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The Examination of Dyed Leather in Cases of Alleged Dermatitis.

BY T. CALLAN, M.Sc., PH.D., F.I.C., AND N. STRAFFORD, M.Sc., A.I.C.

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INTRODUCTION.—Published results of investigations of dermatitis caused by articles of attire have been concerned almost exclusively with furs, which commonly are dyed with organic bases oxidised *in situ* (*cf.* ANALYST, 1923, **48**, 282, 283, 284; 1929, **54**, 694).

Recently, however, there have been several cases of dermatitis alleged to have been caused by leather hat-bands. Investigation of authenticated cases has revealed the fact that the hat-bands in question contained small but appreciable amounts of soluble chromates or chromic acid—the results of faulty after-chroming, that is, a treatment with a dichromate to which dyed leathers are frequently subjected to improve shade and fastness. It is well known that contact of such substances with the skin is liable to cause dermatitis.

The usual dyestuffs for dyeing leather hat-bands are basic colours, such as chrysoidine and Bismarck brown. Since these are derivatives of *meta*-diamines, *e.g. meta*-phenylenediamine or *meta*-toluylenediamine, suspicion has been aroused that, possibly, traces of diamines in the dyestuffs used may also be contributory factors in cases of dermatitis alleged to be caused by dyed leather.

p-Phenylene-diamine is not a constituent of dyestuffs normally employed in colouring leather; nevertheless, it is our experience that, when investigating cases of dermatitis, analysts almost invariably suspect the presence of this substance, and we have known cases of its having been reported, even when the dyestuffs used were derived solely from *meta*-diamines.

It was, therefore, considered of importance to devise tests which would indicate the presence or absence of both *meta*- and *para*-diamines in the dyed leather.

Cox (ANALYST, 1929, **54**, 694) has published valuable methods for the detection of diamines and allied bodies in fur.* In the first place, therefore, the possibility

* Since the present investigation was carried out Forster and Soyka (*J. Soc. Dyers and Col.,* 1931, **47**, 99; ANALYST, 1931, 476) have published similar methods.

of applying these methods directly to dyed leather was investigated. When they were applied both to undyed and to dyed vegetable-tanned leather, it soon became evident that the tannins present in the leather may interfere very seriously with many of Cox's tests, with the result that, unless great caution were taken in interpreting the results, it would be quite possible for the apparent presence of diamines to be indicated, even in an undyed vegetable-tanned leather, whilst in the case of a dyed leather it would be impossible to say with most of these reactions whether they were those of tannin matter or of diamines. We have reason to believe that in several cases where vegetable-tanned leather hat-bands have been reported to contain diamines, the reactions on which this conclusion was based were due to the normally-present tanning materials.

EXPERIMENTAL.—The samples of hat-band leather which we examined were as follows:—

A. Undyed leather which had been tanned with vegetable-tanning materials.

B. Trade-dressed leather tanned as in A and dyed with chrysoidine (a derivative of *meta*-toluylenediamine) shaded with magenta and methylene blue.

C. Trade-dressed leather tanned as in A and dyed with basic leather phosphine shaded with malachite green, magenta and auramine. None of these dyes is a derivative of a *meta*- or *para*-diamine.

D. Vegetable-tanned leather* dyed with Bismarck brown (a derivative of *meta*-toluylenediamine).

The leathers were free from grease. In each case 10 grms. of the leather (cut into small pieces) were extracted for 48 hours in the cold with 40 ml. of 1 per cent. acetic acid. The extracts were then examined by the reactions given by Cox (*loc. cit.*) and by the following additional reagents: aniline and dichromate (indamine reaction); sodium hypochlorite; diazobenzene-*p*-sulphonic acid.

In order to obtain a measure of the reliability and sensitivity of the various tests the reagents were also added to portions of each leather extract, to which had been added a small amount of *para*-phenylenediamine and *meta*-toluylenediamine respectively (equivalent to 0·007 per cent. in the total solution tested, or 0·04 per cent., calculated on the original weight of leather). Control tests were also carried out on solutions containing 0·007 per cent. of *para*-phenylenediamine, 0·007 per cent. of *meta*-phenylenediamine and 0·007 per cent. of *meta*-toluylenediamine, respectively.

In addition, the approximate limiting sensitivity of certain of the tests was determined by reducing the amount of diamine added to the extract.

The following are brief notes on the tests employed:—

REAGENTS REQUIRED.—2 N hydrochloric acid solution; $N/2$ sodium nitrite solution; approx. $N/20$ β-naphthol solution (0·72 grm. of β-naphthol is dissolved in 6 ml. of N sodium hydroxide solution and diluted to 100 ml.); bromine water; $N/10$ sodium hydroxide solution; dilute sodium hypochlorite solution (5 ml. of

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* This leather was of different origin from that employed in tests A to C.

commercial hypochlorite liquor containing 18–20 per cent. of available chlorine, diluted to 100 ml.); 5 per cent. aqueous solution of phenol; 1 per cent. alcoholic solution of *p*-dimethylaminobenzaldehyde; 5 per cent. ferric chloride solution; 1 per cent. aniline hydrochloride solution (1 grm. of aniline hydrochloride crystals dissolved in water and made up to 100 ml.); 2 per cent. potassium dichromate solution; sodium acetate crystals (pure); $N/20$ diazobenzene-*p*-sulphonic acid.

The last reagent is prepared by dissolving 8·65 grms. of purified anhydrous sulphanilic acid in warm water containing sufficient sodium carbonate to make the final solution slightly alkaline to litmus, cooling the solution, and making up to 100 ml. Ten ml. of this solution are pipetted into a 100 ml. beaker containing a few small pieces of washed ice and diluted to about 30 ml. Seven or eight ml. of hydrochloric acid (sp. gr. 1·16) are added while the beaker is cooled externally with ice, and then, rapidly, 10·1 ml. of $N/2$ sodium nitrite solution, previously diluted with an equal volume of ice-cold water. The whole is thoroughly mixed and diluted to 100 ml. with ice-cold water. The diazo solution should be used within an hour of preparation.

DETAILS OF TESTS.—In each case the reagents were added in the order named to (*a*) 1 ml. of the extract and 0·5 ml. of water, (*b*) 1 ml. of the extract and 0·5 ml. of 0·02 per cent. diamine solution.

Cox's TESTS.

No. 1. *Nitrous. Acid.* 0·2 ml. of 2 N hydrochloric acid, 0·5 ml. of $N/2$ sodium nitrite solution.

No. 2. The solution from No. 1, after standing for two minutes in the cold, is added to a mixture of 4 ml. of the $N/20$ β-naphthol solution and 1 ml. of sodium hydroxide solution.

No. 3. *Bromine.* Bromine water is added, drop by drop.

No. 4. *Phenol and hypochlorite.* $N/10$ sodium hydroxide solution, sufficient to make the solution very faintly alkaline to Brilliant Yellow paper, 1 ml. of 5 per cent. phenol solution, 2 to 5 drops of dilute sodium hypochlorite solution.

No. 5. p-*Dimethylaminobenzaldehyde.* 0·2 ml. 2 N hydrochloric acid, 1 ml. of the reagent.

No. 6. *Ferric chloride.* One drop of the ferric chloride solution.

Additional tests.

No. 7. *Aniline and dichromate.* 0·5 ml. of 1 per cent. aniline hydrochloride solution, 1 drop of 2 per cent. potassium dichromate solution.

No. 8. *Sodium hypochlorite.* $N/10$ sodium hydroxide solution, sufficient to give a faintly alkaline reaction to Brilliant Yellow paper, 1 ml. of dilute sodium hypochlorite solution.

No. 9. *Diazobenzene*-p-*sulphonic acid.* One grm. of pure sodium acetate crystals, 1 ml. of $N/20$ diazobenzene-*p*-sulphonic acid solution.

The results are given in the accompanying tables.

TABLE I.   UNDYED VEGETABLE-TANNED LEATHER A.

Test.	Extract from leather.* (X.)	X+p-Phenylenediamine equiv. to 7 parts per 100,000 of soln. or 0·04 per cent. on the leather.	X+m-Toluylenediamine equiv. to 7 parts per 100,000 of solution.	p-Phenylenediamine (7 parts per 100,000).	m-Toluylenediamine (7 parts per 100,000).	m-Phenylenediamine (7 parts per 100,000).	Conclusions.
1. Sodium nitrite.	Deep yellowish-brown.	Deep yellowish-brown.	Deep yellowish-brown.	Pale yellow.	Yellow.	Yellow.	Tannins interfere seriously.
2. Diazotised soln. from (1) + excess alkaline β-naphthol.	Deep brown.	Deep orange-brown.	Deep brownish-orange.	Reddish-brown.	Brownish-red.	Brownish-red.	Tannins interfere seriously.
3. Bromine water.	No precipitate.**	No precipitate.		Very slight white flocculent ppt. (no turbidity).	Turbid solution (no flocks).	Turbid solution (no flocks).	Tannins interfere.
4. Phenol and hypochlorite.	Slight darkening.	Slight darkening. (Rather more than X.)		Immediate violet.	Immediate pink.	Immediate orange.	Tannins interfere (by masking).
5. p-Dimethylamino-benzaldehyde.	Pale yellow, very slowly turning orange and finally red.	Deep orange-red immediately (0·01% on leather, pale orange).	Deep yellow immediately, very slowly turning orange and finally red.	Deep orange-red immediately.	Deep yellow immediately.	Deep yellow immediately.	Tannins slowly develop a red colour which might be mistaken for an indication of the presence of p-diamine.
6. Ferric chloride.	Immediate intense violet-blue.	Immediate intense violet-blue.		Immediate darkening; changes very slowly to pale brownish-violet.	Slight darkening.	Slight darkening.	Tannins interfere seriously.
7. Aniline hydrochloride and dichromate.	Yellowish-brown.	Yellowish-brown.		Immediate blue-green, rapidly turning blue.	No change.	No change (turns brown very slowly).	Tannins present in sufficient quantity to interfere seriously with reaction for p-diamine by masking.
8. Hypochlorite.	No obvious change. No precipitate.	No obvious change. No precipitate.		Very slight flocculent ppt. on long standing.	Transient orange, otherwise no change.	Transient orange, otherwise no change.	This test is much less sensitive than the others. Tannins do, however, apparently interfere (by masking).
9. Diazo-benz-e-p-sulphon-	Deep reddish-brown.		Deep reddish-brown (similar to X.	Light orange-brown.	Reddish-brown (with precipitation).	Deep reddish-brown (with precipitation).	Tannins definitely inter-

TABLE II.   DYED LEATHER B.

Test.	Extract from leather.* (X).	X + p-Phenylenediamine equiv. to 7 parts per 100,000 of soln. or 0·04 per cent. on the leather.	X + m-Toluylenediamine equiv. to 7 parts per 100,000 of solution.	p-Phenylenediamine (7 parts per 100,000).	m-Toluylenediamine (7 parts per 100,000).	m-Phenylenediamine (7 parts per 100,000).	Conclusions.
1. Sodium nitrite.	Slight darkening.	—	Darkens rather more than X.	Pale yellow.	Yellow.	Yellow.	Test not sufficiently sensitive to allow of any definite conclusions being drawn. (Colour of the extract also interferes.)
2. Diazotised soln. from (1) + excess alkaline β-naphthol.	Brownish-yellow.	—	Orange-red (0·02% on leather; brownish-orange).	Reddish-brown.	Brownish-red.	Brownish-red.	No diamines (*meta* or *para*) in the leather.
5. p-Dimethylamino-benzaldehyde.	Yellowish-brown (slight darkening only).	Deep orange-red immediately (0·01% on leather; distinct reddish orange immediately).	Deep yellow (considerably deeper than X.)	Deep orange-red immediately.	Deep yellow immediately.	Deep yellow immediately.	Leather is free from p-diamine and probably also from m-diamine.
6. Ferric chloride.	Immediate greenish-blue coloration.	—	—	Immediate darkening; changes very slowly to pale brownish-violet.	Slight darkening.	Slight darkening.	Owing to the known interference of tannins, no conclusions can be drawn.
7. Aniline hydrochloride and dichromate.	Yellow colour. (Practically no change.)	Immediate blue-green (0·01% on leather: faint olive-green, fading rapidly).	—	Immediate blue-green, rapidly turning blue.	No change.	No change (turns brown very slowly).	Leather contains no p-diamine.
9. Diazo-benzene-p-sulphonic acid.	Deep yellowish-brown.	—	Deep brownish-red (0·02% on leather: deep reddish-brown).	Light orange-brown.	Reddish-brown with precipitation.	Deep reddish-brown (with precipitation).	Leather contains no m-diamine.

* NOTE: The extract itself was light brown in colour.

TABLE III.   DYED LEATHER C.

Test.	Extract from leather.* (X.)	X+p-Phenylene-diamine equiv. to 7 parts per 100,000 of soln. or 0·04 per cent. on the leather.	X+m-Toluylene-diamine equiv. to 7 parts per 100,000 of solution.	p-Phenylenedi-amine (7 parts per 100,000).	m-Toluylenedi-amine (7 parts per 100,000).	m-Phenylenedi-amine (7 parts per 100,000).	Conclusions.
1. Sodium nitrite.	Very slight darkening.	—	Darkens more than X (yellowish colour).	Pale yellow.	Yellow.	Yellow.	Test not sufficiently sensitive to allow of any definite conclusion being drawn. Colour of extract interferes.
2. Diazotised soln. from (1) + excess alkaline β-naphthol.	Yellow.	—	Brownish-red (0·02% on leather: brownish-orange).	Reddish-brown.	Brownish-red.	Brownish-red.	No diamines (meta or para) in the leather.
5. p-Dimethyl-amino-benz-aldehyde.	Very slight deepening of yellow colour (no red).	Very definite orange-red immediately (0·01 % on leather distinct red-dish-orange immediately).	—	Deep orange-red immediately.	Deep yellow immediately.	Deep yellow immediately.	Leather is free from para-diamine and probably also from meta-diamine.
6. Ferric chloride.	Immediate greenish-blue.	—	—	Immediate darkening changes very slowly to pale brownish-violet.	Slight darkening.	Slight darkening.	Owing to the known interference of tannins, no conclusions can be drawn.
7. Aniline hydrochloride and dichromate.	Yellow colour. (Practically no change.)	Immediate blue-green (0·01% on leather: faint olive green fading rapidly).	—	Immediate blue-green rapidly turning blue.	No change.	No change (turns brown very slowly).	Leather contains no p-diamine.
9. Diazo-benzene-p-sulphonic acid.	Golden-yellow.	—	Brownish-red (slight turbidity).	Light orange-brown.	Reddish-brown (with reddish precipitate).	Deep reddish-brown (with precipitation).	Leather contains no m-diamine.

* Note: The extract itself was yellow in colour.

TABLE IV.   DYED LEATHER D.

Test.	Extract from leather.* (X.)	X+m-Toluylenediamine equiv. to 7 parts per 100,000 of soln.	p-Phenylenediamine (7 parts per 100,000).	m-Toluylenediamine (7 parts per 100,000).	m-Phenylenediamine (7 parts per 100,000).	Conclusions.
1. Sodium nitrite.	Slight darkening.	Slight darkening.	Pale yellow.	Yellow.	Yellow.	Test not sufficiently sensitive to detect the presence of added diamine. Colour of extract also interferes.
2. Diazotised soln. from (1) + excess alkaline β-naphthol.	Brownish-yellow.	Brownish-red.	Reddish-brown.	Brownish-red.	Brownish-red.	It is easily possible to detect the presence of added meta-diamine. Colour of extract does not cause serious interference. Leather gives no reaction for meta-diamine.
5. p-Dimethyl-amino-benzaldehyde.	Yellow (colour of reagent).	Deep yellow immediately.	Deep orange-red immediately.	Deep yellow immediately.	Deep yellow immediately.	Colour of extract does not seriously interfere. It is easily possible to detect the presence of added diamine. The leather gives no reaction for meta-diamine.
9. Diazo-benzene-p-sulphonic acid.	Orange-yellow.	Orange-red.	Light orange-brown.	Reddish-brown (with reddish ppt.).	Deep reddish-brown (with precipitation).	It is easily possible (by direct comparison) to detect the presence of added meta-diamines. The leather gives no reaction for meta-diamine.

* NOTE: The extract itself was pale reddish-brown in colour.

DISCUSSION OF RESULTS.—From the results given in Table I, it is evident that the tannins present in the leather may interfere with many of the colour reactions. In some cases the interference is positive; that is, colour reactions are obtained which might easily be mistaken for those given by diamines (Tests 1, 2, 5, 6 and 9). In others, the effect of tannins is to mask, to a greater or less extent, the effect produced by diamines when these are present (Tests 3, 4, 7 and 8).

It is evident, therefore, that very considerable caution is required in interpreting the results of the tests.

From Tables II, III and IV it is noticeable that the extracts from the dyed leathers give much less pronounced reactions with the various reagents than the extract from the tanned but undyed leather. This, of course, is to be ascribed to the fact that a proportion of the soluble tannins has been removed by the dyeing process. Consequently, in certain tests, particularly 5 and 7, the disturbing effect of the tannin reaction is much less noticeable.

By a comparison of the reactions given by the extracts of the dyed leathers with those given by the extracts containing very small amounts of *meta*-toluylene-diamine and *para*-phenylenediamine, it is possible to arrive with a considerable degree of accuracy at a conclusion as to the presence or absence of traces of diamines.

Actually in the three samples of dyed leather referred to in this paper no diamines could be detected.

RECOMMENDATIONS.—Only the tests numbered 2, 5, 6, 7 and 9 should be applied to the extracts from leather which is being examined for the presence of diamines. No. 5 is the most sensitive of the tests, and will detect as little as 0·01 per cent. *p*-phenylenediamine (expressed on the leather) in a coloured extract containing tannins. Test 7 will detect a similar amount, but only if test 6 indicates that more than traces of tannin are present. Tests 2, 5 and 9 will detect about 0·02 per cent. of a *meta*-diamine in a similar extract. This limiting sensitivity of the tests is largely determined by the presence of tannins (indicated by test 6) and colouring material from the leather. The sensitivity of the tests is considerably greater when the reactions are carried out in the absence of these interfering factors.

In view of the fact that the presence of tannins may lead to faulty conclusions being drawn even from these tests, an examination of the extract should always be supplemented by control tests on portions of the extract to which very small amounts of a *meta*- and *para*-diamine, respectively, have been added.

In this way the effect produced by the diamines may be noted with accuracy, and from a careful survey of the whole of the evidence given by the four tests one may draw reliable conclusions as to the presence or absence of diamines in leather.

DISCUSSION.

Dr. H. E. Cox said that the authors had drawn attention to a point which experience showed to be very important; he could quite confirm their findings as to the interference of leather extract or tannin materials. It was very necessary, before making tests by colour reactions, to ascertain what other substances were present and the extent of their possible interference. In his paper, to which the authors had referred, he had given reactions applicable to the pure intermediates, and these were quoted and confirmed by Dr. Callan and Mr. Strafford. He had been particular to indicate that the extracts should be made from the hair and not usually from the fur as a whole. From this point of view furs were quite different from other dyed articles, in that the fibre was impregnated with the appropriate intermediate, which was subsequently oxidised on the fibre; traces of residual or unoxidised bases were easily leached or soaked out.

There was another point which was liable to introduce serious error which the authors had not mentioned; indeed, it did not appear in any of the literature, so far as he knew, that was the decomposition of either oxidation colours or various azo colours during extraction. To take the simplest case, one might consider Bismarck brown, the formula of which was well known to be:
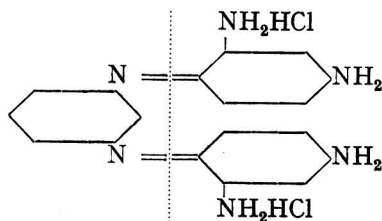
It was made from meta-phenylenediamine and nitrite, and, on reduction with zinc dust or hydrosulphite, split at the double bond, re-forming metaphenylene-diamine. He had established experimentally that digestion of an animal tissue, such as leather, with hot dilute acid effected the same reduction, differing only in degree. In this way it was possible to form by an inappropriate technique one of the substances sought for and so arrive at an erroneous conclusion. This was a simple case. Then, to consider a more complex one, there was a well-known brown leather dye having the constitution (according to the Colour Index)
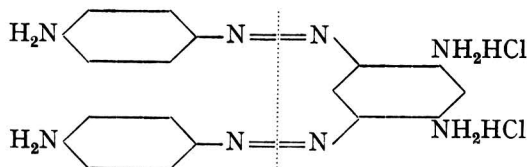
it was made from para-aminoacetanilide and meta-phenylenediamine. On reduction it also split at the double bond, and there were formed two molecules of para-phenylenediamine, which substance was not only not present in the dye, but was not even one of the constituents or ingredients from which the colour was made. He thought that the non-recognition of such facts might explain some difficult results. It was within his own experience, which now extended over some hundreds of specimens, that substances had been occasionally suggested as being present which could not really be there, having regard to the dyes or materials used by the manufacturers.

A similar point arose with oxidation products where the pigment was a complex ring structure, often of imperfectly known constitution; these might be readily decomposed in acid solution with protein matter and free base re-formed. Indeed, one theory of dyeing presupposed the formation of complex but loose compounds with animal bases, and their hydrolytic or reduction products were liable to be misleading unless the possibilities were borne in mind.

He rather mistrusted the indamine reaction because so very many compounds would give it, but every possible test should be applied in these difficult cases.

Dr. H. PHILLIPS said that the British Leather Manufacturers' Research Association had found that the testing of the actual leather extract was unsatisfactory because of the presence of tannins, and they preferred to extract the diamines from the leather extract. Benzene was used for the extraction in a continuous extractor, and for small amounts of diamines 24 hours' extraction was necessary. He had used the same extraction agent as Mr. Strafford, and had found that if semi-chrome leather were painted with a solution of diamines and then allowed to dry, it was not possible, in the case of m-phenylenediamine, to extract the diamine with 1 per cent. acetic acid, although it could be extracted with $N/10$ hydrochloric acid. In testing for p- and m-phenylenediamines a very useful method was to steam-distil the leather with an alkaline solution, using superheated steam. In this manner a colourless distillate was obtained which was very satisfactory for the colour reactions. This method, however, was only suitable for preliminary examination, since, under these conditions, diamines might be generated from normally stable dyes.

Mr. Strafford had mentioned hat-band leathers as a possible cause of dermatitis, owing to the presence of chromates. The greater proportion of hat-bands were made of vegetable-tanned leathers. In experiments which he had made he had been surprised to find that vegetable-tanned leather would fix up to 10 per cent. of its weight of chromate. The presence of chromate in semi-chrome hat-band leather was unlikely to be the cause of dermatitis. Most semi-chrome leathers yielded traces of chromate when extracted with water, and no suspicion was attached to such leathers.

Dr. W. L. DAVIES remarked that, since chromium oxide had been successfully used as a "clue substance" in determining the digestibility of foods, it could not be regarded as an internal poison. Also, did not chromium poisoning depend largely on the individual, one person being affected, whilst another was immune?

Mr. STRAFFORD said that he would like to express his thanks to Dr. Cox for his very valuable comments. Regarding the indamine test there was no doubt that the most important factor controlling the sensitivity of the reaction was the degree of acidity of the solution. Whilst he agreed that the test might not be specific for *para*-phenylenediamine he considered it of value, since in coming to a decision one was guided by the whole of the evidence from the various tests and not by the result of one reaction only. Quite powerful reducing agents were required to reduce azo dyestuffs to amino compounds, and he was surprised to hear the suggestion that leather could act as a sufficiently powerful reducing agent to produce compounds such as *meta*- or *para*-diamines from certain types of azo dyestuffs. This was, of course, theoretically possible with dyestuffs of the constitution outlined by Dr. Cox.

Replying to Dr. Phillips' remarks, Mr. Strafford agreed that the use of superheated steam was rather open to question, since this might cause decomposition of the dyestuff. Acetic acid was chosen for the extraction, following the precedent set by Dr. Cox in the case of dyed furs. The use of this acid more closely conformed to the conditions likely to be met in cases of alleged dermatitis than hydrochloric

acid. Mr. Strafford stated that he was also interested in the question of the separation of diamines from tannins. As a matter of fact, since the completion of the work now presented he had carried out a few experiments on the chemical separation of the diamines from the tannins, and he had obtained reasonably good results by making the extract from the leather distinctly alkaline and extracting with ether.

Dr. Phillips was correct in differentiating between the toxicity of chromium salts and chromates or dichromates. In the case mentioned, soluble chromates or chromic acid had been detected in the leather extract.

The Determination of Small Quantities of Methane.

By H. R. AMBLER, B.Sc., F.I.C.

IN the following paper a convenient and precise technique is described for the determination of methane in gas mixtures; it is particularly applicable to mixtures containing small proportions of methane.

INTRODUCTION.—The determination of methane (and its homologues) is made difficult by its inert character and its lack of specific chemical reactions applicable to analysis. In practice, it has always been finally determined by combustion with oxygen, after removal of interfering gases. Such gases as carbon dioxide, oxygen, and unsaturated hydrocarbons are removed without difficulty; the main concern is the removal of carbon monoxide.

In one method, still much in use, carbon monoxide is absorbed by cuprous chloride or other liquid absorbent, and the hydrogen that is usually present is exploded with air or oxygen, together with the methane, the latter being measured by the amount of carbon dioxide so produced. The accuracy of this method, however, is limited to about 0·2 per cent. on account of incomplete absorption of carbon monoxide. (*Cf.* Ambler, ANALYST, 1925, **50**, 167; Sutton and Ambler, *ibid.*, 172.)

In another method the bulk of the carbon monoxide is removed by absorption, and the remainder by passing over iodine pentoxide at 120°–150° C. The hydrogen and methane are then oxidised by passing over copper oxide at 950°–1000° C., the water so produced removed by phosphorus pentoxide, and the methane determined gravimetrically by absorption of the carbon dioxide in alkali. This method is accurate, but takes some hours, and requires large samples of gas, particularly where the methane content is low.

In the process here described, hydrogen and carbon monoxide are oxidised by means of cupric oxide at about 300° C. (*cf.* Jäger, *J. Gasbeleucht.*, 1898, **41**, 764), the resulting carbon dioxide is removed, and the methane is determined by burning with oxygen in the presence of platinum wire at bright yellow heat.

APPARATUS AND PROCEDURE.—(a) *Removal of Carbon Monoxide and Hydrogen.* —The apparatus for the fractional combustion is shown in the diagram.

A is a glass tube, one end of which contains a mixture of powdered cupric oxide and short-fibre asbestos in equal parts.* The other end of the tube contains calcium chloride, ascarite (a sodium hydroxide and asbestos preparation) and phosphorus pentoxide. If carbon monoxide is to be determined in the same process, the ascarite and calcium chloride are omitted. The end containing the copper oxide is surrounded by an electric furnace. The other end leads to a reservoir, B, of about 150 c.c. capacity, which can be used as a Töpler pump to evacuate the tube A; gas so pumped from A is transferred through the by-pass, C, either to the air or to the measuring part of the apparatus.
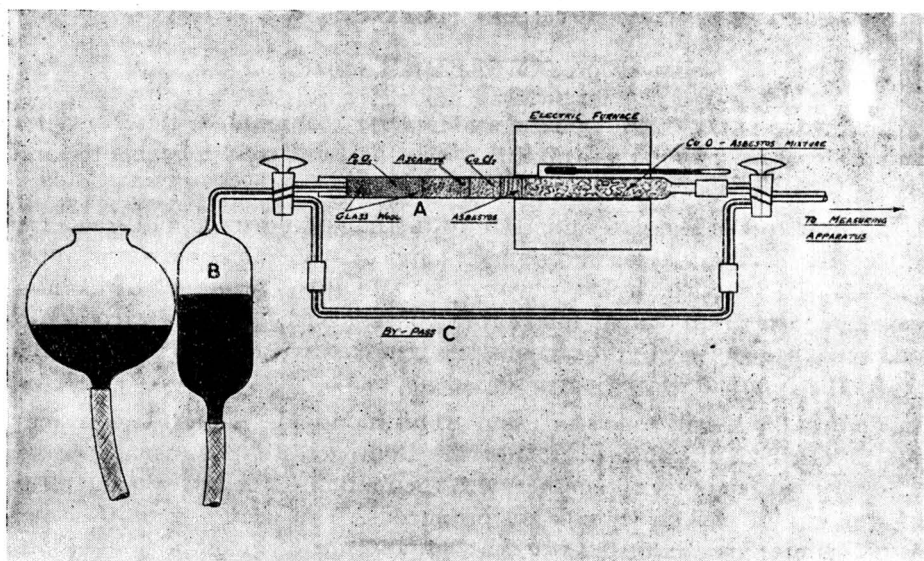
At the beginning of an experiment the furnace is heated to 270°–295° C.,† and the tube A evacuated. A measured sample of gas is drawn slowly through the copper oxide into B, and passed slowly backwards and forwards three times. The gas remaining in the tube is now pumped out and returned through C to a measuring apparatus.

The gas now consists of nitrogen, together with small quantities of methane or its homologues. If the nitrogen content of the original gas is known, it is

* This exposes a much greater surface than the more usual "wire" copper oxide and reduces the time required for the oxidation (see Donnelly, Foott and Reilly, *Proc. Roy. Dublin Soc.*, 1929, **19**, 165).

† Methane is unaffected below 295° C. (Ott and Scherb, *Z. anal. Chem.*, 1926, **68**, 238). It would appear that oxidation may in some cases begin at 300° C. (Terres and Mauguin, *J. Gasbeleucht.*, 1914, **57**, 8). See also Campbell and Gray, *J. Soc. Chem. Ind.*, 1930, **49**, 432т.

unnecessary to measure the volume of sample taken in the first place, since the next process gives the ratio of methane to nitrogen.

(b) *Combustion of Methane.*—The residual gas is measured in a gas analysis apparatus fitted with a platinum wire combustion pipette. The apparatus in use here is one of the Ambler type (ANALYST, 1929, **54**, 517), fitted with a vessel for slow combustion. The Haldane apparatus would also be suitable. A small amount of oxygen or air is let in, the gas measured again and transferred to the combustion pipette. Any carbon monoxide or hydrogen that may have escaped the copper oxide may be detected by heating the platinum wire at very dull red heat for a minute and measuring the gas again. If these gases are present they will burn under these conditions and contraction will be observed; methane is not affected at all (Whitaker, *Fuel*, 1925, **4**, 450). Only in exceptional cases is such contraction greater than 0·1 per cent. on the residual gas.

The gas is now treated with the platinum at bright yellow heat for two minutes, and the volume again measured. Combustion of one volume of methane causes a contraction of two volumes. The gas so burnt can be identified as methane by measuring the amounts of carbon dioxide produced and oxygen remaining. The combustion of ethane gives different ratios, and it can thus be detected and determined by measuring these quantities.

ACCURACY.—With the measuring apparatus used here a contraction of 0·05 per cent. corresponds with a pressure drop on the manometer of about 0·5 mm. This is easily readable, and would be produced by the combustion of 0·025 per cent. of methane in the gases remaining after removal of carbon monoxide and hydrogen, *i.e.* in the nitrogen. For gases of low nitrogen content the sensitivity of the method is increased, since the quantity of gas taken for the final combustion corresponds with a larger quantity of the original gas. If the nitrogen content is, for example, 10 per cent., 0·0025 per cent. of methane in the original sample is easily measurable.

The following duplicate determinations show the degree of concordance obtained. The nitrogen content of the gases was from 16 to 19 per cent., and the volumes of original samples about 70 c.c.:—Sample 1, 0·040 and 0·040; sample 2, 0·089 and 0·090; sample 3, 0·119 and 0·116; sample 4, 0·158 and 0·155 per cent. of methane.

RESEARCH DEPARTMENT,
    WOOLWICH.

The Effect of the Rate of Boiling on the Residual Sulphur Dioxide Content in Mixtures of Sugar and Corn Syrup; also the Effect of Bleaches containing Sulphur Dioxide.

By R. HAROLD MORGAN, B:Sc., A.I.C.

In a former communication (ANALYST, 1930, **55**, 488) I discussed the effect of temperature on the sulphur dioxide content of mixtures of sugar and corn syrup which had been boiled at various temperatures. It was shown that the amount of sulphur dioxide evolved during the boiling process varies with the temperature to which the mixture is raised.

Furthermore, a method was indicated by which an analyst can determine the temperature at which a sample has been boiled, and then work out the limit of sulphur dioxide which should not be exceeded, assuming the original constituents contained their maximum allowance of sulphur dioxide under the Preservatives Regulations.

At the request of the Publication Committee further work has been carried out to determine the effect of variations in the rate at which mixtures of sugar and corn syrup are boiled. The results in the former paper were obtained by rapid boiling. The required temperatures were reached in the shortest possible time, and this is in accordance with industrial practice, as any unnecessary delay in the boiling process, particularly in the case of the "higher boils," causes discoloration of the resulting product.

EXPERIMENTAL PROCEDURE.—The method of boiling and the analytical procedure were similar in every respect to those used in the former investigation (*loc. cit.*). Four ordinary corn syrups (or "confectioners' glucose"), as supplied to the trade, were used. The fourth series of results, *i.e.* with the corn syrup N 381, is worthy of note, as the syrup contained the maximum amount of sulphur dioxide permitted under the regulations.

The times of boiling were chosen arbitrarily, bearing in mind the minima necessary to reach the desired temperatures, as shown by previous results. In each case an endeavour was made to lengthen the time throughout the complete heating process, but if the desired temperature was reached before the time limit had expired, care was taken to maintain the boiling at the correct temperature for the remaining period.

RESULTS.—The following tables show the results obtained:—

I.

CORN SYRUP, B 728.

Total solids, 83 per cent.; sulphur dioxide content, 395 parts per million.

Initial sulphur dioxide content of sugar and corn syrup mixture = 103 parts per million, on dry solids.

Temperature °F.	Time in minutes.	Total solids. Per Cent.	Residual sulphur dioxide, parts per million.		Residual SO₂ per 1,000,000 pts. dry solids.
			Found.	Average.	
250	10	90·5	54	54	60
	10	90·5	54		
	12	90·5	48	48	53
	12	90·6	48		
	14	90·6	46	46	51
	14	90·6	46		
	16	90·6	46	46	51
	16	90·5	47		
270	12	94·4	42	41	44
	12	94·3	41		
	14	94·4	35	35	37
	14	94·3	36		
	15	94·3	35	34	36
	15	94·4	34		
280	13	95·0	29	29	31
	13	95·0	30		
	15	95·0	27	27	29
	15	94·9	28		
	16	94·9	28	27	29
	16	95·0	27		
300	14	97·5	12	13	14
	14	97·3	13		
	16	97·5	7	7	8
	16	97·5	8		
	18	97·6	6	6	6
	18	97·4	6		

II.

Corn Syrup, M 710.

Total solids, 83 per cent.; sulphur dioxide content, 358 parts per million.

Initial sulphur dioxide content of sugar and corn syrup mixture = 94 parts per million on dry solids.

Temperature °F.	Time in minutes.	Total solids. Per Cent.	Residual sulphur dioxide, parts per million.		Residual SO$_2$ per 1,000,000 pts. dry solids.
			Found.	Average.	
250	10	90·5	61	62	66
	10	91·0	63		
	12	91·0	58	57	63 High
	12	90·7	56		results.
	14	90·8	56	56	62
	14	91·0	56		
270	12	95·0	42	41	43
	12	95·0	40		
	14	94·6	35	35	37 High
	14	95·0	36		results.
	15	94·6	33	34	36
	15	94·7	35		
280	13	95·7	22	22	23
	13	95·9	22		
	15	95·5	19	18	20
	15	96·0	18		
	16	95·7	18	17	18
	16	95·9	17		
300	14	97·6	9	9	9
	14	97·5	9		
	16	97·5	7	6	6
	16	97·9	6		
	18	97·9	6	6	6
	18	97·8	7		

III.

Corn Syrup, B 120.

Total solids, 83 per cent.; sulphur dioxide content, 371 parts per million.

Initial sulphur dioxide content of sugar and corn syrup mixture = 97 parts per million on dry solids.

Temperature °F.	Time in minutes.	Total solids. Per Cent.	Residual sulphur dioxide, parts per million.		Residual SO$_2$ per 1,000,000 pts. dry solids.
			Found.	Average.	
250	10	90·9	54	53	59
	10	90·5	53		
	12	90·7	51	51	57
	12	90·4	52		
	14	90·5	49	49	55
	14	90·7	50		
270	12	94·9	37	34	36
	12	95·0	38		
	14	94·7	36	33	35
	14	94·8	35		
	15	94·6	33	34	36
	15	94·7	35		
280	13	95·5	22	22	23
	13	95·7	23		
	15	95·7	21	20	21
	15	95·9	20		
	16	95·9	18	19	20
	16	95·5	20		
300	14	97·3	10	9	9
	14	97·4	9		
	16	97·4	6	6	6
	16	97·4	6		
	18	97·3	6	6	6
	18	97·4	6		

IV.

Total solids, 83·5 per cent.; sulphur dioxide content, 450 parts per million.

Initial sulphur dioxide content of sugar and corn syrup mixture = 117 parts per million on dry solids.

Temperature °F.	Time in minutes.	Total solids. Per Cent.	Residual sulphur dioxide, parts per million.		Residual SO$_2$ per 1,000,000 pts. dry solids.
			Found.	Average.	
250	10	90·8	81	81	89
	10	90·5	81		
	12	90·5	79	78	86
	12	90·8	78		
	14	90·7	77	77	85
	14	90·5	77		
270	12	94·7	60	60	63
	12	94·6	61		
	14	94·7	56	55	58
	14	94·8	55		
	15	94·7	54	54	57
	15	94·6	54		
280	13	95·5	36	37	39
	13	95·7	38		
	15	95·5	36	36	38
	15	95·7	36		
	16	95·5	36	35	37
	16	95·6	35		
300	14	97·8	16	17	17
	14	97·7	18		
	16	97·4	13	13	13
	16	97·5	13		
	18	97·7	11	11	11
	18	97·5	12		

From these tables it will be seen that the additional time taken over the boiling process slightly reduces the residual amount of sulphur dioxide, but that a constant figure is soon reached. With the syrup used for Table I, boiling at 250° F., a fourth trial covering a period of 16 minutes was carried out, but the result was the same as that of the 14 minutes' boiling.

The amounts of residual sulphur dioxide after prolonged boiling bear no relation to each other, taking into account the initial amount of sulphur dioxide present in the mixture. The figures vary, especially in the 250° F. and 270° F. boiling, possibly owing to changes in viscosity. The results obtained from these particular temperatures with corn syrup M 710 are definitely out of proportion when compared with results hitherto obtained. Repeated boiling and analysis

gave similar results, and a possible reason of the abnormality is that this particular corn syrup was obtained from a different source.

BLEACHES.—Only two samples of bleach were obtainable, and these came from recognised trade suppliers.

One was a liquid bleach composed of a practically saturated solution of bisulphite containing free sulphur dioxide. The available sulphur dioxide was 29·5 per cent. (w/v).

The makers recommended the use of 2½ fluid ounces per cwt., which is equivalent to adding 455 parts of sulphur dioxide per million on the dry solids. After carrying out the first series of tests with corn syrup B 728 and adding the equivalent amount, *viz.* 1·35 c.c., the amount of bleach was reduced in subsequent experiments to 0·6 c.c., which is roughly equivalent to 1 oz. per cwt., or an addition of 202 parts of sulphur dioxide per million on the dry solids. Owing to the strength of the bleach, even with the smaller amount, high quantities of residual sulphur dioxide were found.

V.

CORN SYRUP, B 728.

With liquid bleach in the recommended proportion of 2½ fluid ozs. per cwt.
Initial sulphur dioxide content on dry solids was raised from 103 to 558 parts per million.

Temperature °F.	Time in minutes.	Total solids. Per Cent.	Residual sulphur dioxide, parts per million.		Residual SO_2 per 1,000,000 pts. dry solids.
			Found.	Average.	
250	10	90·8	461	462	510
		90·7	464		
280	13	95·9	352	358	373
		95·9	364		
300	14	97·3	209	205	208
		97·2	202		

VI.

CORN SYRUP, M 710.

With liquid bleach in the proportion of 1 fl. oz. per cwt.
Initial sulphur dioxide content on dry solids was raised from 94 to 296 parts per million.

Temperature °F.	Total solids. Per Cent.	Residual sulphur dioxide, parts per million.		Residual SO_2 per 1,000,000 pts. dry solids.
		Found.	Average.	
250	90·9	218	219	241
	91·0	221		
280	95·3	143	141	149
	95·6	140		
300	97·2	64	60	63
	97·6	57		

VII.

CORN SYRUP, B 120.

With liquid bleach in the proportion of 1 fl. oz. per cwt.

Initial sulphur dioxide content on dry solids was raised from 97 to 299 parts per million.

Temperature °F.	Total solids. Per Cent.	Residual sulphur dioxide parts per million.		Residual SO$_2$ per 1,000,000 pts. dry solids.
		Found.	Average.	
250	90·8	224	222	245
	90·9	221		
280	95·9	150	143	154
	95·9	147		
300	97·2	64	62	64
	97·3	61		

VIII.

CORN SYRUP, N 381.

With liquid bleach in the proportion of 1 fl. oz. per cwt.

Initial sulphur dioxide content on dry solids was raised from 117 to 318 parts per million.

Temperature °F.	Total solids Per Cent.	Residual sulphur dioxide, parts per million.		Residual SO$_2$ per 1,000,000 pts. dry solids.
		Found.	Average.	
250	90·9	249	247	273
	90·7	246		
280	95·9	182	184	191
	95·7	186		
300	97·5	106	104	106
	97·7	102		

The other sample of bleach consisted of white powdered hydrosulphite with an available sulphur dioxide content of 53·4 per cent. by weight. The recommended quantity for use was 2 ozs. per cwt., but in the following experiments the equivalent of half this amount was added, viz. 0·5 grm. per boil. This meant the addition of 305 parts of sulphur dioxide per million calculated on the dry solids.

I understand that this powder is sold as conforming with the requirements of the Food and Drugs Adulteration Act, 1928, but, while I do not question its chemical purity, its use does not appear to conform with the spirit of the Public Health (Preservatives in Food) Regulations.

IX.

CORN SYRUP, B 728.

Solid bleach in proportion of 1 oz. per cwt.

Sulphur dioxide content was raised from 103 to 408 parts per million on solids.

Temperature °F.	Time in minutes.	Total solids. Per Cent.	Residual sulphur dioxide parts per million.		Residual SO_2 per 1,000,000 pts. dry solids.
			Found.	Average.	
250	10	90·4	282	280	310
		90·6	278		
280	13	95·5	205	210	219
		95·9	214		
300	14	97·1	120	116	119
		97·2	111		

X.

CORN SYRUP, M 710.

Solid bleach in proportion of 1 oz. per cwt.

Sulphur dioxide content was raised from 94 to 399 parts per million on solids.

Temperature °F.	Total solids. Per Cent.	Residual sulphur dioxide, parts per million.		Residual SO_2 per 1,000,000 pts. dry solids.
		Found.	Average.	
250	90·9	269	270	299 (high)
	90·8	272		
280	95·7	180	176	184
	96·0	172		
300	97·9	94	96	99
	97·8	99		

XI.

CORN SYRUP, B 120.

Solid bleach in proportion of 1 oz. per cwt.

Sulphur dioxide content was raised from 97 to 402 parts per million on solids.

Temperature °F.	Total solids. Per Cent.	Residual sulphur dioxide parts per million.		Residual SO_2 per 1,000,000 pts. dry solids.
		Found.	Average.	
250	90·8	266	267	294
	90·9	269		
280	95·4	182	180	189
	95·8	179		
300	97·3	102	102	105
	97·2	102		

XII.

CORN SYRUP, N 381.

Solid bleach in proportion of 1 oz. per cwt.

Sulphur dioxide content raised from 117 to 422 parts per million on solids.

Temperature °F.	Total solids. Per Cent.	Residual sulphur dioxide, parts per million.		Residual SO₂ per 1,000,000 pts. dry solids.
		Found.	Average.	
250	90·7	282	282	312
	90·7	282		
280	95·7	192	191	200
	95·5	190		
300	97·3	120	121	125
	97·4	122		

The use of these bleaches, even in small amounts, considerably raised the residual sulphur dioxide content of the various boilings when compared with boilings to which no bleach had been added. No definite relationship can be deduced from the above figures, as, no doubt, slight variations in the application of the heat will affect the rates of decomposition of the bleaches.

The position with regard to the use of bleaches in confectionery and allied industries does not appear to be clear, since some manufacturers maintain that a limited amount of the chemicals can be used, providing that the final sulphur dioxide content is not greater than that initially present in the raw materials themselves. On the other hand, other manufacturers have eliminated the use of bleaches, and, after a considerable amount of research work, have altered their processes accordingly.

Public Analysts, while realising that a considerable proportion of the sulphur dioxide goes off during manufacturing operations, as is shown in this and my previous paper, have been unable to detect the addition of bleach excepting in those cases where the sulphur dioxide content is undoubtedly above the maximum initial limit.

It is desirable that a limit should be set for the amount of sulphur dioxide in confectionery. A limit of 100 parts per million would cover all products under this heading, as is shown from the experimental results dealing with boilings at 240° F. and upwards. Of course, such a limit as that suggested would not prevent the use of bleaching agents, but it would restrict the amount which could be added during manufacturing operations, and so define the position for the Public Analyst and form another safeguard in the interest of the general public.

The Examination and Commercial Analysis of Cotton Cloths.

By R. H. KAY.

(Read at the Meeting of the North of England Section, October 25, 1930.)

A LARGE proportion of the work required in the laboratory attached to a manufacturing firm will consist in getting out particulars of cloths for quotation purposes.

Most of the "text book" methods are too long; on the other hand, some of the short methods in use are very inaccurate and may lead to serious mistakes. Hence an attempt has been made to find a method that will give reasonably accurate results in the shortest time. The results have been checked in as many ways as possible, and many hundreds of thousands of yards of cloth have been made in accordance with the particulars obtained by the method described.

EFFECT OF MOISTURE IN THE CLOTH.—Owing to the hygroscopic character of cotton it is practically impossible in any ordinary laboratory to make an accurate analysis of a sample of cotton material without first spending considerable time on drying or conditioning. Even then the results will depend on the prevailing temperature and humidity.

To obtain a constant weight, the Shirley Institute recommends drying over phosphoric anhydride in an evacuated desiccator; by this method it is possible to get a constant weight in 4 to 6 weeks (*J. Text. Inst.*, April, 1930).

In laboratories such as those of the Shirley Institute, some Chambers of Commerce, etc., the humidity is kept as constant as possible (usually 70 per cent.), and temperature and humidity records are kept.

When physical tests—such as strength, elasticity, etc.—are required, the sample is allowed to "condition" in this atmosphere for some time before the tests are made; the length of time required to condition properly is generally considered to be at least 6 hours.

Cotton is said to be in "correct condition" when it contains 7·834 per cent. of moisture; this is equal to a regain of 8½ per cent. on the dry weight. In yarn and cloth analysis it is a usual custom to dry the sample at 105° C. and to calculate the correct condition weight by allowing 8½ per cent. regain on the dry weight. In actual practice it is quite unusual to find a sample that is in "correct condition." The patterns received for analysis are in practically any condition, and it is quite usual to get one that has been carried about in someone's pocket for an hour or so.

Heavily-sized cloths naturally contain excess moisture, but this is reckoned as part of the size. Ordinary grey cloth, containing 10–20 per cent. of size on the warp, rarely contains excess moisture, and in most cases it is bought and sold

without any special moisture content being specified. The patterns received are generally tested as soon as possible, and the results are handed in as referring to "in condition received."

ANALYSIS OF GREY CLOTH.—As a description of the methods of analysis for all the various cloths passing through the laboratory would occupy too much space, this paper is confined to the method used for an ordinary grey (*i.e.* unbleached and unfinished) cloth.

The particulars of a grey cloth required for quotation are:—Weave; warp threads per inch; weft threads per inch; count of warp; percentage of size on warp; count of weft; weight of cloth for stated width and length. It is also a help to know the percentage of size on the cloth.

Weave.—This is the way in which the threads are interlaced—plain, twill, sateen, drill, percale, poplin, leno, etc., etc.

Warp Threads per Inch.—The warp threads are those that run parallel along the *length* of the piece; it is usual to count in several places if the pattern is large enough, and it is not usual to find much variation, as the threads are accurately spaced by the healds and reed of the loom. Occasionally a thick place is found, and, if the pattern is a very small one and the thick place comes in the portion that has to be weighed, the calculated weight of the cloth will be on the heavy side.

A sized warp thread can usually be detected at once by testing with iodine, since the size nearly always contains starch.

Weft Threads per Inch.—Weft threads are those that run across the cloth from edge to edge. When the thread has been drawn across the cloth by the shuttle it is "beaten up" to the preceding thread before the shuttle comes back again.

This beating up is sometimes uneven, and, for this reason, it is quite usual to find a considerable variation in the number of weft threads per inch; in such a case the only thing to do is to count the threads in as many places as possible and to take an average.

Count of Warp and Weft.—The count of a yarn is another term for the size or thickness of the thread. Roughly speaking, there are two systems of fixing the count:—(1) *Fixed weight systems*, in which the number of hanks, leas, cuts, or some other definite measure of length, required to weigh 1 lb., or some other fixed weight, determines the count; *i.e.* the higher the count number, the finer the yarn; and (2) *fixed length systems*, in which the unit of length is fixed, and the count number is determined by the weight of that unit length, *i.e.* the coarser the yarn, the higher the count.

Cotton belongs to the first group, and the count is based on the number of hanks of 840 yards that are required to weigh 1 lb. For example, a 16^s yarn means that 16 hanks of 840 yards weigh 1 lb.; that is, there are 16 × 840 or 13,440 yards of this particular yarn in 1 lb. A 16^s yarn is twice as heavy as a 32^s yarn, and so on.

Unfortunately there are different systems of fixing the count for different materials. Linen and wool belong to the same group as cotton, but the count is based for linen on the number of hanks of 300 yards that are required to weigh 1 lb., for wool on the number of skeins of 256 yards, and for worsted on the number of skeins of 560 yards required to weigh 1 lb. Jute, silk and rayon belong to the second group, i.e. with a fixed length and a varying weight. For jute the count is based on the weight of a spindle of 14,400 yards; i.e. a 4½ lb. jute means that 14,400 yards weigh 4½ lbs., and a 9 lb. jute would be twice as heavy (or thick) as the 4½ lb. yarn. For silk and rayon the count* is based on the weight of a skein of 476 metres in deniers.†

When testing the count of cotton yarn it is customary to reel off a number of small hanks of 120 yards; these are called "leas," and are 1/7th of a hank proper. They are weighed to the nearest ¼ grain and the count calculated. At least six tests should be made, more if possible, and the results averaged. For instance, twelve tests made on a sample of 18ˢ yarn may show a variation of 17½ to 18½, or even more, but the average may be 18·1, or thereabouts. This result may be inaccurate unless the yarn has been previously conditioned in an atmosphere that will give a moisture content of about 7½ per cent., or the moisture has been determined and the count calculated "in correct condition weight."

When the count of a yarn is found by weighing a few inches or yards, more often than not a figure representing a half or quarter count may be obtained. For example, the count of a yarn may be found to be 43¼, but as no such uneven count is spun, it can only be inferred that it is 42ˢ or 44ˢ. If size has been removed by "boiling out," it will probably be 42ˢ, as there is always a slight loss on boiling out.

Size on Warp.—Practically all single warps are sized to enable the threads to withstand the strain and friction of weaving. There are many special sizing preparations on the market, but they mostly consist of starchy material which has been rendered more soluble by previous treatment (such as "quellin," dextrin, "textiline," "frog starch"), together with tallow substitute—often nothing but soap—or sulphonated tallows. Gums and waxes, such as tragasol, spermaceti, paraffin wax, etc., may also be used, and china clay is often present.

For weaving the percentage of size is always calculated as gain on 100; i.e. 20 per cent. of size means that 100 lbs. of yarn, when sized, will weigh 120 lbs., not that 100 lbs. of sized yarn contain 20 lbs. of size and 80 lbs. of yarn.

In heavily-sized goods one or more of the following salts are usually present:— magnesium chloride, zinc chloride, magnesium sulphate, sodium sulphate, and, possibly, calcium chloride or barium sulphate. Zinc chloride is generally used with "anti" (magnesium chloride) to prevent the growth of mould. The newest antiseptic is salicylanilide, sold under the name of "Shirlan."

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* A comparison may be of interest:—8ˢ cotton = 22·4ˢ linen; = 26·25ˢ woollen; = 12ˢ worsted; = 2·14 lbs. jute; = 660 denier silk or rayon.

† A denier = 0·0531 grm.

Weight of Cloth.—This is usually given in lbs. (so many lbs. for, say, 36″ wide by 100 yards long). Sometimes the weight may be required in kilos. for so many cm. wide by so many metres long.

The cloth is usually measured and weighed at the mill, and the weight is generally given to the nearest ¼ lb.

Here, again, absolute accuracy is practically impossible, as the weight of any particular piece will vary from time to time according to the humidity and temperature of the place it happens to be stored in.

METHOD OF ANALYSIS.—The following is an outline of the method used for an ordinary grey cloth, made of single yarns and containing a sized warp. The lengths of yarn and dimensions of pattern given below are for guidance only and will, of course, vary with the size of the sample submitted.

1. Count the number of warp threads and weft threads per inch.

2. With a dissecting needle tease out sufficient warp and weft threads to give 4 yards of each. These should be made into small bundles for cutting to the desired length. For example, take 4 lots of 9 threads and trim each little bundle to exactly 4 inches. Before cutting, stretch the threads sufficiently taut to pull out the waviness introduced by weaving, but do not stretch as "tight as possible." The heavier the yarn the fewer the number of threads that should be cut together. To distinguish between warp and weft tie the warp bundle together with a single thread and loosely knot the weft bundle. Note whether the weft is spun "twist way" or "weft way."

3. Trim a piece of the cloth to form a square, 4″ by 4″. The use of a template is not recommended; it is better to pull out the side threads until the desired size is obtained and then to trim. All the creases and folds should be carefully smoothed out, but undue stretching avoided. When templates are used it is difficult to get the cloth at the correct tension and to cut it without dragging.

4. Weigh the warp, weft and cloth accurately.

5. "Wet out" the warp and cloth in hot water, and, if salts such as magnesium chloride, etc., are present, give several rinsings, as such salts destroy the activity of the malt extract in which the yarn and cloth are to be placed.

6. Steep in a solution of malt extract and water at 60° C. for at least 15 minutes, or in a solution of "Rapidase" at about 90° to 95° C. for a few minutes. No particular strength of malt solution need be specified, but it should be fairly strong; 5 to 6 grms., stirred into about 200 c.c. of water, will give a strong enough solution. There is no need to keep the temperature constant; the yarn and cloth can remain in the cooling solution. All the starches are quickly converted into dextrin and sugars and can be removed with comparative ease.

7. Wash with warm water and "work" well.

8. Boil in soap solution for 3 to 5 minutes. (This consists of about 1 to 1·5 grm. of Hudson's soap dissolved in 200 c.c. of water.) This quickly

gets rid of the converted starch and also helps to remove any China clay. The duration of boiling should be as short as possible, to keep the "scouring loss" down to the minimum.

9. Wash thoroughly, working and squeezing well. By squeezing out the water and letting it drop into a beaker standing on a dark bench it is quite easy to see when all the china clay has been removed. It is always advisable to boil the cloth and yarn separately; some threads come away from the cloth and very easily get entangled with the warp threads if not kept separate. All loose threads must be carefully collected and kept with the cloth.

10. Dry in the water oven; the time taken will, of course, vary according to the weight of the cloth, but, roughly speaking, from 30 to 45 minutes is long enough. If all possible speed is required, soak the yarn and cloth first in alcohol and then in ether and dry in the oven for about 10 minutes.

11. Condition in a cool room for at least $1\frac{1}{2}$ hours—longer if possible.

12. Again weigh. The losses in weight are calculated as the percentage of size on cloth and warp. It is necessary to convert grms. to grains, if the warp, weft and cloth have been weighed in grms.

To find the count of a yarn the calculation is:

$$\frac{\text{Yards taken} \times 7000}{\text{Grains found} \times 840} \quad \text{or} \quad \frac{\text{Yards} \times 25}{\text{Gr.} \times 3} = \text{Count.}$$
$$(\text{Grms.} \times 15\cdot432)$$

To find the weight of the cloth the calculation is:

$$\left(\frac{\begin{array}{c}\text{Weight in grs. of test piece}\\ (\text{grms.} \times 15\cdot432)\end{array}}{\text{Size of test piece in inches}}\right) \times \left(\frac{\begin{array}{c}\text{reqd. width} \times 36 \times \text{reqd.}\\ \text{length}\end{array}}{7000\ (\text{grs. in 1 lb.})}\right) = \text{Weight in lbs.}$$

Say, $4'' \times 4'' = 1\cdot376$ grm.; find weight for $36'' \times 100$ yards;

$$\frac{1\cdot376 \times 15\cdot432 \times 36 \times 36 \times 100}{4 \times 4 \times 7000} = 24\cdot57 \text{ lbs.}$$

From the particulars obtained the weights of warp and weft required for the cloth are calculated. These, when added together, should give approximately the same weight as the "after boiling" weight already found, and the addition of the percentage of size found on the warp should give a weight approximately equal to the "before boiling" weight.

The calculated results should come within about $\frac{1}{2}$ lb. of the weight found by analysis. The full analysis can be completed in just over 3 hours. Three or four patterns can be started in the morning, and are easily ready for the final weighings early in the afternoon.

NOTES ON THE METHOD.—Taking it for granted that the analysis has to be done quickly, it is impossible to allow any great length of time for conditioning,

re-conditioning or drying; on the other hand, sufficient time must be allowed after the boiling out and drying for the yarn and cloth to attain to something like a normal condition.

In most contracts where a definite weight is specified, that weight has to be "not less than x pounds," and care is usually taken that the cloth is woven with yarns that will give a weight slightly over that specified, so that, even under the driest conditions, the cloth will not be too light.

As the result of many tests it has been found that, after the yarns and cloth have been boiled out and dried, conditioning for $1\frac{1}{2}$ hours will allow the cotton to regain sufficient moisture for its condition to be considered fairly normal. For instance, a yarn may show 18·75^s after $1\frac{1}{2}$ hours' conditioning; if left overnight, in the same atmosphere, and re-weighed, it may then show 18·3^s. This slight difference is immaterial to the manufacturer, as, whatever result is given to him, he will still base his price on 18^s yarn.

"*Boiling out.*"—The treatment with malt diastase, or other solution containing diastase, followed by a few minutes' boiling with soap solution, does not . damage the yarn or cloth, and the loss in weight of the cotton, apart from the removal of sizing materials, is only very slight. Blank tests on yarns free from size showed losses ranging from 2·5 to 4·0 per cent., according to the quality of cotton from which the yarns were manufactured. (*Cf.* Fargher, Hart and Probert, *J. Text. Inst.*, Jan., 1927).

As the sized yarn will always lose some of the size during weaving, the scouring loss due to boiling out should not be deducted from the percentage of size found by analysis, but should be taken to balance roughly the amount lost during the weaving.

At the same time an allowance should always be made for the fact that the count of yarn and weight of cloth found after removal of size are from 2 to 3 per cent. on the light side.

A New Development in Filter Papers.

By E. J. GUILD.

(*Demonstrated at the Meeting, May 6, 1931.*)

MY justification for bringing this filter paper (Whatman No. 54) to the notice of the meeting is that I believe it to be unique in its properties; these, briefly stated, are as follows:

(1) Extraordinary strength in water, *i.e.* when wet; its strength when wet transcends that of any usual filter paper.

(2) Great resistance to alkaline solutions, such as caustic soda, ammonia, etc.

(3) Rapidity of filtration. It will deal with large quantities of liquid where the matter in suspension is coarse or gelatinous. It will not retain fine particles; unfortunately, no one has yet succeeded in combining retentiveness and rapidity of filtration in one paper, but I may add that papers which are retentive and possess this outstanding wet strength are also available (*viz.* No. 52, which is medium retentive, and No. 50, which is highly retentive).

(4) High degree of purity. The alpha-cellulose is 99 per cent. or over, and the copper number is as low as 0·12 (Schwalbe–Braidy method).

(5) Low ash content. The percentage of ash is about 0·04, and this is mainly of an inert nature, so that the paper is suitable for all but the most highly delicate analytical work.

It will be appreciated that this paper should be very valuable for filtrations on a large scale, as it will withstand the pressure of large volumes of water or other liquid without risk of bursting.

DISCUSSION.

In reply to questions by the President and various members, Mr. Guild said that the paper was not cheap; it cost the same as acid-washed paper, but was more effective. He had not tried the paper for filter-press work, but saw no reason why it should not serve the same purpose as cloth. He had filtered caustic soda solutions up to 50 per cent. in strength without the paper showing signs of attack.

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.

THE TITRATION OF QUININE IN ULTRA-VIOLET LIGHT.

IT is well known that if a minute amount of quinine is added to sulphuric acid, the acid may be titrated with alkali, the end-point being reached when the fluorescence due to the quinine sulphate is destroyed. If the titration is carried out in a dark room provided with a source of ultra-violet light, the change is very striking, and gives an accurate end-point in solutions of 0·0001 N or less strength.

So far as I am aware, this method has not hitherto been applied to the determination of quinine itself. Anhydrous quinine was prepared by extraction of an ammoniacal solution of quinine sulphate with chloroform, the extract was evaporated, and the residue dried at 105° C. until constant in weight. A weighed portion (300 mgrms.) was then dissolved in 200 c.c. (*i.e.* an excess) of 0·01 N sulphuric acid, 20 c.c. were pipetted into a beaker, and titrated with 0·01 N sodium hydroxide

solution under a vertical beam of ultra-violet light. The end-point is reached when the excess of sulphuric acid over that required for the formation of quinine sulphate, $(C_{20}H_{24}N_2O_2)_2,H_2SO_4$, is neutralised. Further addition of alkali liberates free quinine, the presence of which produces a marked decrease in fluorescence of the quinine sulphate, which is easily seen by the naked eye in ultra-violet light. The end-point is not so sharp as in the direct acid-alkali titration with quinine as indicator, since it involves only a decrease in the fluorescence and not its complete disappearance; but, with practice, an accuracy of at least 0·1 c.c. of 0·01 N alkali is attainable, especially if comparison is made with two similar solutions adjusted previously one to each side of the end-point.

It is an advantage to standardise the alkali against the acid to the same end-point by addition of a minute amount of quinine to the latter, and titration with the former until the fluorescence, viewed in ultra-violet light, disappears. This end-point is, of course, extremely sharp, and the amount of quinine required is so small as not to affect the accuracy of the titration by using up the acid to form sulphate.

It is advisable to carry out the titration in a beaker placed on a white tile underneath the source of filtered ultra-violet light, since, if a conical flask or a horizontal beam of light is used, any fluorescence from the glass itself may obscure the end-point.

The result is obtained from the usual factor, i.e. 10 c.c. of 0·01 N sulphuric acid $\equiv$ 0·0324 grm. of quinine. Of the 20 c.c. of solution pipetted out for the titration, about 10 c.c. are used up by the quinine under the above conditions.

Comparative tests of the method against ordinary back-titration with brom-cresol purple as indicator showed that the same degree of accuracy is obtainable. Additional advantages are:—(1) Non-fluorescent substances (including slight colour and turbidity) which may obscure the indicator end-point do not interfere. (2) Errors inherent in indicator methods (e.g. due to the acidity or alkalinity of the indicator solution added, or to salt errors, etc.) are eliminated, since the substance titrated serves as indicator. (3) The purple colour of brom-cresol purple in solutions of about pH 6 is unstable on account of absorption of carbon dioxide from the air, and fading at the end-point often occurs if the solution is vigorously stirred; the method described has no such disadvantage.

Disadvantages are:—(1) The inconvenience of working in a dark room illuminated only by ultra-violet light, and especially of reading the burette near the end-point. I have found that if a small area of the bench is enclosed with dark curtains the determination may be made in the lighted laboratory, the burette being arranged so that the upper portion projects through the top for reading purposes. (2) As already stated, the end-point is not sharp to the unpractised eye, but this is to some extent offset by the fading of brom-cresol purple, and a number of titrations made in duplicate by means of the two methods gave identical results.

Extensions of the method suggest themselves and are being examined at the Hackney Technical Institute, London, E.8, where the above observations were made.

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                                                                    JULIUS GRANT.

POISONING BY AMMONIA.

ON December 13th, 1929, a female (Tamil) coolie, aged 32 years, employed on a rubber estate, was admitted to hospital, suffering from shock, having attempted to commit suicide by taking some poison. She is said to have taken curry and

rice at 7.0 p.m. and to have swallowed the poison half an hour afterwards. She died at 1.45 a.m. on December 14th. There was no vomiting or purging. The *post-mortem* examination was carried out at 3.15 p.m. on December 15th, about 36 hours after death, by which time decomposition was somewhat advanced. There were no external signs of injury. The outer wall of the stomach, left lobe of the liver, and several feet of adjacent small intestine were congested and dis-coloured dark red. There was congestion and marked reddening of the mucous membrane of the mouth and gullet. The other internal organs were normal, in-cluding the lungs. The stomach, on opening, smelt strongly of ammonia; it was found to contain a quantity of partly digested rice, reddened with blood, together with shreds of detached mucous membrane from the stomach lining. The stomach lining itself was highly inflamed and of a deep red colour, and the mucous mem-brane was severely corroded and partly destroyed.

The stomach and contents were examined separately. After mincing, half was diluted with water and distilled with steam until the distillate no longer re-acted alkaline to litmus.

An aliquot portion of the distillate, which smelt strongly of ammonia, was titrated with $N/10$ sulphuric acid, with methyl orange as indicator. By this method 17·5 grms. of ammonia were found. After communication with the police, it was found unnecessary to examine the remainder of the viscera. The quantity of ammonia found indicates that at least 25 c.c. of strong aqueous ammonia had been taken. Strong ammonia is readily obtainable on some rubber estates, where it is used as an anti-coagulant and preservative of latex.

<div align="right">R. W. BLAIR.</div>

INSTITUTE FOR MEDICAL RESEARCH,
    KUALA LUMPUR, FEDERATED MALAY STATES.

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 special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1931.

OF the 1274 samples examined under the Food and Drugs Act, 134 were formal and 1140 informal. Seventy-nine samples were incorrect or adulterated.

CRYSTAL MINTS.—A sample contained 850 parts per million of sulphur dioxide. From the composition it was calculated that not more than 150 parts should be present. The vendor was cautioned, and intimated that immediate steps were taken to conform with the Preservatives Regulations.

AMMONIATED QUININE TABLETS.—Ten samples of ammoniated quinine tablets were taken. These are manufactured as a substitute for the liquid tincture and are usually made by mixing the requisite weights of quinine sulphate and ammonium carbonate with sufficient binding material to form a tablet. Of 9

samples, made with quinine sulphate and ammonium carbonate, all of which were probably originally of correct composition, 6 had lost practically all the ammonia, and 2 had average losses of about 80 per cent. The remaining sample was made with ammonium chloride instead of ammonium carbonate, the proportion of the two substances being declared on the label. These proportions were found to be as stated, ammonium chloride not being volatile.

In one case the wholesale dealer, at the request of the manufacturers, agreed to attach a label to the bottle worded as follows: "These tablets contain the same percentage of quinine as in a dose of the tincture, but no guarantee can be given in respect to the quantity of ammonia owing to its volatile nature."

H. H. BAGNALL.

GIBRALTAR.

REPORT OF THE CITY ANALYST FOR THE YEAR 1930.

THE total number of specimens and samples examined was 4776. Of the 124 foods and drugs examined, 18 were below the standard. A careful watch was kept on the purity of the drinking waters of Gibraltar, 354 samples being examined bacteriologically.

GOATS' MILK.—The statutory limit for milk-fat, fixed by the Public Health Ordinance, is 3·5 per cent. The average composition of the 47 samples examined was: Fat, 4·18; solids-not-fat, 8·89 per cent. Ten were deficient in milk-fat as the result of skimming by the vendor. This is an increase of 11 per cent. over last year's figures. Vendors appear to be at liberty to take off the fat which rises quickly to the surface after boiling, and offer the skimmed or partly skimmed milk to the public at the same cost as whole milk. The law is evaded by declaring to the Sanitary Inspectors at the time of purchase that the milk is skimmed. No such statement appears to be made to the general public, who unwittingly are deprived of some of the milk-fat. It is satisfactory to report that no sample of goats' milk was offered to the public unboiled. A bacteriological examination was made to ascertain whether a milk vendor was effectively sterilising goats' milk sold in bottles as "sterilised." The following results were obtained:

	Sample before sterilising.	Sample sold as "sterilised."	Sample after correctly sterilising.
B. coli	1,000,000 per c.c.	not in 10 c.c.	not in 10 c.c.
Streptococci	1,000 per c.c.	not in 10 c.c.	not in 10 c.c.
" Enteritidis " change ..	in 30 c.c.	not in 30 c.c.	not in 30 c.c.
Organisms at 37° C. per c.c. ..	42 millions	520	12
Organisms at 22° C. per c.c. ..	75 millions	152	13

The serological agglutination test was carried out on the 162 goats living on the "Rock." All gave negative results for undulant fever.

METALLIC CONTAMINATION OF AERATED WATERS.—Continued supervision of the manufacture of aerated waters in Gibraltar revealed the presence of lead in harmful quantities in the soda water of one factory. Solder containing lead was found in the carbonator and has been removed.

TESTING OF SHIPS: *Inflammable and Poisonous Vapours.*—The City Analyst is entrusted with the testing of compartments of oil-carrying ships and others for dangerous gases. Such work was first undertaken for Naval Authorities in 1928,

but has since been extended to local shipping agents. Gas-free certificates are necessary before ships of this class enter dry dock for repairs.

Two ships were examined:—(1) A tanker of nearly 6,000 tons, which was certified gas free. (2) A cargo ship on which a fire had occurred in the mixed cargo of foodstuffs, etc. The ship had been flooded. Inflammable and poisonous gases were present beneath the decomposing materials, and the agents were warned of the risks to the men when entering the holds to unload.

A. G. HOLBOROW.

CITY AND COUNTY OF KINGSTON-UPON-HULL.

ANNUAL REPORT OF THE PUBLIC ANALYST AND BACTERIOLOGIST FOR THE YEAR 1930.

DURING the year 1930 the number of samples of all kinds examined was 6902, of which 1620 were samples for chemical analysis, and 5282 were specimens for bacteriological examination. Of the 1247 samples examined under the Food and Drugs Act, 20 were suspicious and 48 adulterated.

"DIRT" IN MILK.—Thirteen of the 652 samples of milk received from the Sampling Officers under the Adulteration Acts were found to contain unwarranted amounts of extraneous matters (dirt), a percentage of 2·0. This figure is slightly lower than that recorded last year (2·3 per cent.). Three of these thirteen samples were the unsatisfactory ones of a total of 12 milks taken specially for examination for dirt; these were three-pint samples, allowing after division one pint for the determination of extraneous matters. These three samples were found to contain 5·5 parts of dirt ·(sand and dung), 4·0 parts (partly dung), and 2·0 parts (sand, etc.) per 100,000.

CURDS.—The sale of wet milk-curds for making curd cheese-cakes is common in the City, and an examination of twelve samples was made during the year. They contained from 74 to 81 per cent. of water, and all were free from foreign additions, including alum. It has frequently been stated that alum is used in curdling the milk for curd-making, but if used, it is carefully washed out. It is very necessary that such washing of the curds with water should be thoroughly done, as the presence of alum in foods must be regarded as an adulteration. It would be a better practice to use a rennet preparation rather than alum for making these curds. There is no doubt that by carefully draining the washed curds, the amount of extraneous water can be reduced, and perhaps 75 per cent. might be regarded as a maximum. On such a basis, about half the samples examined contained water in slight excess.

DRIPPING.—Twelve out of fifteen samples were of satisfactory composition, being sound edible beef-fats free from water and other extraneous substances. One of the three unsatisfactory products was unsound, since it contained 7·2 per cent. of free fatty acids and gave definite reactions showing a rancid condition. The vendor was cautioned. Two other samples (informal and formal samples from the same vendor) were returned as adulterated, and proceedings instituted, since the "dripping" supplied contained 15·3 and 22·8 per cent. of water, with tissue, salt and other extraneous ingredients. These samples were obviously pork dripping with much of the gelatinous gravy mixed with the fat, and it was contended by the defence that the ordinary standards could not apply to a product which was sold at a good price because of its superior flavour, due to the presence of the meat extractives. The case was dismissed, but the position, as left by the decision,

was not quite satisfactory, since it cannot be denied that "the fat which drips from roasting meat" is a reasonable definition of dripping. However, as a result of discussions with representatives of the trade concerned, the vendors of such products have agreed to label them as "pork dripping with gravy."

SHREDDED SUET.—Forty-three samples examined in the City Laboratories during the last six years showed an average addition of rice or other flour of 11·5 per cent., and more than one-third of these samples contained not more than 12 per cent. It is clear that 10 to 12 per cent. of flour is a reasonable amount if the addition is declared on the label, and that an allowance of another three per cent. (15 per cent. addition in all) should cover all reasonable variations.

SPONGE CAKE MIXTURES.—Six samples were composed of cereal or other flours (wheat, maize, potato and mixtures of these) and sugar, together with small amounts of baking-powder ingredients. Four of these mixtures were coloured with a permissible coal-tar dye (yellow or pink). Some little time may be saved by using these products in cake-making, but they are costly in proportion to the amount of nutriment purchased. The ingredients cost (retail prices) approximately, on the average, perhaps 2d. per lb., whilst the mixtures were sold at prices ranging from 9d. to 10½d. per lb.

POTTED MEATS.—All the twenty-one samples of loose potted meats, sold with a fatty covering, were sound products as regards freedom from souring, and from objectionable ingredients other than farinaceous material and excess of water. Only one sample contained a slight excess over the proportion of water, regarded as reasonable; this meat contained 72·8 per cent. of water as compared with 51 to 70 per cent. in the remainder. The last-mentioned figure should not be exceeded. Eight of the samples contained an added starchy constituent, frequently amounting to about 10 per cent. of the foodstuff, but the remaining 13 samples contained no such addition. Potted meat should be cooked meat, finely minced, and containing nothing else but the natural extractives (gravy) of the meat. The best makers conform to the standards here laid down. Other products containing extraneous additions should be sold as meat pastes. It is time that these standards were enforced in the City, and that those products not conforming to such standards were considered adulterated within the meaning of the Food and Drugs (Adulteration) Act, 1928.

GLASS PARTICLES IN FOODS.—No sample of glass-packed food has shown any appreciable traces of glass particles. Since the year 1924, when the matter was first mentioned in these Reports, there has been a progressive improvement in the quality of the glass containers used for packing foodstuffs, and there is now little likelihood of this form of contamination except as an accidental occurrence.

BACTERIA IN COMMERCIAL MILK.—Nine samples of ordinary *commercial milk*, submitted by the Medical Officer of Health, were examined bacteriologically. Judged by the standards for Grade "A" milk, two samples were somewhat unsatisfactory, showing under 200,000 organisms per c.c., but having *Bacillus coli* in 1/100th c.c. of the milk.

PETROL IN SEWAGE.—In connection with an investigation into the cause of a serious explosion in West Dock Street, undertaken in October at the request of the Deputy City Engineer, samples of the sewage and "air" in the main sewer of this street were collected for examination. The "air" contained a considerable quantity of vapour inflammable at the ordinary temperature, and the sewage was found to have, floating on its surface, a light oily layer with an odour of petrol, and which showed on distillation an initial boiling point of 56° C. The presence of liquid and vaporised light petroleum spirit in the sewer thus proved that the

explosion was caused by the ignition, in some way, of petrol which had obtained access to the sewer. The dangerous mixture of air and petrol-gas formed in the sewer would be at least one thousand times the volume of any petrol run into the sewer. The City Engineer caused a warning notice to be issued to all persons concerned.

SUNLIGHT (ULTRA-VIOLET RAYS) OBSERVATIONS.—These recordings have been continued throughout the year at the Central observation station. It has become increasingly evident that, whilst useful results can be obtained with the acetone and methylene blue solution, provided that due care is taken, the method involves several fallacies, and that, unless these are guarded against, the results may be much too high.

The table below gives the maximum and minimum daily averages for various towns:—

Records of Ultra-Violet Light.

Place.	Units of Fading. Daily average throughout the months mentioned.	
	Maximum.	Minimum.
Hull (Central)	5·5 (June)	0·08 (Dec.)
Cardiff (Central) ..	2·8 (June)	0·4 (Dec.)
Edinburgh	2·3 (Aug.)	0·2 (Feb.)
Lytham St. Anne's ..	3·2 (May)	0·3 (Dec.)
Lowestoft	9·9 (June)	0·9 (Dec.)
Prestatyn	6·1 (June; Aug.)	1·4 (Dec.)
Rochdale (8 months only)	1·1 (Aug.)	0·03 (Dec.)
Skegness	7·0 (Aug.)	0·9 (Feb.)
Stirling (Central) ..	3·3 (June)	0·2 (Jan.)
Walsall (7 months only)	3·2 (Aug.)	0·02 (Dec.)

A. R. TANKARD.

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.

VALIDITY OF PATENT FOR TREATMENT OF CHEESE.

ON July 17th the Judicial Committee of the Privy Council (comprising the Master of the Rolls, Lords Tomlin, Russell of Killowen and Macmillan, and Sir L. Sanderson) gave judgment in the appeal by James Lewis Kraft, the Kraft Cheese Co. (Incorporated) and the Kraft Cheese Co. Proprietary, Ltd., in the matter of their patent (No. 1620 of 1916) in Australia, for a process of making cheese of the Cheddar type keep permanently. (A similar patent exists in Great Britain.) The respondents were Oliver Kenneth McAnulty, carrying on business as the Maxam Cheese Factory in Australia.

The Master of the Rolls (Lord Hanworth), in giving judgment, said that this was an appeal from a decision of the High Court of Australia reversing a decision of the Supreme Court of Queensland in favour of the appellants. It was alleged

by the appellants that their patent for treating cheese in such a way that it would keep indefinitely, and without spoiling, had been infringed by the respondents.

The respondents denied that they had infringed the patent, and claimed that it was invalid for reasons which included want of subject matter, want of utility, and further claimed that the patent specification was ambiguous and misleading. The Court of Queensland held that the patent was valid, but on appeal this decision was reversed by the High Court of Australia, by a majority of three judges to two, on the grounds:—(a) That the patent was invalid because the representation or promise of complete sterilisation at about 175° F. was not true; (b) that the specification was ambiguous and misleading and did not disclose, or prescribe, a method whereby the object aimed at could be achieved.

Special leave to appeal was given, and the hearing was on June 15th, 16th, 18th, and 19th. The Master of the Rolls pointed out that two views were presented upon the construction of the specification. The one that the main desideratum was complete sterilisation; the other dwelt upon the statement: "the invention consists in the process of rendering the cheese . . . permanently keeping."

The majority in the Court of Appeal held that the phrase "permanently keeping" was used to denote cheese that had been both completely sterilised and so placed as to maintain complete sterilisation. They were unable to cut down the meaning of sterilisation to the degree for which the appellants contended. Then came the question, was the cheese, in spite of that, a permanently-keeping cheese?

The Judicial Committee held that they could not accept the view of the Queensland Court and of the two judges of the High Court of Australia, that the evidence proved that cheese made by the Kraft process was "permanently keeping."

Their Lordships found themselves in agreement . . . that the evidence suggested to "say the least, a very modified permanence." They also pointed out that in both claims there was some insufficiency in the description of the process to be followed. The principle in patent law was clear, that a patentee must define the nature of the invention and disclose a process which would produce the result aimed at.

Their Lordships would humbly advise His Majesty that the judgment of the High Court be affirmed and the appeal dismissed with costs to be paid by the appellants.

ARTIFICIAL PRODUCT SOLD AS GRAPE VINEGAR.

AT Liskeard Police Court, on September 2nd, a manufacturer, trading as the Grape Vinegar Co., was summoned for selling pure grape vinegar which was not of the nature, substance and quality demanded by the Cornwall County Council's inspector; there was a further summons for affixing a false label. Inspector James said that he took a sample in course of delivery from one of the defendant's casks, which was labelled: "Pure Grape Vinegar." The defendant's invoice bore a picture of a bunch of grapes, and this liquid was supplied by a retailer (who was also summoned), when asked for grape vinegar. The Public Analyst, Dr. H. E. Cox, said that, on analysis, the sample was found to consist of diluted and coloured acetic acid, and was artificial vinegar; it contained no phosphate, tartrate or inositol, which would be found in small quantities in the product of the grape. So far as he knew, there was no grape vinegar manufactured in England, though it was known on the Continent and valued for its flavour.

The defendant urged that by calling his product "Grape Vinegar" he had only given it a name and did not intend to imply that it was derived from the grape. The grape was a symbol of purity and excellence; if he had called it "Pyramid Vinegar," would the Public Analyst have expected to find traces of the pyramids in it?

The Bench imposed a fine of 40 shillings, with two guineas costs.

The retailer was fined £1 for adding 20 per cent. of water to the vinegar.

EGG POWDER—GUARANTEED TO CONTAIN EGG.

AT Saltash Police Court, on August 25th, a retail grocer was summoned for a breach of Section 2 of the Sale of Food and Drugs Act, in that he sold to the Cornwall County Council's Inspector two tins of egg powder which were not of the nature, substance and quality demanded. The powder in question was labelled: "——'s Real Egg Powder, Double Strength, Guaranteed to contain the Real Yolks of Eggs." It also bore a facsimile of a certificate of a Fellow of the Institute of Chemistry, dated March, 1894, which certified "that an essential ingredient of its composition is sound yolk of egg." The certificate of the Public Analyst, Dr. H. E. Cox, showed that the powder was composed of tartaric acid, acid sodium pyrophosphate, bicarbonate of soda, rice starch and a yellow dye, and that it contained no egg. He said that a powder described as real egg powder containing eggs, as this one was described, ought to contain a substantial proportion of egg; the sample in question was really an egg substitute; the expression "double strength" was meaningless in application to this material.

Mr. C. Knight, for the County Council, explained that the retailer had not pleaded a warranty, and the wholesaler or manufacturer was not in the county, so he was obliged to proceed against the retailer. Mr. Wolferstan, for the defendant, agreed that the composition given by the County Analyst was correct, but urged that the powder had been manufactured for about 40 years from the same formula, although he did not know how it came about that acid pyrophosphate was present, a product which was not in use 40 years ago. It had been awarded various gold medals. A representative of the manufacturers said that the analyst's certificate appearing on the label had since been withdrawn.

The Bench intimated that the offence had been proved, but as they sympathised with the retailer, who had no intention of committing an offence, they imposed a fine of only ten shillings.

The National Physical Laboratory.

REPORT FOR THE YEAR 1930.*

THE volume includes the Report of the Executive Committee; a Comparison of Tests for the last three years; a list of Official and Unofficial Published Papers, and the detailed reports of the Physics, Electricity, Metrology, Engineering, Aerodynamics and Metallurgy Departments, and also that of the William Froude

National Tank.   From the mass of material a few investigations may be specially quoted.

PHYSICS: *Maintenance of Standards.   Optical Pyrometer Scale.*—The work on melting points at high temperatures has been continued by obtaining a black-body radiator, consisting of a tube immersed in an ingot of the metal which can be held a sufficient time at the melting point to allow observations by the pyrometer to be taken.   The small ingots are heated either by indirect induction by means of a heating unit consisting of molybdenum foil wrapped round a thoria tube fixed in a silica tube, or by direct induction by heating by a coil providing the maximum ampère turns per unit length, fitted in an alundum tube into which is inserted a cylindrical thoria crucible containing the ingot (0·6 cm. in diameter and 1·8 cm. long), threaded with a thin-walled alumina tube.   The black-body radiator consists of a small fragment of alumina nearly of the same cross section as the tube at its centre.   Although reliable determinations were obtained with these small ingots of platinum, the work is to be repeated with a thoria crucible and radiator presented by the Bureau of Standards, permitting the use of ingots, 1·6 cm. in diameter by 3·5 cm. long, and, if successful, the radiator might at the same time be used as a standard of photometric intensity.

GOVERNMENT RESEARCH, ETC.—Work has been carried out for the Food Investigation Board on heat transmission to cold pipes, and a single pipe is being studied in air of varying humidity and with speeds up to 30 ft. per second.   The Determination of Water in Fogs (work carried out for the Atmospheric Pollution Research Committee) having been impeded by lack of natural fog, artificial continuously dense fogs have been used.   Owing to difficulties experienced with Kohler and Owen's apparatus, a gravimetric method has been tried which measures the water as droplets by aspirating the air at about 60 cb. ft. per hour through U-tubes of 2 in. bore, containing wetted glass wool, and measuring the volume by a dry gas meter.   A dew-point method has also been used in which the foggy air is heated to evaporate the droplets, and the dew-point is determined on the fog-free air.

Work for the Building Research Board was done on transmission tests for various materials, including wall sections of closely thatched straw, cement faced one side and plastered the other, and one of reeds instead of straw.

Action of Heat on Iron Oxides.—In collaboration with the Research Association of British Paint, Colour and Varnish Manufacturers, the effect of heat on iron oxides was made the subject of X-ray examination.   Freshly prepared hydrated iron oxide ($Fe_2O_3,2H_2O$) was amorphous; Fe_2O_3,H_2O, prepared commercially, gave a diffraction pattern corresponding with a structure not yet worked out, and, on heating, the water was not wholly removed under 300° C., after which the structure of the oxide (Fe_2O_3) was a cubic one, resembling that of Fe_3O_4, but with a slightly different intensity distribution.   Further heat treatment caused a change to trigonal Fe_2O_3, beginning at 500° C. and complete at 600° C.

COLOUR MEASUREMENT AND STANDARDISATION.—The three-colour mixture curves, based on the spectrum observations of seven observers, are so far confirmed in their accuracy that the data have been put into a form for general use, and specific proposals based on these and other published data are being put forward for the definition of the "normal" eye.   The standardisation of the 57 colours, scheduled as standard for ready-mixed paints by the British Engineering Standards Association, has been completed and results incorporated in the British Standards Schedule of Colours for Ready-mixed Paints.   The Pharmacopoeia Commission

was assisted in its colour specification for the antimony trichloride test for cod-liver oil, and the Fuel Research Station in specifying a set of colour standards for testing coal ash.

ELECTRICITY DEPARTMENT: *Photometry Division.*—The investigations relating to heterochromatic measurements have been continued and the visual spectrophotometer has been described (*J. Scientific Instruments*, 1930, **7**, 305). It is sufficient to calibrate the standard lamp at one standard wave-length, and the calibration for other wave-lengths is deduced from Wien's law. The transmission of the Ives yellow and blue solutions for determination of the Y/B ratio for different observers has been measured, and records made on glasses for photometric determinations, so that a study of flicker photometry for large colour differences may be made. The spectrophotometer is being used for measuring the effective wave-lengths of coloured glass, which can be found from two measurements at different colours. A change of 20° C. in room temperature will lead to an error of 4° C. in the deduced melting point of platinum, owing to the influence of temperature on the red glasses of optical pyrometers.

PHYSICAL INSTRUMENTS.—Work on the new standard barometer (ANALYST, 1930, **55**, 512) has been continued, and comparisons with other standards are shortly to begin. Relative weights of the Laboratory standards of Mass have been re-determined and comparisons made with the standards of the Standards Department of the Board of Trade. The ampère balance has been reconditioned, and can now be used for accurate determinations of the moment of inertia of the suspended system.

VOLUMETRIC GLASSWARE AND HYDROMETERS.—The drafting of specifications for the adoption, throughout the Empire, of uniform specifications and methods of testing glassware used in the examination of milk and milk products is in hand. Methods of testing centrifuge tubes for the determination of dirt in milk are being investigated, and the leakage test for burette stopcocks is under review. In collaboration with the Standardisation of Tar Products Tests Committee, specifications for glassware and hydrometers to be used in testing tar and its products have been prepared, and a series of experiments made to enable suitable hydrometers to be specified for tar and tar distillates.

ENGINEERING DEPARTMENT: *Lubrication.*—The Investigation for the Lubrication Research Department Committee into the characteristics of boundary lubrication for surfaces under relative reciprocating motion has been continued, and a machine constructed in which the frequency of oscillation has been reduced to 10 per minute, in order to reduce the inertia of the moving parts of the mechanism.

The work on "doped" lubricating oils for the Aeronautical Research Committee has shown that addition of lead ethyl and such substances to lubricating oils reduces the coefficient of friction and raises the seizing temperature, but that the opposite occurs with castor oil. Three samples of oil from an asphaltic base showed a marked reduction of the minimum friction to be produced by oxidation or by addition of lead ethyl, but, if they had been previously oxidised, no further reduction occurred.

METALLURGY DEPARTMENT.—The X-ray spectrometer has been particularly applied to the study of the aluminium-copper system, and two new lattice structures have been discovered, probably corresponding with definite phases in the region between 20 and 30 per cent. of aluminium. Variations detected in the lattice parameter of iron-chromium alloys are being further investigated, and the work on gold-copper alloys of composition approaching that of the compound AuCu has shown that the depression of the transformation temperature is due to slight

absorption of oxygen. Experiments in the determination of elastic constants of inter-metallic compounds by production of acoustical vibrations in small specimens are in progress.

Work on the production of single crystals of pure metals has been continued, together with further work on the preparation of pure metals, particularly iron, with a view to preparing larger quantities for corrosion research work. The surface tension of mercury has been measured between 0° C. and −37° C., and that of tin-lead alloys down to 240° C. Investigation on aluminium alloys have shown that the dimensional changes occurring on machining are greatly reduced by quenching in boiling water or oil, and that there is no change in mechanical properties.

The work on the removal of dissolved gases from molten aluminium alloys. The good results obtained by passing volatile chlorides, particularly titanium tetra-chloride, have been published (*J. Inst. Metals*, 1930, **44**, 305), and the laboratory results have been confirmed on a large industrial scale, so that ingots and castings have been obtained substantially free from gas cavities.

Welded joints in aluminium alloys are under investigation, as are also the mechanical properties and resistance to corrosion of magnesium alloys. A paper dealing with the results of work on nickel-chromium and iron-nickel-chromium alloys has been published (*J. Iron and Steel Inst.*, 1930, **121**, 225), and it has further been found that the greatest resistance to prolonged stress at high temperatures is exhibited by an alloy containing: Silicon, 1·0; carbon, 1·5; tungsten, 4; nickel, 30; chromium, 30; and iron, 33·5 per cent.

The important study of the resistance of various steels to oxidation by flue gases has been begun. An investigation into "creep" is in progress, and work on gases in steels and on the cracking of boiler plates is also being carried out for the Metallurgy Research Board. Continuous immersion in tap-water has been found to reduce the life of boiler plates by 30 to 40 per cent.

<div align="right">D. G. H.</div>

Government of Madras.

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1930.

In his Annual Report to the Local Self-Governing Department of Madras, Lieut.-Col. C. Newcomb, M.D., F.I.C., mentions that in the course of 1931 the Chemical Examiner was to be relieved of his professorial work at the Medical College, leaving him free to attend to his medico-legal work, and to undertake research on the identification of certain poisons which are not very uncommon in India, but are almost unknown in Europe.

The total number of articles examined during the year showed a slight reduction on 1929 (5406, as compared with 5844), but the human poisoning and the stain cases showed an increase, and there are no indications that this increase will not continue in future.

HUMAN POISONING CASES.—The number of cases investigated was 271, in which 330 persons were affected and 207 died. In 133 cases poison was found, mercury being identified in 21, arsenic in 10, atropine (or datura) in 18, and opium

in 16 cases. Among the less common poisons detected were oduvan (2 cases) and madar (1 case). The tests found the most useful for the detection of these poisons were as follows:—

ODUVAN LEAVES.— The acid ethereal extract gives a green colour with strong hydrochloric acid and kills a frog when injected under its skin. The reaction can often be obtained from the stomach contents in cases of poisoning.

MADAR.—(1) The juice itself or the stomach contents, freed from the alcohol in which they are preserved, give a green colour with strong nitric acid.

(2) On boiling the juice with alcohol under a reflux condenser an extract is obtained with a peculiar and rather characteristic smell. With stomach contents the difficulty in applying this test is that the offensive smell of the decomposing organic matter frequently obscures the rather pleasant odour of the madar, but sometimes the odour is recognisable even in the stomach contents.

(3) We have not had much success with the crystallisation test. In this the above alcoholic extract is allowed to evaporate in a glass dish, when crystals, resembling cauliflower, are stated to form. In our experience, the crystals are not at all characteristic in form.

(4) Should a considerable quantity of madar juice be available the resin can be extracted and purified, and its properties compared with that obtained from known madar juice, but in poisoning cases there is rarely enough of the poisonous substance available for this· procedure.

It is not, of course, possible with either oduvan or madar poisoning to be certain from these tests of the exact nature of the poison, but the tests indicate the probable presence of the poison. This, together with the medical evidence of the symptoms, is often sufficient to establish with a fair degree of certainty the poison used.

ANIMAL POISONING CASES.—Thirty-three cases with 122 articles were investigated. In 17 of the cases poison was detected. Arsenic was found in 8 cases, and yellow oleander (or its active principle) in 7. In 2 of the cases an unidentified poison was found.

STAIN CASES.—During the year the number of stain cases investigated was 749 with 3217 articles. The number again exceeded that of the previous year, and was the largest on record. The Imperial Serologist examined 2296 specimens of bloodstains, of which 2182 were human blood.

DETECTION OF SEMINAL STAINS BY MEANS OF ULTRA-VIOLET LIGHT.—The use of an ultra-violet lamp, with a shade and a glass screen cutting off nearly all the visible light, has been very useful in finding semen stains on white or light-coloured cloths. On black or dark-coloured cloths ultra-violet light is useless, and one has to decide which portions to cut out for examination by eye and feel in the usual way—a tedious business with a large cloth. A white cloth can be passed rapidly through a beam of ultra-violet light, and any seminal stains will at once shine with a bluish fluorescence. A great many other stains which are not seminal show up too, and it is surprising what a number of different stains will appear when viewed in ultra-violet light on a cloth which, by ordinary examination, is fairly clean. Ultra-violet light is no test for semen, except in the sense that it shows one to which portion of the cloth to confine one's attention. This, however, when dealing with a large cloth, is no small advantage.

Florence's Test for Semen.—The number of rape cases in which we can find no semen (and by no semen I mean not only no spermatozoa, but no stains which will give Florence's test), is always a little surprising. One expects to fail to find spermatozoa in many seminal stains, as spermatozoa are extremely fragile and

readily decomposed and have been shown to disappear quickly from stains known to be seminal, but if a seminal stain is dried and kept dry—as most of those we get are—one expects to get Florence's test from it. If one does not, it is very unlikely that the stain is really seminal. I think a large number of rape cases must be false cases, and I am supported in this opinion by the fact that in many of the alleged seminal stains we examine, we find that the stains are those of starch.

EXAMINATION OF BOMBS.—Thirty-five miscellaneous medico-legal cases, with 160 articles, were investigated. Most of these cases were bombs of the type common in these parts, *viz.* a round packet containing red sulphide of arsenic, potassium chlorate, and small stones or nails, all tightly packed together in cloth and bound with string or cotton. Such a bomb explodes on percussion, and though, as bombs go, it is not of a particularly dangerous type, a well-made one can do considerable damage and can easily kill a man if it strikes near a vital part. In some of the bombs sent to us the bomb-maker had been deceived, by a super-ficial resemblance, into using the wrong materials. In one case what should have been potassium chlorate was found on analysis to be tartaric acid, and in another the red sulphide of arsenic had been replaced by potassium dichromate—a red substance somewhat resembling it. Neither of these bombs would have exploded.

DETECTION OF ERASURE BY MEANS OF ULTRA-VIOLET LIGHT.—In one of these miscellaneous cases we were sent a bus licence for examination for alteration of the figures on it. It was suspected that in the figure "$1\frac{1}{2}$ tóns" the "$\frac{1}{2}$" had been erased and subsequently re-inserted. On examination in ultra-violet light this suspicion was confirmed, and the erasure and subsequent insertion of the figure "$\frac{1}{2}$" could be distinctly seen.

Ceylon.

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1930.

IN his report on the work of the Government Analyst's Department, Mr. C. T. Symons mentions that, in the absence of any alterations with regard to staff and accommodation, and in view of the necessity for retrenchment, it became necessary towards the end of the year to inform the departments concerned that the work of the Department would in future be limited to the scope laid down in general orders, wherein the work of the Government Analyst is defined as: (*a*) Analyses arising out of criminal investigations; (*b*) examinations and other duties under the Petroleum Ordinance; (*c*) analyses of water or milk sent by a Government Depart-ment; with a proviso that, should an analysis of any other kind be required by the Head of a Department he should apply to the Government Analyst, showing special cause for his application.

The work discontinued includes scientific investigation of crime (other than chemical analysis), examination of firearms, examination of stains, analysis of food and drugs, analysis of sewage effluents, etc.

The following notes are given on some of the remarkable cases dealt with during the year.

POISONING CASES.—Specimens were examined in 104 cases, and in 33 of them poison was identified. Ten involved arsenic (in one case with a barium salt, and in another as Paris green), 8 prussic acid (in one case with morphine), 4 mercury,

as metal or as salt, 2 phenols, and 1 each, *Gloria superba*, morphine, chenopodium oil, zinc chloride, a copper compound, and powdered glass. A case of some interest was one in which no prussic acid was found in the viscera of a man who had undoubtedly died from the ingestion of potassium cyanide. Traces of the poison were found in the tumbler he used and in other receptacles in his room.

BULLETS AND FIREARMS CASES.—Twenty-three cases were investigated, necessitating the examination of 108 articles.

Imprint of Cloth on Bullet.—In one case from Colombo a man who was wearing a coat and shirt was shot through the arm. The bullet went through his arm, but after that did not penetrate the shirt and coat a second time. The next day a revolver bullet was found in the rubbish heap behind an adjoining bungalow. It was suspected that the man had been shot, at fairly close range, by a man using a revolver and intending to shoot someone else who was standing near. The suspected person admitted that he had fired several shots that night from the window of his bungalow, with the intention, he said, of frightening away a riotous crowd who were damaging his house and trying to break in, but he denied having wounded or fired at any person. A visit to the scene soon showed that his story was false, so far as it concerned the assault on his house. The slight damage had been done with the object of simulating an assault on the house. In addition, the wounded man was conclusively proved to have been standing in a position which could not have been reached by shots fired from the window, and finally, by means of the comparison microscope and bullet comparator, it was found possible to demonstrate that the bullet picked up in the rubbish heap had been fired through the accused person's revolver, and that it had actually penetrated through a piece of cloth of exactly the same texture as that of the coat of the wounded man. This was possible from the impression of the cloth left on the end of the lead bullet when it hit the man's arm, and from the rifling marks on the bullet, and its irregular entry into the barrel.

In another case, the problem sent up was more in the nature of a jig-saw puzzle, since the productions consisted of two tubular pieces of metal, a chopper, and some fragments of wood and metal, and the Analyst was asked whether the fragments originally constituted the stock and barrel of a gun, and whether the chopper had been used to cut it up. After some trouble the pieces of wood were fitted together to form a passable gun stock, and by a piece of good fortune a flaw in the blade of the chopper was found to contain a fragment of the same wood as the stock, an unusual kind of wood to use for firewood.

SPECTROSCOPIC IDENTIFICATION OF TELEPHONE WIRE.—In the past many cases have been initiated in the courts, charging various persons with the theft of Government copper telephone and telegraph wires. Most of these cases have been dismissed, on account of the difficulty of proving the identity of the seized wire with Government samples, in view of the defence that the wire was quite legitimately purchased from local importers. We were consulted on this subject, and by means of the Féry quartz spectroscope we were able, in a recent case, to demonstrate quite conclusively that the seized sample contained traces of certain ingredients which were present in Government wire, but not in any other samples obtained locally. This evidence is obtained very rapidly by a photographic process, and can be demonstrated by prints, showing that the finding is not a matter of opinion, but one of fact.

IDENTIFICATION OF CLOTH BY MEANS OF ULTRA-VIOLET LIGHT.—An extraneous torn piece of common white cloth was found in a house where a burglary had been committed. Another piece of similar cloth was found in a suspected

person's house.   Each piece showed the same material, the same state of dirt, a similar seam and fresh tearing, but this was not sufficient to establish identity of source where such commonly used cloth was concerned.   Examination under Wood's light, however, showed up certain stains, invisible to the naked eye, which extended over the freshly torn edges, and formed continuous stains when these edges were placed together.   The nature and conformation of these stains conclusively established the fact that the two pieces of cloth had originally formed one piece.

In future, such cases as this will not be dealt with in the Government Analyst's Department.

PROOF OF FRAUD BY MEANS OF RECEIPT STAMPS.—In one case it was possible to prove and demonstrate fraud clearly by means of the perforation on receipt stamps.   Three promissory notes were produced in support of an insolvency case and purported to have been made at two different places and at intervals of time covering about a year.   The signatures were genuine, but were all written with the same pen and ink, which had been specially prepared to produce an appearance of age.   The pen was not a fountain pen.   The pen points showed progressive deterioration throughout the three documents, but not in the proper order.   But the most conclusive proof was from the stamps, which, by the irregular tearing of the perforations, were shown to have formed originally one block of three stamps. (Cf. Mitchell, Documents and their Scientific Examination, p. 178.)

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Method for the Determination of Small Quantities of Mixed Reducing Sugars and its Application to Determination of Products of Hydrolysis of Starch by Taka-Diastase. E. M. Widdowson. (Biochem. J., 1931, 25, 863–879.)—Preliminary investigations on the carbohydrates in the developing apple have shown that the concentration of sugars in the fruit is less than 1 per cent. during the first weeks of growth, and that the maximum starch concentration reached at any time is only about 2 per cent.   Since starch appears to be most satisfactorily determined by measurement of the glucose and maltose produced by hydrolysis with taka-diastase, a method for the determination of small quantities of reducing sugars has been investigated.   In order to determine two mixed reducing sugars it is necessary to employ two methods of determination, and to solve the pair of simultaneous equations obtained from the results of the determinations. Hagedorn and Jensen (Biochem. Z., 1923, 135, 46) have used the method of oxidation by alkaline ferricyanide for the determination of amounts of glucose ranging from 0·02 to 0·36 mgrm. in 2 c.c.   Hanes (Biochem. J., 1929, 23, 99; ANALYST, 1929, 54, 349) has applied this method to the determination of quantities of glucose and maltose up to 3·8 mgrms. in 5 c.c.; also, Macleod and Robison (Biochem. J.,

1929, **23**, 517) have shown that the oxidation of reducing sugars by hypoiodite can be satisfactorily carried out in solutions of similar concentration. The Hanes modification of the Hagedorn and Jensen method with alkaline ferricyanide, when combined with the iodimetric method, has been satisfactorily applied to the determination of small quantities of mixtures of glucose and fructose and of glucose and maltose (concentrations of about 3 mgrms. per 5 c.c.). In the oxidation of sugars by alkaline ferricyanide a cooling procedure is adopted to prevent loss of iodine and consequent introduction of serious error. The methods have also been applied to the determination of the glucose and maltose obtained by the hydrolysis of starch by taka-diastase. Tests with pure starch showed that the method was accurate to within 1 per cent. It has been shown that there is no loss of sugar when a solution of glucose and maltose is cleared with basic lead acetate and sodium phosphate. It has been shown that cleared, coloured solutions obtained from alcoholic extracts of young apples should be boiled with a preparation of charcoal such as "Suchar" before determinations of the fructose and glucose by oxidation with alkaline ferricyanide and hypoiodite are made. The combination of the two methods of oxidation appears to give satisfactory results for the determination of small quantities of glucose and fructose and glucose and maltose, and could probably be applied to mixtures of any two sugars, provided that the ratio between the factors for the two sugars given by one method of oxidation differs sufficiently from the corresponding ratio given by the other method. The method is convenient, since the same thiosulphate solution is used for both sets of titrations.

P. H. P.

Composition of Karité Butter. J. Bougault and G. Schuster. (*Compt. rend.*, 1931, **193**, 362–364.)—Two samples of different origin gave acid value, 0·67 to 0·73 per cent. (as palmitic acid); iodine value, 44 to 46; saponification value, 200; unsaponifiable matter, 1·3 per cent. They were examined by the method of Hilditch (oxidation with potassium permanganate in acetone solution, *cf.* ANALYST, 1931, 406), which left unattacked 7·3 per cent. of totally-saturated glycerides made up of tributyrin (3·10), dibutyro-stearin (3·10), and arachido-dipalmitin (0·96 per cent.); separation was achieved by fractional crystallisation from alcohol at 0° C., then from mixed ether and acetone, and finally from petroleum spirit. The 92·7 per cent. of incompletely-saturated glycerides were oxidised to glycerides which were separated by fractional crystallisation and were shown to contain at least one molecule of azelaic acid. The results indicated the presence of dipalmito-olein (19), dibutyrolein (54), and palmito-diolein (19 per cent.) in the original fat. Small amounts of other glycerides may also be present, but the data given, which are only approximate, leave room for not more than 5 per cent. of other substances.

J. G.

Expressed Brazil Nut Oil. H. A. Schuette and W. W. F. Enz. (*J. Amer. Chem. Soc.*, 1931, **53**, 2756–2758.)—The value of the oil from the seeds of *Bertholletea excelsa* depends upon the extraction process used. Virgin oil, colourless to pale yellow, may be obtained by expression, whereas extraction of the residual

pulp by solvents will yield a darker inferior product, and, although the superior oil solidifies the more readily, a detailed examination of the saturated and unsaturated acid fractions shows that the linolin and palmitin contents of both grades are of the same order of magnitude. The approximate percentage composition of virgin Brazil nut oil was: Myristin, 0·48; palmitin, 13·74; stearin, 5·45; olein, 42·79; and linolin, 26·54. Myristin is present in the virgin oil only to one-fourth of the proportion in the lower-grade product, but there is twice as much stearin.

<div align="right">D. G. H.</div>

Kapok Oil and the Halphen Test. H. P. Trevithick and W. H. Dickhart. (*Oil and Fat Ind.*, 1931, **8**, 305 and 317.)—A sample of kapok oil, crushed from imported seeds, gave the following analytical results:—Moisture and volatile matter, 0·45; insoluble impurities (meal), 0·36; unsaponifiable matter, 0·66; free fatty acids (oleic), 12·13; and refining loss, 35 per cent.; sp. gr. at 15·5° C., 0·9221; iodine value (Wijs), 94·9; saponification value, 194·5; colour (refined oil) 35 yellow, 7 red; titre (refined oil), 28·1° C.; titre (soapstock acids), 30·2° C.; Halphen test, strong and immediate. Owing to the similarity of this oil to cottonseed oil, tests were made to determine the effects, on the Halphen reaction, of adding each oil in small proportions to sesame, olive, palm kernel, and coconut oils. In every case the colour developed in this reaction by kapok oil was much deeper than that caused by the same percentage contamination with cottonseed oil. The colour obtained with any mixture containing kapok oil in a certain proportion is equivalent to that furnished by a mixture containing ten or more times such proportion of cottonseed oil. Mixtures of oils containing either 5 per cent. (or more) of cottonseed oil or 1 per cent. (or more) of kapok oil yield Halphen colorations which are too deep to allow the percentage contamination to be estimated. T. H. P.

Tonka-bean Oil. C. D. V. Georgi and G. L. Teik. (*J. Soc. Chem. Ind.*, 1931, **50**, 318T.)—*Dipteryx odorata*, which yields tonka beans, is indigenous to S. America, and has recently been introduced into Malaya, where the conditions appear suitable to it. A sample of the beans showed the average weight per fresh bean to be 3·4 grms. or per fresh kernel 3·2 grms. The kernels contained: Moisture (loss at 100° C.) 43·1 per cent., and oil (petroleum spirit extract) 26·5 per cent. The oil began to melt at 7·2° C., and was completely fused at 11·8° C.; sp. gr. at 99°/15·5° C. 0·878; saponification value, 198·5; iodine value (Wijs), 72·6; n_D^{27}, 1·4680; acid value, 1·0; and unsaponifiable matter, 0·5 per cent. The fatty acids had the solidifying point (titre value), 42·0° C.; mean molecular weight 302·9, and iodine value (Wijs) 76·9. Partly on the basis of the high saponification value, 257, given by Duyk (*Répert. Pharm.*, 1908, 193), the oil has previously been classified with the coconut oil group, but the above results, showing normal saponification and low iodine values, indicate that it should be regarded as a non-drying oil. Since coumarin can be manufactured synthetically, and since there are available for edible purposes enormous quantities of other oils of the same class, *e.g.* arachis oil, extensive demand for tonka beans seems unlikely. T. H. P.

Oil from the Seeds of *Putranjiva Roxburghii*, Wall. S. Krishna and S. V. Puntumbekar. (*J. Indian Chem. Soc.*, 1931, **8**, 301–306.)—The putranjiva or jiputa tree (*Putranjiva Roxburghii*, Wall., N. O. *Euphorbiaceae*) is an evergreen tree of tropical India, where in certain parts the leaves and stones of the fruit are officinal and given in decoctions for colds and fevers. The stones of the ripe fruits contained 46 per cent. of kernels, yielding 25 per cent. of oil, that obtained by cold expression being light yellow and clear, but deepening to orange on keeping, with deposition of a fine curdy precipitate. The values obtained from a sample of freshly extracted oil (1) and one extracted in 1925 (2) were as follows:—Sp. gr. at 30°/30° C., 0·9108, 0·9233; n_D^{25}, 1·4615, 1·4623; saponification value, 189·9, 198·5; iodine value (Hanus), 93·8, 79·49; acetyl value, 9·5, 43·3; Hehner value, 95·4, 96·2; unsaponifiable matter, 0·75, 0·73 per cent.; acid value, 0·9, 11·13. The fatty acids were separated by Twitchell's lead salt and alcohol method, and the groups of mainly-saturated and mainly-unsaturated acids were converted into the methyl esters, which were systematically fractionated. The mixed fatty acids had a mean molecular weight of 292·5, and an iodine value (Hanus) of 101·9, and consisted of 21·4 per cent. of saturated, and 78·6 per cent. of unsaturated acids. The largest of the ester fractions of the unsaturated acids were hydrolysed, the soaps oxidised with potassium permanganate in dilute cold solution, and the hydroxy acids (obtained by neutralising the mixture with sulphur dioxide) were extracted with petroleum spirit. Various compounds, regarded as isomeric acids, of the formula $C_{18}H_{36}O_6$ were obtained. A portion of the liquid acids was brominated and found to consist of 80 per cent. of oleic acid and 20 per cent. of linolic acid. The methyl esters of the saturated acids were also fractionated, and stearic and lignoceric acids were identified. The phytosterol of the unsaponifiable matter was identified as sitosterol. D. G. H.

Determination of Iodine and Chlorine in Iodised Oils. T. T. Cocking and G. Middleton. (*Quart. J. Pharm.*, 1931, **4**, 175–177.)—Commercial iodised oils are normally prepared by the action on a fixed oil containing unsaturated fatty acid radicals (usually sesame oil) of solutions of iodine chloride in glacial acetic acid or of iodine and mercuric chloride in strong alcohol. Absorption of halogens is additive in the dark, but some substitution occurs in sunlight, and, since the 2 halogens are seldom present in equivalent proportions, the total halogen content does not enable the amount of iodine to be obtained. If 1 grm. of oil is boiled under a reflux condenser for 1 hour with 10 c.c. of glacial acetic acid and 1 grm. of zinc filings, the halogens are converted into zinc salts. The condenser is then washed down with 30 c.c. of hot water, and the mixture filtered through cotton-wool, two 20 c.c. portions of water being used as washings. The combined cold filtrates are titrated with 0·05 M potassium iodate solution (1 c.c.≡0·01269 grm. I) in the presence of 100 c.c. of concentrated hydrochloric acid, a few c.c. of chloroform being added when the solution becomes light brown, and the end-point being taken when, on shaking, the chloroform is colourless and the aqueous layer yellow. The total halogens (and thence, by difference, the chlorine) are determined by

titration of the acid aqueous liquid with silver nitrate (Volhard). Agreement to within 0·2 per cent. of iodine was obtained by comparison against Middleton's method (ignition with alkali and oxidation to iodate, see *id.*, 1929, **2**, 536). A mixture of sesame oil and Wijs solution allowed to react for 1 hour was also shown by the authors' method to contain as much iodine (to within ± 0·001 grm.) as the Wijs solution alone.   J. G.

Non-Volatile Organic Acids in Barley, Maize, Oats and Rye Plants. E. K. Nelson and H. H. Mottern. (*J. Amer. Chem. Soc.*, 1931, **53**, 3046–3048.)— The cereal plants used in these investigations were cut when they were beginning to form heads. The non-volatile acids were isolated as lead salts and then converted into ethyl esters, which were separated by fractional distillation. Barley plants were found to contain aconitic, malic, citric, malonic, tricarballylic and oxalic acids. The oxalic acid, calculated on the fresh material, amounted to 0·019 per cent. Maize plants contained aconitic, malic, citric, tricarballylic and oxalic acids. The oxalic acid was found to be 0·029 per cent. (on the fresh plants). Oat plants contained aconitic, malic, citric, malonic, and oxalic acids. The amount of oxalic acid calculated on the fresh material was 0·04 per cent. Rye plants contained aconitic, malic, citric and oxalic acids. The oxalic acid amounted to 0·048 per cent. The occurrence of aconitic acid in these cereals, as well as in sugar cane and sorghum, is noteworthy.

Detection of Bilberry Juice by means of Plahl's Reaction modified for Use with Sweet Wines. R. Ofner. (*Chem. Ztg.*, 1931, **69**, 666.)—Plahl's reaction (ANALYST, 1907, **32**, 92; 1908, **33**, 191) is suitable for the detection of bilberry juice only in completely fermented wines, and is modified as follows for sweet wines:—The residue from the alcohol or volatile acid determination (or 100 c.c. of the sample) is warmed with 5 grms. of decolorising charcoal for 5 minutes, evaporated to half its volume on the water-bath, diluted to 100 c.c., and filtered by suction. The sugars are removed by 6 washings with hot water, and the residual charcoal heated for 2 minutes, with shaking, with 100 c.c. of water and 5 c.c. of 2 N sodium hydroxide solution. The brown filtrate from the cooled liquid (40 c.c.) is shaken with 2 c.c. of N hydrochloric acid and 2 c.c. of lead acetate solution and filtered. The filtrate, which is still alkaline, should be colourless, otherwise the treatment is repeated, 10 c.c. of the final filtrate being mixed with 1 c.c. of concentrated hydrochloric acid. No colour results, but, on warming for 15 seconds, the lead chloride dissolves, and, in the presence of bilberry juice, a blue colour appears. The test may be applied in conjunction with Werder's (sorbitol) fruit wine test, in which charcoal is also used.   J. G.

Colorimetric Method for Determination of the Preservative Value of Hops. J. M. French. (*J. Inst. Brewing*, 1931, **37**, 436–439.)—The coloured solutions of the lead salt of humulon, prepared according to Guthrie and Philip's directions (ANALYST, 1930, **55**, 703), become turbid with certain hops, but this trouble is avoidable by the use of 0·7 per cent. uranium nitrate solution in place of

uranium acetate. The standard solutions made up with uranium acetate in methyl alcohol are found to be unstable in daylight. Hence a series of standard solutions was prepared, with contents of 0·005, 0·0055, 0·006, 0·0065, 0·007, 0·0075, 0·008, 0·0085, and 0·009 grm., respectively, of the α-resin in 100 c.c. of re-distilled industrial methylated spirit (the first 150 c.c. of distillate from 1 litre being discarded). Ferric chloride solutions to match the colours of this standard series were then made up and have been retained as the standards for use in the test.

The procedure has been simplified as follows:—Ten grms. of the finely minced hops are extracted with 100 c.c. of redistilled methylated spirit for 10 minutes in a corked bottle, with occasional shaking. The hops are allowed to settle, and 0·5 c.c. of the liquid is transferred by means of a graduated 1 c.c. pipette into a Nessler tube marked at 50 c.c. About 10 to 15 c.c. of the redistilled alcohol and 7 c.c. of the uranium nitrate solution (0·7 per cent.) are then added, followed by the same alcohol to the mark. The colour of the liquid is matched with that of one of the standard ferric chloride solutions. In comparing the colours of these two solutions, it is found permissible to withdraw a measured quantity from the solution which may be slightly the darker. This method gives results virtually identical with those furnished by Guthrie and Philip's procedure, and allows of the estimation of a difference of one unit in the preservative value. Owing to changes which occur in the hop extract and in the coloured solutions, all determinations must be made as soon after the extraction as possible.

Various grades of pure alcohol and industrial methylated spirit may be used without diminishing the accuracy of the method, provided that one and the same alcohol is used in the test and in preparing the standards. The uranium nitrate solution keeps well in bottles of amber-coloured glass. T. H. P.

The Resin of Ipomoea: Mexican Scammony Root: its Solubility in Ether and the Acid Value as a Test for Rosin. C. E. Corfield and W. R. Rankin. (*Pharm. J.*, 1931, **127**, 76.)—Practically the whole of the scammony resin of commerce now comes from the Mexican scammony root (*Ipomoea orizabensis*, Ledanois) and that from *Convolvulus scammonia* is rare. The value of the determination of the ether-soluble solids of the resin is discussed, the test being regarded as useful provided the conditions are fixed. One grm. of resin and 50 ml. of ether (sp. gr. 0·720) are suggested, and the standard should be in the form of a limit test of not more than 40 per cent. of ether-soluble resins. The determination of the acid value is recommended for ensuring the absence of colophony.

D. G. H.

Assay of Official Balsams. T. T. Cocking. (*Pharm. J.*, 1931, **127**, 73–74.)—The official method for the assay of cinnamic acid in prepared storax fails to extract all the acid, owing to the hardening of the matrix under prolonged boiling, and the consequent protection of the inner portions from complete extraction, and no methods involving the addition of various substances to keep the resinous mass semi-liquid were successful. A simpler modification of the magnesia method for the extraction of balsamic acids is described, whereby the total acids

from the saponified balsams are converted into the corresponding magnesium salts, which are separated from the resin acid salts by filtration. Any incompletely separated aromatic alcohols are separated from an ethereal solution by extraction with a solution of sodium bicarbonate, and the balsamic acids are finally extracted from an acidified solution with ether, and are weighed after drying *in vacuo* over sulphuric acid. With varying preliminary treatment the free balsamic acids in balsam of tolu and benzoin may be similarly determined.   D. G. H.

Determination of Strychnine in Easton's Syrup. L. A. Haddock and N. Evers. (*Pharm. J.*, 1931, 127, 72.)—The total alkaloids are dissolved in 20 c.c. of hydrochloric acid, washed into a separator with a further 5 c.c. of acid, followed by 25 c.c. of a saturated solution of sodium chloride, and the acid liquid is extracted by shaking for five minutes with five successive portions of 25 c.c. of chloroform. The chloroform extract is shaken for five minutes with 5 c.c. portions of an equal volume of *N* hydrochloric acid and saturated sodium chloride, and the combined washings extracted with 10 c.c. of chloroform, which are added to the first extract. After shaking with a mixture of 20 c.c. of water and 5 c.c. of 10 per cent. ammonia, the chloroform extract is separated, washed with 5 c.c. of water, the chloroform distilled off, 1 c.c. of alcohol added, the residue left on evaporation is dried at 100° C. The residue in the flask is washed with three portions of 2 c.c. of a mixture of 2 volumes of ether and ône volume petroleum spirit previously saturated with strychnine, the solvent being decanted each time through cotton wool, and any alkaloids on the wool are washed back into the flask with 3 c.c. of chloroform. One c.c. of alcohol is added, the liquid evaporated, and the residue of strychnine dried and weighed. If the original syrup is used, 50 c.c. of syrup are taken with 50 c.c. of saturated sodium chloride solution and 5 c.c. of concentrated hydrochloric acid, and double quantities of chloroform throughout the process.
                                                                    D. G. H.

Quantitative Methylation of Theobromine and Theophylline, and the Determination of these Substances in Theobromine Sodium Salicylate and Theophylline Sodium Acetate. P. A. W. Self and W. R. Rankin. (*Pharm. J.*, 1931, 127, 75–76.)—A method is described whereby 99·5 per cent. of caffeine may be obtained from theobromine and 98·0 per cent. from theophylline. Theobromine may be determined in theobromine sodium salicylate by dissolving 1 grm. of theobromine sodium salicylate in 10 c.c. of water, adding 2 c.c. of *N* sodium hydroxide and 0·6 c.c. of dimethyl sulphate and shaking for 5 minutes. After 30 minutes 3 c.c. of *N* sodium hydroxide solution are added, the mixture shaken for 1 to 2 minutes, transferred to a separator with chloroform and a little water, and the caffeine extracted by shaking with successive portions of chloroform, and washing each extract with about 10 c.c. of water. The chloroform is evaporated, and the residue of caffeine dried at 100° C. and weighed; each grm. of anhydrous caffeine is equivalent to 0·9278 grm. of theobromine. Theophylline may be determined in theophylline sodium acetate by mixing 1 grm. of the substance with 4 c.c. of *N* sodium hydroxide solution, 5 c.c. of water and 0·8 c.c. of

dimethyl sulphate, shaking for 5 minutes or until a clear solution is obtained, and leaving for 1 hour with frequent shaking, when 3 c.c. of N sodium hydroxide solution are added, the mixture shaken for 2 minutes, the caffeine extracted as described above and the same factor used for conversion to anhydrous theophylline.

D. G. H.

Theophylline Sodium Acetate of Commerce. G. J. W. Ferry. (*Pharm. J.*, 1931, **127**, 74–75.)—Twelve samples offered as theophylline sodium acetate were analysed qualitatively and quantitatively; only three actually consisted of this compound, which should contain not less than 60 per cent. of anhydrous theophylline, and not more than 5 per cent. of water. The examination of theophylline sodium acetate is discussed with particular reference to its distinction from theobromine sodium acetate and to variations in composition, since many samples are deficient in theophylline, owing mainly to the presence of excess of water. Neither the formula usually given for the anhydrous salt nor that for the monohydrate accurately represents the actual composition of most specimens, and the introduction into the British Pharmaceutical Codex of monographs on theophylline and theophylline sodium acetate is recommended. D. G. H.

Colorimetric Evaluation of *Folia Digitalis* **according to the Method of Knudson and Dresbach.** B. J. Okeloen and J. C. Timmers. (*Pharm. Weekblad,* 1931, **68**, 820–824.)—Ten c.c. of an infusion of the powdered leaves, 10 c.c. of water and 2·5 c.c. of a 10 per cent. solution of neutral lead acetate are thoroughly mixed, made up to 25 c.c. in a flask, filtered, and 12·5 c.c. of the filtrate precipitated with 1·25 c.c. of a 10 per cent. solution of (crystalline) disodium hydrogen phosphate. The new mixture is also diluted to 25 c.c. and filtered, and 5 c.c. of the bright filtrate are pipetted into a small tube (diameter 20 mm.). A mixture of 95 c.c. of 1 per cent. picric acid and 5 c.c. of 10 per cent. sodium hydroxide solutions is then added from a burette until the colour, which changes from yellow to orange, reaches a maximum and constant degree of intensity. After 25 to 40 minutes the colour may be matched against that produced from 5 c.c. of a standard ouabain solution by 5 c.c. of the picric acid reagent according to the method of Knudson and Dresbach (ANALYST, 1923, **48**, 76), but any error due to the uncertain strength of this standard is avoided if a solution of potassium dichromate is used alone. This may be titrated with 0·1 N sodium thiosulphate solution after liberation of iodine by addition (to 10 c.c.) of 5 c.c. of N sulphuric acid and 0·5 grm. of potassium iodide. Five, 3, and 1 per cent. infusions of a sample having a Focke physiological value of 4 (Baljet, *Chem. Weekblad*, 1918, **55**, 457) required 15·2, 9·2 and 3·0 c.c. of thiosulphate, respectively. Diffused daylight is preferable, and artificial light is unsuitable, for matching purposes. Ten samples, including *D. ambigua, lanata, lutea, purpurea* (1929-season), gave results showing a maximum divergence from the Focke values (4 to 9) of 0·5; the *D. lanata*, which had a Focke value of 18·2, gave a colorimetric value of 17·1. The Martindale–Westcott method was found suitable for identifying these varieties. Addition of 100 mgrms. of dextrose, laevulose, sucrose, lactose, mannose, maltose and arabinose

to 5 c.c. of picric acid reagent gave a negative colour reaction in the cold in all cases except for laevulose, and positive on warming in all cases except for maltose.

J. G.

Biochemical.

Blackening of Potatoes after Cooking. C. K. Tinkler. (*Biochem. J.*, 1931, **25**, 773–776.)—Potatoes sometimes darken considerably on the surface after cooking. This darkening is distinct from that which occurs with raw potato on exposure to air, and is a matter of considerable importance to those concerned in the growing and sale of potatoes. A simple test has been devised by means of which it is considered possible to tell by examination of a raw potato whether or not a similar potato will blacken after cooking. It was found that all potatoes examined contain a substance (or substances) in greatly varying amounts, which on treatment with nitrous acid followed by an alkali, gives a fine red colour. The amount of the red substance produced in this test was found to vary exactly with the amount of blackening which takes place on cooking. The test is as follows:— A transverse section of potato, about 5 mm. thick, is peeled thinly and covered with 7 per cent. sodium nitrite solution (about 25 c.c.) in a small porcelain basin. About 2 c.c. of dilute hydrochloric acid (1 volume of concentrated hydrochloric acid to 2 volumes of water) are added, and the mixture left for 5 minutes. The liquid is then poured off and the section of potato covered with 16 per cent. sodium hydroxide solution (about 25 c.c.). The red colour develops in about 5 minutes, at first chiefly on the outer and inner edges of the fibro-vascular layer of the potato, then through the whole of this layer, but it often extends towards the centre. It is strongly marked where there are eyes in any potato. After some time the coloured substance is partly extracted by the sodium hydroxide solution. The reaction has not yet been investigated fully. It may be that the nitrous acid reacts with a primary amino-compound, and that coupling of the diazo-compound thus produced takes place with a phenoxide on the addition of the sodium hydroxide, or the colour may be due partly or entirely to reactions between the nitrous acid and lignocellulose. It seems probable that the production of the colour in the test described is in some way connected with the blackening which takes place after cooking, for if the fibro-vascular layer of a potato which would darken, which gives most colour in the test, is completely removed before cooking, very little blackening of the remainder is usually noted after cooking. It is extremely probable that the blackening is due to oxidation; its cause as distinct from darkening due to enzymic oxidation is discussed, and attention is drawn to the fact that iron may have a pronounced influence on the degree of blackening observed.   P. H. P.

Free and Bound Water Determinations by the Heat of Fusion of Ice Method. W. Robinson. (*J. Biol. Chem.*, 1931, **92**, 699–709.)—The dissolved materials and the colloids which are present in the water of the tissues have the effect of modifying some of the properties of the water in which they occur; consequently the water of the tissues does not behave in all respects like water in its

pure state, and it is commonly spoken of as "bound" water. Any variations in the concentration of substances in solution and any changes in the water-binding capacity of the colloids, which take place as a result of the processes of normal physiology or of pathology, may affect the degree of force with which the water is bound. The conception has been held by some investigators in this field that part of the water in the tissues is bound and the remainder free, and that an equilibrium is maintained between these two conditions. According to other theories (Briggs, unpublished data, 1931) all the water in the tissues is bound and changing conditions affect only the force with which it is bound. Whichever view is adopted, the method of Rubner (*Abhandl. Preuss. Akad., Physik-Math. Klasse,* No. 1, 1 (1922)) for bound water determinations can be applied to any series of comparative tests. The colloids and dissolved materials hold water with an actual tenacity and resist any force which tends to pull the water away. In Rubner's method a definite and constant desiccating force is used which withdraws the "free" water and leaves the "bound." The method for free and bound water determinations, which is described in detail, is modified from the description given by Thoenes (*Biochem. Z.,* 1925, **157**, 174) and by Robinson (Colloid Symposium Monograph, 1928, **5**, 199), but does not differ materially from the principles of the method of Rubner. A known weight of specimen, preferably between 0·4 and 0·8 grm., is placed in a prepared tin-foil container of known weight, frozen at a constant temperature of −20° C. for several hours, and transferred to a calorimeter where a determination is made of the number of calories required to melt the ice formed within the tissues (based upon the fact that to melt 1 grm. of ice without raising its temperature requires 80 calories). By calculation the amount of free water per grm. of solid is determined. For the final step in the method the material is dried to constant weight as a measurement of total water content. The difference between the total and the free water values indicates the amount of bound water in the specimen. In the freezing process an efficient desiccating force is provided, since at temperatures below zero water tends to leave the colloids and dissolved materials to form ice crystals of pure water. The force exerted by this means is definite and constant at any given temperature below the freezing point of the tissue, and increases with fall in temperature, but the tendency of the water to crystallise is retarded by the dissolved and colloidal substances present. Therefore, at any given temperature below freezing the amount of water which crystallises out is a measure of the water-binding capacity of the tissue. With the use of the technique described, results with homogeneous material may be obtained which are reproducible within a small range of error. The number of data necessary for each determination makes a separate work sheet essential for each specimen, and the form of that used by the author is shown. The formulae necessary for the calculations are given. P. H. P.

Simplification of Okey Method for Determination of Cholesterol by Oxidation of the Digitonide. M. E. Turner. (*J. Biol. Chem.,* 1931, **92**, 495–498.)—The method of Okey (*J. Biol. Chem.,* 1930, **88**, 367; ANALYST, 1930, **55**,

654) for the determination of cholesterol by means of oxidation of the digitonide is an intricate procedure, especially in the precipitation of the cholesterol digitonide. The need for special and difficultly obtainable apparatus and for practice in the technique of making numerous transfers and filtering and washing small amounts of material discourages general application of the method. A simplification has been developed in which the precipitation, washing, and oxidation are accomplished in the one centrifuge tube (a 15 c.c. centrifuge tube with conical bottom and with well-fitted ground stopper). A table shows the figures for the recovery of free cholesterol from artificial and natural plasma extracts, as well as comparison figures with the colorimetric method of Autenrieth and Funk (*Münch. med. Woch.*, 1913, **69**, 1243). The limits of error in the oxidative method are $+2$ to $+4$ per cent. for 0·5 to 1·5 mgrm. of free cholesterol, and in the colorimetric method $+8$ to $+12$ per cent. The method described is applicable to the determination of free and combined cholesterol, and also lends itself to use in the determination of sterols of those plant extracts for which the colorimetric methods cannot be used.

P. H. P.

Activation of Ergosterol with Radium Emanation. **R. B. Moore and T. De Vries.** (*J. Amer. Chem. Soc.*, 1931, **53**, 2676–2681.)—A sample of reasonably pure ergosterol prepared in the United States (m.pt., 148° C., specific rotation in chloroform $-100°$), and one from Germany (m.pt., 157° C., specific rotation in chloroform $-121°$) were activated with radium emanation on four different occasions, and the activated samples were tested on rachitic white rats. Results showed that the degree of potency obtained was about 0·01 of that of a good grade of ergosterol radiated with ultra-violet light, and the activation of the samples appeared to be permanent. Stirring the sample during activation increased the speed of activation, but not appreciably the potency reached, and a twenty-fold excess of activation caused no appreciable loss in potency; some decomposition products were, however, present in all the experiments. D. G. H.

Influence of Solvents on the Activation of Ergosterol. **C. E. Bills, E. M. Honeywell and W. M. Cox, Jr.** (*J. Biol. Chem.*, 1931, **92**, 601–604.)—Previously described biological and spectrographic measurements made on alcoholic solutions of ergosterol after different periods of irradiation have shown that the quantity of vitamin D in the photochemical reaction product rapidly rises to a maximum and gradually declines to zero. The spectrographic changes are no measure of anti-rachitic potency, and thus, to gain knowledge of the rise and decline of potency, it is usually necessary to prepare an activation curve. The authors have investigated the influence of solvents on the activation of ergosterol, with the use of cyclohexane and ether in comparison with alcohol. At least 100 rats were used for each activation curve, so that the probable error for the curves was only ± 4 per cent. The three curves, which are given, had the same general shape, but widely different dimensions. Of the three solvents, ether permitted by far the greatest activation. With alcohol, the maximum cod-liver oil coefficient was reached in the shortest time, 22·5 minutes, but the maximum

was the lowest (250,000), and the decline in potency was the most rapid. After 3 hours and 18 minutes all antirachitic activity disappeared. With cyclohexane, the maximum was reached in 27 minutes, but the maximum was somewhat higher (330,000). The decline was much more gradual; the reaction product showed a cod-liver oil coefficient of 25,000 even after 14 hours of exposure. With ether the maximum was reached in 4 hours, 12 minutes, but the maximum was by far the highest (710,000). The decline in potency was relatively more rapid than with cyclohexane, yet even after 18 hours of exposure the reaction product showed a cod-liver oil coefficient of 25,000. In ether the attainment of maximum potency required an hour more of exposure than was required in alcohol for the entire cycle of rise and decline. The authors have no satisfactory explanation of the observed influence of solvents on activation. The three solvents used are transparent to the short wave-length side of the ergosterol absorption curve, and each, when pure, transmits a high percentage of radiations between $230\mu\mu$ and the visible region, and hence might be expected to give similar results under similar conditions of exposure. One might presume that the different solvents had different protective, anti-oxidative actions. P. H. P.

Experiments on Nutrition. X. Comparative Vitamin B_1 Values of Foodstuffs. Cereals II. R. H. A. Plimmer, W. H. Raymond and J. Lowndes. (*Biochem. J.*, 1931, **25**, 691–704.)—In previous experiments by Plimmer, Rosedale, Raymond, and Lowndes (*Biochem. J.*, 1927, **21**, 114) on the testing of cereals for their vitamin B (B_1) value, rearing of young by pairs of adult pigeons was taken as the standard of comparison. It was shown that a greater amount of foodstuff containing vitamin B was needed for rearing than for maintenance, and this fact has been again observed in subsequent experiments. Therefore the standard of maintenance for a period of at least 26 weeks was adopted with satisfactory results by Plimmer, Raymond and Lowndes (*Biochem. J.*, 1929, **23**, 546) in their trials with pulses and nuts. In order to bring cereals into proper comparison it was necessary to test them again on this standard, and the results obtained are given. Some experiments were also made on the extraction of vitamin B from wheat germ, and marmite was again tested for comparison with the cereals, and for ascertaining if its value is the same after a period of 5 or 6 years. There is no essential change in the vitamin B value of marmite in a period of 6 years; it may lose in value if kept for long periods, but freshly manufactured marmite seems always to have approximately the same value. The term "vitamin B" is now used to include several unknown factors. In the tests the symptoms of head retraction of pigeons were taken as the sign of insufficient vitamin B, *i.e.* vitamin B_1 in the modern nomenclature. With the use of the same standard of comparison as in the work on pulses and nuts, the comparative vitamin B values of cereals, etc., are as follows:

	Percentage amount in diet for maintenance.	Comparative vitamin B value.
Dried yeast	4	100
Marmite	6	67

				Percentage amount in diet for maintenance.	Comparative vitamin B value.
Wheat germ ("bemax")	..			6–7	62
Middlings	..	..	..	10	40
Baker's yeast		..	..	12	33
Bran	..	..	..	20	20
Buckwheat	..	..	..	20	20
Millet ..	..	..	..	30	13
Oatmeal	..	..	..	35	11
Wheat	..	..	..	40	10
Barley	..	..	..	40	10
Malt	..	..	..	40	10
Rye ..	..	..	..	40	10
Dari ..	..	..	..	40	10
Brown rice	..	..	..	40	10

Cereals are thus not quite so rich in vitamin B as pulses, which have a comparative value of 13.

P. H. P.

Investigations on Vitamin B_2. I. Sources of Vitamin B_2. II. Stability of Vitamin B_2. III. Chemistry of Vitamin B_2. B. C. Guha. (*Biochem. J.*, 1931, 25, 945–959.)—The values as sources of vitamin B_2 have been investigated of milk powder and aqueous extracts of brewer's yeast, baker's yeast, fresh ox-liver, beef muscle and Eli Lilly's liver concentrate No. 343. The fresh ox-liver extract is apparently the most potent of those. An aqueous extract (20 per cent.) of the liver concentrate is also very potent, being effective in a daily dose of 40 to 60 mgrms. for the growth of young rats. The advantages of this liver concentrate over yeast as a source of vitamin B_2 are pointed out; it can be readily prepared from a stock of the solid liver concentrate whenever required. The stability of vitamin B_2 preparations obtained from different sources towards heat and alkali shows curious discrepancies. The vitamin B_2 in aqueous extracts of yeast and fresh ox-liver is much less stable than that in marmite and in the commercial liver concentrate. Probably the stability of certain preparations is connected with the presence of some kind of protective material in them. An aqueous extract of the liver concentrate, autoclaved at pH 9 for half an hour at 124 to 125° C., provides an excellent source of vitamin B_2 free from vitamin B_1; it is preferable to autoclaved marmite, for it contains less solid matter and is more palatable to the rats. A chemical study of vitamin B_2 in a cold aqueous extract of the liver concentrate has been made. Picric acid, benzoyl chloride, phosphotungstic acid and flavianic acid do not precipitate the vitamin. Nitrous acid neither precipitates nor inactivates it. Lead acetate and silver nitrate precipitate it partially. Esterification leaves about 40 per cent. of the vitamin in the non-esterified fraction; the esterified fraction is inactive. It is not attacked by trypsin. Norit charcoal adsorbs the vitamin at the normal pH (4·6) of the aqueous extract of the liver concentrate; it was not possible to elute it effectively by aqueous alcohol, 30 per cent. propyl alcohol or dilute saponin solution. The possibility of a relationship between vitamin B_2 and the factor in liver specific for pernicious anaemia is discussed; the chemical behaviour of the vitamin, however, is in contrast to that of

the factor for pernicious anaemia. On the basis of the present evidence it may be provisionally concluded that the vitamin is probably not a base, acid or peptide, but a neutral substance. Preliminary experiments on the electro-dialysis of the vitamin support this tentative conclusion. The partial precipitation by lead acetate and silver nitrate is probably due to the adsorption of the vitamin on the precipitates formed. The vitamin is stable to sulphur dioxide, hydrogen peroxide and ozone. Some of the rats which were maintained at a weight between 60 and 80 grms. over periods of 12 weeks or so, and were not undergoing a drastic deprivation of vitamin B_2, developed a curious form of depilation, which was cured by administration of the liver-extract. Haemin, haemoglobin and lactalbumin could not ameliorate the above symptoms or produce growth in absence of vitamin B_2. P. H. P.

Quantitative Method for Determination of Vitamin C. K. M. Key and G. K. Elphick. (*Biochem. J.*, 1931, **25**, 888–897.)—A method is described for the determination of the antiscorbutic potency of a substance in terms of the potency of a standard such as lemon juice or orange juice. Different doses of orange juice were given to a series of guinea-pigs and the amount of protection from scurvy produced in each animal was determined by means of an arbitrary scale. The test on the animals was continued for 14 days, when the growth response, *post-mortem* observations and structure of the roots of the incisors were examined, but the method finally used was based solely on the histological appearance of the roots of the incisors. A curve was constructed relating the average amount of protection afforded to the dose of orange juice given. A straight line was obtained, and this was used as a curve of reference for evaluating results on an unknown substance. Some disadvantages of the use of decitrated lemon juice as a standard are pointed out. Evidence is given which suggests that the anti-scorbutic potency of orange juice is constant, and orange juice is palatable to guinea-pigs and can be given to them directly without previous treatment. The method gives results more accurate than those obtained from the minimum protective dose method, and is useful for determinations of the antiscorbutic potency of substances containing little vitamin C. Satisfactory results, which were obtained in experiments on Bramley's Seedling apples and tomato juice of unknown strength, are recorded.
P. H. P.

Influence of the Ration of the Cow upon Vitamin B and Vitamin G Content of Milk. C. H. Hunt and W. E. Krauss. (*J. Biol. Chem.*, 1931, **92**, 631–638.)—It was shown by Hunt and Krauss (*J. Biol. Chem.*, 1928, **79**, 733; ANALYST, 1928, **53**, 668) that milk contains a relatively large amount of vitamin G (B_2), whilst the amount of vitamin B (B_1) is small. Sherman and Axtmayer (*J. Biol. Chem.*, 1927, **75**, 207; ANALYST, 1927, **52**, 721) found that dried skim milk was apparently richer in vitamin G than in vitamin B. Aykroyd and Roscoe (*Biochem. J.*, 1929, **23**, 483) made the observation that milk was a poorer source of the antineuritic vitamin than of the antipellagric factor. In view of these observations it was decided to study the influence of the ration of the cow upon the

relative potency of milk in these two known factors of the vitamin *B* complex. The milk was tested on rats. Two experiments were carried out: (1) A comparison of pasture grass with dry feed as to their effect on the vitamin *B* and vitamin *G* content of milk; (2) the influence of the stages of maturity of pasture grasses upon the vitamin *B* and vitamin *G* content of milk. The vitamin *B* and vitamin *G* content of the pasture grasses was also investigated. The results show that milk from cows on pasture has a higher vitamin *G* content than milk from cows on dry feed, although the quality of the hay used in dry feeding may be a determining factor. The vitamin *B* content of the milk is not so affected. Cows on early pasture during its vigorous state of growth produce milk higher in vitamin *G* than do cows on an over-mature pasture. Whilst the vitamin *B* content is not so easily affected, there are slight indications that fresh tender grass produces a milk higher in vitamin *B* than does over-mature pasture grass. It appears that vitamin *G* is synthesised during the process of rapid growth, and then is dissipated as the plant matures. On this basis the highest quality of hay would be produced by cutting it while the plant is still immature, and this appears to be in keeping with practical observations and feeding results.   P. H. P.—

Organic Analysis.

Determination of Small Proportions of Hydrocarbon in Alcohol containing Acetone. R. W. Hoff. (*J. Soc. Chem. Ind.*, 1931, **50**, 242–244T.)— Since most of the grades of alcohol containing hydrocarbons now legalised by the Canadian Government are denatured with wood spirit (*e.g.* "Specially Denatured Alcohol" or "Grade No. 1 Benzine," and "Fully Denatured Alcohol" or "Grade No. 2 Benzol") the method proposed by Babington and Tingle (ANALYST, 1919, **44**, 297), which fails in the presence of acetone, cannot be used. The acetone is therefore converted into a non-volatile compound as follows:—(1) A freshly-prepared amalgam, made by immersing 5 grms. of pieces of aluminium sheet in a saturated solution of mercuric chloride, is lightly washed with water and warmed in a 500 c.c.-Kjeldahl flask with 100 c.c. each of the sample and of 2 *N* potassium hydroxide solution for 1 hour on the water-bath under a reflux condenser (minimum length 2 feet). The mixture is then cooled, the condenser rinsed with 20 c.c. of 90 per cent. alcohol, and then with 200 c.c. of water, and the liquid is distilled at the rate of 1 c.c. per minute through a vertical condenser. The hydrocarbon distillate is collected in two 20 c.c. portions in 50 c.c. stoppered ("Eggertz") tubes graduated to 0·1 c.c., 15 c.c. of a 1/6-saturated potassium dichromate solution and 2 c.c. of hydrochloric acid (sp. gr. 1·2) added in each case, and the whole mixed. After about 15 minutes, when the mixture is olive-green in colour, exactly 10 c.c. of petroleum spirit of low b. pt. are added, and the volume of the petroleum layer read after mixing. If the tube is inverted, any greasiness produced in it during the distillation is avoided. The volume of hydrocarbon is obtained by deducting 10 c.c. from the reading, 0·1 c.c. or less being found in the second fraction. In the case of "petroleum benzine" containing 0·5 to 1·5 grm. of acetone per 100 c.c., the

only error recorded was −0·05 per cent. of hydrocarbon (1 to 2 per cent. present). Solvent naphtha from coal tar, however, gives high results, owing to the greater solvent action for dilute alcohol of the higher benzene hydrocarbons. The factor 0·95 then gives results with a maximum error of 0·09 per cent. (2) When the continuous evolution of hydrogen is liable to cause loss of volatile hydrocarbons, the sample (100 c.c.) is freed from pine oil (e.g. by distillation) and mixed with more hydroxylamine hydrochloride (e.g. 2 grms.) than will combine with the acetone present, and with sufficient potassium hydroxide solution to give a permanent pink colour with phenolphthalein. The mixture is diluted to 400 c.c., distilled, and 40 c.c. of the distillate collected and treated as in (1). The maximum error is +0·05 per cent. of benzene (2 to 2·5 per cent. present). The methods (subject to criticism) are to be adopted for fiscal purposes in Canada.   J. G.

Determination of Small Proportions of Butyl Chloride and Diethyl Phthalate together in Ethyl Alcohol. R. W. Hoff (*J. Soc. Chem. Ind.*, 1931,. **50**, 244T.)—The new Canadian Government "Specially Denatured Alcohol, No. 1-F" (Rubbing Alcohol), contains butyl chloride, diethyl phthalate (0·98 c.c. of each per 100 c.c.), brucine sulphate and quassin as denaturants, the solids being present in amounts insufficient to affect the analytical results if the following procedure is used:—One hundred c.c. are distilled from a 500 c.c. Kjeldahl flask at 3 c.c. per minute through a vertical condenser into a similar flask. The first 70 c.c. contains the butyl chloride, which is determined, after dilution to 400 c.c., by the method proposed for benzene in ethyl alcohol by Babington and Tingle (ANALYST, 1919, **44**, 297). The diethyl phthalate is determined by hydrolysis of the residue by heating on the water-bath under a reflux condenser for 1 hour with 50 c.c. of 0·5 N alcoholic potassium hydroxide solution (*i.e.* an excess equivalent to more than twice the amount of ester probably present). The liquid is cooled, diluted and back-titrated with 0·5 N sulphuric acid in the presence of phenolphthalein, allowance being made for any blank on the reagents. If 1·126 is the sp. gr. of the phthalate at room-temperature, the volume present is given by (c.c. of 0·5 N alkali used × 0·0555/1·126). The results obtained are accurate to within about 0·01 c.c. for the phthalate and 0·07 for butyl chloride (per 100 c.c.).
          J. G.

Reduction of Aromatic Ketones and Benzils by Triphenylmagnesium Bromide. W E. Bachmann. (*J. Amer. Chem. Soc.*, 1931, **53**, 2758–2763.)—The Grignard reagent, triphenylmagnesium bromide, reduces aromatic ketones such as benzophenone, 4-chlorobenzophenone, 4-phenylbenzophenone, 4.4-di-phenylbenzophenone, fluorenone, and xanthone, to pinacols. The reaction proceeds through the intermediate formation of radicals, according to the equation: $RRC{=}O + (C_6H_5)_3CMgBr \rightarrow RRC{-}OMgBr + (C_6H_5)_3C$. The ketyl radicals then associate to the pinacolate: $2RRC{-}OMgBr \rightleftharpoons RRC(OMgBr)(OMgBr)CRR$. Benzils are reduced by the reagent to the bromo-magnesium salt of stilbene-diols: $RCOCOR + 2(C_6H_5)_3CMgBr \rightarrow RC(OMgBr){=}(OMGBr)CR + 2(C_6H_5)_3C$.
          W. P. S.

Anhydrous Distillation Method for the Determination of Mercury in Organic Compounds. E. P. Fenimore and E. C. Wagner. (*J. Amer. Chem. Soc.*, 1931, **53**, 2468–2475.)—A method for the determination of mercury in such compounds as diacetatomercuriphenol, mercury *p*-ditolyl, *n*-butyl mercury mercaptide, mercuric cyanide, etc., consists in decomposing the compound with concentrated sulphuric acid and ammonium or potassium persulphate, distilling the mercury as mercuric chloride in a current of hydrogen chloride, precipitating the metal as zinc mercuric thiocyanate and subsequently determining it iodimetrically. In the presence of iodine, the mercury in the distillate must first be precipitated with zinc-dust, the excess zinc dissolved in hydrochloric acid, the residual amalgam dissolved, and the mercury determined by the iodate method. The presence of chlorine or bromine does not interfere. W. P. S.

Copper Determination in Organic Matter. S. Ansbacher, R. E. Remington and F. B. Culp. (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 314–317.)— A critical and very detailed study has been made of methods for determining very minute amounts of copper in organic materials generally, *e.g.* milk, fruit, vegetables, oysters, etc. After destruction of the organic matter by wet or dry oxidation depending on the bulk of the sample, precipitation of the copper by hydrogen sulphide in the presence of co-precipitated sulphur under controlled conditions of acidity has been found the most suitable method for separating the smallest traces of copper from other elements, *e.g.* iron, interfering with the final determination, for which a choice of four tested methods is given. *Destruction of Organic Matter. Wet digestion.*—To a small sample, moistened with water, in a Kjeldahl flask, are added 15 c.c. of concentrated sulphuric acid, and the whole heated until the residue becomes black and sulphur trioxide is evolved. After cooling, 5 c.c. of dilute perchloric acid (20 per cent.) and 2 c.c. of nitric acid are added, and the flask again heated until sulphur trioxide fumes are evolved and the liquid is colourless, more nitric and perchloric acids being added, if necessary, and the heating repeated. *Ashing of the sample.*—Larger samples are ashed in a silica dish in an electric muffle at a temperature not exceeding 400° C., followed by evaporation of the residue to dryness with fuming nitric acid; the product is dissolved in 10 c.c. of concentrated sulphuric acid. *Precipitation of the copper as sulphide and its re-solution.*—The acid liquid is transferred to an Erlenmeyer flask, diluted to give an acid concentration of 15 per cent. by volume, and heated to boiling; a few drops of nitric acid are added and hydrogen sulphide passed through the solution until cold. After the precipitate has settled it is filtered off on a small crucible with a porous bottom, washed with very dilute acetic acid saturated with hydrogen sulphide and finally dissolved in fuming nitric acid; this solution is evaporated to dryness (care being taken not to decompose the copper nitrate), and the residue is dissolved in water, giving a neutral solution containing the copper in the sample. *Determination by Xanthate reagent.*—An aliquot part of the solution is transferred to a Nessler tube containing 10 c.c. of potassium ethyl xanthate solution (0·1 per cent.) and water. To a similar tube containing the same quantity of reagent and

water, standard copper solution (about 50γ of copper per c.c.; $1\gamma=0\cdot001$ mgrm.) is added until an approximate match is obtained after the contents of the tubes have been diluted to the same volume with water. The true amount of copper is obtained by preparing six colour standards containing different amounts of copper very close to the amount indicated, and choosing the one nearest in colour to the unknown. The most reliable results are obtained when from 100γ to 200γ of copper are present in the solutions compared. (This method is a modification of Supplee and Bellis's process for copper in milk, *J. Dairy Sci.*, 1922, 5, 455). *Determination of copper with the "Biazzo" reagent.*—An aliquot part of the solution is transferred to a 25 c.c. separating funnel, and into another funnel is run an approximately equivalent amount of standard copper solution (judged from the appearance of the original copper sulphide precipitate). To each of the funnels are added about 10 c.c. of water, 25 drops of glacial acetic acid, 30 drops of pyridine, 3 c.c. of potassium thiocyanate solution (10 per cent.), and 2 c.c. of bromobenzene (b.pt., 154–155° C.), and the mixture is well shaken. Some of the bromobenzene layer is drawn off and the depths of the two colours compared in a colorimeter. This method works best with 50 to 150γ of copper (Note by Abstractor, *cf.* Chalk, ANALYST, 1930, 55, 187). *Determination of Copper by Carbamate reagent.*—The directions are the same as for the xanthate method, this reagent being replaced by 10 c.c. of sodium diethyldithiocarbamate solution (0·1 per cent.) (*cf.* Callan and Henderson, ANALYST, 1929, 54, 650). A fourth alternative given is a titrimetric method employing "nitroso chromotropic acid" (1, 8-dihydroxy-2-nitroso-3, 6-naphthalene disulphonic acid), for details of which, and the preparation and standardisation of the reagent, the original memoir should be consulted. (*Cf.* Cherbulier and Ansbacher, *Helv. Chim. Acta*, 1930, 13, 187). Good results were obtained by each of the different methods of finishing the determination.

<div align="right">S. G. C.</div>

Determination of Sodium in Organic Compounds by the Uranyl Acetate Method. D. L. Tabern and E. F. Shelberg. (*Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 278–279.)—The paper is concerned with the application of the now well-known uranyl acetate precipitation method to the analysis of sodium salts of organic acids, the determination of sodium in some of which, more particularly barbiturates, *e.g.* "Nembutal" [sodium ethyl-(1-methylbutyl) barbituric acid], "sodium Neonal" (sodium ethyl-*n*-butyl barbituric acid), and "sodium Amytal" (sodium ethyl-*iso*-amyl barbituric acid) gave inexplicably low results by the ordinary sodium sulphate method. The following process is given:—To 0·1 grm. (containing from 5 to 20 mgrms. of sodium), dissolved in 5 to 10 c.c. of water or alcohol, are added 3 c.c. of reagent for each mgrm. of sodium expected [reagent: uranyl acetate 33 grm.; magnesium acetate, 100 grm.; acetic acid, 20 c.c.; alcohol (90 per cent.), 500 c.c.; water, to make 1000 c.c.; filtered at 20° C. before use]. The beaker is placed in ice-water for half-an-hour with occasional stirring of the liquid, the precipitate is filtered off on a Gooch crucible, washed with 5 to 10 c.c. of the reagent, and finally with alcohol (95 per cent.), and dried at 105° C.; 1 grm. of the precipitate is equivalent to 0·0153 grm. of sodium. The results obtained with a

number of sodium salts of various organic acids compared well with the theoretical values and with those obtained with a special electrometric titration method.

S. G. C.

Irregularities in Sodium Determination by Sodium Sulphate Method (in Organic Compounds). G. W. Collins. (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 291.)—The determination of sodium in the sodium salts of certain barbituric acids by the direct sulphate method gives low results (*cf.* preceding abstract). Sodium can be determined accurately in these compounds if the aqueous solution of the sample is acidified and the organic radicle is removed by extraction with ether before the evaporation with sulphuric acid. It is concluded that the direct sulphate method gives low results in the presence of the five-carbon side-chain of malonyl urea; no definite explanation of this is put forward. S. G. C.

Determination of Silica in Vegetable Substances by Mixed Nitric and Perchloric Acids. L. Lematte, G. Boinot, E. Kahane and M. Kahane. (*Compt. rend.*, 1931, **192**, 1459–1462.)—Organic matter can be conveniently destroyed by heating with a mixture of nitric and perchloric acids, and the silica is left in an insoluble form. The following method has been found suitable for cereals, straw, bran, pine-needles, and sawdust:—A mixture of 20 c.c. of fuming nitric acid (sp. gr. 1·49) and 30 c.c. of perchloric acid (sp. gr. 1·61) is poured on to 5·0 grms. of the sample contained in a 500 c.c. *beaker*. The oxidising action generally starts in the cold, but the mixture may be heated from the start, care being taken to prevent too abundant frothing. When the nitric acid has been dispelled, as shown by the appearance of white fumes, the heating is continued for 30 minutes (the beaker being covered). After cooling, about 100 c.c. of water are added, the liquid is boiled, and the silica filtered off, calcined and weighed. The table of results shows interesting differences between the silica contents of different kinds of straw, etc. S. G. C.

Note.—The use of a beaker is emphasised because there is a risk of explosion if a flask is used.—EDITOR.

Inorganic Analysis.

Diphenylaminesulphonic Acid as an Indicator. L. A. Sarver and I. M. Kolthoff. (*J. Amer. Chem. Soc.*, 1931, **53**, 2902–2905, 2906–2909.)—The properties of diphenylaminesulphonic acid are similar to those of diphenylamine, but it gives a much sharper end-point, as the introduction of the sulphonic group increases the solubility. The new indicator, unlike the base, can be used in the presence of tungstate; its oxidation is very much accelerated by ferrous ion. It is used in the form of its barium salt (3·17 grms. in 1000 c.c. of water). A comparative study of the indicators diphenylamine, diphenylbenzidine, and diphenylaminesulphonic acid was made in the determination of ferrous iron by means of dichromate, and of dichromate and vanadate by means of ferrous sulphate. The very small corrections required to allow for the amount of indicator added are tabulated. Preference is given to diphenylaminesulphonic acid on account of

its rapid, brilliant, and reversible colour changes, which are unaffected by tungstate. This property is of importance in connection with the analysis of alloy steels.

W. R. S.

Inaccuracy in the Determination of Mercury by Direct Precipitation as Mercury Sulphide from Acid Solution. E. P. Fenimore and E. C. Wagner. (*J. Amer. Chem. Soc.*, 1931, **53**, 2453–2456.)—Direct precipitation of mercury from an acid solution by means of hydrogen sulphide yields an impure precipitate and the results obtained are too high. Under the most favourable conditions the error may be 0·34 per cent., and this error is increased by the presence of salts in the solution, particularly by the presence of iodides. Volhard's method is accurate with solutions containing little else than mercury, but in the presence of salts it also gives results which are too high. W. P. S.
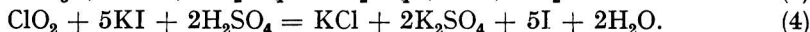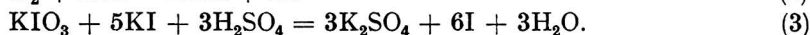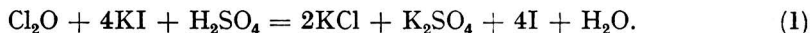
Quantitative Separation of Copper and Cadmium by Reduction with Potassium Formate. E. I. Fulmer. (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 257–258.)—On evaporation of a solution containing copper sulphate and cadmium sulphate (2 grms.) and potassium formate (15 grms.) to dryness and heating the residue at 155° to 160° C. for $1\frac{1}{2}$ hours, the copper is liberated as metal, and the cadmium remains in a form which can be dissolved in water. In a test of the process, good results for copper were obtained by filtering the aqueous extract of the residue and weighing the copper remaining as metal; the results for cadmium are not stated. S. G. C.

Volumetric Determination of Chromium and Nickel in the Same Solution. L. H. James. (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 258.)—The method depends on the discovery by Willard and Cake (*J. Ind. Eng. Chem.*, 1919, **11**, 480) that boiling perchloric acid oxidises tervalent chromium to the sexavalent state, which can be titrated by ferrous sulphate in the diluted solution; nickel can then be titrated in the same solution by the well-known Moore cyanide method. *Method for "Chrome-Nickel" and Stainless Steel.*—To 1 grm. of "chrome-nickel" or 0·2 grm. of stainless steel contained in a tall 500 c.c. beaker are added 20 c.c. of an acid mixture containing 250 c.c. of nitric acid (sp. gr. 1·42), 750 c.c. of hydrochloric acid (sp. gr. 1·19) and 1000 c.c. of water; after heating until the material is dissolved, 20 c.c. of perchloric acid (20 per cent.) are added. The solution is boiled until white fumes are given off, and then 10 minutes longer. After cooling, 100 c.c. of water are added, the liquid is boiled for 2 minutes and again cooled. Twenty-five c.c. of dilute sulphuric acid (sp. gr. 1·22) and an excess of 0·1 N ferrous sulphate solution are added, and the unused ferrous sulphate titrated with 0·1 N potassium permanganate solution. The nickel is then determined by the Moore cyanide titration method. The method needs modification for dealing with nickel-chromium iron containing an appreciable percentage of silicon; after the boiling with perchloric acid, which should in this case be continued for 20 minutes, 50 c.c. of water are added after cooling, the silica is filtered off and washed with dilute perchloric acid (1 per cent.). Chromium and nickel are then determined in the filtrate as described above. S. G. C.

Analysis of Mixtures of Chlorine Monoxide and Chlorine. J. W. T. Spinks. (*J. Amer. Chem. Soc.*, 1931, **53**, 3015–3016.)—The gas is absorbed in potassium iodide solution, after which the solution is acidified with a known excess of standard acid, and titrated with thiosulphate. This gives the iodine equivalent of chlorine and the monoxide according to equations (1) and (2):

$$Cl_2O + 4KI + H_2SO_4 = 2KCl + K_2SO_4 + 4I + H_2O. \qquad (1)$$
$$Cl_2 + 2KI = 2KCl + 2I. \qquad (2)$$
$$KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 6I + 3H_2O. \qquad (3)$$
$$ClO_2 + 5KI + 2H_2SO_4 = KCl + 2K_2SO_4 + 5I + 2H_2O. \qquad (4)$$

The excess acid over that equivalent to the monoxide according to (1) is then ascertained by reaction (3) after addition of a slight excess of standard iodate solution. Hence the standard acid can be standardised iodimetrically against the same thiosulphate solution. Mixtures of chlorine peroxide and chlorine can be analysed by means of the above method, equation (4) giving the necessary stoichiometric data.   W. R. S.

Iodimetric Titration of Iodide and Nitrite. C. A. Abeledo and I. M. Kolthoff. (*J. Amer. Chem. Soc.*, 1931, **53**, 2893–2897.)—The reaction $HNO_2 + HI = H_2O + NO + I$ occurs only in acid medium. In the presence of oxygen the nitric oxide is oxidised to nitrogen dioxide, which partly reacts with water, forming nitrous and nitric acids. The conditions for applying the reaction to the accurate determination of iodide and nitrite were ascertained. *Iodide.*—The solution is treated in a glass-stoppered flask with about 1 grm. of urea (to remove nitrous acid and nitric oxide), 5 c.c. of 0·5 *N* sodium nitrite, and 5 c.c. of 4 *N* sulphuric acid, and the flask then stoppered and frequently shaken during 10 minutes. After addition of 1 to 2 grms. of potassium iodide, the solution is titrated with thiosulphate. For very small amounts of iodide, the additions are 0·5 grm. of urea, 1 c.c. of 0·2 *N* nitrite solution, 5 c.c. of chloroform, and 5 c.c. of 4 *N* acid; the stoppered flask is left for 30 minutes before the addition of the iodide and titration. Chlorides do not interfere; if the bromide present exceeds the equivalent of the iodide, results are high. *Nitrite.*—The solution is run into a glass-stoppered flask containing 10 to 12 grms. of sodium bicarbonate, 3 grms. of potassium iodide, 0·5 to 1 c.c. of amyl alcohol (to prevent foaming), and 25 c.c. of water; the ingredients are thoroughly mixed, after which 4 c.c. of glacial acetic acid are distributed, without agitation, through the solution from a pipette. The stopper is loosely inserted, and the flask gently rotated after the evolution of carbon dioxide has nearly ceased. When the bicarbonate has again settled, 6 to 7 c.c. of 20 *N* sulphuric acid are quickly added, and the stopper inserted as before. When most of the gas has escaped the flask is shaken, the stopper rinsed, and the solution titrated with thiosulphate. If in either determination there is a return of the starch-iodine colour, the operation should be repeated.   W. R. S.

Determination of Fluorine. P. Mougnard. (*Compt. rend.*, 1931, **192**, 1733–1735.)—Two modifications of the calcium fluoride method for the determination

of fluorine have been studied—(a) Rose's method, in which some calcium carbonate is made to precipitate with the calcium fluoride, and (b) Carrière and Rouanet's method (*Compt. rend.*, 1929, **189**, 1281), in which precipitation of calcium fluoride in boiling ammoniacal solution is employed. The subsequent removal of the calcium carbonate from the precipitate in (a), by treatment with acetic acid, is uncertain; some calcium acetate is retained in it, and the precipitate slowly loses weight during ignition, owing to decomposition of the calcium acetate. Pure calcium fluoride remained unchanged on ignition at 800° C. for two hours. Loss of hydrofluoric acid is liable to occur in Rose's method by the action of the acetic acid during the removal of the calcium carbonate from the calcium fluoride. Method (b) suffers from the disadvantage that calcium fluoride becomes contaminated, during the precipitation, with calcium carbonate formed by the boiling ammoniacal solution absorbing carbon dioxide.

The solubility in water of (a) precipitated calcium fluoride dried at 100° C. is 18·3 mgrms. at 18° C., and that of (b) calcined calcium fluoride is 15·1 mgrms. (the volume of water used, not stated, is presumably 1 litre). The values for the solubility of calcium fluoride (not calcined) in various solutions (in mgrms. per litre, temperature not stated) are as follows:—In acetic acid, 30·8 (0·083 N), 38·3 (0·166 N), 40·7 (0·333 N), 49·8 (0·833 N), 58·6 (1·66 N); in ammonium chloride, 20·8 (0·25 N), 25·8 (0·5 N), 27·8 (N), 27·8 (1·66 N); in ammonium acetate, 20·3 (0·333 N), 21·9 (0·71 N), 34·5 (1·42 N), 25·5 (1·66 N); in ammonia, 17·6 (N), 17·5 (1·66 N).

S. G. C.

Microchemical.

Micro-crystallographic Identification of Barbituric Alkaloids. G. Denigès. (*Mikrochem.*, 1931, **9**, 316–323.)—The microscopic appearance of the crystals of veronal, soneryl, rutonal, luminal, dial, allyl-*iso*-propyl malonylurate, and allonal are described with the aid of drawings. A fraction of a milligram of the alkaloid is taken for the tests, and is dissolved on a slide in a small drop of ammonia, and then precipitated by a drop of dilute sulphuric acid (1:10 by volume). The crystals are examined with a magnification of about 60 diameters; those of veronal consist of rectangular plates, isolated or in groups, and those of soneryl consist of long needles generally radiating from a centre. Rutonal has characteristic isolated, regular hexagonal plates, or groups of crystals, with the appearance of foliage. Luminal gives crystals in the form of rosettes. Dial gives hexagonal plates, often with sides of irregular length, and groups of rhomboids. Allyl-*iso*-propyl malonylurate gives elongated hexagonal plates, or small rhomboids, and allonal, which is a compound of the preceding alkaloid with pyramidon, is identified by the formation of the allyl-*iso*-propyl malonylurate crystals, whilst the pyramidon part of the molecule is identified by the crystals formed with picric acid, which are yellow elongated prisms, radiating more or less regularly from a centre. The only two crystal formations which might be confused are those of dial and rutonal. These are differentiated by adding a drop of a 2 per cent. solution of sulphuric acid, and

heating gently on a slide. The phenyl substituted alkaloids, such as rutonal and luminal, give an intense brown coloration and yield a precipitate on dilution with cold water. The non-phenyl group gives a slight red-brown colour, with no formation of a precipitate on adding cold water.   J. W. B.

Determination of Solubility Number: Micro Method for Measuring the Extent to which a Cellulosic Material has been Chemically Modified or Degraded. C. R. Nodder. (*J. Text. Inst.*, 1931, **22**, T416, T424.)—For detecting chemical attack of cellulosic materials, the cuprammonium viscosity method is considerably more sensitive and reliable than the solubility number method in the initial stages of the attack, that is, when the solubility number is less than about 5 for linen goods (log. of the viscosity of 2 per cent. solution less than 1) or less than 2 or 3 for cotton goods (log. viscosity less than about 0·5). For general purposes, however, especially with linen goods, the solubility number method is highly suitable and is decidedly the more simple. The method now described, using 0·1 grm. (or less, if necessary) of material, has been employed for some years as a routine test for the examination of defective materials, for control purposes at the bleach-green, and for purposes of general research.

The material is first boiled for 6 hours in 2 per cent. sodium hydroxide solution under a reflux condenser, in order to remove non-cellulosic impurities and cellulose degradation products soluble in the dilute alkali. It is next washed free from alkali, carefully dried, and cut into fine shreds. With a cloth, Birtwell, Clibbens and Geake's method is satisfactory (ANALYST, 1928, **53**, 672). Thus, it is often convenient to cut about 10 strips of the cloth, $1 \times \frac{1}{4}$ inch, parallel to the warp or weft, and to cut, from these, very thin shreds (not more than 1 mm. wide) at an angle of 45° to warp and weft. The shreds are then broken down to a powder between finger and thumb. With yarn, short lengths (less than 1 mm.) are cut from the ends of a small bundle. The air-dry powder (exactly 0·1 grm.) is weighed into a test-tube (conveniently $5 \times \frac{5}{8}$ inch), having a ground-in glass stopper. The powder is tapped into the bottom of the tube and 1 c.c. of 10 N sodium hydroxide is added in drops distributed as evenly as possible; uniform wetting may be promoted by tapping the tube smartly with the finger-tips, but, if wetting is difficult, stirring with a thin glass rod is advisable. As soon as possible the tube is immersed in a water-bath at 15° C. (vacuum flasks are satisfactory), and after 15 minutes 4 c.c. of water are added to dilute the alkali to 2 N strength. The tube is left at 15° C., with occasional shaking, for the further period of an hour. For filtering the solution a small fritted glass filter (Schott and Co.'s 30aG3), cut down to within 2 mm. of the disc, is used. This filter is attached to the lower end of a 2 c.c. pipette with thick-walled rubber tubing and immersed in the contents of the tube. The pipette is filled by gentle suction from the water-pump, and the filtered solution (2 c.c.) is run into a 100 c.c. flask and treated with 10 c.c. of 0·5 N potassium dichromate solution containing 230 c.c. of concentrated sulphuric acid per litre. The flask is closed with a glass-pear stopper and *immersed* for one hour in a vigorously boiling water-bath, being shaken occasionally. The contents of the flask

are then cooled and titrated with $0 \cdot 1$ N ferrous ammonium sulphate solution, with potassium ferricyanide as external indicator. If 10 c.c. of the $0 \cdot 5$ N acid dichromate solution require a, and the contents of the flask b, c.c. of $0 \cdot 1$ N ferrous ammonium sulphate, the solubility number $= 1 \cdot 688$ $(a - b)$. This result may be corrected for the moisture content of the air-dry material, if thought desirable.

If carefully bleached to a full white by normal processes, a linen damask or sheeting has a solubility number of about 6; a value above 8 is highly undesirable as regards resistance to wear, and a value greater than 10 definitely indicates unsatisfactory bleaching. The maximum desirable solubility number for bleached yarns depends on the counts and quality of the yarn, the degree of bleaching, and the nature of its treatment after weaving, as well as on the use for which the material is intended. In general, the normal value for a yarn of 35's leas bleached "three-quarter white" may be taken as 7, although a value not exceeding 4 is obtainable. With less advanced bleaching or finer yarn, a lower solubility number is desirable, whilst with coarser yarn a somewhat higher number is permissible. With bleached damasks the loss in weight in repeated washes, which has proved a reliable guide to the wearing qualities, is proportional roughly to the square root of the solubility number (S) or, more nearly, to $S^{0 \cdot 53}$.

In almost every case the test will show if damage or tendering is the result of chemical attack or of some other action, *i.e.* mechanical or that of micro-organisms. With damaged damasks, sheetings, towellings, etc., which have been repeatedly laundered, comparison of the solubility number of the sewing thread in the hem with that of the cloth will usually show whether general chemical damage was caused in bleaching or in laundering. Further, comparison of the solubility number of the general cloth (or warp and weft separately) with that of the selvedge threads (commonly cotton) will often indicate whether the yarn bleacher or the piece bleacher was responsible for the over-bleaching of materials woven from partly bleached yarns and bleached further in the piece.   T. H. P.

The Alkaline Earth Metals. Methods of Qualitative and Quantitative Micro-analysis. K. Heller and Z. Stary. (*Mikrochem.*, 1931, 9, 451–520.)— A description with full references of recently developed micro-methods of determination of the alkaline earths. Spectroscopic, colorimetric, nephelometric, and electrometric methods, as well as gravimetric and volumetric methods, are given. The qualitative methods include a number of the new "spot" tests. The methods are described chronologically, with more detailed description of the work since 1926.
                                                                      J. W. B.

Detection of Small Quantities of Perchlorates. D. Krüger and E. Tschirch. (*Z. anal. Chem.*, 1931, 85, 171–176.)—Monnier's methylene blue test for perchlorates (ANALYST, 1917, 42, 51) is applied on the micro-scale, and details of the sensitiveness of the test in different conditions are investigated. On the macro-scale, using 1 c.c. of test solution in a test tube, the smallest amount of perchloric (ClO_4') ion detectable is 1000γ, and the limit of dilution 1 : 1000. For the micro-test one drop of the solution under examination is evaporated to dryness

on a slide, and one drop of a 0·2 per cent. aqueous solution of methylene blue is added. Blue and blue violet, needle-shaped crystals and crystal aggregates are formed in the presence of perchlorates, and may be seen under the microscope. The smallest amount recognisable is 3γ of ClO_4', and the limit of dilution is $1:17000$; sulphate and acetate ions do not interfere. The test is more sensitive in a saturated solution of sodium acetate, when $0·5\gamma$ of ClO_4' is detectable in a $1:100,000$ dilution. In the presence of cellulose acetate $2·5\gamma$ of ClO_4' is detectable in a dilution of $1:20,000$. The test has been applied in an investigation of the use of perchloric acid as a catalyst in acetylations of cellulose. When sulphuric acid is used as a catalyst the cellulose acetate contains some sulphate in the form of ester, but when perchloric acid is used the perchlorate contamination in the cellulose acetate is undetectable by the methylene blue method, and is therefore less than 0·01 per cent.

J. W. B.

Physical Methods, Apparatus, etc.

Measurement of the Viscosity of Solutions of Cellulose in Cuprammonium Hydroxide Solution: A Capillary Tube Viscometer. R. W. Kinkead. (*J. Text. Inst.*, 1931, **22**, T411, T415.)—For measuring accurately the viscosity of solutions of cellulose materials in cuprammonium hydroxide solution, the falling sphere method proves satisfactory when the viscosity is relatively high, *i.e.* when the logarithm of the viscosity of a 2 per cent. solution is above 0·5. With lower viscosities, however, none of the methods previously described gives reliable results. In such cases, the author uses the capillary tube viscometer shown in the figure.
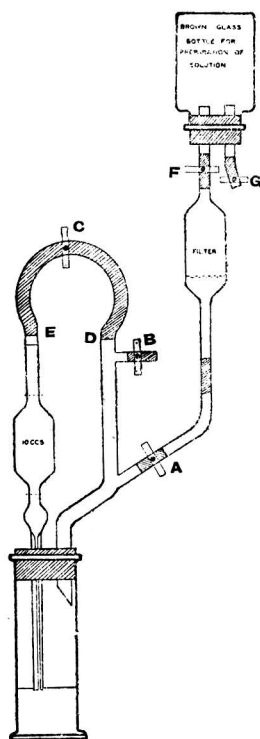
The reservoir is a specimen jar of 12 cm. height, 3 cm. diameter and 90 c.c. capacity, and approximately 50 c.c. of solution are used. The bore of the side tube, D, is 0·7 cm., and the capillary has a bore of 1 mm. and is 10 cm. long below the lower bulb. The upper tube is 7 cm. long above the bulb and its diameter is 0·5 cm. The main bulb has the capacity 10 c.c. between the marks, and the lower bulb, of approximately 1·5 c.c. capacity, assists in preserving the head of liquid. All rubber joints are of pressure tubing. To facilitate emptying and filling, the side-tube is made as wide as possible, and its end below the rubber stopper is cut off at an angle. The volume of the reservoir and side-tube should be such that, when the viscometer is inverted, there is more than sufficient liquid present to fill the bulb tube and the side-tube. The same reservoir is always used with any one bulb in order to avoid errors due to differences in diameter.

The viscometer is connected at B with a supply of hydrogen and a high vacuum exhaust pipe. The vessel containing the solution of cellulose material in the cuprammonium solution is joined to the reservoir at A, a fritted glass filter of the coarsest grade obtainable being interposed if necessary. The hydrogen supply and pump are also connected at G with the solution vessel, which has all air replaced by hydrogen during the preparation of the solution. The viscometer and filter are exhausted, washed twice with hydrogen through B to remove all air, and again exhausted, screw clip B being then closed. Clip F on the solution vessel is opened and the viscometer reservoir filled through A, the solution being washed through with hydrogen by opening clip G, so that the space in the viscometer above the liquid is filled with hydrogen. Clip A is then closed, and the viscometer disconnected at A and B and inverted. Pressure on the rubber tube, ED, forces the hydrogen from the side-tube, which fills with the solution on releasing the pressure, the liquid flowing up the bulb tube and filling the capillary and bulb. Clip C is then closed and the viscometer is placed upright in a thermostat. Pressure on the rubber tube between C and D removes all the liquid from the side tube up to the clip. Clip C is now opened and the solution allowed to flow through the capillary until the level is slightly below E. When the solution has assumed the standard temperature the capillary is adjusted so that its lower end is just below the surface of the liquid in the reservoir. Any gas bubble trapped under the end of the capillary is removed by applying slight pressure to the rubber tube CD. When clip C is opened the solution flows through the capillary against the back pressure of the rising level in the reservoir and is timed between the marks.

Inversion and filling of the bulb may be repeated as many times as is desired. Repeated observations of the time of flow do not differ by more than 1 or 2 seconds in a flow of 60 to 200 seconds. The filling of the bulb and capillary occupies less than a minute, and the drop in temperature due to removal from the thermostat is very slight, but the viscometer is left in the thermostat for at least five minutes before making a second determination. The instrument may be calibrated by means of a solution containing 40 grms. of cane sugar per 100 grms. of solution.

T. H. P.

Report on Tintometer Standardisation. W. D. Hutchins. (*Oil and Fat Ind.*, 1931, **8**, 303–304.)—The Colour Committee of the American Oil Chemists' Society makes the following recommendations concerning the standardisation of apparatus and procedure for determining the colour of oils. The tintometer shall be a light-proof metal box with dull black interior. Lovibond red and yellow glasses are to be used, the minimum standard set to consist of: Red, 0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7, 0·8, 0·9, 1·0, 2·0, 2·5, 3·0, 3·5, 4·0, 5·0, 6·0, 7·0, 7·6, 8·0, 9·0, 10·0, 11·0, 12·0, 16·0, and 20·0; yellow, 1·0, 2·0, 3·0, 5·0, 10·0, 15·0, 20·0, and 35·0. For examining maize (corn) and soya bean oils, yellow 30 and red 70 glasses are also required. The red glasses are to be standardised by the U.S. Bureau of Standards. The colour tubes shall have flat, smooth, polished bases of clear colourless glass, and the dimensions: Length 154 mm. over-all, inside diameter, 19 mm.; the tubes are to be marked to show an oil column of 133 mm.

One of the tubes is to be filled, to a depth of 133 mm., with the clear transparent oil at 20° to 24° C., previously filtered, if necessary, through good, heavy grade, close-textured filter paper at 20° to 24° C.; filtration should be noted on the report made. If the oil or fat is not completely liquid at 20° C., it should be liquefied by heating and the colour should be read at a temperature exceeding that of complete liquefaction by not more than 10° C. In matching the colour of the oil with the coloured glasses, use is to be made of only one yellow glass, not more than two red glasses up to and including 13 red, and not more than three red glasses above 13. When only two coloured glasses are used, a colourless glass also must be inserted. T. H. P.

Determination of the Hydrolytic Acidity of Decolorising Earths: New Means of ascertaining their Decolorising Power. H. Utermöhlen. (*Chem. Ztg.*, 1931, **55**, 625–626.)—Determination of the hydrolytic acidity of a number of active decolorising earths of German, English, and American origins by the method commonly adopted with soils shows that this acidity increases with the decolorising effect of the earths on a sample of soya bean oil, previously treated with dilute sodium hydroxide solution. To determine the hydrolytic acidity, 100 grms. of the earth are mechanically shaken for an hour with 250 c.c. of N sodium acetate solution in a Stohmann 500 c.c. flask. After filtration, 125 c.c. of the liquid are titrated with 0·1 N sodium hydroxide solution in presence of phenolphthalein. The number of c.c. of the alkali used represents the hydrolytic acidity. If a result is required quickly, the earth and acetate solution may be shaken together by hand for a few minutes, after which time the reaction is nearly complete. It should be borne in mind that the preparation of highly active decolorising earths involves treatment with acid, small proportions of which are always retained, even after thorough washing. The value found for the hydrolytic acidity must be corrected by subtraction of the corresponding value for this acid. Many earths exhibit such marked absorptive properties that insufficient filtrate is obtained; in such cases 75 c.c. are titrated and the number of c.c. required is multiplied by 2. Further, with highly active earths, the titration is best carried out with N alkali. T. H. P.

Reviews.

SOLVENTS. By T. H. DURRANS, D.Sc., F.I.C. Pp. xv+180. Revised Second Edition. London: Chapman & Hall, Ltd. 1931. 10s. 6d.

The first edition of this book, extremely useful within its restricted scope, was welcomed by us in November last (1930, **50**, 726). We can welcome this second edition, with its extra 36 pages, and with the satisfaction of knowing that its appreciation by chemists and manufacturers has resulted in so practical an expression.

The book still discusses solvents primarily from the point of view of their utility in the manufacture or use of cellulose esters. There is thus little or no mention of their value as extractors of drugs and in the preparation of tinctures, as fat extractors in the food and allied industries, as rubber solvents and in the rayon industry, as dry-cleaning agents, or of their multifarious applications to more purely chemical operations, such as crystallisation, in works and laboratory.

We could not really cavil at these omissions, did not the very general title suggest the book to have a wider scope than is the case.

Although Part II of the book, dealing with specific solvents, is largely a compilation from tables of constants and manufacturers' lists, it should be very convenient to many technicians as well as to lay heads of departments. It is, however, to be regretted that certain commercial products have not been analysed, so that statements like " 'Palatinol A' and 'Anozol' are reputed to consist of di-ethyl phthalate" might have been replaced by exact information.

Part I consists of a series of general, and fairly elementary, chapters on the chemical and physical properties and influence of solvents—solvent action, solvent power, plasticising action, solvent balance, viscosity, vapour pressure, inflammability and toxicity. In Part II organic solvents are treated individually under their respective main groups.

The production of the book is excellent, and the publishers are to be congratulated and thanked for having added 36 pages to it without increasing the price.

A. L. BACHARACH.

RECENT ADVANCES IN MICROSCOPY. BIOLOGICAL APPLICATIONS. Edited by A. PINEY, M.D., with contributions by five authors. Pp. vii+260, with 83 illustrations. London: J. & A. Churchill. 1931. Price 12s. 6d.

Owing to the ever-increasing specialisation necessary in science at the present time it would be difficult for any one reviewer to deal fully with the whole of the

contents of this work, since it treats of results obtained in the more remote and limited departments of microscopy.

The volume is intended to give a general idea of the more recent developments in the applications of the microscope to biological structure and phenomena, and whilst of considerable value to the microscopist and biologist, from the nature of the subjects dealt with would probably prove difficult reading for the layman.

The first section of the book is contributed by the editor, and after a brief but useful introduction is devoted to general discussions of the cytology of various animal tissues and glands. In the "Microscopy of the Living Eye," by B. Graves, an excellent description is given of the use of the recently developed slit lamp in conjunction with the microscope for the detection and observation of abnormal conditions and pathological changes in various parts of the human eye. The methods of illumination illustrated in this section not only demonstrate in an able manner the use of the instrument to the oculist, but in addition would also provide excellent test exercises for advanced students of optics or microscopy. The remaining two sections, by E. W. MacBride, H. R. Hewer and E. C. Barton-Wright, comprise about two-thirds of the volume and are devoted to the study of animal and vegetable cytology and illustrate the remarkable developments taking place in the minute study of the simple cell. Not only are the results of a number of investigations in this exacting branch of science given, but able and erudite comments, criticisms and comparisons are made by the authors on the conclusions reached by the various workers. From these sections one gains an insight into the vacuome, nucleus, mitochrondria, Golgi apparatus and other internal structures of the living cell in various species of animals and plants, together with information on the development of ova, spermatozoa, spores and the chromasomes which play so great a part in the study of genetics. The whole of the text is well written and serves as an admirable summary of the progress being made in subjects involving difficult technique, the results of which are at present in many cases in the early controversial stage, but which point the way to further developments which cannot fail to become of value. The authors have succeeded in converting into a coherent and lucid form much matter which might otherwise have appeared decidedly unattractive, but the value in this respect would have been much enhanced by the provision of a comprehensive glossary, since many of the newer terms used are known to relatively few, and are not to be found in any dictionary. The book is generously illustrated with excellent diagrams, and the principal sections are provided with bibliographies. The text appears to be free from errors of any kind, and the index is accurate and reasonably complete. To those interested in the subjects dealt with the volume will prove exceedingly good value for the price charged.

T. J. WARD.

A STUDY OF HAIRS AND WOOLS. By JOHN GLAISTER, Junr., D.Sc., M.D. Pp. 172, with 35 plates. Cairo: University Press. 1931. Price 40s.

This elaborate work originates from the Faculty of Medicine of the Egyptian

University, and has been published with the financial assistance of the Egyptian Government. Its scope is confined to the hairs and wools of the mammalia, considered from the medico-legal aspect, and its aim has been to provide a reference atlas by means of which hairs of unknown animals can be recognised and distinguished from those of man.

In his introduction Professor Glaister rightly lays stress upon the point that a photographic record is essential for the legal demonstration of the identity of a hair, but against this must be set the fact that the distinctive features of a hair can often be brought out more clearly by means of a camera lucida drawing than by photo-micrography, and that, subject to the permission of the Court, a photo-micrograph may well be supplemented by a diagram. Useful directions for preparing cross-sections of hairs are given, and the photographic methods used are described in detail.

The photo-micrographs of the hairs of the various animals have been arranged in accordance with the zoological classification of Flower and Lydekker, and valuable explanatory details of the characteristics of each order elucidate the plates; it is safe to assert that never before has such a complete collection of reproductions of the hairs of mammalia, ranging from the duck-bill platypus to man, been made available, and the author may be congratulated on having completed such a laborious task. Although some of the animals whose hairs are photographed and described are unlikely ever to form the subject of a criminal investigation, yet there is justification for including them in a medico-legal atlas of hairs and wools, since a witness might well be asked in cross-examination whether the hair attributed to one animal could not possibly have come from another. The series of plates of human hair represent photomicrographs of hairs at various ages and from different parts of the body, but the reproductions are somewhat disappointing, as many of them fail to bring out the distinctive structure of the cortex. There is also no account of the racial differences to be found in certain human hairs, such as those of the Australian aborigines, or of characteristic affections of human hair, such as ringed hair, and so on.

From what has been said it will be gathered that this atlas will sometimes be found helpful by those who have to make microscopical examinations of hairs and fibres, but that each investigator should supplement it by his own photo-micrographs and drawings. The absence of an alphabetical index (as distinct from the list of the contents of the plates) is a drawback.

EDITOR.

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RECENT ADVANCES IN ORGANIC CHEMISTRY. By A. W. STEWART, D.Sc. Vols. I and II. London: Longmans, Green & Co. Price 21s. net each Vol.

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FORENSIC CHEMISTRY AND SCIENTIFIC CRIMINAL INVESTIGATION. By A. LUCAS, O.B.E., F.I.C. 2nd Edition. London: Edward Arnold & Co. Price 18s. net.

THE SCIENTIFIC DETECTIVE AND THE EXPERT WITNESS. By C. AINSWORTH MITCHELL, D.Sc. 2nd Edition. Cambridge: W. Heffer & Sons Ltd. Price 3s. 6d. net.

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A BRIEF INTRODUCTION TO THE USE OF BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE. By E. M. HUNTRESS, Ph.D. London: Chapman & Hall. Price 5s. net.

DIE ARBEITSMETHODEN DER TRINKWASSER BIOLOGIE. By H. BEGER. (Abderhalden, Handbuch der biologischen Arbeitsmethoden, Lieferung 366.) Berlin: Urban & Schwarzenberg. Price RM.5.50.