irregularity.

## TABLE III.

EFFECT OF DECREASING TEMPERATURE AND INCREASING RELATIVE HUMIDITY.

| Still Air. | | | | Air moving at a velocity of 5 feet per sec. | | | |
|---|---|---|---|---|---|---|---|
| D.B. | W.B. | R.H. | P. | D.B. | W.B. | R.H. | P. |
| 68·0 | 61·5 | 69 | 16 | 68·0 | 61·5 | 69 | 50 |
| 67·0 | 60·5 | 69 | 16 | 66·5 | 60·5 | 71 | 46 |
| 65·0 | 60·0 | 72·5 | 14 | 65·5 | 59·5 | 70·5 | 46 |
| 64·5 | 59·5 | 74·5 | 12 | 64·5 | 59·0 | 72 | 43 |
| 63·5 | 59·5 | 79 | 12 | 63·5 | 58·5 | 74 | 40 |
| 63·0 | 58·0 | 77 | 10 | 62·5 | 58·0 | 76·5 | 38 |
| 62·0 | 58·0 | 79 | 10 | 61·5 | 57·5 | 78·5 | 38 |
| 61·5 | 58·0 | 81 | 10 | 60·5 | 57·0 | 81 | 36 |

In this series the readings are more regular. Here the decreasing temperature and increasing relative humidity tend to balance each other, though the effect of the latter is more marked, and so the general tendency is a reduction in the number of pulsations.

## TABLE IV.

EFFECT OF DECREASING RELATIVE HUMIDITY AT NEARLY CONSTANT TEMPERATURE; AIR MOVING AT A VELOCITY OF 4 FEET PER SEC.

| D.B. | W.B. | R.H. | P. |
|---|---|---|---|
| 58·5 | 52·5 | 66·5 | 36 |
| 58·7 | 51·8 | 60·5 | 42 |
| 59·5 | 50·5 | 53·5 | 48 |
| 59·7 | 50·3 | 50·5 | 50 |
| 59·9 | 49·4 | 46·0 | 55 |

The number of pulsations increases as the relative humidity decreases.

## TABLE V.

EFFECT OF AIR MOVEMENT; RELATIVE HUMIDITY AND TEMPERATURE NEARLY CONSTANT.

| Velocity: Feet per sec. | D.B. | W.B. | R.H. | P. |
|---|---|---|---|---|
| 12·0 | 65·0 | 55·5 | 54 | 82 |
| 8·3 | 64·5 | 54·5 | 51·5 | 74 |
| 6·3 | 64·0 | 55·0 | 56·0 | 64 |
| 5·0 | 63·0 | 54·5 | 55 | 62 |
| 4·0 | 63·5 | 55·0 | 55 | 58 |

The number of pulsations decreases as the velocity of the air flow decreases.

"EFFECTIVE TEMPERATURE" CHART.—The foregoing results show that, whilst the air tester is not an instrument of precision, its indications certainly do vary according as changes in temperature, humidity, and air movement occur in the air of the space in which it is placed. Much work on the collective influence of these three factors has been done in America by the Research Laboratory of the American Society of Heating and Ventilating Engineers, in co-operation with the United States Bureau of Mines and the United States Public Health Serivce. To this

collective influence they have given the name "effective temperature," and have drawn up an effective temperature chart; included in this chart is what is termed a comfort zone, a term which is self-explanatory.   This chart is reproduced in a recent paper by Yaglou (*J. Ind. Hyg.*, **8**, 5).   It is, however, not applicable to this country; indeed, what would be considered ideal conditions here do not fall within the comfort zone at all, as people in America, speaking generally, favour a considerably higher temperature and relative humidity than we do.

The makers of the air tester acknowledge the assistance of this research in the preparation of the "comfort zone" table supplied with the apparatus, and state that the rates laid down have also been influenced by the work of English investigators, and that, in consequence, there have been included in the comfort zone somewhat lower temperatures than those in American practice.   Such experience as he has had of the apparatus inclines the author to the view that the figures laid down are more suited to conditions in America, and that the comfort zone table should be revised for use in this country.

As a general conclusion, the author is of opinion that, in the investigation of ventilation conditions an air tester, empirically standardised in the light of the more exact methods available in conjunction with personal observation, would yield additional data of some interest.

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# Sweet Potato Starch in Cornflour and Arrowroot.

## BY J. R. STUBBS, M.Sc., F.I.C.

THE author's attention has been recently called to this subject by finding sweet potato starch in a sample submitted as arrowroot.   There does not appear to have been any reference lately to admixtures of this kind; consequently the following notes may be of interest and service.

Sweet potato (*Ipomoea batatas*, Poir) , a climbing plant, cultivated in tropical countries, has thickened roots which contain large quantities of starch.   It was commonly eaten in Europe previous to the widespread cultivation of the ordinary potato, which has now taken its place.   Little prominence is given to the sweet potato in the literature dealing with starches.   Hassall does not even mention it in his *Food and its Adulterations*, neither does Clayton in *A Compendium of Food Microscopy*, nor Greenish in *Food and Drugs* (1903 edition).   Greenish and Collin (*Anatomical Atlas of Vegetable Powders*, p. 18) say that the name "Brazilian arrowroot" is given to it in commerce.   Hassall, on the other hand, applies this name to the flour of *Manihot utilissima*.

Greenish and Collin, after remarking that the starch granules of sweet potato are very variable in size and shape, describe them as follows:—"A few are rounded,

some are conical, others resemble a sugar-loaf cut obliquely, others again are cap or bell-shaped or even polyhedral."

The author ventures to describe them in a manner admittedly less technical, but easily followed by anyone familiar with the common starches, suggested by the impression made on his mind when first meeting with sweet potato as an ingredient of foodstuffs in 1921. A sample then submitted as cornflour, examined microscopically (mounted in glycerin and water, 1:1), contained granules some of which resembled tapioca, sago, maize, and rice, with possibly some like tacca arrowroot. Mixtures of these might be said to correspond roughly with the sample, but it was always possible, on careful examination, to distinguish between
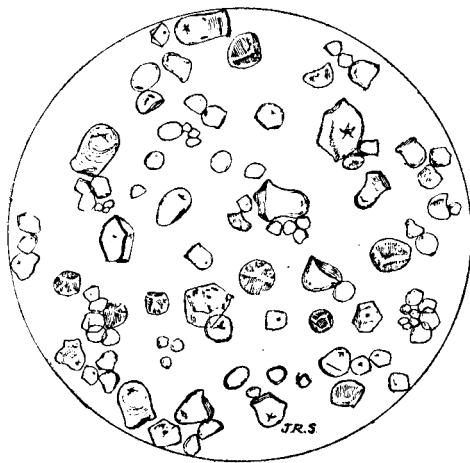


the sample and the mixtures. In addition, there were some granules present in the sample, but not present in any mixture of the above, which showed what might be called "facets." They were present in sufficient amount to be easily seen and to constitute a distinctive feature.

Most of the granules show a hilum and some are striated, both features becoming less marked after being mounted in glycerin and water for several hours. They vary so much in size (from $4 \cdot 5\mu$ to $47\mu$) that measurements can be of little diagnostic value.

The granules of sweet potato starch, then, are very varied in shape and size, often having a hilum and more or less suggesting a mixture of tapioca, sago, maize, and rice, with others showing "facets." The outlines of the granules are drawn in the illustration, and an attempt has been made to show the "faceted" ones.

One brand only of cornflour, in the last seven years, was found to contain this starch, and then it was a case of complete substitution for maize. Proceedings were instituted, and at the hearing of the case it was said that it was a war-emergency article which the Government had allowed. An undertaking was then given (in 1921) to discontinue selling it as cornflour.

At the end of 1921 a sample of arrowroot was received which consisted of a mixture of maranta and sweet potato starches. In two other instances (one in 1925 and the other in April, 1926) similar mixtures have occurred. In these cases "war-emergency" can scarcely be advanced as an explanation or excuse. It would seem that stocks of sweet potato are liable to be "worked off" by being mixed with maranta starch. No case of complete substitution has been met with.

One hundred and thirty-nine samples of cornflour have been examined, and, of these, 133 consisted entirely of maize starch. Of 235 samples of arrowroot, 231 consisted solely of maranta starch. Whatever may be the view taken as to whether the presence of sweet potato, wholly or in part, in cornflour and arrowroot constitutes adulteration, it is clear from the above figures that in a large area, comprising both industrial and agricultural districts, in the majority of instances it is the practice to supply maize starch when cornflour is demanded, and maranta starch when arrowroot is purchased.*

Enquiry of one of the largest firms in Liverpool dealing with cornflour and arrowroot elicited the reply that sweet potato is not now quoted on the market as a foodstuff, so far as they know. It was quoted in 1921, and the price was then much lower than that of either cornflour or arrowroot.

I am indebted to Mr. G. D. Elsdon, B.Sc., F.I.C., Public Analyst for Lancashire, for permission to publish this note.

THE LANCASHIRE COUNTY COUNCIL LABORATORY,
LIVERPOOL.

# Notes.

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

## "BLOWING" OF CANNED FRUIT DUE TO CHEMICAL ACTION.

SEVERAL cans in a consignment of imported canned loganberries were recently found on arrival to be "blown." Bacteriological examination showed that the contents were sterile.

The gas from five of the cans was collected and analysed, with the following results:

|  | 1. | 2. | 3. | 4. | 5. |
|---|---|---|---|---|---|
| Volume of gas in c.c. (not corrected) | 38·8 | 85 | 33·2 | 41·4 | 49·6 |
| Carbon dioxide, per cent. | 3·6 | 1·6 | 3·0 | 3·4 | 4·0 |
| Oxygen, per cent. | 0·5 | 1·6 | 1·2 | 1·0 | Nil |
| Hydrogen, per cent. | 69·6 | 75·6 | 69·9 | 73·7 | 73·5 |
| Nitrogen (by difference) | 26·3 | 21·2 | 25·9 | 21·9 | 22·5 |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |

* Much of the cornflour on the market however consists of pure rice starch.—EDITOR.

The cans were lacquered on the inner surface.  The greater part of the lacquered surface was intact, but in each can there were several longitudinal dark streaks where the lacquer had apparently given way and from which the tin had been dissolved, leaving the iron exposed.  The iron in these places had been extensively corroded, and had presumably been dissolved by the fruit acids, with production of hydrogen.  Corrosion was most pronounced along the edges of the seam.  The cans contained about 550 grms. of fruit and liquor, and the total quantities of tin and iron in the contents of each can were as follows:

|  | | | | 1. | 2. | 3. | 4. | 5. |
|---|---|---|---|---|---|---|---|---|
| Tin (mgrms.) | .. | .. | .. | 19 | 66 | 19 | 20 | 16 |
| Iron (mgrms.) | .. | .. | .. | 150 | 175 | 80 | 100 | 85 |

These figures, of course, include any iron which may be natural to loganberries.  Forty c.c. (corr.) of hydrogen is theoretically equivalent to 100 mgrms. of iron.

The occurrence of corrosion in well-defined lines parallel to the long axis of the can may be due to the lacquer having been applied to the tinplate before the can was made, and to cracks or scratches having been produced in the film during the process of bending the plate round and machining the seams.

G. W. MONIER-WILLIAMS.

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## FRESHLY GROUND COFFEE AND "BLOWN" TINS.

THE phenomenon described by Dr. Shaw and Mr. R. C. Frederick (ANALYST, 1926, 308) has been known to me for some time, and has been made the subject of special investigation in these laboratories.  I have, in fact, taken out a provisional specification entitled "An improved method of, and means for, the packing of roasted and ground coffee" (No. 2520/28.1.26), based on the evolution of gas from freshly ground coffee, and, taking into account the inert character of the gas evolved. I do not consider that the evolution of gas from ground coffee is due to action of air on the coffee, but to the gradual liberation from the coffee of gas evolved during the roasting process, and held under pressure in the whole roasted bean. This gas can be seen to escape when whole roasted coffee is crushed below a layer of paraffin oil.

The evolution begins at once; the greater proportion of the gas is evolved in 6 to 7 hours with the ordinary degree of grinding, and ultimately ceases after a shorter or longer period according to the conditions.  The amount of gas evolved is much greater than is suggested in the abstract and varies according to the degree of grinding, the severity of roasting, the lapse of time, etc.  The gas also contains a quantity of carbon monoxide as well as carbon dioxide.

The following results are typical of those obtained under favourable conditions:—A quantity of pure Costa Rica coffee was roasted and allowed to stand for eight days, after which it was ground.  Some of the ground coffee was transferred as quickly as possible to a suitable apparatus for determining the evolution of gas, and the following results were obtained:

| Time: Hours. | Gas evolved from 200 grms. of coffee. c.c. |
| --- | --- |
| 1 | 52 |
| 2 | 67 |
| 3 | 78 |
| 4 | 85 |
| 5 | 90 |
| 6 | 93 |
| 7 | 95 |
| 24 | 109 |
| 48 | 132 |

It should be noted that these figures represent amounts actually collected, and do not include any gas, which may have been considerable, evolved during grinding.

Some preliminary experiments made over a year ago suggested that coffee would keep better in its own gas than in air, particularly under tropical conditions, and I have at present a number of different lots undergoing incubation tests to decide this point.

J. W. BLACK.

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## INVERT SUGAR AS A REAGENT FOR BORIC ACID DETERMINATIONS.

IN reply to Mr. van Liempt's note (ANALYST, 1926, 293), I wish to state that I discovered the value of invert sugar as a reagent in 1919 when employed in the laboratory of the Maypole Dairy Co., Ltd.  At that time a considerable number of boric acid determinations were being made daily, and, as mannitol was used in the titrations, the reagent was becoming quite an expensive item.  When the discovery was made, I replaced mannitol by invert sugar, and this reagent has been in continual use since.

This more or less accidental discovery stimulated my interest in the nature of the reactions between polyhydric bodies and boric acid, resulting in a paper I read before the Chemical Society in November, 1920 (see *Proc. C.S.*), and published in THE ANALYST, 1921, **46**, 3.  In this paper I pointed out the value of invert sugar as a reagent, after having had about a year's experience in its use. I also gave a method for its preparation.  At this time I had not seen van Liempt's paper (*Rec. trav. chim.*, 1920, **39**, 358), which, I might mention, deals mainly with the electrometric titration of boric acid in the presence of glycerol, mannitol and fructose; only one titration is shown in which invert sugar was used, and the author, referring to the use of invert sugar, says " Je n'ai pas eu le temps de mettre cette méthode au point pour la pratique."

J. Boeseken and H. Couvert in a paper entitled "Configuration of some sugars (use of invert sugar in titrating boric acid)" (*Rec. trav. chim.*, 1921, **40**, 354), pointed out the value of invert sugar as a reagent, and gave a method for preparing it, although, from reading van Liempt's note, one would expect to find this in his paper.  As my paper was published before that of Boeseken and Couvert, I think I am perfectly justified in claiming that I was the first to show the effectiveness and cheapness of invert sugar as a reagent in the titration of boric acid.

I might add that the effect of the addition of fructose, etc., to boric acid solutions was studied by Lambert as far back as 1889 (*Compt. Rend.*, **108**, 1016). It is rather surprising that all this time intervened before the value of invert sugar as a reagent was realised.

G. van B. Gilmour.

## MODIFICATION OF THE KJELDAHL METHOD FOR DETERMINING ORGANIC NITROGEN IN SEWAGE EFFLUENTS, ETC.

It is known that the Kjeldahl process for the determination of organic nitrogen gives unsatisfactory results in the presence of nitrites and nitrates.

It is suggested that large amounts of free and saline ammonia should be first removed by distillation as usual; then nitrites by distillation after acidifying with 2 c.c. of dilute (1 in 4) sulphuric acid.

When nitrites cease to appear in the distillate the reduction of nitrates may be effected by adding 0·5 grm. of zinc dust in the form of an ammonia-free suspension, together with the usual quantity (10 c.c.) of sulphuric acid. The solution should then be "refluxed" for 15 minutes. By this time the whole of the nitric nitrogen will have been reduced to ammonia, and the process may now be completed in the usual manner. (As much as 0·01 grm. of nitrogen has been reduced in 15 minutes). After deduction of the necessary blank amounts the results may be relied upon to give an accurate determination of the organic and nitric nitrogen present.

The accuracy of the final organic nitrogen determination is naturally influenced by the relative amounts of these two forms of nitrogen, a low nitric value being desirable.

The occasional failure of somewhat similar reduction processes is attributable to the fact that, although the reagents employed do eventually produce ammonia, some loss of nitrogen occurs in the intermediate nitrous stage, in which form it readily escapes from the heated acid liquid. By means of the reflux condenser used in this modification the intermediate forms are returned to the flask and finally reduced to ammonia without loss. The amount of acid necessary for the reduction stage of this process is not more than 2 c.c. of the strong acid. It might obviously be suggested that after reduction the nitric nitrogen could be determined as ammonia by distilling the liquid after rendering it slightly alkaline. Experience, however, proves that by this time some albuminoid ammonia may have been liberated and would in consequence distil over with that from the reduced nitric nitrogen.

Wakefield.                         J. W. Haigh Johnson.

## THE VOLATILITY OF BENZOIC ACID.

As a result of the writer's note on salicylic acid (Analyst, 1926, 79), it was suggested that benzoic acid should be examined in a similar way.

No very exact statements appear to be available as to the temperature at which the acid is volatile. Allen (*Organic Analysis*) states that it volatilises at a temperature much below its boiling point (249° C.), whilst Leach says that sublimation occurs slightly above its melting point (120° C.). Actually, of course, benzoic acid can be rapidly and completely volatilised at 100° C., as in Hinks's method for benzoate estimation (Analyst, 1913, **38**, 555).

In the writer's experiments, three quantities of 0·5 grm. of pure benzoic acid were dissolved, one in dry methylated ether and two in ether saturated with water. After spontaneous evaporation and exposure for 24 hours in air at room temperature (about 15° C.), the residues weighed 0·503, 0·504 and 0·503 grm. It was noticed that the dry ether gave much smaller and finer crystals than the moist solvent. The residues were then heated in the oven for observed periods of time and at various temperatures.

Two hours at 40° C. reduced the residues to 0·500, 0·501 and 0·500 grm., respectively. On further heating at 40° C. for 12 hours loss occurred at the slow rate of about 0·001 grm. per hour, the weights then being 0·490, 0·491 and 0·489 grm. This rate of loss increased but slowly as the temperature was raised to 50° C., but above that temperature the rate of volatilisation increased fairly quickly. At 70° C. the above residues were losing weight at a rate of more than 0·020 grm. per hour.

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# 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.*

## COUNTY OF KENT.

### REPORT OF THE COUNTY ANALYST FOR THE FIRST QUARTER, 1926.

DURING the quarter ended March 31st, 1926, the total number of food and drugs samples submitted was 941, of which 42 (4·5 per cent.) were adulterated. Only 7 samples of drugs (all genuine) were submitted.

MILK.—Of the 420 samples taken under the formalities of the Acts, 19 were adulterated, the worst sample containing 25 per cent. of added water.

A sample found to contain 13 per cent. of added water and to be 25·3 per cent. deficient in fat was reported by the vendor to have been produced by his own cows. The mixed sample, taken at his request (from 3 heifers and 1 cow), was found to be low in fat, and it was then discovered that one of the heifers was yielding up to 1 gallon per day of an exceedingly poor milk. Two samples of the milk from this heifer gave the following results:—Fat, 1·37, 1·50; protein, 2·68, 2·55; milk sugar, 0·47, 0·56; mineral matter, 0·98, 0·98 per cent. Total solids, 5·50, 5·59 per cent. The milk was thin and grey, and poured out like slimy water. Microscopical examination indicated that it consisted largely of pus cells, and therefore could not in any way be regarded as milk, although it was a secretion obtained from the udder of a cow. The milk of this animal cannot now be sold for human consumption, as we reported the cow as one which might probably be tubercular.

*Rate of Rising of Cream.*—A sample of milk was found to be 47 per cent. deficient in fat, but the owner of the dairy was unable to account for the deficiency,

until it was discovered that the milk was taken out in two churns, the second of which was not drawn upon until the contents of the first had been sold. The milk was drawn from a tap near the base of the churn. In an experiment to ascertain the probable rate of the rising of the cream in this churn a sample of the mixed milk was taken from the churn at 7 a.m., and was then found to contain 3·0 per cent. of fat. The lid of the churn was sealed and it sent out according to the usual practice. A sample drawn from the tap at 8.45 a.m. contained only 2·0 per cent. of fat, and a second sample, taken some time later, showed a deficiency of 64 per cent. in fat. After a considerable amount of the milk had been sold another sample was taken from the churn an hour later, and the percentage of fat was then 3·1. This case indicates the necessity for keeping the milk thoroughly stirred while it is being sold. The High Court has held that it is not a good defence to allege that a fat deficiency has arisen through milk being allowed to stand in a vessel (cf. ANALYST, 1925, 50, 288).

*Fat in Grade "A" Milk.*—The Grade "A" milks examined had an average fat content of 3·66 per cent., the average figure for the county during the quarter being 3·68 per cent. There is no doubt that the opinion is prevalent that cleanliness is the sole factor to which attention should be paid, and that the cows selected to produce Grade "A" milk are selected for the quantity of milk they yield without attention to quality. It may be said that producers are justified in adopting that attitude, since no fat requirement is laid down in the standard enabling a producer to obtain a Grade "A" licence.

SEPARATED MILK.—One genuine sample contained 0·3 per cent. of fat. In two other cases, however, when milk was demanded from a seller, the inspector was informed that the two cans contained separated milk. Analysis did not confirm this statement, as the samples contained 3.23 and 3.37 per cent. of fat, respectively. It is probable that small quantities of water had been added to this milk, and that the seller thought that the term "separated milk" would cover the addition.

CREAM.—Two samples were of genuine quality and free from preservative. One sample, from a Danish consignment, contained only 25·3 per cent. of fat, whereas the other, cream of English production, contained 36·6 per cent. The difference between the two fat contents again emphasises the necessity for fixing a fat standard, or the adoption of grades of cream in accordance with their fat content.

BUTTER.—Boric acid was present in 63 per cent. of the 67 samples examined, the amounts ranging from 0·14 to 0·40 per cent. (average 0·24 per cent.).

IMPORTED APPLES.—Of the 55 samples examined, an excess of arsenic was found in the following four instances: "Jonathan," 1/40 grain; "Jonathan," 1/50 grain; "Newtown," 1/35 grain; and "Winesap," 1/25 grain.

F. W. F. ARNAUD.

# Legal Notes.

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

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## ARSENIC IN APPLES:   ALLEGED INSUFFICIENCY OF ANALYST'S CERTIFICATE.

On May 31 a fruiterer was summoned at Bow Street Police Court for the sale of apples containing 1/64 grain of arsenic per lb., contrary to the Sale of Food and Drugs Acts.

The solicitor for the defence raised the objection that the analyst's certificate did not disclose any offence, as required by the Act.   This certificate merely stated the amount of arsenic present, whereas it should have given sufficient material to enable the magistrate to form a judgment whether any offence had been committed.   It was a recognised thing, he asserted, that apples did contain a certain amount of arsenic.

Mr. H. Hawkes, for the Holborn Borough Council, contended that the analyst's certificate was sufficient, since it stated that the apples contained "a percentage of foreign ingredients," and specified the amount of arsenic present.   The Magistrate, observing that the point was a tiresome one, reserved judgment.

At the adjourned hearing on June 9, the Magistrate (Mr. Fry) said that he was not prepared to hold that the certificate did not comply with the Act.

The solicitor for the defence said that the apples were American " Jonathans," and that steps had been taken to guard against the presence of arsenic in future. The defendant had carried out the advice of the Ministry of Health to wash the apples, but it had been found that this did not always cure the trouble.

Mr. Hawkes agreed that the proportion of arsenic present was not serious, and the Magistrate dismissed the summons on payment of £5 costs.

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## BORIC ACID IN SAUSAGES: LABEL AN INSUFFICIENT DECLARATION.

On June 1st a firm of grocers was summoned at Kensington, under Sec. 3 of the Sale of Food and Drugs Act, 1875, for having sold sausages which contained 21·4 grains of boric acid per lb., and were therefore injurious to health.

Evidence was given by an agent of the inspector that he had bought ½ lb. of sausages, and had handed them to the inspector at the shop.   The vendor, when told that the sample was for analysis, had pointed out that the sausages were labelled that they contained boric acid, but the inspector informed him that the purchase had been completed, and that no declaration had been made to the deputy who purchased the sausages.

The Medical Officer gave evidence that he regarded this amount of boric acid as injurious to health.                                    •

The Town Clerk, in reply to a question of the defendant, stated that boric acid was prohibited unless its presence was disclosed.

The Chairman of the Bench asked why there was no disclosure, to which the defendant replied that there was a label round the sausages stating that they contained preservative.

The Town Clerk then observed that the question of disclosure could not be raised in this case; at any rate, disclosure was made too late.

The Chairman said that there would be a conviction, and imposed a fine of £3, with £2 2s. costs.

## SULPHUROUS ACID IN SAUSAGES.

A GROCER was summoned at Derry for selling sausages containing sulphurous acid equivalent to 5·4 grains per lb., whilst the Public Analyst stated that the amount for meat preparations should not exceed 3 grains per lb.

The solicitor for the defence argued that no regulation had been made by the Ministry as to the exact amount of sulphurous acid which could be used in the manufacture of sausages, and, in the absence of any regulations, it would be a great hardship that a respectable firm should be convicted in a case of the sort. The Analyst had said that not more than 3 grains should be used, but he had not suggested that an additional 2 grains would make the sausages inferior.

Sir H. Miller, for the prosecution, said that, although no definite quantity of preservative had been fixed by legislation, a Royal Commission had fixed the amount of preservative to be permitted in sausages, and an excessive amount of that preservative had been used in this case.

The solicitor for the defence pointed out that no effect had yet been given to the findings of that Commission, and until that was done it would be a harsh thing to inflict a penalty.

Mr. Glass (R.M.) remarked that the magistrates in that Court had given effect to the Commission's findings on two occasions at least. In fining the defendant £5 they recognised that he was not making the sausages himself, but was purchasing them from a wholesale firm.

# Government of Madras.

## REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1925.*

ACCORDING to the Report of Major Clive Newcomb, M.D., F.I.C., the total number of analyses made during the year was 4227, as compared with 4125 in 1924, and an average of 3624 per year for the previous 20 years. There was a remarkable increase in the number of stain cases (507 with 2018 articles), and the number of human poisoning cases (246) was also a record. It does not necessarily follow that these increases indicate an increase in crime, since they may also indicate an increasing readiness on the part of the police and magistrates to make use of scientific methods of examination.

HUMAN POISONING CASES.—In the 246 cases of suspected poisoning investigated, poison was detected in 135, giving a percentage of detections of 54·9, as against 42·7 in 1924, and an average of 50·5 during the last 20 years. The poison most commonly found in 1925 was again opium, being detected either alone or in association with other poisons in 33 cases. Arsenic came next (23 cases), and then mercury (18), aconite (16), and atropine (14 cases). Of the rarer poisons, there was one case each of the following: *Cerbera odallum*, madar, *Gloriosa superba*, and copper sulphate; three cases of picrotoxin poisoning, and one case in which *Cryptostigia grandiflora* was apparently used. Organic poisons were found in

* G.O. No. 767, P.H., May 4th, 1926.

37 per cent. of the total poisoning cases, the decline in the use of inorganic poisons (chiefly arsenic and mercury), noted in the Report for 1924 (ANALYST, 1925, **50**, 450), being still noticeable.

PICROTOXIN POISONING CASES.—The method of extraction given in Lyon's *Medical Jurisprudence for India*, 1914, p. 558, was found satisfactory. Briefly, this consists in extraction with alcohol and evaporation of the extract nearly to dryness; addition of acidified water; filtration; extraction with ether and evaporation of the ether. Of the tests recommended, the following gave good results when applied to an extract of *Cocculus indicus* berries:

(1) The extract injected under the skin of a frog caused convulsions and death.

(2) Solid potassium nitrate and sulphuric acid, followed after a short time by an excess of potassium hydroxide gave a brick red coloration (Wynter Blyth, *Poisons*).

(3) Strong sulphuric acid gave a yellow solution, and solid potassium dichromate added to this gave a *green* coloration (not a violet, as stated by Lyon, *loc. cit.*).

In one of these poisoning cases a well was poisoned and several persons who drank the water suffered from "vomiting and purging and a burning sensation in the mouth," but none died. A brown powder was found sticking to the sides of the well, and this gave the above-mentioned reactions.

In the second case the crushed berries were taken with suicidal intent, but the patient recovered, probably owing to prompt vomiting. The berries were identified as *Cocculus indicus*, and a substance extracted from the vomit gave the three reactions mentioned above.

In the third case a wandering beggar, who pretended to some medical knowledge, had given a medicine to two women which caused abdominal pain. Some berries found in the beggar's stock of drugs were identified as *Cocculus indicus*, but it was not certain that this poison was in the dose given to the women.

CERBERA ODALLUM POISONING.—Some of the fruit of this plant was taken, crushed up with jaggery, with suicidal intent. A sample of the fruit was identified from its appearance as *Cerbera odallum*, and its extract gave reactions similar to those given by yellow oleander (*Cerbera theretia*), but these reactions were not obtained with the vomit. The symptoms noted in this case were nausea, pain in the abdomen, and drowsiness, followed by vomiting some four hours after the poison had been taken.

CRYPTOSTIGIA GRANDIFLORA POISONING.—This plant was believed to have been used in a fatal case of suicide. The leaves of the plant, on extraction with acid and alkaline ether, yielded extracts which were poisonous to frogs, but which did not give precipitates with either Meyer's reagent or phosphotungstic acid. Poisonous extracts could not be separated from the stomach contents.

INDIAN HEMP POISONING.—A troupe of fourteen actors and actresses were invited to a meal, and all of them subsequently became giddy and drowsy. With three of the stomach washes or vomits Bean's test for ganja was obtained, and from this fact and the observed symptoms it is probable that this was the poison used.

MARKING NUT JUICE.—Experiments were made on the detection of the juice of the marking nut, *Semecarpus anacardium* (*cf.* ANALYST, 1925, **50**, 450). The vesicating principle—which, without prejudice to its subsequently proving a mixture, may be termed *cardol*—can be extracted from the pericarps of the nuts themselves or from articles imbued with their juice with alcohol. This extracts at least two substances—*cardol* and *anacardic* acid—which can be separated by

precipitation with freshly prepared lead oxide, the cardol going into solution (as suggested in Lyon's *Medical Jurisprudence for India*, 1914, p. 528). On evaporating the filtrate nearly to dryness, adding a little water, extracting with ether, and evaporating the extract, the cardol is left as a thick yellow oil. The most characteristic test for it is its vesicating action, which often takes a long time to be felt (*e.g.* 48 hours and 4 days in two instances), but eventually causes a painful and persistent rash.

Other tests for cardol which, however, are not distinctive, are:—(1) Its solubility in alcohol and ether; (2) a blue coloration with potassium hydroxide solution (not bright green, as stated in Lyon's book (*loc. cit.*)); (3) a black coloration with ferric chloride; (4) a scanty black precipitate with baryta water, but this is probably due to the presence of unseparated traces of anacardic acid, since cardol can be recovered from the filtrate.

ANIMAL POISONING CASES.—Poison was detected in 16 of the 42 cases (38·1 per cent.). In 1925 there were more cases of arsenic poisoning (8) than of yellow oleander poisoning (7), which for some years has been the most common cattle poison. The poison found in the remaining case was strychnine, which is not common.

STAIN CASES.—Semen was detected with certainty (spermatozoa found) in 6 cases, and was probably present (positive Florence test) in 5 cases, of the 39 cases examined. All the stains in which spermatozoa were found gave a pronounced result in Florence's test. During the year, 1398 specimens of blood stains were sent to the Imperial Serologist, Calcutta, who reported that 1293 of them were of human blood.

In two cases there were articles which gave absorption spectra somewhat resembling blood spectra. In one of these a red silk cloth was sent the dye of which when treated in the method used for obtaining a haemochromogen spectrum (extraction with water, heating and addition of potassium hydroxide, followed by yellow ammonium sulphide) showed a band from 520 to 570 $\mu\mu$, so that the blood bands, if present, would have been obscured. The Imperial Serologist reported the stain to be of blood, although it was not possible to decide whether it was human blood.

In the other case some moist earth was sent, which, on treatment as described above, gave a very definite band from 540 to 555 $\mu\mu$, which persisted at great dilutions, thus closely resembling the more definite of the haemochromogen bands shifted a little towards the violet. There were also faint indications of a less definite band about 515, enhancing the resemblance to blood. All the other tests tried failed to give any indications of blood, beyond an indefinite blue coloration with guaiacum and turpentine, such as a soil commonly gives. The earth had been packed moist, so that if it had been blood stained originally it is improbable that the blood would have survived decomposition. It is of interest, however, to note the occasional necessity of a fairly accurate wave length scale.

SALIVA STAIN.—A cloth supposed to have been used to gag a person in an attempted murder case was submitted for examination for the presence of human saliva. The Imperial Serologist reported that, owing to the presence of mucin and the low protein content, precipitin tests cannot be successfully applied to saliva.

EARTH FROM "SALT LICKS."—Specimens of earth from "salt licks"—the places in the jungle to which wild animals resort at intervals, as it was presumed, to lick the earth to obtain salt—have been examined. In the seven specimens analysed the amount of sodium chloride is very small (*viz.* 0·01 to 0·27, average 0·09 per cent.), and it seems doubtful whether an animal could get any material amount of salt

from such a source. Each of the earths contained a fair proportion of iron (3·6 to 9·4, average 6·0 per cent. as $Fe_2O_3$). Four of them contained from 5 to 10 per cent. of calcium as CaO, but the other three contained traces, at most.

COBALT CHLORIDE AS INDICATOR FOR WATER.—A rough test for the amount of water in alcohol may be useful when only a small amount of the sample is available. When 0·4 c.c. of a saturated solution of cobalt chloride is added to 10 c.c. of the alcohol at 30° C. the colour varies from blue in absolute alcohol to pink in 90 per cent. alcohol.

WHITE PHOSPHORUS IN MATCHES.—For the first time for many years a sample of matches gave a faint, but distinct, result with Mitscherlich's test for white phosphorus (phosphorescent vapour on boiling with sulphuric acid in the dark). The manufacturers contended that this was not due to white phosphorus, and pointed out that phosphorus sulphide may also give Mitscherlich's test. Experiments were made with phosphorus sulphide prepared in the laboratory, but this did not give the test immediately after its preparation, but it is possible that under certain conditions phosphorus sulphide may decompose in the match composition, producing traces of white phosphorus sufficient to give the test. The Act requires that white phosphorus shall not have been used in the preparation of matches, so that a slight positive reaction in Mitscherlich's test may not be a proof of its use. The samples giving a positive result in Mitscherlich's test were examined by means of the apparatus officially used in Germany (Lunge's *Technical Analysis*, Vol. II., Part I., p. 568). None of them gave a reaction for white phosphorus, but the method is admittedly much less delicate.

# City of London.

## REPORT OF THE MEDICAL OFFICER FOR THE YEAR 1925.

IN his annual report the Medical Officer of Health (Dr. W. J. Howarth) deals with the numerous questions affecting the public health in the area of the City of London. There has been a progressive decline in the night population since 1861, when the census gave 112,063 persons, whilst the estimated night population for the year 1925 was 13,706 persons. The census taken in 1921 showed a day population of 436,721 persons.

ATMOSPHERIC POLLUTION.—A table is given showing the monthly results obtained by the Public Analyst (Mr. E. A. Pinchin) which have been recalculated into metric tons per sq. kilo. In the month of February the amount of deposit registered was equivalent to 22·27 tons per sq. kilom. (= 57 tons avoirdupois), of which approximately 26·3 tons were soluble, and 30·7 tons were insoluble, and consisted of tar, carbon and grit. Determination of the impurity at noon by a dry method from January 1 to December 31, gave results varying from 0·5 mgrm. to 6 mgrms. per cb.m. of air, the higher figure including times when there was a fog.

SUPERVISION OF FOOD AND DRUGS.—During the year, 1022 samples were submitted to the Public Analyst, 690 of which were informal samples; of these 18 were adulterated. Of the formal samples, 20 of the 332 taken were found to be adulterated. Nine samples of drugs did not conform with the requirements of the B.P. There were two prosecutions, and in other instances cautions were issued.

COLOURING MATTERS USED IN FOOD PRODUCTS.—A number of dyes, principally used by butchers and confectioners, were analysed. No poisonous metals were found in samples of rose pink, Bismarck brown, Indian red, and a polony dye. Six samples of cheap sausages, 6 of anchovy paste, 4 of anchovy essence, 5 of caramel, 4 of cheap chocolates, 3 of burnt almonds, and 2 of potted meat, were also free from poisonous metals.

*Armenian Bole.*—The first sample, purchased in the neighbourhood of Smithfield, contained 800 parts per million of arsenious oxide, and another sample contained 40 parts, whereas two others contained none. The first sample also contained 5·76 per cent. of zinc. Steps were immediately taken to prevent further supplies of the contaminated bole being sold for food purposes.

ARSENICAL APPLES.—The only imported apples bearing indications of what appeared to be arsenical deposits were "Jonathans" from America. Samples of these examined by the Public Analyst were found to contain 1/700 grain of arsenious oxide per lb.

MILK SAMPLED AT RAILWAY STATIONS.—Two series of samples of milk were collected on arrival at the railway stations from the country, one series in March and the other in September. In the March series only 1 sample of the 42 samples was found to be infected with the tubercle bacillus. Two samples were definitely dirty, and two more contained a moderate amount of dirt, whilst 11 samples were quite clean. The chemical analysis showed that, with one exception, all the samples were genuine.

Of the 42 samples taken in September, one was found to be infected with the tubercle bacillus. Thirty-one were free from dirt, whilst the remainder showed some blackish specks in the deposit. There was no really dirty sample. Only one of the samples was adulterated.

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# ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

# Food and Drugs Analysis.

**Tin Corrosion and Blackening in Certain Marine Products. D. B. Dill and P. B. Clark.** (*Ind. Eng. Chem.* 1926, **18**, 560, 563.)—Free oxygen and volatile bases do not appear to be significant factors in the corrosion of tins by marine products such as crabs, lobsters, shrimps, salmon, etc., but there seems to be some connection between the hydroxyl-ion concentration and corrosion ; all the products which corrode tins have a reaction on the alkaline side of $P_H$ 6·5. The mechanism of blackening is dependent on a neutral or alkaline reaction in the presence of a fairly high concentration of sulphide sulphur. The conversion of organic sulphur into sulphide sulphur is accelerated by the metal of the container, due to the disturbance of the equilibrium between these forms of sulphur by the precipitation of ferrous sulphide, and blackening increases rapidly with rise of temperature.                                                   W. P. S.

**Stability of Evaporated Milk during Sterilisation. A. G. Benton and H. G. Albery.** (*J. Biol. Chem.*, 1926, **68**, 251–263.)—The stability of protein solutions when heated is an intricate problem in colloid chemistry, particularly in

biological fluids where conditions are complicated by the presence of difficultly controlled factors. Experiments are described from which the authors draw the following conclusions : The milk of individual cows varies considerably from day to day in $P_H$ value and resistance to heat coagulation. Thus each sample, whether mixed or from a single cow, must be regarded as a separate colloidal system, and necessary experimental controls must be run on the sample in question. Stability under sterilisation is considerably affected by addition of citrates, due more to the buffer action and peptising effect than to the specific effect of the citrate. Borates act similarly. In a milk which can be stabilised in this manner, the maximum increase in stability is easily over-reached, and over-treatment may reverse the effect. The $P_H$ effect may completely overshadow any action of the buffer solutions studied, especially if the sample lies above or below a $P_H$ range of about 6·58 to 6·65. Within this range changes in salt balance are very important ; outside it, changes in $P_H$ produce more marked effect. The fact that the alcohol test is positive or negative does not prove anything as to the heat stability of milk. When an alcohol-positive milk is turned negative by citrates or other buffers the stability is not increased unless the optimum combination of $P_H$ and salt balance is approached. This optimum is probably the resultant of several variables and thus is an expression of the colloidal peculiarities of the particular sample. It is different in different milks. In the majority of the samples studied, the optimum lies at or near the point where the milk is positive to 75 per cent. alcohol and negative to 70 per cent.                    P. H. P.

**Yogurt as a Dietetic Food and Medicine.** T. Stathopoulo. (*J. Pharm. Chim.*, 1926, **118**, 415–423.)—Yogurt is scientifically prepared by boiling or condensing the milk, lowering the temperature to about 30° C., adding a known quantity of pure culture of selected ferment, and allowing it to stand at about 25° C. for 24 hours, and is thus a milk which has undergone a complex lactic fermentation. About 880 grms. of yogurt are prepared from 1 litre of milk. A yogurt is also made from separated milk and placed in bags to strain off the liquid portion. Milk of different animals may be used, with a consequent difference in composition of the resulting yogurt. The following table gives typical analyses of commercial samples and of yogurt made by the author :

|  | Bowl Yogurt as sold. | Bag Yogurt as sold. | Cow. | | Sheep. | | | | Goat. | |
|---|---|---|---|---|---|---|---|---|---|---|
| Water | 87·44 | 81·54 | 86·20 | 65·29 | 80·44 | 64·27 | 82·48 | 72·51 | 83·22 | 73·54 |
| Fat-free extract | 10·07 | 18·24 | 9·30 | 20·01 | 11·77 | 18·35 | 12·15 | 17·68 | 11·02 | 14·45 |
| Ash | 0·86 | 1·16 | 0·79 | 0·87 | 0·93 | 1·80 | 0·97 | 1·02 | 0·86 | 1·10 |
| Fat (butter) | 2·46 | 0·22 | 4·50 | 14·70 | 7·79 | 17·38 | 5·37 | 9·80 | 5·75 | 12·01 |
| Milk sugar | 3·40 | 3·37 | 4·30 | 2·53 | 3·70 | 2·93 | 3·42 | 2·46 | 3·96 | 3·58 |
| Nitrogenous matter | 4·68 | 12·65 | 3·37 | 12·03 | 7·32 | 13·37 | 8·15 | 10·50 | 6·00 | 9·23 |
| Acidity (lactic acid): | | | | | | | | | | |
| 1st day | 1·26 | — | 1·01 | — | 1·50 | — | 1·50 | — | 1·25 | 1·00 |
| 2nd day | 1·54 | 2·43 | 1·36 | 2·25 | 2·00 | 2·07 | 1·89 | 2·20 | 1·40 | 1·66 |
| 3rd day | 1·91 | — | 1·49 | — | 2·20 | — | 2·40 | — | 1·45 | — |
| Calories | 56 | 67 | 72 | 204 | 117 | 228 | 97 | 145 | 91 | 152 |

The header row "Laboratory samples prepared from milk of" spans the Cow, Sheep, and Goat columns.

D. G. H.

**Illicit Beverages.   R. T. Feliciano.**   (*Philippine J. Sci.*, 1926, **29**, 465–472.)—The principal sources of the material used in the manufacture of illicit beverages seized in the Philippine Islands are nipa and coco palms, and the beverages contain considerable proportions of secondary fermentation products, as the fermentation is spontaneous and uncontrolled, and the methods of distillation primitive.   Typical analytical results are as follows :

Grms. per 100 litres of 100-proof spirit.

| Sp. gr. at 27·5° C. | Alcohol per cent. | Total solids. | Ash. | Higher alcohols as amyl. | Aldehyde. | Total acids as sulphuric. | Volatile acids as acetic. | Esters. |
|---|---|---|---|---|---|---|---|---|
| 0·9580 | 32·10 | 115·42 | 19·78 | 109·91 | 69·65 | 232·74 | 196·86 | 207·11 |
| 0·9589 | 31·16 | 91·42 | 13·46 | 113·36 | 43·07 | 150·01 | 176·62 | 158·03 |
| 0·9515 | 36·14 | 32·92 | 6·08 | 141·66 | 6·19 | 118·54 | 141·58 | 219·75 |
| 0·9512 | 37·56 | 30·48 | 8·65 | 114·22 | 42·55 | 111·23 | — | 204·32 |
| 0·9727 | 15·14 | 527·79 | 83·23 | 368·09 | 124·76 | 495·17 | 578·93 | 472·16 |
| 0·9792 | 14·18 | 576·48 | 95·90 | 442·06 | 122·61 | 526·50 | 629·56 | 528·80 |

It is recommended that all distilleries producing alcohol for beverage purposes should be required to produce an alcohol containing not more than the following proportions of impurities in grms. per 100 litres of 100-proof spirit :  Higher alcohols, 35 ;  aldehydes, 6·5 ;  esters, 113 ;  total acidity, 5·4 ;  total solids in solution, 2·6 ;  total solids, suspended, 0.                                       T. H. P.

**Separation of Formic Acid in Food Products by Distillation with Xylene.   J. K. Morton and G. C. Spencer.**   (*J. Assoc. Off. Agric. Chem.*, 1926, **9**, 221–224.)—The method employed by Grotlisch (ANALYST, 1921, **46**, 96) for acetic acid may be applied to the separation of formic acid from food materials. Use is made of a 500 c.c. pyrex distilling flask provided with an air inlet closed by a pinchcock and connected through a condenser with a filter flask containing a suspension of 2 grms. of barium carbonate in 50 c.c. of water :—One hundred c.c. of a liquid material, or 50 grms. of a semi-solid together with 50 c.c. of water, are distilled, in presence of a few pieces of unglazed porcelain and 0·5 grm. of tartaric acid, under reduced pressure and at as low a temperature as possible, preferably in an oil bath.   When the solution is concentrated as far as practicable without charring, the heating is interrupted and, when the flask is cold enough, 100 c.c. of xylene are added and the distillation is continued ;  another addition of 100 c.c. of xylene is made later, the whole of the formic acid being thus driven over into the barium carbonate suspension.   Without separation of the xylene, the excess of barium carbonate is filtered off by suction and washed with 20 to 30 c.c. of water.   The filtrate is transferred to a 500 c.c. Erlenmeyer flask, made acid with acetic acid, mixed with 10 c.c. of 30 per cent. sodium acetate solution and 10 c.c. of a solution containing 100 grms. of mercuric chloride and 30 grms. of sodium chloride per litre.   The flask is fitted with two feet of quarter-inch tubing as an air condenser and heated on a steam bath for 2 hours.   The liquid is then filtered hot by suction through·an asbestos mat in a Gooch crucible, the flask and precipitate being washed thoroughly with hot water.   The precipitated mercurous chloride

should be white, a dark or yellow colour indicating contamination or the presence of reducing substances other than formic acid. The whole contents of the crucible, including the asbestos mat, are transferred to the flask again, not more than 10 to 15 c.c. of water being used. The liquid is then treated with 30 to 40 c.c. of concentrated hydrochloric acid and 10 c.c. of chloroform and titrated with a solution containing 2·326 grms. of potassium iodate per litre until the violet colour of the chloroform is discharged and does not return after one minute of brisk agitation.

T. H. P.

**Detection of Olive Oil obtained by Extraction with Solvents.** S. **Fachini.** (*Giorn. Chim. Ind. Appl.*, 1926, **8**, 178–179.)—Olive oils obtained with the help of solvents and those which have been extracted from the pressed residue and then refined are readily identified, even when present in small proportion, in olive oil obtained by pressure, by the following reaction, which is similar to Morawsky's reaction for resins. Two or three c.c. of the oil are heated in a test-tube, with an equal volume of acetic anhydride, the liquid being then shaken for a short time, cooled, and filtered through a small filter previously wetted with acetic anhydride. When brought into contact in a porcelain dish with a few drops of concentrated sulphuric acid, the filtrate soon yields a cherry-red coloration. Addition of a few c.c. of water to the product of this reaction gives a more or less intense green coloration, which gradually disappears. T. H. P.

**Determination of Milk Fat by means of the " Butyric Acid Value."** J. **Grossfeld.** (*Z. Unters. Lebensm.*, 1926, **51**, 203–213.)—Details of further experiments on the application of this method are given (*cf.* ANALYST, 1926, 305). It is shown that the probable proportion of butter fat (M) can be calculated from the " butyric acid value " (*b*), and the saponification value (*v*), by means of the formula $M = 5·115 b - 0·085 v$. Ten commercial samples of margarine showed butyric acid values of 0 to 0·59, with saponification values of 194 to 223, corresponding to a calculated butter fat content of 0 to 1·1 per cent. If less than 5 grms. of butter fat or coconut oil are used for the determination, the results when calculated upon 5 grms. will be too high. Conversely, when a larger amount than 5 grms. of fat is used, the results are too low. Decomposition of the soaps at higher temperatures than 20° C., causes a reduction in the value for butter fat, whilst at temperatures below 20° C. there is an increase in the value (about 0·1 per cent. for each 1° C. between 17° and 31° C.). The influence of temperature on the value obtained with coconut oil is considerably greater, though still relatively small. The effect of oils containing highly unsaturated fatty acids upon the determination of small amounts of butter fat in oils can be eliminated by separating the liquid fatty acids in the form of their insoluble magnesium salts. Finally it is shown that the method affords a means of effecting a sharper separation of butyric acid from its higher homologues than has hitherto been possible.

**Evidence of Decomposition in Oils and Fats.** J. **Stamm.** (*Bull. Soc. Pharm. Esthonia*, 1925, **5**, 181 ; *J. Pharm. Chim.*, 1926, **118**, 214–215.)—Phenyl-hydrazine (2 mol.) and urethane (1 mol.) react to form diphenylcarbazide. To

10 drops of the oil, or a little of the melted fat mixed with vaseline are added 5 drops of the reagent obtained by mixing 0·1 grm. of diphenylcarbazide in 10 c.c. of pure vaseline oil, and the mixture is heated for 3 minutes. Fresh oils give no coloration ; a faint pink colour results in the presence of 1 to 1·5 per cent. of free acidity, and if flavour and taste are satisfactory the oil is to be regarded as of good quality. If a red colour results, even if the oil is organoleptically sound, rancidity will soon develop.                                                D. G. H.

**Piperonal in Vanilla Extract. C. B. Gnadinger.** (*Ind. Eng. Chem.,* 1926, **18**, 588–589.)—The use of piperonal (heliotropine) in vanilla extracts is largely due to the mistaken belief that this substance is a natural constituent of vanilla beans. Bourbon, Mexican, Java, and South American beans do not contain piperonal ; vanillons (obtained from the vines of *V. pompoma, V. guianensis,* etc.) and Tahita beans contain traces of piperonal, but these differ markedly from the true beans, are inferior in flavour, and it is questionable whether the use of either should be permitted in the preparation of vanilla extract. The gallic acid test, described by Labat (*Bull. Soc. chim.,* **5**, 742) is recommended for the detection of piperonal, since it will yield a reaction with 0·01 mgrm. of the substance. One hundred c.c. of the extract are de-alcoholised by evaporation at ordinary temperature before a fan until the volume is reduced to 40 c.c., and this residual solution is extracted with 50 c.c. of ether ; the ethereal solution is separated, washed three times with 2 per cent. sodium hydroxide solution and once with water, and then shaken with 30 c.c of 15 per cent. sodium hydrogen sulphite solution. After two hours the sulphite solution is separated, rendered alkaline (to litmus) with sodium carbonate, extracted with 25 c.c of ether, and the ethereal extract evaporated. The residue is dissolved in 1 c.c. of alcohol, and 0·1 c.c. of this solution is mixed with 0·1 c.c. of 20 per cent. alcoholic gallic acid solution and 2 c.c. of concentrated sulphuric acid, and the mixture is heated at 100°C. for two minutes. An emerald to blue coloration developes if piperonal is present.                          W. P. S.

**Cade Oil. R. Huerre.** (*J. Pharm. Chim.,* 1926, **118**, 314–318.)—Analysis of oil of cade should include determination of the quantities of oil distilling under normal pressure between 150 and 200°C, 200–250° and 250–300° (at least 65 per cent. should distil over this range) ; polarimetric examination after elimination of the portion soluble in dilute alkalis and treatment with steam (a laevo reading is always given by genuine cade oil) ; treatment of the alkali-insoluble portion of the oil with glacial acetic acid saturated with hydrochloric acid should yield in the case of a good sample crystalline cadinene hydrochloride. Thuja oil distils at temperatures much lower than cade oil (e.g. 100–150°C., 39 per cent. ; 150°–230°C., 34 per cent. ; residue, 27 per cent.), and, after extraction with alkali in the cold, shows a slight laevo rotation. The oil of *Juniperus Virginiana* distils at practically the same temperatures as the oil of *J. oxycedrus,* but the portion insoluble in alkalis does not show any crystallisation with hydrochloric acid.                                                             D. G. H.

# Biochemical, Bacteriological, etc.

**Separation of Histidine and Arginine.　H. B. Vickery and C. S. Leaven-worth.**　(*J. Biol. Chem.*, 1926, **68**, 225–228.)—A statement in a recent paper by Kossel and Edlbacher (*Z. physiol. Chem.*, 1920, **110**, 241) indicates that it is possible to precipitate all of the histidine from a mixture of the silver salts of histidine and arginine by the addition of barium hydroxide to give a faint alkaline reaction to phenolphthalein, without precipitation of any of the arginine.　The authors have applied the observations of Kossel and Edlbacher during the course of an analysis of the bases from wheat gliadin.　They found that a large part of the arginine present in such a mixture is thus precipitated together with the histidine. They likewise investigated a mixture of the pure amino-acids and also a solution of pure arginine carbonate, and in every case a large part of the arginine was precipitated.　It seems possible, however, that further investigation will show that a separation can be effected by proper control of the hydrogen ion concentration, since histidine comes out first completely, further cautious addition of alkali gives no precipitate, and the precipitation of arginine begins when a stronger excess of barium hydroxide has been added.　It will be necessary to determine the exact point at which the precipitation of histidine silver is complete and that at which the precipitation of arginine silver begins.　　　　　　　　　　　P. H. P.

**Titration of Organic Acids in Urine.　W. W. Palmer.**　(*J. Biol. Chem.*, 1926, **68**, 245–249.)—The titration method for the determination of organic acids in urine, described by Van Slyke and Palmer (*J. Biol. Chem.*, 1920, **41**, 567), has proved satisfactory in many cases, but in a more extended use of the method for pathological urines, limitations and sources of error have been discovered which need consideration.　The organic acids in the urine, both free and as salts, are determined by titration, with the use of suitable indicators, between the hydrogen ion concentrations represented by $P_H$ 8 and $P_H$ 2·7, respectively.　All carbonates, phosphates and protein must first be removed.　The phosphates and carbonates are generally removed by means of calcium hydroxide, but if carbonates are present in appreciable amounts, 10 per cent. hydrochloric acid should be added and the sample vigorously shaken to drive off the carbon dioxide liberated.　Small amounts of albumin are taken out by calcium hydroxide, but most of the protein is removed if one to three drops of concentrated hydrochloric acid are added to 100 c.c. of urine, the solution is then brought to boiling-point and filtered.　The action is discussed of certain salts and indicators.　Whilst tropaeolin 00 is the most satisfactory indicator for general use, occasionally urine specimens contain some unknown substance which produces fading as the end-point is reached.　Such specimens should be checked by the use of another indicator, preferably bromophenol blue, with which fading has never been noted.　With this, however, at $P_H$ 2·7 the end-point is not sharp, and the greenish-yellow colour is influenced by the urinary pigment.　　　　　　　　　　　　　　　　　　　P. H. P.

# Toxicological and Forensic.

**Carbon Tetrachloride Poisoning. L. A. Dingley.** (*Lancet*, 1926, **210**, 1037.)—The driver of a motor-bus, observing that a fire extinguisher was leaking, pulled the handle to empty it, when the gas and fluid were driven up into his face. He speedily became unconscious, respiration ceased, and the pulse was imperceptible. After artificial respiration had been applied for 25 minutes, breathing began again, and the patient was sent to the hospital, where he soon recovered. On enquiry it was learned that the fire extinguisher had contained carbon tetrachloride of 99·95 per cent. purity, and was free from acid or alkali. The following previous references to the toxic action of carbon tetrachloride are recorded :— In the early years of this century, carbon tetrachloride was used as a shampoo, but Colman (*Lancet*, 1907, **1**, 1709) issued a warning that it was dangerous to life ; a fatality from its use for this purpose has been reported (*J. Amer. Med. Assoc.*, July 31st, 1909), and one case in England. A case of poisoning from its use in the preparation of golf balls is on record (*Brit. Med. J.*, Sept. 25th, 1920). Several cases of non-fatal poisoning were reported by Starr (*J. Indust. Hyg.*, 1922–3, **4**, 203), but the symptoms appear to have been mainly due to benzine. The use of carbon tetrachloride for treating hookworm has been shown by Meyer and Pessoa (*Amer. J. Trop. Med.*, 1923, **3**, 177), to involve possible risk (*cf.* ANALYST, 1926, 260). The pharmacology and toxicity of carbon tetrachloride have been thoroughly investigated by Lamson and his co-workers (*J. Pharm. Exper. Therap.*, 1923–4, 215), who have found that if large amounts are inhaled respiration stops, and the blood pressure falls rapidly. Alcohol should not be given, as it greatly increases the rapidity of absorption and toxicity. Strong tea or coffee, and such cardiac stimulants as are used in chloroform poisoning should be given.

**Changes Undergone by Alkaloids of the Tropine Group in Putrefying Organic Media. M. Magnette.** (*J. Pharm. Belg.*, 1925, **7**, 757–767, 781–783, 797–805, 821–823 ; *J. Pharm. Chim.*, 1926, **118**, 429–430.)—Alkaloids such as atropine and its direct derivatives, such as hyoscyamine and tropococaine, are very resistant to putrefaction, and may be found in the decomposing material, but those alkaloids which hydrolyse to ecgonine, such as benzoylecgonine, cocaine and ecgonine itself, cannot be identified in decomposing bodies, although they may occasionally be found as methyl alcohol, or else may decompose in corpses into benzoic acid. Factors such as low temperature, dryness, contact with air, and, above all, an acid medium, retard hydrolysis of the alkaloid. Extreme caution is necessary in identifying alkaloids of this class in putrefying media, and conclusions must be based on the sum of the positive reactions, and particularly on specific reactions. D. G. H.

# Agricultural Analysis, etc.

**Mechanical Analysis of New Zealand Soils.** R. E. R. Grimmett. (*N. Z. J. Sci. and Techn.*, 1926, **8**, 118–125.)—A modification of the method adopted by the Chemical Committee of the Agricultural Education Association (*J. Agric. Sci.*, 1905, 470) has been found suitable for the mechanical analysis of New Zealand soils. Among the difficulties encountered were the following : (a) Certain soils with a considerable proportion of clay may show little, if any, suspension after one or two days' standing, but, on continued treatment with ammonia, clay appears, and may increase to a maximum after two to three days. The presence of as much as 20 per cent. of clay may thus be obscured. The results obtained in the analysis of some soils by the long-tube method, as described by Sven Oden (*Soil Sci.*, **19**, 1), in which only a short time (one operation) is allowed for dispersion or flocculation, may therefore be inaccurate. (b) In pumice soils the individual particles are often so soft or brittle as to be broken up when rubbed with a rubber pestle to separate the fine gravel and coarse sand. This source of error was eliminated by washing the residues with a strong finely-spread jet of water; for example, one soil which gave 0·8 per cent. of fine gravel and 21·6 per cent. of coarse sand when a rubber-tipped pestle was used, gave 1·9 to 2·3 per cent. of fine gravel and (1) 25·4, (2) 25·4 per cent. of coarse sand by the spray method. (c) In bringing the soil into suspension before pouring off the silt from the fine sand it is essential that the liquid should be free from any motion of rotation. This has been effected by the use of a stirrer on the principle of the milk mixer (a perforated metal disc at the end of a rod). A simple apparatus by means of which six soils may be treated simultaneously has been devised. The system of classification adopted for New Zealand soils is, in the main, that of the U.S.A. Bureau of Soils (1904), with certain additions and modifications. The American classification of " loams " for example, would include several distinct types of New Zealand soils, which could be more definitely classified, and the types " sandy silt," fine sandy silt," and " silt," have therefore been introduced. The term " fine gravelly sand " has been introduced to denote what are probably the coarsest series of soils in New Zealand, namely, certain of the pumice soils of the North Island. " Sandy silt " differs from sandy loam in containing less than 5 per cent. of clay, and the term is applicable to another type of pumice soil.

**The Fluosilicates as Insecticides.** S. Marcovitch. (*Ind. Eng. Chem.*, 1926, **18**, 572–573.)—Commercial calcium fluosilicate appears to be very effective against many insects, especially those which cannot be controlled by arsenical compounds; sodium fluosilicate, sold as a 75 per cent. mixture with alumina, is also useful. These fluosilicates do not injure foliage to an appreciable extent and are quite as toxic as are the arsenical preparations towards certain insects, although arsenic trioxide is from 100 to 300 times more poisonous than sodium fluoride towards higher animals. Calcium fluosilicate does not appear to react to any great extent with lime-sulphur or Bordeaux mixture, but sodium fluosilicate precipitates

sulphur from lime-sulphur, and the two are, therefore, not compatible, especially for use on apple trees. A Bordeaux and sodium fluosilicate mixture is not injurious to potato foliage, but is toxic to the larvae of the potato beetle. Mixtures of sodium fluosilicate and calcium arsenate or Paris green are not safe for foliage, owing to the liberation of soluble arsenic (arsenic pentoxide). W. P. S.

# Organic Analysis.

**Determination of Halogen in Organic Compounds. C. F. van Duin.** (*Rec. trav. chim.*, 1926, 45, 363.)—For the determination of halogens Stepanow recommends the use of 20 to 40 c.c. of absolute alcohol and 25 times the calculated proportion of sodium for 0·2 grm. of the compound to be analysed. The author finds that, where the halogen is firmly bound (*e.g.*, in substituted dibromohydro-cinnamic acids and their esters), twice as much sodium as recommended by Stepanow is required, the proportion of alcohol remaining the same. It is necessary to " reflux " the solution over a free flame. W. R. S.

**Determination of Arsenic in Organic Compounds. H. ter Meulen.** (*Rec. trav. chim.*, 1926, 45, 364–367.)—The method consists in heating the material in a current of pure, dry hydrogen and weighing the sublimate of elementary arsenic. The operation takes place in a transparent silica glass tube 45 cm. long ; the central part of the tube, containing a column of pure asbestos, is heated to redness in a Fletcher furnace ; the part near the hydrogen inlet contains the porcelain boat with the weighed substance. The part near the outlet end is empty ; to it is ground a small narrow silica tube containing a spiral of platinum foil at its extremity near the outlet, which is loosely closed with an asbestos pad. The small tube is weighed with its contents. The substance is gradually heated by means of a burner, and the arsenic trioxide driven through the red-hot asbestos. The sublimate of reduced arsenic is driven into the small tube, the platinum spiral in which is kept red-hot. The arsenic deposits before reaching the spiral, which decomposes a minute quantity of hydrogen arsenide and retains the arsenic. When the operation is concluded the small tube is washed with a little petroleum spirit, which removes the small quantity of solid hydrocarbons sometimes formed ; it is then dried in a current of dry air and again weighed, the increase giving the arsenic. Organic compounds containing metals should be mixed in the boat with bisulphate or sulphuric acid before treatment. The detection of minute quantities of arsenic in organic substances by this method renders destruction of the organic matter unnecessary. A silica tube of greater diameter is used, to accommodate a larger amount of material. This is heated gently in hydrogen until all moisture is expelled ; the temperature is then gradually raised. The small receiver tube is heated near the joint with a Bunsen burner, and cooled by a small wet cloth at the other end ; the formation of a black ring in the cooled portion indicates arsenic. The small tube should be cleaned in *aqua regia* or by being heated in a current of hydrogen, not air ; the platinum spiral is heated in a glass tube in a current of air. W. R. S.

**Determination of Mercury in Organic and Inorganic Compounds.**
**H. ter Meulen.** (*Rec. trav. chim.*, 1926, **45**, 368–370.)—Mercury can be deter-
mined in the manner described for arsenic determinations in the preceding abstract ;
the ground-on receiver tube is modified, being a U-tube partly immersed in cold
water.  Mercuric sulphide is most easily reduced ; halogen compounds should be
mixed in the boat with finely powdered sodium sulphide and a little water, the wet
mass being dried on a steam bath ; organic halogen derivatives are treated like-
wise.  As in the determination of arsenic, the receiver must be washed with
petroleum spirit when organic compounds are analysed ; care should be taken to
avoid loss of minute drops of mercury in this last operation.              W. R. S.

**Polymerised Linseed Oil.   K. H. Bauer.**   (*Chem. Ztg.*, 1926, No. 59, 411.)
—The polymerised product resulting from the action of heat on a normal linseed
oil was found to have saponification value of 206, and to be soluble in acetone and
chloroform to the extent of 37·7 and 44·7 per cent. respectively.  The fatty acids
liberated on saponification had an acid value of 200, an iodine value of 98·7, and
molecular weights of 685·0 and 321·0 in benzene and camphor solutions, respec-
tively.   Corresponding values for the acetone-soluble acids were 197, 100·6, 453·0,
and 244·0, respectively ; and, for the chloroform-soluble acids, 193·7, 93·3, 447·0,
and 241·0, respectively.   No hexabromides were produced.   The molecular weight
values indicate that the camphor solutions were almost monomolecular.  J. G.

**Detection of Resins, especially in Linseed Oil Varnishes.   K. Brauer.**
(*Chem. Ztg.*, 1926, 371–372.)—The blue coloration developed when ammoniacal
phosphomolybdic acid is added to resins suspended or dissolved in ether, is suggested
as a general reaction.  The colour, which in the test experiments was given by
amber, dammar, dragon's blood, colophony, Borneo, Manila and Zanzibar copals,
mastic and shellac, is not substantially altered by acidification.  Diazotised
sulphanilic acid in potassium hydroxide solution gives red colorations with
resins, such reactions being characteristic of the phenolic hydroxy group.
Finely powdered ammonium molybdate in concentrated sulphuric acid also
gives stable blue and green colours with the various resins.  After subsequent
neutralisation with ammonia, shellac gives a lilac colour which is easily visible
in the presence of linseed oil and is not masked by the weaker colours produced
by any other resins present.  Ammoniacal phosphotungstic acid gives green and
lilac colours with colophony and shellac respectively, but is inert towards other
resins.   Both colours disappear on acidification.                    J. G.

**Test for Mercerised Cotton.   H. Mennell.**   (*J. Textile Inst.*, 1926, **17**,
T 247.)—Mercerised cotton is more readily acted on by sulphuric acid of sp. gr.
1·375 than unmercerised cotton.  If 320 c.c. of sulphuric acid at 120° Tw. are
diluted with 260 c.c. of 40 per cent. formaldehyde solution a solution at 75° Tw. is
obtained, which has a much increased effect on mercerised, but little or no action
on unmercerised cotton.  The cotton to be tested is immersed for two minutes at
room temperature in this solution, well washed and neutralised with hot dilute soda

solution. The effect is best shown by dyeing the treated sample with a very dilute boiling solution of a substantive dye (chlorazol sky blue G.W.) made alkaline with a little sodium carbonate. The colour produced on the sample to be tested is compared with that of samples of known treatment. If a dyed sample is to be tested the dye may be stripped with sodium hypochlorite or hot alkaline hydrosulphite.                                             R. F. I.

# Inorganic Analysis.

**Use of Hydrazine Sulphate for the Preparation of Ammoniacal Cuprous Chloride.** E. Cattelain. (*J. Pharm. Chim.*, 1926, 118, 321–322.)—Ten c.c. of 10 per cent. copper sulphate solution ($CuSO_45H_2O$) are mixed with 20 c.c. of 10 per cent. sodium chloride solution and 2 c.c. of concentrated hydrochloric acid added, and, when the mixture is boiling, 2 grms. of powdered hydrazine sulphate are slowly added. Boiling is continued until reduction of the copper salt is complete and the liquid colourless. The solution is filtered while hot into a flask filled wth copper turnings, and the exact quantity of concentrated ammonia solution required is added when cold.                                             D. G. H.

**Methyl Orange Error in the Determination of $P_H$ Values by Comparison with Clark's Buffer Solutions.** I. M. Kolthoff. (*Rec. Trav. Chim.*, 1926, 45, 433–435.)—$P_H$ determinations on various buffer solutions ($P_H$ values ranging from 3·52 to 4·19) by means of methyl orange, bromphenol blue, and the quinhydrone electrode, show that the two latter methods are in substantial agreement, the maximum recorded error being 0·07. Methyl orange, however, gives values from 0·13 to 0·23 too high, compared with these. In Clark's potassium biphthalate buffer solutions, of concentrations ranging from 0·02 $M$ to 1·0 $M$, the difference between the extreme $P_H$ values when methyl orange is used is 1·1. If Sörensen's potassium monocitrate buffer solutions of the same concentrations are used, however, the difference is only 0·4. Sörensen's solutions are therefore to be preferred for use with methyl orange. Dimethyl yellow also shows divergencies, but methyl red is satisfactory if used with phthalate solutions having $P_H$ values of about 5.                                             J. G.

**Dissociation Constants of Various Acids in the Presence of Boric Acid** J. Böeseken and J. Coops. (*Rec. Trav. Chim.*, 1926, 45, 407–413.)—The property of boric acid of forming acid compounds with various organic substances is used to elucidate the structure of certain hydroxy and ketonic acids, and of vicinal diols having rigid, open, or flexible ring structures. The dissociation constants of various organic acids in 0·5 $M$ boric acid solution are calculated, and shown to be 10 to 20 per cent. less than those for the same aqueous solutions. From these the decomposition constants of the compounds are calculated and shown to have no simple connection with the strength of the acid, and to be independent of the concentrations of the decomposition products. All acids (except α- and o-hydroxy acids)

form partly dissociated acidic compounds with boric acid in aqueous solutions, as is shown by the alteration in conductivity on the addition of the acid. For the purpose of these calculations it is assumed that the conductivity of a dilute boric acid solution is due to the ions $H^{\cdot}$ and $B(OH)'_4$, in the presence of the amphoteric compound $B(OH)_4H$. This combines with the anion $(Z')$ of the organic acid to form the weakly acidic compound $Z.B.(OH)_3H$. This, in equilibrium with its decomposition products, is the cause of the decrease in the dissociation constant on the addition of boric acid. J. G.

**Stable Colorimetric Scales for the Measurement of $P_H$ Values.** P. Bruère. (*J. Pharm. Chim.*, 1926, **118**, 377–379.)—A yellow solution (A) corresponding to the tint in Clark and Lubbs's scale for $P_H = 6.0$ may be made by mixing 2 c.c. of a 20 per cent. solution of cobalt nitrate with 98 c.c. of a 0.03 per cent. potassium dichromate solution, whilst a blue solution (B) corresponding to Clark and Lubbs's tint for $P_H = 7.6$ results from mixing 5 c.c. of the cobalt nitrate solution with 95 c.c. of a 10 per cent. copper sulphate solution. Intermediate tints are obtained by mixing volumes of the two solutions, A and B, as follows :—

|  | Yellow. | Greenish yellow. | | | Green. | Bluish green. | | | Blue. |
|---|---|---|---|---|---|---|---|---|---|
| $P_H =$ | 6.0 | 6.2 | 6.4 | 6.6 | 6.8 | 7.0 | 7.2 | 7.4 | 7.6 |
| Solution A. | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | 0 |
| Solution B. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |

D. G. H.

**Analysis of Boron Alloys.** N. Tcshischewski. (*Ind. Eng. Chem.*, 1926, **18**, 607–608.)—An electrolytic method for the separation of metals in the analysis of iron-boron alloys is described. One grm. of the alloy is dissolved in 15 c.c. of dilute (1 : 3) sulphuric acid and the solution is heated until a black, flaky precipitate is formed ; five drops of 30 per cent. hydrogen peroxide are then added, and the solution is diluted to 100 c.c. Twenty-five c.c. of this solution are neutralised with sodium hydroxide solution, five drops of concentrated sulphuric acid are added, and the solution is transferred to a beaker containing a 3 cm. layer of mercury. A platinum wire extending into the mercury serves as the cathode, whilst the anode consists of another platinum wire passing down the centre of a glass stirrer, the end of the wire below the bottom of the stirrer being bent into the form of a spiral. The stirrer is rotated at 350 revolutions per minute, and with a current of 5 amps, and 10 to 15 volts, all the iron, manganese, nickel, etc., is precipitated and amalgamated with the mercury. The solution is then drawn off while the current is still passing. The solution is neutralised to methyl orange, and the boric acid then titrated in the presence of glycerol, phenolphthalein being used as indicator. W. P. S.

**Gravimetric Determination of Copper as Cuprous Iodide.** I. M. Kolthoff and H. A. Kuylmann. (*Chem. Weekblad*, 1926, **23**, 185–186.)—Winkler's method of determining copper as cuprous iodide (*Z. anal Chem.*, 1923, **63**, 324)

gives good results, even in a strongly acid solution, provided that, after the precipitation and boiling, the cooling is effected in an atmosphere of carbon dioxide. If any air is present, oxidation of the iodine takes place, with the result that some cuprous iodide dissolves. The method is also satisfactory when used in presence of large amounts of ferric salts, so that it should prove of value for determining copper in pyrites, etc.

**The Bismuthate Method for the Determination of Manganese. B. Park.** (*Ind. Eng. Chem.*, 1926, **18**, 597–598.)—In this method sulphuric acid may be used with advantage in place of nitric acid ; among the defects accompanying the use of nitric acid are the necessity of removing oxides of nitrogen, the instability of permanganic acid in nitric acid solution, and the tendency of nitric acid to react with ferrous iron. Oxidation in sulphuric acid solution is particularly adapted to the determination of manganese in iron ores. From 0·5 to 3 grm. of the ore is dissolved in hydrochloric acid, 10 c.c. of concentrated sulphuric acid are added, and the mixture is heated until copious fumes of sulphuric acid are evolved ; a small quantity of nitric acid may be added before the sulphuric acid if the ore contains organic matter. After cooling, more sulphuric acid is added to bring the volume up to 8 c.c., the mixture is diluted with 100 c.c. of water, the solution heated to dissolve sulphates, cooled to below 50°C., and treated with 0·5 grm. of sodium bismuthate. The solution is filtered, after one minute, through asbestos, the insoluble portion and the filter are washed with 3 per cent. sulphuric acid, the filtrate is treated with a weighed excess of ferrous ammonium sulphate, and the excess of ferrous iron is titrated with standardised permanganate solution.

W. P. S.

**Determination of Aluminium Oxide in Aluminium. W. H. Withey and H. E. Millar.** (*J. Soc. Chem. Ind.*, 1926, **45**. 170 T.) The sample is heated in a combustion tube at 300–400°C. in a current of dry hydrogen chloride, when the metallic aluminium is volatilised and any alumina is unattacked and left in the boat. This residue contains also other impurities and must be further analysed. Before the combustion tube is heated the air in the apparatus is displaced by a stream of hydrogen. Several experiments showed that metallic aluminium does not contain more than a trace of oxide, which is probably only present as a thin surface film, not disseminated throughout the mass.          R. F. I.

**Determination of Chloride in Commercial Cyanides. A. Bock.** (*Chem. Ztg.*, 1926, **57**,)391.)—Use is made of the reaction of hydrogen peroxide with potassium cyanide, whereby the cyanide is transformed into cyanate and finally into potassium bicarbonate and ammonia. Fifty c.c. of a 2 per cent. solution of the cyanide are treated in the cold with 10 to 15 c.c. of hydrogen peroxide (10 vol. free from chlorine) and gently warmed. Evolution of ammonia denotes that sufficient hydrogen peroxide has been added. Excess is removed by boiling, and the solution is slightly acidified with nitric acid. The chloride can then be determined in the usual way volumetrically or gravimetrically.          R. F. I.

**Determination of Fluorine.** **F. G. Hawley.** (*Ind. Eng. Chem.*, 1926, **18** 573–574.)—The fluorine is precipitated as lead chlorofluoride, the precipitate is decomposed, and the chlorine titrated ; the quantity of chlorine thus found is a measure of the fluorine present. A weighed amount of about 0·5 grm. of the sample of ore is fused with 8 grms. of a mixture of sodium and potassium carbonates in a platinum crucible, the fused mass is treated with hot water until disintegrated, the solution is filtered, and the insoluble portion boiled with a small quantity of concentrated sodium carbonate solution and filtered. The total filtrate, measuring about 250 c.c., is treated with 16 drops of concentrated hydrochloric acid, heated at 30°C., and neutralised with nitric acid, methyl orange being used as indicator. Three drops of nitric acid, 10 drops of glacial acetic acid, and 25 c.c. of 10 per cent. lead acetate solution containing 1 per cent. of acetic acid are added, the precipitated lead chlorofluoride is collected after thirty minutes, and washed three times with cold water saturated with lead chlorofluoride, and then twice with water. The precipitate is dissolved in 25 c.c. of hot 25 per cent. nitric acid (if much lead sulphate remains undissolved it is removed by filtration)), the solution is treated with a known excess of standardised silver nitrate solution, the silver chloride is collected on a filter, and the excess of silver is titrated in the filtrate. Each c.c. of 0·1 silver nitrate solution used to precipitate the chlorine is equivalent to 0·0019 grm. of fluorine. W. P. S.

**Quantitative Colorimetric Determination of Nitrates.** **L. W. Haase.** (*Chem. Ztg.*, 1926, 372.)—The ordinary brucine sulphate reagent used in the colorimetric determination of nitrates develops, on standing, a dark yellow colour which renders it useless. Autenrieth and Koenigsberger's directions for the preparation of the reagent are impossible to follow, inasmuch as they overlook the extreme insolubility of brucine in water. The author adds to 10 c.c. of the liquid under investigation, 0·2 c.c. of a solution of 5 grms. of brucine in 100 grms. of pure chloroform. Twenty c.c. of concentrated sulphuric acid are added, and the heat developed then drives off most of the chloroform. Intense and stable colours are thus produced, the sensitiveness of the reagent being 0·5 mgrm. of $N_2O_5$ per litre. Solutions containing more than 20 mgrms. of $N_2O_5$ per litre should be diluted. J. G.

**Volumetric Determination of Hypophosphites.** **D. Köszegi.** (*Z. anal. Chem.*, 1926, **68**, 216–220.)—Permanganate titration in acid solution leads to negative errors (1 to 4 per cent.), but titration in neutral solution is recommended as an accurate process. The solution (20 c.c.) is boiled for 5 minutes in a graduated 100 c.c. flask with 40 c.c. of $0·1N$ permanganate ; if lime is not already present, 20 to 25 c.c. of calcium sulphate solution are added, to promote settlement of the manganese precipitate. After cooling, the volume is made up and the solution filtered, 50 c.c. being titrated with thiosulphate after addition of 1·5 grm. of potassium iodide and dilute hydrochloric acid. One c.c. of $0·1N$ permanganate = 0·00165 grm. $H_3PO_2$. W. R. S.

# Physical Methods, Apparatus, etc.

**Temperature Corrections of Baumé Hydrometer Readings. C. F. Snyder.** (*Circular No. 295. U.S.A. Bureau of Standards.*)—In several disputes in which the Bureau of Standards has acted as referee the Bureau's Baumé scale for sugar solutions has been accepted. This scale, drawn up by Bates and Bearce, is standard at 20°C., and is based on the specific gravity values of Plato and on the modulus 145. The table of Bates and Bearce (*Table No. 31, Circular No. 44, U.S.A. Bureau of Standards*, comes between the " old " or " Holland " table and the " new " or " Gerlach " table, agreeing closely with the former up to about 13°, and being from 0·1° to 0·2° higher from that point on. The following table shows the corresponding degrees Baumé for the three scales in the neighbourhood of 42° Bé.

| Bureau of Standards. Scale. Modulus. | "Old" or "Holland" Scale. Modulus. | "New" or "Gerlach" Scale. Modulus. |
|---|---|---|
| 145 | 144 | 146·78 |
| 40·00 | 39·9 | 40·6 |
| 41·00 | 40·8 | 41·6 |
| 42·00 | 41·8 | 42·6 |
| 43·00 | 42·8 | 43·6 |
| 44·00 | 43·9 | 44·6 |

A table for correcting temperatures to the standard 20°C. is given. This is based on the values of the thermal expansion of sugar solutions of Plato, the instrument being assumed to be of Jena 16$^{III.}$ glass. It is given as supplementary to the Bearce and Bates table (*loc. cit*), and to the table of temperature corrections for Brix hydrometers (Table II. B.S. Circular No. 44).

**Determination of the Concentration of Liquid Soaps by the Immersion Refractometer. L. F. Hoyt and A. Verwiebe.** (*Ind. Eng. Chem.*, 1926, **18**, 581–582.)—The refractive index of aqueous potassium soap solutions is directly proportional to their total solids content, and the instrument can therefore be used in the routine analysis of such materials. The upper limit of the instrument corresponds with about 22 per cent. of total solids, and 1 per cent. of potassium coconut oil soap gives a reading of 4° on the scale. In the case of soaps made from other oils it is necessary to standardise the instrument with soaps of known composition, since the refractive index of the original oil or fatty acid comes into account. **W. P. S.**

**Measurement and Significance of the Surface Tension of Sugar Solutions. P. Honig.** (*Chem. Weekblad*, 1926, **23**, 265–269.)—Measurements of the surface tension of sugar solutions have been made by means of Traube's stalagmometer (drop-weight method) and of the du Nouy apparatus (*J. Gen. Physiol.*, 1919, **1**, 521), and it has been found that, contrary to the opinion of Lindfors

(*Ind. Eng. Chem.*, 1925, **17**, 1155), a method of determining the percentage of colloidal substances in sugar juices cannot be based on this variable value.    Apart from the many experimental difficulties in the way of applying the principle to general analysis in technical laboratories, it has been established that there is no relation between the surface tension value and the particular colloidal impurities occurring in solutions of raw sugars.    Comparative determinations on the adsorbent action of active carbon (" norit ") and kieselguhr upon sugar solutions have shown that the former is more effective.

**Preparation of Nickel Membranes for Ultra-filtration,   J. Manning.** (*J. Chem. Soc.*, 1926, 1127–1132.)—Membranes for fractional ultra-filtration, which may be used at high temperatures and in the presence of most organic solvents, are prepared by nickel-plating phosphor-bronze or nickel gauze (200 mesh), so that the deposit partly fills up the holes of the gauze.    The membranes are most effective when 50 grms. of nickel sulphate and 80 grms. of nickel chloride are dissolved in 1500 c.c. of water with 5 c.c. of concentrated sulphuric acid.    Electrolysis is carried out at 1·1 to 0·4 amps per 4 sq. in., with the use of 3·5 volts for 1 hour and 2 volts for 18 hours.    The finest membranes obtained contain pores of 50 to $80\mu\mu$, increasing to $300\mu\mu$ with an increase in the nickel sulphate content of the bath.    Successful ultra-filtrations of colloidal silver, arsenic sulphide, ferric hydroxide, cellulose acetate in water and acetone, casein, gelatin, and sodium stearate have been carried out.                                                J. G.

**Investigations into the Standardisation and Calibration of Collodion Membranes I.   C. Lundsgaard and S. A. Holbll.**   (*J. Biol. Chem.*, 1926, **68**, 439–456.)—During the course of an investigation into the action of insulin *in vitro*, the specific rotation angle of the glucose in a mixture containing blood had to be determined, and attempts were made to prepare the glucose in a form suitable for polarimetric determinations by dialysis through collodion membranes.    The collodion membranes used had to keep back the proteins and pigments of the blood with certainty, and to let the glucose pass through them rapidly.    This work led to the problem of making and standardising uniform membranes.    Previous work on the subject is discussed, and the work carried out is described in detail.    The laws governing the passage of glucose through a given collodion membrane were investigated, and it appears that when the volumes of the liquids on both sides are the same the diffusion follows the equation: $\dfrac{dx}{dt} = c\left(\dfrac{K}{2} - x\right)$, where K is the initial concentration of the inner liquid, $x$ is the increase in concentration in the outer liquid in the time, $t$, and $c$ is the diffusion coefficient of glucose for the given membrane.    Determinations were made of the diffusion coefficients for a series of collodion membranes which had been immersed in solutions of alcohol in accordance with the instructions of Walpole (*Biochem. J.*, 1915, **9**, 287).    The solutions used contained 70, 80 and 90 per cent. alcohol.    The diffusion coefficient was found to be the same for membranes prepared in the same manner, but varied according

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to the concentration of alcohol used. It decreased with rising alcohol concentration. A useful method has thus been devised for the determination of the yield of a given membrane, and proof has been furnished that it is possible to standardise collodion membranes by varying the strength of the solution of alcohol in which they are immersed. Membranes were found to retain their properties after being kept for a week, but were not tested further in this respect.          P. H. P.

# References to Scientific Articles not Abstracted.

SOLIDIFICATION OF HELIUM. By W. H. Keesom. *Nature*, 1926, **118**, 81 (July 17).

> Helium solidified in narrow brass tube forming communication between two German silver tubes—Liquid helium as cooling bath—Solidification took place at 4·2° K. at 140 atmos., and at 1·1° K. at 26 atmos.—Solid helium is homogeneous transparent mass, refractive index of which is probably little different from that of the liquid.

CARBOHYDRATE METABOLISM IN HEALTH AND DISEASE. By H. MacLean, M.D. (The Oliver-Sharpey Lectures). *Lancet* (June 26, 1926).

> Different curves with sugar tolerance tests—Factors affecting the curve—Pituitary gland—Thyroid gland—Metabolism in diabetes—Oxidation of fat in diabetes and its bearing on diet—How are the fatty acids oxidised?—Insulin and diabetes—Mode of action of insulin.

# Reviews.

THE CHEMISTRY OF THE PROTEINS AND ITS ECONOMIC APPLICATIONS. By DOROTHY JORDAN LLOYD, M.A., D.Sc., F.I.C. Introduction by Sir FREDERICK GOWLAND HOPKINS, M.B., D.Sc., F.R.S. Pp. xii.+279. London : Churchill & Co., 1926. Price 10s. 6d. net.

Though it is no longer possible to claim for any one class of chemical constituents of the living cell that they form the physical basis of life, yet it is certain that only in a protein milieu can compounds assume that degree of activity which distinguishes their behaviour *in vivo* from that *in vitro*. It is not surprising, therefore, that the proteins should possess the most highly complex and varied chemistry. Hitherto no book in this language has attempted to give an account of the proteins from the side both of structural and of physical chemistry; indeed, these two aspects, owing to their difficulty and specialised nature, have hitherto tended to form separate subjects of treatment, with the result that each has often missed the illumination which a knowledge of the other side might have afforded.

The author of this work, who is herself a specialist on the physical side of the subject, has also the advantage of being a trained biologist; consequently all chemical and physical phenomena associate themselves naturally with biological problems, making the book not only a highly useful storehouse of information, but also a real source of suggestion and stimulus to the biochemist; her special knowledge of the leather industry lends to her applications of the subject to

industrial problems a cogency and force which a purely academic writer could not achieve.

The first part of the book deals with the subject from the purely chemical aspect. The assemblage of facts on the structure of the protein molecule as a whole, and of its degradation products are clearly presented, the modern work on the proteolytic enzymes and the linkages in the protein molecule being particularly well dealt with. The chapter on protein foods is valuable, and incorporates much hitherto scattered information on the relative merits of different proteins which is not to be found in other text books.

Considering that both parts of the subject are condensed into some 266 pages, it is perhaps too exacting to complain of omissions; nevertheless something more on the synthesis of proteins by the vegetable and animal cell, respectively, would be welcome, even at the expense of the chapter on food preservation, which is rather too fragmentary to add much to the value of the book.

In Part II. the author has faced and solved a difficult problem in scientific literature. She has here collected and arranged in a masterly way the very diverse work on the physical chemistry of the proteins so as to make it available for the non-specialised reader. Every aspect of this part of the subject is dealt with, and its bearing on biological and industrial problems indicated in a highly suggestive manner; no worker in biochemistry or in any branch of industrial chemistry connected with proteins can fail to derive help from this able presentation of varied and complex physico-chemical phenomena.

Though covering a range considerably broader than that required by the honours' student in chemistry, yet to him, also, this book will be valuable, as he will be able to gain from it a clear view of the essentials of the subject, even if a proportion of the material is outside his requirements. By assembling this diverse material in so clear and readable a form the author has rendered a real service to biochemical and industrial research.                                    M. STEPHENSON.

THE SYNTHESIS OF BENZENE DERIVATIVES. By S. C. BATES, B.Sc., F.I.C. Pp. xi.+229. London: Ernest Benn, Ltd. 1926. Price 21s. net.

This book fills a gap which has long been felt in chemical literature, and the modest statement of the author that there exist, in the German language, books similar to his is, as regards the form, at least, not correct. Mr. Bates's book is, in fact, the first attempt to give a short but concentrated survey of the different methods which lead to the many derivatives of benzene. The book is divided into the following different chapters: Hydrocarbons, Nitro Compounds, Amines (primary and secondary), Diazo Compounds, Nitroso and Azo Compounds, Halogen Compounds, Sulphonic and Sulphinic Acids, Phenols, Alcohols, Aldehydes, Ketones, Carboxylic Acids, Chlorides and Anhydrides, Amides, Esters, Nitriles, Isonitriles, and the Triphenylmethane group.

The examples are very well chosen, and very little remains to be desired if one considers that the volume has only 229 pages. There are, however, certain statements which are not quite correct, at all events in the form given. On page 22, for example, Mr. Bates says that: " In no case have more than three nitro groups

been inserted in one benzene nucleus." This is not correct, because tetranitro-benzene is well known (*cf. Ber.* **34**, 56); also, tetranitroaniline has been proposed by Flürsheim as a very good detonator for T.N.T. and other stable explosives. (See *e.g. Explosives* by Barry Barnett, London, 1919, pp. 6, 30, and 59.)

Another point to be criticised is that the index is a little too short, and that compounds like phenylhydroxylamine and para-amidophenol are not to be found in the list. These are, it is true, trifles, but "the trifles matter," and Mr. Bates, while he has to be congratulated on his very useful work, will doubtless make it complete when a second edition is required. Even if a new edition should be a little larger, the price should not be augmented. H. E. FIERZ.

LECTURES ON CERTAIN ASPECTS OF BIOCHEMISTRY. By J. C. DRUMMOND, D.Sc.;
    A. V. HILL, Sc.D., F.R.S.; H. H. DALE, M.D., F.R.S., and L. J. HENDERSON,
    A.B., M.D. London: University of London Press, Ltd. Pp. viii+313.
    Price 12s. 6d. net.

This book fulfils the claims of its title. It reproduces, in printed form, four sets of lectures on certain aspects of biochemistry, given under the auspices of the University of London. In the preface it is stated that the lectures have been printed in the form in which they were delivered, and that no attempt has been made to give them the finality of a text book. This method of treatment has made a book which is essentially readable, and which titillates the imagination by the incompleteness of its stories.

The first series of articles by Dr. H. H. Dale on "The Chemical Control of Certain Bodily Functions" is a model of lucid thought and clear expression. Dr. Dale deals with "The Control of the Circulation in the Capillary Blood Vessels," " The Active Principles of the Pituitary Body," and "The Pancreas and Insulin." The account of the work gives a vivid picture of the difficulties which beset the path of the biochemist who is trying to track out the nature of substances which can produce marked biological reactions in concentrations as low as $1 \times 10^{-11}$, and shows how biological reactions can be adapted for analytical purposes. For instance, the active extract of the pituitary body produces eight recognised physiological effects. Are these due to eight different substances? The distribution of the biological reactivities among different fractions obtained by such recognised chemical methods as differential solubilities, differential precipitation or dialysis, provides a qualitative test that shows that the existence of three different substances must be assumed. Again, by defining very carefully the conditions which produce a certain biological response, it is even possible to standardise such an apparently unpromising reagent as a rabbit, which then provides a unit for the determination of insulin.

The second section, by Prof. J. C. Drummond, deals with "Modern Views on the Mechanisms of Biological Oxidations," "Certain Aspects of the Role of Phosphates in the Cell," and "The Vitamins." Theories of biological oxidations are at present undergoing considerable change. It is now recognised that adsorption at an interface has a profound influence on the oxidation of substances like cystine and glycine by gaseous **oxygen, and that the activation of both hydrogen and**

oxygen which occurs at such interfaces, is a similar process in both living and non-living systems. Many biological oxidations are now recognised to be of the type of a Canizzaro's reaction, *i.e.* two molecules of a substance divide between them the elements of water, the one being oxidised, the other reduced. The theory of the existence of "hydrogen acceptors" as part of the mechanism of many biological oxidations is now becoming generally accepted. Oxygen itself is one of the most important of the biological hydrogen acceptors. And, in the presence of a suitable hydrogen acceptor, water can function as an oxidising agent.

Prof. L. J. Henderson contributes to the symposium three lectures on "The Blood and Circulation from the Standpoint of Physical Chemistry." The blood is a system into which oxygen diffuses from the air, and out of which it diffuses into the tissues. Conversely, carbon dioxide diffuses inwards from the tissues and outwards to the air. In a highly detailed account in which the correlation of all the variables is analysed with meticulous care, Prof. Henderson points out to what a high degree of efficiency the body is organised through the influence of one reaction on another. For instance, the oxidation of haemoglobin to oxyhaemoglobin makes this protein a stronger acid. This change in properties is one which accelerates the diffusion outwards of the carbon dioxide, and this loss of carbon dioxide, in its turn, influences the oxygen dissociation curve of haemoglobin in such a way that a further absorption of oyxgen from the air takes place. An analysis of the physico-chemical properties of the blood leads to the interesting conclusion that the body must obtain the increased oxygen supply required when working, by increasing the area of the total diffusing surface, both in the lung and to a still greater extent in the body. This deduction, derived from analytical figures, is fully confirmed by Krogh's discoveries of the opening and closing of the capillaries, a process which he considers one of the major physiological activities.

Prof. A. V. Hill contributes two lectures on "The Physical Environment of the Living Cell," and on "Lactic Acid as the Keystone of Muscular Activity." In the former it is made clear that the dimensions of cellular systems have in themselves important bearings on the nature of the physical and chemical changes that occur within them, and that "the living cell is not so much a thing as a process, a chain of chemical events organised in a peculiar way. The second lecture is a most readable account of one such chain.

The book is printed in clear and pleasing type, and the diagrams are especially well reproduced.                                      D. JORDAN LLOYD.

THE CHEMISTRY OF DRYING OILS. By R. S. MORRELL, M.A., Ph.D., F.I.C., and H. R. WOOD. Pp. 224. London: Ernest Benn, Ltd., 1925. Price 21s. net.

This interesting volume, fourth of the series of monographs edited by Dr. Morrell on "Oil and Colour Chemistry," surveys in a comprehensive and, to a certain degree, critical manner the chemical aspects of the drying oils. About one half of the book is devoted to the purely chemical side, considered in three chapters, dealing respectively with the acids whose glycerides constitute the drying oils, the composition of the oils themselves and the question of their oxidation, including, of course, the action of metallic driers. The only comment called for is that the

limited state of our knowledge of this last subject is not concealed. It may be added in connection with the oxidation of oleic acid that Lapworth has recently determined the conditions under which the yield of dihydroxy-stearic acid is raised to almost the theoretical value at the expense of the dibasic acids which are usually produced at the same time.

On the technical side, the means of production of linseed and China wood oils. the refining processes and the various products of heat treatment are described in some detail, as are also the uses of the oils in the linoleum, electrical and patent leather industries. The endeavour to end up on the high note of colloid chemistry is considerably marred by the fact, acknowledged by the authors, that most of the examples of colloidal phenomena cited have had perforce to be drawn from other types of compounds than the oils in question.

Perusal of the somewhat brief chapter on the analysis of drying oils leaves an impression that the personal touch of the authors is lacking; this is particularly noticeable in the descriptions of the hexabromide test, and of the methods of examination of mixtures of fatty acids, where reference is made to numerous papers, often contradictory, without critical distinction. A typographical error gives undue prominence to the dispersive power of China wood oil, while no satisfactory iodine value for a drying oil will be obtained using 0.5 grm. with the quantity of reagents quoted. On the whole, however, misprints are comparatively few; more rigorous revision would have eliminated, in addition, a number of redundancies and ambiguities. The scheme of collecting references at the end of each chapter possesses certain advantages, but it renders them decidedly awkward of access.

It may be pointed out that the specifications for paint and varnish materials now in process of publication by the British Engineering Standards Association occasionally differ in some minor details from the requirements put forward in this volume.

To the chemist associated in any way with the drying oils, this book presents a useful survey of the subject; it should also exercise an appeal to those engaged in other branches of chemistry, and it is, therefore, a matter for regret that the price could not be made substantially lower; it may be noted in this connection that the volume is offered in America at an appreciably lower figure. B. A. ELLIS.

THE CHEMISTRY OF RUBBER MANUFACTURE. By LOTHAR E. WEBER, Ph.D. Pp. xii.+365. London: Charles Griffin & Co., Ltd., 1926. Price 21s. net.

The volume under review was commenced, as the author tells us in his preface, as a revision of his father's *The Chemistry of India Rubber*, originally published over 20 years ago. It soon became apparent, however, that as a result of the profound changes which the rubber industry has undergone during the past two decades, a complete re-writing was required, and the present work is described as "based" on the fifth edition of Carl Otto Weber's classical book. It is not remarkable that, on the whole, but little remains of the matter as presented by Weber *père*; that the general "atmosphere" and tone of Weber junior's publication are essentially different from those which are so characteristic of the prior work. Dr. Lothar

Weber reminds us that "Twenty years ago there was no plantation rubber industry, reclaimed rubber was in its infancy, and organic accelerators had not yet been conceived.   Many of our most valued compounding ingredients, whilst available, were not appreciated, and the individual function of such compounding ingredients as were in active use was by no means clearly understood." .... He might have gone further, and pointed out that, from a scientific point of view also, so much has been achieved in the realms of rubber chemistry and physics, that, in many respects, an entirely new perspective has been developed.   Whilst the outlook of the original work was mainly scientific and philosophical, that of the present publication is largely technical; nevertheless, the author has given a fair exposition of many of the more recent researches dealing with such objects as the nature of latex and of coagulation, the physical and technical properties of crude rubber, vulcanisation, the synthesis of rubber, reinforcing agents, softeners, organic accelerators and the chemical and physical examination of vulcanised rubber.   There are useful appendices dealing with rubber solvents and with textiles.

The analyst will note that the chapters on the examination of crude rubber and the chemical examination of vulcanised rubber contain a good deal of new matter, and that the latter, more particularly, has been entirely re-cast and brought up to date.   The sections dealing with the physical examination of crude and vulcanised rubber might with advantage have been handled jointly, inasmuch as the more important tests of the raw material involve vulcanisation, and the separation of these sections by some two hundred pages may possibly, in the mind of the non-expert reader, cause some little confusion.

The treatment of the matter is quite practical, and Dr. Weber's volume is one which should prove distinctly useful to the analyst and rubber work's chemist, and may be cordially recommended to them.          PHILIP SCHIDROWITZ.

RUBBER AND ITS USES IN BUILDING WORKS.   By H. P. STEVENS, M.A., D.Sc. (Consultant to the Rubber Growers' Association), and B. D. PORRITT, M.Sc. (Director of Research to the Research Association of British Rubber and Tyre Manufacturers).   Pp. 32.   London: Propaganda Department of the Rubber Growers' Association, 2 to 4, Idol Lane, E.C.3, 1926.

This little brochure is described as being a "short account of the preparation and properties of rubber, with particular reference to its uses in the building and allied industries.   When it is stated that it also contains a section on "the treatment and storage of rubber goods," a glossary of terms, a bibliography, a list of educational and rubber trade institutions and associations, and several excellent illustrations, it will be realised, having regard to the standing of the authors, that we have here a veritable *multum in parvo*.   On page 6 there is an obvious arithmetical slip, inasmuch as, in connection with the tensile strength of crude rubber, the figure of 3 tons per square inch, calculated to original section, and 15 tons, calculated to section at break, are mentioned.   The intention, no doubt, was to write 0.3 tons and 1.5 tons respectively.   The booklet should be distinctly useful to the various sections of the building trade interested in well-tried and novel applications of rubber in its various forms.          PHILIP SCHIDROWITZ.