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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 6th, the President, Mr. F. W. F. Arnaud, in the chair.

Certificates were read in favour of Sydney Emsley, B.Sc., F.I.C., George Frederick Hall, M.B.E., B.Sc., A.I.C., Walter Maurice Keightley, A.I.C., Dorothy Mary Mathews, B.Sc., Reginald Percival Page, F.I.C., Hilda Mary Perry, M.Sc., A.I.C., Arthur Dudley Powell, A.I.C., Winifred Ethel Smith, B.Sc., A.I.C.

The following were elected members of the Society:—Willard E. Baier, B.S., Adam Dunsmore, A.I.C., Donald Clarence Garratt, B.Sc., Ph.D., F.I.C., Colston James Regan, B.Sc., F.I.C., Robert Henry Slater, D.Sc., Ph.D., F.R.S.E., A.I.C.

The following papers were read and discussed:—"A Specific Gravity Apparatus," by the late C. H. Cribb, B.Sc., F.I.C. (read by T. McLachlan, F.I.C.); "The Excretion of Aloes," by G. F. Hall, M.B.E., B.Sc., A.I.C., and W. M. Keightley, A.I.C.; "The Chemical Examination of Furs in Relation to Dermatitis. Part IV. The Chemical Reactions of Dyeing with *p*-Phenylenediamine and *p*-Aminophenol," by H. E. Cox, M.Sc., Ph.D., F.I.C.; "The Use of the Air-Damped Balance for the Determination of Total Solids in Milk," by John Golding, D.S.O., F.I.C.; "A Rapid Method of Determining Minute Quantities of Nitrites," by G. G. Rao and K. M. Pandalai.

NORTH OF ENGLAND SECTION

A MEETING of the Section was held in Sheffield on December 2nd, 1933. The Chairman (Mr. John Evans) presided over an attendance of thirty. Dr. J. T. Dunn gave an account of the appearance, before the Departmental Committee on Food Law, of the Society's representatives.

The following papers were read and discussed:—"Note on Nitrates in Milk," by W. F. Elvidge, B.Sc., F.I.C.; "The Effect of Certain Salts in Fermentation in Dough," by R. M. Callow, M.Sc., A.I.C.; and "Note on Freezing-point Determinations," by E. V. Jones, F.I.C.

Death

WITH deep regret we record the death, on December 11th, of William Partridge. An obituary notice will be published later.

Obituary

ALFRED EDWARD JOHNSON

ALFRED EDWARD JOHNSON, who died on the 30th September, at the age of 75, was educated at the City of London School, and subsequently, from 1878 to 1881, he was at the Royal College of Science, Ireland, where he obtained his Associateship.

In 1883 he went to Wolverhampton as assistant to the late E. W. T. Jones, and continued to hold that post until Mr. Jones's death in 1922. He then went into partnership with the writer, with whom he was appointed Joint Public Analyst for the County of Stafford and the Boroughs of Stoke-on-Trent, Wolverhampton, and Newcastle-under-Lyme, which appointments they held until October, 1929. At that date, upon the County Council setting up their own laboratory, the partnership was dissolved, Mr. Johnson taking over the whole work of the above-mentioned boroughs.

He obtained his F.I.C. in 1888, and in 1901 gained the London B.Sc. degree. In 1923 he joined the Society of Public Analysts, and was elected a member of the Council for 1931–32.

Mr. Johnson made a valuable contribution to chemical literature in the excellent *Analyst's Laboratory Companion*, of which he was the author, and which is now in its fifth edition. In collaboration with Mr. W. Lincoln Sutton he revised the tenth and eleventh editions of *Volumetric Analysis* by Francis Sutton, and also contributed several articles to the *Chemical News*.

He was an able analyst, always willing to give help to another, and was a most industrious and conscientious worker, who carried on his work to the day of his death.

Mr. Johnson was exceedingly musical, being an accomplished organist and pianist. He leaves a widow and one son.

ERNEST V. JONES

The Chemical Examination of Furs in Relation to Dermatitis

By H. E. COX, M.Sc., Ph.D., F.I.C.

PART IV

THE CHEMICAL REACTIONS OF DYEING WITH *p*-PHENYLENEDIAMINE AND *p*-AMINOPHENOL

(*Read at the Meeting, December* 6, 1933)

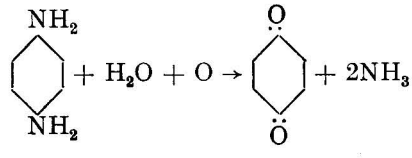
In previous papers of this series it has been shown, as a result of investigating a large number of cases of fur dermatitis, that at least 45 per cent. of these cases were due to *p*-phenylenediamine-dyed furs. There are good reasons for knowing that this particular fur base is concerned in a still higher percentage, and is more important than all the other potential causes put together. For this reason a detailed study of this substance, its properties and those of its oxidation products has been made, with the object of gaining some slight knowledge of the mysterious phenomenon of idiosyncrasy, and of determining whether the dye itself acts as the primary irritant or only through certain intermediate oxidation products. Is the action of *p*-phenylenediamine a normal chemical action? Is a fur dyed with it potentially irritant because of any free diamine or because of the chance presence of some special bye-product which is peculiarly irritant? Moreover, the properties of this, the most important member of the fur-dye group, are likely to differ only in detail from those of the other amino compounds which are used.

Some account has already been given (Analyst, 1933, **58**, 743) of *p*-phenylenediamine in relation to its transfusion through living and dead tissue, and of its reactions with blood or serum and substances occurring therein. It is the purpose of the present paper to discuss the identity of the dye formed on fur treated with *p*-phenylenediamine or *p*-aminophenol, and also to determine what bye-products are actually formed, and so may be present in an imperfectly dyed or washed fur; the properties of these bye-products are considered in so far as they bear on the causation of dermatitis.

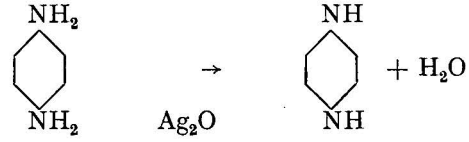
Little has been published on the chemistry of fur dyeing; it has generally been assumed that the black dye is Bandrowski's base, though Austin (*Fur Dressing and Dyeing*, p. 163) does suggest an azine type without giving any reference to experimental evidence for it, and A. G. Perkin, in an appendix to Dr. Parsons's report on the subject in 1924, states that the further stages of colour development are unknown, but the final product is probably a complex azine, as in the case of aniline black.

In considering the possible products of oxidation of diamines on furs, certain conditions must be borne in mind which limit the range of possible reactions. These are that: (1) the temperature must always be low, not exceeding approximately blood heat; (2) the liquors must not be acid or strongly alkaline; and

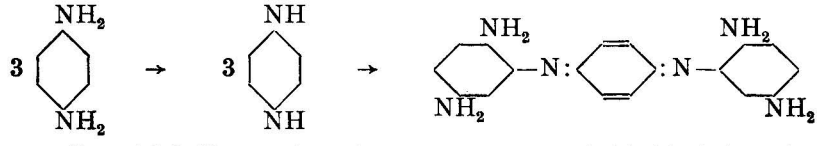
(3) the oxidising agent in practice is nearly always hydrogen peroxide, though dichromate, copperas, copper sulphate and other metallic compounds may be used as mordants. Traces of bleaching powder may occasionally be included. In strongly acid solution the oxidation of *p*-phenylenediamine yields quinone and ammonia almost but not quite quantitatively (*cf.* Erdmann, *Ber.*, 1904, **37**, 2908; Green and Johnson, *ibid.*, 1913, **46**, 3772) thus:



If neutral solutions are employed and water is rigorously excluded, the product of mild oxidation is quinone di-imine, which substance is at once decomposed by water (*cf.* Willstätter and Pfannenstiel, *Ber.*, 1904, **37**, 4605)



In weakly alkaline solutions, with hydrogen peroxide, there are several products of which the best known is tetra-aminodiphenyl-*p*-azo-phenylene, well known as Bandrowski's base.



Erdmann (*loc. cit.*) indicates that about 80 per cent. of this black base is formed, but Heiduschka and Goldstein (*Arch. Pharm.*, 1916, **254**, 584), who studied it in detail, show that, at best, only about 30 per cent. of the black base results; even in the presence of excess of peroxide some 50 per cent. of the diamine remained unchanged, and there was a residuum of about 20 per cent. of non-identified products. All these published experiments deal with the pure diamine, and do not take into consideration the complicating effects of the presence of animal fibre. In my experiments, examples of which follow, some idea of the nature of the dye has been obtained, and a quantitative determination of the oxidation products has been made, so that all the products are known, and approximately 100 per cent. of the diamine used is accounted for.

THE COMPOSITION OF THE DYE ON THE FUR.—It has been shown (by Heiduschka) that the maximum yield of black dye is obtained when about three molecular proportions of hydrogen peroxide are used to one of *p*-phenylenediamine. I find when this is done that there always remains a slight excess of peroxide in the liquid, so that more would be useless. This corresponds with the general directions for using fur dyes, which include about 15 parts of 10 volume peroxide to 1 part of the intermediate; this ratio leads to a fairly pure form of Bandrowski's base, whether fur be present or not. For the quantitative study of the reaction I have

taken advantage of the fact that Bandrowski's base is almost insoluble in water, but freely soluble in hot pyridine, so that it can be filtered out of the liquor extracted from the fur, and its purity controlled by observation of the m.pt. This procedure gives a clear filtrate, in which the total nitrogen can be determined and the forms in which it is present ascertained by the ordinary methods of analysis; they were proved to be unoxidised *p*-phenylenediamine, with traces of quinone and ammonia. There remains the fur. It is found to be strongly dyed, and the dye is not extractable by any solvent—including pyridine, 60 per cent. acetic and formic acids—and can only be removed by decomposing the hair with caustic soda. Subsequent acidification enables one to examine it in the usual way to ascertain, not its entire constitution, but at least its class and general reactions. It is found that the pigment in a fur dyed in the usual way consists of three parts:

(i) Bandrowski's base *on* the fibre; (ii) an insoluble azine combined *in* the fibre with the protein substance; (iii) a small quantity of azine *on* the fibre.

The products remaining in the dye bath consist of: (iv) Bandrowski's base in suspension; (v) Bandrowski's base in solution; (vi) free *p*-phenylenediamine; (vii) a small amount of ammonia; (viii) a small amount of quinone; (ix) a small excess of hydrogen peroxide.

The following details of an experimental dyeing, which follows the general instructions given with fur dyes, show the quantitative relationships. Sodium carbonate was used in place of ammonia (which is more usual) because of the complicating effect of ammonia in the subsequent analyses.

Ten grms. of rabbit fur, clipped from the hide so as to eliminate difficulties due to skin and its protein or fats, were soaked for 24 hours in a bath containing copper sulphate 2 grms., acetic acid 1 grm., water 500 ml. Next day the fur was removed and rinsed.

Determination of the copper showed that the fibre had absorbed 0·4 per cent. of its weight of copper (as Cu)—an observation which gives an indication of the amount of mordant likely to be found in black dyed fur.

The fur was then immersed in a dye-bath made from *p*-phenylenediamine, 4·00 grms.; sodium carbonate (dry), 1·50 grm.; water, 400 ml.; and 60 ml. of hydrogen peroxide (10 vol.) were added. After 24 hours at 25° C. the fur was collected on muslin, well squeezed out and washed in repeated changes of water, until substantially free from *p*-phenylenediamine. The total volume of liquor amounted to 1100 ml. This was filtered; the insoluble base, which weighed 0·935 grm., was found to have m.pt. 237° C., and to give all the reactions of Bandrowski's base; it consisted of fairly pure base. The total nitrogen, determined on the filtrate, was found to be equivalent to 1·27 grm. of *p*-phenylenediamine. Hence it follows that the fur contained altogether the equivalent of 1·77 grm. of the diamine in water-insoluble forms. The liquid was examined qualitatively, and found to contain traces of peroxide, ammonia, quinone and much unoxidised *p*-phenylenediamine. Determination of the quantity of the *p*-phenylenediamine by Callan and Henderson's method failed, owing to the interference of the other substances, but it was readily determined by weighing the quinone dichloro-di-imine formed with sodium hypochlorite, and was found to amount to 0·590 grm. Ammonia was determined by distillation with magnesia as usual, and found to be

0·10 grm., which with its equivalent quinone is equal to 0·36 grm. of *p*-phenylenediamine. Quinone was determined by titration of the iodine liberated from potassium iodide in acid solution; its quantity was 0·40 grm.

It was also needful to examine the dyed fur; this weighed 11·6 grms.; it was extracted with hot pyridine in a Soxhlet extractor until the extracts were almost colourless; this yielded 0·690 grm. of a black powder which melted at 235° C., showing it to be Bandrowski's base, but there was a small residuum of black compound which had m.pt. not below 280° C. The extracted fur now contained 1·06 grm. of a black dye which was not soluble in any solvent. The colour of the fibre was as black after the extraction of the Bandrowski's base as before; evidently the real dye is not this base (see below). The base extracted with pyridine was boiled with *N* hydrochloric acid which, as has been shown, decomposes and dissolves Bandrowski's base, and the insoluble compound was filtered off (weight, 0·042 grm.); it had m.pt. not below 280° C., and the reactions described below indicated that it was an azine. These results may be expressed as a balance sheet and show that the *p*-phenylenediamine added is completely accounted for within experimental error.

p-Phenylenediamine			Per cent. of diamine added
Added	Found		
4·00 grms.	as unoxidised diamine	0·59	14·8
	as Bandrowski base in suspension	0·95	23·8
	as ammonia and quinone	0·36	9·0
	as Bandrowski base in solution	0·18	4·5
	as azine *in* the fur	1·08	27·0
	as Bandrowski base *on* the fur	0·67	16·8
3·87	as azine *on* the fur	0·04	1·0
Unaccounted for 0·13 grm.	Total	3·87	96·9

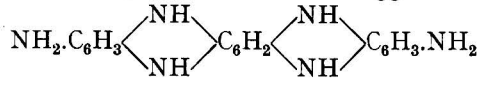
Other experiments of a like kind have been made, and the results definitely indicate that the final product is an azine combined with the protein of the fur. A large excess of peroxide does not improve the result, but yields more insoluble azine outside the fibre.

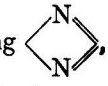
One or two practical points may be mentioned. In neither Bandrowski's base nor the azine can the nitrogen be accurately determined by the Kjeldahl method. I have tried several modifications, including the well-known Jodlbauer procedure, but the results are always low. (Heiduschka also mentions that the direct Kjeldahl process is inapplicable to this base, but apparently did not try modifications.) Bandrowski's base, when dissolved in pyridine, gives a deep red solution which forms an intense blue with hydrochloric acid. The azine is practically insoluble, and forms no colour on the addition of acid. It is decolorised by hydrosulphite or titanous chloride, but re-oxidises readily in air.

PROPERTIES OF THE DYED FUR.—Fur which is coloured only with Bandrowski's base externally can be readily recognised either by extracting the base with hot pyridine or by decomposing the base on the fibre by boiling with dilute hydrochloric acid. This method is applicable to most furs on which stripes have been dyed by the familiar paint-brush procedure. But when the azine

stage is reached it is found that nothing is yielded, even to boiling pyridine or on treatment with acid or with any other solvent. The azine character of the dye is only determinable by decomposing the fibre with caustic soda, then acidifying and reducing with titanous chloride or boiling the fibre with the usual sodium formaldehyde sulphoxylate solution. It is then decolorised, but the colour is at once restored on exposure to air, as is characteristic of azines.

Experiments on the quantitative reduction to the leuco base have been made by boiling some of the fur containing a known weight of the azine with caustic soda, then acidifying with hydrochloric acid, adding pyridine and titrating with titanous chloride in an atmosphere of carbon dioxide. It was found that the amount of hydrogen required to reduce it was only 0·18 per cent. by weight. This observation seems to disprove the formula suggested by Austin:



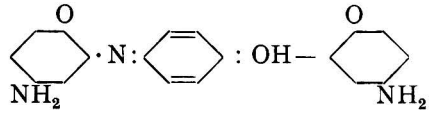
since the addition of even one hydrogen atom would require 0·31 per cent. of the element. In order that 0·2 per cent. of hydrogen may suffice to form the leuco compound, the substance must have a molecular weight of at least 500. As it has been shown that there are no side-products, except in quite small traces, it follows that the structure of the azine must be a multiple of the three molecules of Bandrowski's base; this implies nine benzene rings as a minimum. It has been shown by Green and others that the aniline blacks have chains of as many as eleven benzene rings. The oxidation product of *p*-phenylenediamine must have at least nine, and, of course, the azine structure requires the grouping  , in which at least one nitrogen is free, and can take up a hydrogen atom to form a leuco compound. This does not appear in Austin's suggested formula.

Experiments have also been made to ascertain whether dyeing could be effected by means of Bandrowski's base, whether this substance is the necessary intermediate product in the production of the azine, and whether it can be further oxidised without the presence of fur or other organic matter. If this base is the intermediate product and no side reactions occur, it forms additional evidence of the number of rings in the structure of the azine; it must be a multiple of three. A quantity of finely-powdered Bandrowski's base was suspended in water, and kept warmed at blood-heat with excess of hydrogen peroxide; there was found an azine not melting below 300° C. and resembling that already described, and no other products were detected by analytical processes. Evidently the azine is capable of being formed direct from the base without side-reactions. Heiduschka and his colleague observed that when they oxidised *p*-phenylenediamine with excessive quantities of peroxide at high temperatures they obtained mixtures which they could not analyse; evidently these included the azine and Bandrowski's base, as well as the products already enumerated. This experiment also suggests the presence of multiples of three benzene rings in the structure of the azine.

It was not found possible to dye fur by soaking it in a suspension of the Bandrowski's base with excess of peroxide; it is clearly necessary for the *p*-phenylenediamine or the base to be absorbed into the hair substance and oxidised therein.

A successful dyeing experiment was effected by dissolving 1 grm. of the base in 20 ml. of pyridine, then soaking fur (2 grms.) in it, adding 20 ml. of water, and later 10 ml. of hydrogen peroxide; under these conditions Bandrowski's base enters the protein substance, and is oxidised therein, with the production of the azine. The colour of fur so dyed is similar to, but weaker than, that dyed directly with *p*-phenylenediamine, so that this method affords a method of dyeing without the direct application of *p*-phenylenediamine, and would appear entirely to preclude the possibility of the presence of the free amine. There are certain obvious reasons why such a method presents difficulties in commercial practice; if they could be overcome, cases of fur dermatitis would arise less frequently.

DYEING WITH *p*-AMINO-PHENOL.—In order to ascertain whether the azine formation just described is a general result of the oxidation of fur dyes, another set of experiments was made, using *p*-amino-phenol instead of *p*-phenylenediamine. When oxidised in acid solution, this substance is converted quantitatively into quinone, and in solution in dry ether it is convertible into quinone mono-imine by silver oxide, but, when oxidised in alkaline solution by air or hydrogen peroxide, it forms a compound of which the detailed structure does not appear to have been elucidated. Bandrowski, who first described it (*Monatsh.*, 1889, **10**, 124), gives $C_{18}H_{15}(NO)_3$. It is a dark brownish-black crystalline substance which melts at 228° C., and there are reasons for thinking it may have the formula:



A fur dyed with *p*-amino-phenol will usually contain some of this base, but the true pigment is found to be an oxazine analogous with the azine produced from *p*-phenylenediamine. A quantitative study of the distribution of the amino-phenol has been made following the same procedure as has been already described, except that the unoxidised amino-phenol was determined by Powell's method (ANALYST, 1919, **44**, 52) as quinone chloro-imine, which is formed on adding hypochlorite to the acid solution and is more soluble than the dichloro-di-imine. The clipped fur, mordanted with copper, was treated with *p*-amino-phenol in exactly the same manner as in the *p*-phenylenediamine experiments. The results were as follows:

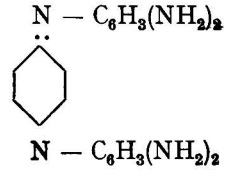
p-Amino-phenol				
Added		Found		Amine added Per Cent.
4·00 grms.	as unoxidised amine		1·91	47·7
	as base in suspension		0·54	13·5
	as ammonia and quinone		0·42	10·5
	as base in solution		0·18	4·5
	as oxazine in the fur		0·53	13·2
	as base on the fur	}	0·64	16·0
4·22	as oxazine on the fur	}		
Error +0·22			4·22	105·4

The pyridine-extracted fur dyed with the oxazine is of a deep brown colour—not black; the dye is not extractable by solvents and undergoes the same changes with reagents as the azine dye formed from *p*-phenylenediamine. Analogy indicates that the pigment is an oxazine resembling the azine formed from the diamine.

The significance of these observations in relation to fur dyeing and dermatitis lies in the demonstration that the true object of the fur-dyeing process is the formation of this azine in the fur fibre itself, and not merely the development of Bandrowski's base, as has hitherto been supposed by writers on this subject. The ideal process should form the azine and subsequently remove not only any remaining unoxidised amino compound, but also the base which is loose on the fibres. Clearly, if this be done, there can be no question of any dermatitis developing from irritant properties of the fur. I have examined several hundred dyed furs in detail and find that this objective is attained only in quite a small percentage of cases. A fur in which Bandrowski's base is present, but no free diamines, may be truly said to be well dyed and washed, but it is a less perfect product than one in which all the dye is fast. Patterns, such as lines or spots, are often dyed on to fur by a sort of painting process, in which the peroxide is applied also with a brush; it is manifestly very difficult, if not impossible, to secure complete azine formation in such circumstances.

In Part II of this series (ANALYST, 1933, **58**, 738) it was mentioned that in **12**, out of about 216 furs, it had not been possible to identify the actual fur base used. When the amount of the dye is small and the colour not very dark, it appears that the whole of the original intermediate may have been converted into the azine or oxazine and so become completely insoluble. This state of affairs is readily recognisable, but, as the dye compound cannot be split up or re-formed into its original components by ordinary means, it becomes impossible to recognise the original amine. This probably accounts for the cases not identified.

DECOMPOSITION OF BANDROWSKI'S BASE.—In earlier parts of these papers reference has been made to the re-formation of free *p*-phenylenediamine from Bandrowski's base by action of hydrochloric acid, and figures were given showing the approximate extent of such reaction (Cox, *J. Soc. Dyers and Color.*, 1932, **48**, 124), which was referred to as hydrolysis. It is difficult to see just how a compound of the formula



can be re-formed into $C_6H_4(NH_2)_2$ without the presence of a reducing agent to supply hydrogen. When wool or fur is present this may happen readily enough. The reaction has now been investigated further, and it is found that, on boiling Bandrowski's base with dilute (*N*) hydrochloric acid, *p*-phenylenediamine hydrochloride is the principal product, and there are also formed ammonia, hydroquinone, hydrogen cyanide and carbon dioxide.

It has been shown that this liberation of *p*-phenylenediamine does not occur as a result of exposure either to water or to perspiration, but the reaction is of practical importance from the analyst's point of view, because it shows that a fur must not be extracted with warm mineral acid, or there may be produced a whole range of substances which were not already there—including *p*-phenylenediamine, quinone, hydroquinone and cyanide; hence an erroneous conclusion as to the method of dyeing might be reached.

The action of hydrochloric acid in this way is also of theoretical interest, as it involves the unusual phenomenon of a breaking down, not only of a quinone group, but actually of a benzene ring, by so simple a reagent as dilute hydrochloric acid. It is being further investigated, and I hope to discuss it in detail on another occasion. It may be remarked, however, that Heiduschka and Goldstein (*loc. cit.*) found that, although a definite salt was formed with sulphuric acid, they were unable to say what happened when hydrochloric acid was used. They noted the bright red colour which develops at an early stage, but did not isolate any compounds.

OTHER OXIDATION PRODUCTS.—It remains to consider what oxidation products other than Bandrowski's base and the azine may be produced, and whether any of them are liable to be present in imperfectly treated fur. Various substances are suggested from time to time, notably quinone di-imine. I propose to comment only on a few substances, considering whether they are specially irritant, and what evidence that they are ever present in dyed fur.

It has been shown that quinone is a minor bye-product of the oxidation, and, of course, hydroquinone is easily formed from it. Quinone is very irritating to the nose and throat, and in alkaline solution is an active reducing agent*; it seems likely that it might cause skin irritation if present, but as a result of the examination of very many furs dyed with *p*-phenylenediamine, which have been definitely known to have caused dermatitis, I have never found any quinone or quinol, and I do not think these are ever likely to be present unless as actual ingredients of a dyeing mixture; it is easily washed out or removed in the finishing processes.

Quinone di-imine is known to be the immediate precursor of Bandrowski's base; it is very poisonous when taken internally (*cf.* Erdmann, *Ber.*, 1904, **37**, 2908). I prepared this substance by the method of Willstätter and Pfannenstiel (*loc. cit.*), and have described some of its reactions with blood in Part III. It is almost instantly decomposed by water, forming the usual insoluble black base with no free *p*-phenylenediamine. It thus appears impossible that it should ever be present in a dyed fur; it would not be detected by the ordinary processes of analysis, but could be extracted with anhydrous ether, in which it forms a yellowish solution which gives a brown-black solid on the addition of a few drops of water. To test its effect on the skin, I applied an ethereal solution of the di-imine first on the back of a mouse. The mouse suffered no apparent inconvenience; the imine quickly formed a brownish black stain by absorption of moisture from the air, but, on later killing the animal and preparing sections of the skin, no evidence was obtainable of any penetration even of the ethereal solution; the outer layer

* Quinone is commonly regarded as an oxidising agent, but in alkaline solution it quickly reduces Fehling's solution, silver nitrate or permanganate solution.

of the epidermis was stained, but there was no penetration or apparent effect on the cells underneath. Having satisfied myself by experiments on mice, I applied a few drops of a concentrated ethereal solution of the di-imine to my own arm; a brown stain was quickly formed, which subsequently became almost black, but there was no irritation at all.

Quinone dichloro-di-imine ($C_6H_4N_2Cl_2$) has been under suspicion in the minds of one or two writers. That it should be present pre-supposes the use of bleaching powder or sodium hypochlorite as the oxidising agent. So far as I know, these are never used in ordinary practice. The substance is readily prepared by adding sodium hypochlorite to a slightly alkaline solution of *p*-phenylenediamine; it is nearly insoluble in water; suspended in water and acidified with nitric acid it does not give any precipitate with silver nitrate; on boiling with dilute nitric acid quinone is formed, which is easily recognisable by its odour or colour reactions, and a chloride reaction is obtainable. In this way it can be easily detected, if present on a fur. Applied to the skin, it had no apparent effect.

I have searched for this substance in many furs, but have never found any to be present. It is my opinion that *p*-phenylenediamine itself, and not any intermediate oxidation products, is the active irritant in fur dermatitis.

SUMMARY OF PART IV.—A quantitative study of the oxidation of *p*-phenylenediamine with hydrogen peroxide in the presence of fur shows that the principal pigment formed is an azine combined with the fur proteins. Some Bandrowski's base is found on the surface of the fibres, and there exists in the solution in the dye bath much free unoxidised *p*-phenylenediamine, together with some Bandrowski's base and traces of quinone and ammonia. Similar data are given in respect of *p*-amino-phenol, which forms an oxazine in an analogous manner. The azine from *p*-phenylenediamine forms a leuco compound, with the addition of only 0·18 per cent. of hydrogen, by action of titanous chloride; it can be formed by direct oxidation of Bandrowski's base in solution, and has at least nine benzene rings in its constitution.

A preliminary account is given of the reaction of Bandrowski's base with dilute hydrochloric acid, whereby free *p*-phenylenediamine is formed. This base is not, as has usually been assumed, the desired product in fur dyeing. The occurrence and properties of the other intermediate oxidation products are discussed in relation to dermatitis.

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Acidimetry of Wines

By JAMES HOSSACK

In the analysis of wine the usual practice is to make determinations of the "total acids" and of the "volatile acids" independently, while the "fixed acids" are calculated by difference. This practice does not commend itself to the writer. The usual defence for it seems to be summarised in a short passage in Allen's "Commercial Organic Analysis" (5th Ed., Vol. 1, p. 228), where the contention is made that a determination of "fixed acids" is of necessity inaccurate. The reasons given appear illogical. A little clear thinking will show that the term "fixed acids" can be more rigidly defined than can the term "volatile acids." The latter are separated by steam distillation. The point at which this operation should be suspended is often one of convention only. The exact result may be affected by the rate at which the steam is driven, and by other factors. Acid remaining after evaporating on the water-bath and drying at 105° C. is a much more definite quantity.

The real cause of discrepancy in the past seems to have been as much the uncertainty of end-points in titration as anything else. When red wines in particular are to be titrated for "total acids," an external indicator is generally used. European practice seems to favour litmus paper. In the U.S.A. azo-litmin solution (essentially "refined litmus") should be employed, though in certain cases a mixture of solid phenolphthalein with sodium sulphate may be substituted. (*Vide* "Methods of Analysis," A.O.A.C., 3rd Ed., p. 140.)

Neither litmus nor any of its constituents is a reliable indicator when organic acids are being titrated, and any end-point obtained externally is likely to lack precision.

When the determination of "fixed acids" is made on such materials as are here under discussion, there is the same end-point difficulty as for "total acids." When "volatile acids" are being determined, the point at which steam distillation is to cease may also be uncertain.

If the trouble due to colouring matter could be overcome and a suitable internal indicator used, good independent determinations of all three factors could be made. If only two were considered necessary the "total" and "fixed" acids could be determined more quickly and conveniently than "volatile" acids. With these ideas in mind the writer has worked out the following procedure:

Total Acids.—Measure 50 ml. of the wine to be tested into a 250 ml. graduated flask, add 10 ml. of saturated barium chloride solution, then 50 ml. of $N/10$ sodium hydroxide solution free from carbonates and sulphates. Almost all natural colouring matter will be precipitated. Make up to the mark with water (free from carbon dioxide), mix well and filter through a rapid paper. Reject the first 10 ml. of filtrate, and from the remainder pipette 100 ml. into a separate flask for titration. Acidify by adding 25 ml. of $N/10$ hydrochloric acid, then titrate back with $N/10$ sodium hydroxide solution in the usual manner, using phenolphthalein solution as indicator. The end-point is quite distinct.

An approximately $N/10$ solution of sodium hydroxide which will automatically maintain its freedom from carbonates is most conveniently obtained by adding to 100 ml. of normal sodium hydroxide approximately 10 ml. of saturated barium chloride solution, diluting to 1 litre and decanting the clear liquid (or, if necessary, filtering through a rapid paper) before standardisation. Such a solution is best not used in titration against sulphuric acid, though the presence of sulphates in the wine will not cause error.

FIXED ACIDS.—Evaporate 50 ml. of wine to dryness on the water-bath. Finish drying in an oven at 105° C. Dissolve the residue in a convenient amount of water, transfer to a graduated 250-ml. flask and proceed as for the determination of "Total Acids" described above.

CALCULATION OF RESULTS.—If X = ml. of $N/10$ NaOH used in the final titration, then 20 ml. of wine contain (X − 5) ml. of $N/10$ acid. This can be converted further to such terms as the analyst may prefer.

For purposes of comparison, analyses of four wines are given below. All determinations were made directly, "total" and "fixed" acids as above, "volatile" as described in "Methods of Analysis, A.O.A.C., 3rd Ed., p. 140, "Method I." Samples 1 and 2 were fortified sweet red wines (port type), No. 3 was an unclarified fortified yellow wine (sherry type), and No. 4 was a spoiled wine (red Burgundy type). Results are expressed as ml. of $N/10$ acid equivalent to 20 ml. of wine.

Sample No.	Total acid found	Fixed acid found	Volatile acid found
1	19·9	16·5	3·36
2	20·3	16·0	4·28
3	18·4	12·7	5·80
4	19·0	14·8	4·08

The figures in the last column are 2/5 of those read from the burette on titration, since a conventional 50-ml. sample was taken for distillation.

When this method of analysis is applied to fruit juices, or to wines, the total acidity of which is greater than decinormal, larger volumes of alkali than those here mentioned must be added before the filtration. Precipitation of the colouring matter can only be assured in alkaline solution.

If thymol blue is substituted for phenolphthalein in these determinations, a direct titration of the aliquot portion of the filtrate against $N/10$ hydrochloric acid may be made with advantage, somewhat simplifying both the procedure and the calculation, but the latter indicator is so much more popular that it was thought best to adapt the directions to its peculiarities.

If barium hydroxide is substituted for sodium hydroxide, no barium chloride need be used at any point. The merits of barium hydroxide in many routine operations do not seem to be appreciated at the present day.

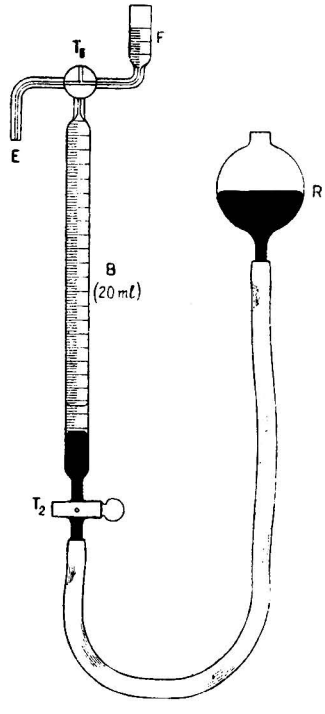
The thanks of the writer are due to Dr. Alfred Tingle, Chief of the Customs-Excise Laboratory, for making possible the performance of the work here recorded and for suggestions which have contributed to a successful issue.

CUSTOMS-EXCISE LABORATORY
DEPARTMENT OF NATIONAL REVENUE
OTTAWA, CANADA

A Rapid Colorimetric Method for the Detection and Determination of Small Quantities of Oxygen in Gases

By H. R. AMBLER, Ph.D., F.I.C.

A colorimetric method has been worked out for the detection of oxygen in mixed gases, and for its determination where present in quantities between 0·01 and 0·5 per cent. The volume of sample required is 20 ml. or less, depending on the oxygen-content.



The principle of the process depends on the colour imparted by oxygen to alkaline pyrogallol solution, which is compared with that of iodine solution of known strength (Pfeiffer, *J. für Gasbeleuchtung*, 1897, **40**, 354).

The apparatus used is shown in the diagram. B is a burette of about 20 ml. capacity, fitted at the bottom with a tap, T_2, and at the top with a three-way tap, T_1, which can be set to connect any two (or all three) of the following:—the burette, B, a funnel, F, of about 2 ml. capacity, and the gas entrance, E. It is desirable, but not essential, for B, and also F, to be graduated in tenths of a ml.; the tap and the connections should be about 1·5 mm. in bore. T_2 is connected by pressure-tubing with a mercury-reservoir, R.

At the beginning of an analysis, B and the bore of T_1 contain mercury only. A small volume of a freshly prepared aqueous solution of pyrogallol (1 : 3) is placed in F, and a measured amount (say, 0·3 ml.) is run into the burette through T_1; F is now washed out with dilute acid and water successively, these being expelled through E; a small quantity of strong potassium hydroxide solution is placed in F, and about 0·6 ml. of this run into B, where it mixes with the pyrogallol. It is advisable at this stage to wash out F with dilute acid and water as before.

The solutions in B are further mixed by inverting the burette with T_1 and T_2 closed. The mixed solution should be almost colourless; with good distilled water and reagents this result can be attained without any special precautions.

E is now connected with the source of the gas to be tested; if an ample supply of this is available it is blown off through F until the connections have been cleared of all air; T_1 is then turned so as to connect E with B, and the appropriate volume of gas is drawn into B. If the amount of gas sample is limited it is best contained

in a vessel such as the Huntly sampler (Huntly, *J. Soc. Chem. Ind.*, 1910, **29**, 312), fitted with a three-way tap, the common end of which is close-connected with E by rubber tubing, and the connections are cleared of air by running mercury from F through the three-way tap of the sampler.

When the required volume of gas (20 ml. or less) has been taken, T_1 is turned so as to close B, T_2 is closed, and the burette is inverted once or twice to ensure complete absorption of the oxygen. The colour of the solution is then matched with iodine; this is most conveniently done by running $N/10$ iodine solution, drop by drop, from a burette into a small measuring cylinder of the same diameter as B, previously containing a small volume of water (say, 1 ml.). The iodine solution contains two parts of potassium iodide to one of iodine (Pfeiffer, *loc. cit.*). The colour matching should be done in fairly strong transmitted light, and at a standard time, say two minutes after admission of the gas.

From the strength of the solution of iodine matching the pyrogallol solution the amount of oxygen is derived by an empirical relation, which, for precise work, should be determined under the exact conditions of normal use with gases of known oxygen content. For approximate work, the relation given in the following table may be used:

Volume of oxygen (at N.T.P.) absorbed by unit volume of mixed solution	Iodine solution of equal colour depth
0·01	0·01 *N.*
0·02	0·025
0·03	0·04
0·04	0·055
0·05	0·065
0·06	0·08
0·07	0·095

Within the range of the above figures good colour matches are obtainable. For strengths above about 0·1 *N* iodine the solutions are too deep in colour for accurate matching, whilst below 0·01 *N* the colours are appreciably different in quality. For a considerable way below this strength, however, the colour of the pyrogallol solution is sufficient to provide a definite qualitative test. The range may be extended in both directions by varying the volumes of reagent and of gas sample. Ferric chloride, and also mixtures of ferric, copper and cobalt salts have been tried as comparison solutions, but are found to have no advantage over iodine.

The principle of the method was applied originally to coal-gas (Pfeiffer, *loc. cit.*), hydrogen, hydrocarbons and oxides of carbon not interfering. Nitrous oxide, also, has been found not to interfere. Hydrogen sulphide (which gives a red colour) and oxidising gases, such as chlorine, must not be present.

RESEARCH DEPARTMENT
WOOLWICH

The Analysis of Magnesium Alloys

By L. C. NICKOLLS, M.Sc., D.I.C., A.R.C.S., A.I.C.

THE analysis of magnesium alloys presents no difficulties except when the alloys contain aluminium. As most common commercial alloys do contain aluminium it has been necessary to devise methods for determining aluminium in the presence of comparatively large quantities of magnesium. Blum (*Sci. Papers*, No. 286, *Bureau of Standards*) has shown that precipitation of the aluminium hydroxide is dependent on the p_H value of the solution lying within narrow limits, while Lassieur (*Compt. rend.*, 1926, **182**, 384) has stated that, provided that the p_H value of the solution does not exceed 7·0, aluminium may be separated completely from magnesium by precipitation with ammonia as hydroxide. There is more difficulty in separating these metals when the ratio of the magnesium to the aluminium is as high as is usually found in commercial magnesium alloys, and Hackney (*Quantitative Analysis of Inorganic Materials*, p. 322) states that such a separation is practically impossible. Berg (*Z. anal. Chem.*, 1927, **71**, 369) and others have used 8-hydroxyquinoline to effect a separation, but the use of this reagent usually hinders the direct determination of other metals possibly present.

A method has been employed in the Government Laboratory which is free from this defect and is superior to the precipitation at a known p_H value of the aluminium as hydroxide with ammonia. It depends upon the fact that alkali sulphides precipitate aluminium hydroxide from solutions of aluminium salts, whilst magnesium gives the soluble hydrosulphide. There is no tendency to co-precipitation, although the p_H value of the solution is about 7·5. The only difficulty is the mechanical one of washing the bulky aluminium hydroxide precipitate free from magnesium salts. Excess of ammonium chloride does not appear to be necessary to keep the magnesium in solution, which agrees with the results of Lassieur (*loc. cit.*), but we have considered it advisable not to dispense with it.

PROCEDURE IN THE ABSENCE OF MORE THAN TRACES OF MANGANESE, ZINC OR NICKEL.—In the absence of manganese, nickel or zinc in considerable amount, a comparatively simple method is adopted. One grm. of the alloy is dissolved in 1:1 hydrochloric acid containing a little nitric acid or bromine, and the solution is evaporated on the water-bath to dryness to fix the silica. The chlorides are taken up in 100 ml. of hot water, sufficient hydrochloric acid to dissolve the magnesium oxychloride and 20 grms. of ammonium chloride are added, and the silica is filtered off, ignited, and weighed. Hydrogen sulphide is passed through the filtrate, and the precipitated Group II sulphides are filtered off and examined in the usual manner. Usually there is only a trace of copper. To the filtrate, which should smell of hydrogen sulphide, ammonia is added until the liquid turns a dark green colour, due to ferrous sulphide, and a precipitate is formed. Hydrochloric acid is then carefully added, with stirring, until the precipitate just dissolves, but the dark tint of the iron sulphide is not entirely discharged. Five ml. of 6 *N* sodium sulphide solution are added, hydrogen sulphide is passed to saturate the solution,

and the beaker is heated on the water-bath for an hour. The precipitate is filtered off and well washed with dilute ammonium nitrate solution to remove magnesium salts. Calcium, strontium and barium may be determined in the filtrate by precipitation with ammonium carbonate. The filter paper and precipitate are returned to the beaker, 20 ml. of hydrochloric acid and a few ml. of bromine water are added, and the beaker is heated on the water-bath to dissolve the precipitate. This solution now contains all the iron, aluminium and the traces of manganese, nickel and zinc. The iron, aluminium and manganese are precipitated by adding ammonia, heating the liquid to boiling, filtering, and igniting the precipitate in the blowpipe flame. The iron is determined by fusing the precipitate with potassium bisulphate, extracting with water, and titrating with titanous sulphate solution, and its amount is deducted from the weight of alumina. Nickel is determined in the filtrate with dimethyl glyoxime, and the zinc in the filtrate from the nickel is determined with pyridine thiocyanate. When manganese is present it should be determined on a separate portion with sodium bismuthate and the necessary amount deducted from the weight of the ignited alumina. The magnesium in the sample is obtained by difference.

Modified Procedure in the Presence of Manganese, Zinc or Nickel.—In the presence of comparatively large amounts of zinc, manganese or nickel, the adjustment of the neutrality of the solution after filtering off Group II sulphides is more difficult. Zinc and manganese sulphides do not dissolve until the solution is distinctly acid. Instead of adding hydrochloric acid, as previously, till the precipitate just disappears, it is best, after the liquid has been made slightly ammoniacal, to add hydrochloric acid until the tint of the iron sulphide begins to fade, then to add the sodium sulphide solution, and to continue as before. Nickel gives an intensely black insoluble precipitate which completely obscures the neutral point. When nickel is present, ammonia is slowly added until a permanent black precipitate is formed, and then 2 or 3 more drops are added before the treatment with sodium sulphide. The filtrate from the alumina in all these cases should be tested by adding a little ammonia to ensure that the iron has been completely precipitated. It is advisable, moreover, when zinc, manganese or nickel is present in considerable quantity, or if more than 7 per cent. of aluminium is present, to dissolve the precipitate and repeat the sodium sulphide separation. The double precipitation does not require much more time, since it is not necessary to wash the first precipitate free from chlorides. The mixed precipitate is treated as described above for the determination of the various metals present.

Experimental.—The method was tested by adding known amounts of alum solution to a solution of four grms. of magnesium chloride in water together with, in certain cases, some zinc, nickel or manganese salts. The results for aluminium tended to be slightly high, even though the precipitated alumina was ignited in a muffle furnace. When tested for magnesium, however, by fusing the alumina with potassium bisulphate, dissolving the mass in dilute sulphuric acid, and precipitating the magnesium as phosphate in ammoniacal tartrate solution, it was shown that magnesium was absent. It should be pointed out that Hahn and Scheiderer (*Ber.*, 1924, **57**, 1854) state that magnesium in small amount is not precipitated

under these conditions. Our experiments have shown, however, that one per cent. of magnesium in aluminium can be accurately determined as phosphate in ammoniacal tartrate solution, and that 0·5 per cent. can be determined with substantially accurate results, provided that the solution is allowed to stand for 48 hours. The absence of a positive test for magnesium on the alumina precipitate shows, therefore, that the percentage of magnesium is less than the experimental error.

The results are given only to the first decimal place, as it is not considered that the second place has any significance.

	Percentage of aluminium	
	Added	Found
One precipitation	10·0	10·5, 10·3, 10·4, 10·2, 10·6
	8·0	8·5, 8·3, 8·3, 8·4
	6·5	6·6, 6·7, 6·7, 6·5, 6·5
	5·0	5·0, 5·0, 5·0, 4·9
Two precipitations	9·9	9·9, 9·9, 10·0
	7·9	8·0, 8·0, 8·1
Nickel present (one precipitation) ..	5·0	5·4
,, ,, (two precipitations) ..	5·0	5·0
Zinc ,, (one precipitation) ..	5·0	5·1
Manganese ,, (,, ,,) ..	5·0	4·9

I have to thank Sir Robert Robertson, the Government Chemist, for permission to publish this paper, and Mr. Gaskin of this department for assistance in the experimental work.

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Nitron as a Precipitant for Nitrates

BY J. E. HECK, H. HUNT, AND M. G. MELLON

(*Contribution from the Department of Chemistry, Purdue University*)

THE entrainment* of material by precipitates formed in solution presents one of the most disturbing problems confronting the analytical chemist, particularly when he is concerned with gravimetric precipitation processes. That the matter has had serious attention is evident from the literature, where one may find much work relating to the analytical significance of the phenomenon.

In recent years there has been an increasing use of various organic compounds as precipitating agents, such as benzidine, cupferron, dinitroresorcinol, 8-hydroxyquinoline, nitron, nitroso-β-naphthol, phenylthiohydantoic acid, pyridine and salicylaldoxime. In view of the voluminous character and the complex structure of some of the precipitates formed by certain elements with these precipitants,

* Entrainment is used in the general sense, without any commitment regarding the specific nature of the mechanism of the process involved.

it seemed that the specific surfaces and polarities of the compounds formed might be such as to exhibit interesting entraining capacities.

Saylor[1] concluded that, in some degree, all solid substances entrain from their mother liquor ions of electrolytes, molecules of solvent and dissolved non-electrolytes. The extent of this entrainment is known to vary greatly for different substances and for different conditions,[2] but we are without sufficient basis for calculating it quantitatively in any given cases. France[3] stated that no simple rule has yet been found that enables one to predict what foreign materials will be appreciably entrained by any given crystalline substance.

The object of this study was to determine whether precipitates, such as those mentioned above, entrain certain cations, and, if so, whether the magnitude of contamination is sufficient to influence seriously the precision of analytical determinations. In addition, an inspection of part of the previous work indicated, for some of the precipitates at least, the desirability of checking the reproducibility of individual determinations and the reliability of the methods under different conditions.

From the organic reagents available, nitron, a precipitant for the nitrate radical, was chosen for the first work. This compound seemed particularly promising, on account of the possibility of oxidising and volatilising the precipitate of nitron nitrate, leaving as a residue only material which had been entrained or incompletely removed during washing. This residue could then be examined spectroscopically or taken up in a solvent and tested colorimetrically. Nitron nitrate is appreciably soluble, and must, therefore, be treated with only a limited amount of washing medium. For this reason it was thought foreign material might be present from incomplete washing, if not from entrainment.

On account of the solubility of nitron nitrate Gutbier[4] expected low results with the method. Not finding this to be the case, he concluded that nitron acetate, the precipitant, might have been "occluded" sufficiently to compensate for the solubility. The results of others[5], from the time when the method was originally proposed by Busch, have indicated disagreement concerning errors, both in magnitude and direction. Some agreed well with what theoretically should have been obtained, even when the precipitation occurred in the presence of various other constituents, as reported by Vasiliev; some were low and some were appreciably high, as reported by Hes.

Experimental Work

Material and Apparatus.—The salts were recrystallised, except ferric chloride, which was prepared by passing dry chlorine gas over heated pieces of pure iron wire.[6] Conductivity water was used to prepare the solutions. To determine their metallic content, portions of 25 or 50 ml. were analysed by standard methods, as given in the reference for each of the following elements: Aluminium,[7] barium,[8] cadmium,[9] cobalt,[10] copper,[11] iron,[12] lead,[13] magnesium,[14] nickel,[15] potassium,[16] and sodium.[17] From the content of metal found the equivalent content of nitrate was calculated. The analytical data are not included.

A freshly prepared and filtered 10 per cent. solution of nitron in 5 per cent. acetic acid served as the precipitant.

The spectroscopic examination of precipitates was made by means of a Hilger instrument (E-3), with the use of an arc-spectrum and ortho plates.* To identify the metals, a search was made for their "persistent" lines in spectrograms according to the procedure of Holt.[18]

PRECIPITATIONS.—For precipitating the nitron nitrate Gutbier's modification[4] of Busch's original procedure[5] was used in most of the work. A solution containing about 0·12 grm. of nitrate in 100 ml., acidified with 12 to 15 drops of dilute sulphuric acid (2 : 3), was heated almost to boiling. To this were added, all at one time, 12 ml. of a 10 per cent. solution of nitron in 5 per cent. acetic acid. After being cooled to room temperature the beaker was placed in ice-water for an hour and a half. The precipitate was quickly transferred to a porcelain crucible with porous bottom, small portions of the filtrate being used to remove the last traces of precipitate. For the washing, not more than 12 ml. of ice-cold water were used, 2 to 3 ml. at a time, and the precipitate was drained as completely as possible after each washing. Finally, the precipitate was dried at 105° C., and the nitrate was calculated by means of the theoretical factor 0·1653. In some cases acetic or hydrochloric acid was substituted for sulphuric acid, the latter being unsuitable for the nitrates of lead or of the alkaline earths because of the low solubility of the corresponding sulphates.

Since both Gutbier[4] and Treadwell and Hall[19] suggested a possible "occlusion" of precipitant by the precipitate, the process of precipitation was reversed in certain cases to determine the effect upon the weight of precipitate found. No other direct means of testing this source of entrainment suggested itself.

By adding to the solution of a nitrate a salt having the same cation, but a different anion, a few precipitations were made in the presence of a concentration of cation greater than that equivalent to the nitrate present. A few precipitations were also made in solutions containing mixtures of several salts likely to be encountered in ordinary analyses, as others have found that from a mixture of electrolytes a particular ion is entrained less than if present alone. Furthermore, entrainment of a cation is influenced by the nature of the anion present.

Two modifications of the procedure were tried, one due to Vasiliev[5] and the other to Treadwell and Hall.[19] In the former the precipitate was washed mainly with a cold, saturated solution of nitron nitrate, and finally with 3 to 5 ml. of ice-cold water. In the latter the precipitate stood for 24 hours in the dark at room temperature before filtration, after which it was filtered off and washed with 50 ml. of a saturated solution of nitron nitrate at room temperature. In this case an empirical factor 0·1679 was used.

As a check on the gravimetric method with nitron nitrate several determinations were made by means of two adaptations of the Kjeldahl method and by Kolthoff's new method.[20, 21, 22] For all these titrimetric procedures 25 ml. of a solution of sodium or potassium nitrate were used.

Of the various methods tried for decomposing the nitron nitrate, preparatory to testing for entrained cations, the most workable procedure was heating with a mixture of concentrated sulphuric and nitric acids.[23] Since it proved long and troublesome, however, it was discarded in most of the work in favour of direct

* The spectroscopic examination was made by H. Hunt.

spectrographic examination. Examinations were made of precipitates obtained from each solution of a pure nitrate and from all solutions in which changes of acidity or other constituents were made, 0·01 grm. samples being used.

In order to obtain more concentrated samples the organic matter was completely oxidised, by the method mentioned above, in 0·3 grm. samples of a few precipitates obtained from solutions containing mixtures of salts. The inorganic residue was dissolved in a small amount of dilute hydrochloric acid and transferred to the anode.

A summary of the results for all precipitations made of nitron nitrate and of evidence of entrainment of cations found on examination of the respective precipitates is given in Table I. Table II contains the comparative results for the several methods of determining the nitrate radical.

TABLE I

DATA FOR PRECIPITATES OF NITRON NITRATE

No. of detns.	Cation added Grms.	Weight of NO_3: Assumed present Grm.	Weight of NO_3: Average found Grm.	Maximum deviation from mean Grm.	Difference Grm.	Acid used: Kind	Acid used: Vol.	Acid used: Conc.	Spectroscopic evidence
				Aluminium nitrate					
4		0·1186	0·1177	±0·0003	−0·0009	H_2SO_4	15 dps.	2:3	No Al
				Barium nitrate					
1		0·1193	0·1191		−0·0002	HCl	25 ml.	0·2 *N*	
1*		0·1193	0·1190		−0·0003	HCl	25 ml.	0·2 *N*	No Ba
1	0·133 Ba(*a*)	0·1193	0·1193		0·0000	HCl	25 ml.	0·2 *N*	Tr. Ba
1*	0·133 Ba	0·1193	0·1188		−0·0005	HCl	25 ml.	0·2 *N*	
				Cadmium nitrate					
2		0·1239	0·1225	±0·0000	−0·0014	H_2SO_4	15 dps.	2:3	Tr. Cd
2	0·110 Cd(*b*)	0·1239	0·1224	±0·0001	−0·0015	H_2SO_4	15 dps.	2:3	Tr. Cd
				Cobalt nitrate					
2		0·1182	0·1178	±0·0001	−0·0004	H_2SO_4	15 dps.	2:3	Tr. Co
2*		0·1182	0·1175	±0·0002	−0·0007	H_2SO_4	15 dps.	2:3	Tr. Co
				Copper nitrate					
2		0·1460	0·1443	±0·0000	−0·0017	HOAc	10 ml.	0·5 *N*	Tr. Cu
2		0·1460	0·1440	±0·0004	−0·0020	HOAc	50 ml.	0·5 *N*	Tr. Cu
2		0·1477	0·1453	±0·0001	−0·0024	HCl	25 ml.	0·2 *N*	Tr. Cu
2	0·122 Cu(*c*)	0·1477	0·1454	±0·0000	−0·0023	HCl	25 ml.	0·2 *N*	Tr. Cu
				Potassium nitrate					
4		0·1202	0·1192	±0·0001	−0·0010	H_2SO_4	15 dps.	2:3	No K
2		0·1202	0·1195	±0·0001	−0·0007	No acid used			No K
2	0·038 K(*d*)	0·1202	0·1194	±0·0001	−0·0008	No acid used			No K
				Magnesium nitrate					
2		0·1199	0·1193	±0·0001	−0·0006	H_2SO_4	15 dps.	2:3	No Mg
2		0·1348	0·1337	±0·0002	−0·0011	HCl	25 ml.	0·2 *N*	No Mg
3	0·053 Mg(*e*)	0·1348	0·1338	±0·0003	−0·0010	HCl	25 ml.	0·2 *N*	No Mg
2	0·133 Mg	0·1348	0·1338	±0·0001	−0·0010	HCl	25 ml.	0·2 *N*	No Mg
2		0·1348	0·1333	±0·0000	−0·0015	H_2SO_4	15 dps.	2:3	No Mg
2		0·1348	0·1334	±0·0001	−0·0014	HOAc	10 ml.	0·5 *N*	No Mg
2		0·1348	0·1334	±0·0001	−0·0014	HOAc	50 ml.	0·5 *N*	No Mg
2	0·061 Cu(*c*)	0·1348	0·1339	±0·0001	−0·0009	HCl	25 ml.	0·2 *N*	Tr. Cu

TABLE I—*continued*

No. of detns.	Cation added Grms.	Weight of NO_3 Assumed present Grm.	Weight of NO_3 Average found Grm.	Maximum deviation from mean Grm.	Difference Grm.	Acid used Kind	Acid used Vol.	Acid used Conc.	Spectroscopic evidence
				Nickel nitrate					
3		0·1197	0·1193	±0·0003	−0·0004	H_2SO_4	15 dps.	2:3	Tr. Ni
1*		0·1197	0·1193		−0·0004	H_2SO_4	15 dps.	2:3	
1	0·057 Ni(*f*)	0·1197	0·1199		+0·0002	H_2SO_4	15 dps.	2:3	
1*	0·057 Ni	0·1197	0·1191		−0·0006	H_2SO_4	15 dps.	2:3	Tr. Ni
				Sodium nitrate					
4		0·1201	0·1194	±0·0001	−0·0007	H_2SO_4	15 dps.	2:3	
2	0·016 Al(*g*) 0·057 Ni(*f*) 0·061 Cu(*h*)	0·1201	0·1197	±0·0001	−0·0004	H_2SO_4	15 dps.	2:3	Tr. Ni Tr. Cu
2	0·016 Al(*g*) 0·057 Ni(*f*) 0·061 Cu(*h*)	0·1201	0·1196	±0·0002	−0·0005	H_2SO_4	15 dps.	2:3	Tr. Ni Tr. Cu
2	0·133 Mg(*e*) 0·057 Ni(*f*) 0·061 Cu(*h*)	0·1201	0·1197	±0·0001	−0·0004	H_2SO_4	15 dps.	2:3	Tr. Ni Tr. Cu
2	0·133 Mg(*e*) 0·057 Ni(*f*) 0·061 Cu(*h*)	0·1201	0·1192	0·0000	−0·0009	H_2SO_4	15 dps.	2:3	Tr. Ni Tr. Cu
2	0·133 Ba(*a*) 0·485 Pb(*i*)	0·1201	0·1199	±0·0002	−0·0002	HCl	25 ml.	0·2 *N*	No Ba No Pb
2	0·133 Ba(*a*) 0·047 Fe(*j*)	0·1201	0·1191	±0·0003	−0·0010	HCl	25 ml.	0·2 *N*	Tr. Fe
2	0·047 Fe(*j*)	0·1201	0·1196	±0·0001	−0·0005	H_2SO_4	15 dps.	2:3	Tr. Fe
2	0·047 Fe	0·1201	0·1192	±0·0001	−0·0009	H_2SO_4	15 dps.	2:3	Tr. Fe
				Lead nitrate					
2		0·1192	0·1194	±0·0001	+0·0002	HCl	25 ml.	0·2 *N*	No Pb
2*		0·1192	0·1195	±0·0002	+0·0003	HCl	25 ml.	0·2 *N*	No Pb
2	0·485 Pb(*i*)	0·1192	0·1190	±0·0001	−0·0002	HCl	25 ml.	0·2 *N*	No Pb
2		0·1192	0·1192	±0·0000	0·0000	HOAc	10 ml.	0·5 *N*	No Pb
2	0·970 Pb	0·1192	0·1194	±0·0001	+0·0002	HCl	25 ml.	0·2 *N*	No Pb
2	0·970 Pb	0·1192	0·1190	±0·0003	−0·0002	HOAc	10 ml.	0·5 *N*	No Pb
2		0·1192	0·1192	0·0000	0·0000	HOAc	50 ml.	0·5 *N*	No Pb

* Solution of the nitrate added at boiling temperature to the solution of the nitron.

Cations added in the form of the salts indicated:—(*a*) $BaCl_2$; (*b*) $CdSO_4$; (*c*) $CuSO_4$; (*d*) K_2SO_4; (*e*) $MgSO_4$; (*f*) $NiCl_2$; (*g*) $Al_2(SO_4)_3$; (*h*) $Cu(C_2H_3O_2)_2$; (*i*) $Pb(C_2H_3O_2)_2$; and (*j*) $FeCl_3$.

DISCUSSION OF RESULTS.—The significance of the data presented may be considered from two view-points: (i) Evidence of entrainment by the precipitate of nitron nitrate, and (ii) evidence bearing upon the general reliability of the method for the gravimetric determination of the nitrate radical.

The two sources of entrainment considered here were cations present in the solution from which the precipitate separated, and the precipitant itself, nitron. An inspection of the results presented in Table I and of the spectrogram shows little evidence of the presence, in the precipitate, of appreciable amounts of the metals present at the time of precipitation. The order of mixing solution and precipitant did not affect the results of these tests. Even in the case of the concentrated samples the amounts of metals detected were still quantitatively unimportant. In nearly all cases the spectrograms showed more sodium and

silicon than the other constituents which it was thought might be present. For this reason precipitates obtained from sodium nitrate were not examined spectroscopically for sodium.

TABLE II

THE NITRATE IN NITRATES BY DIFFERENT METHODS

No. of detns.	Method	Nitrate: Assumed present Grm.	Nitrate: Average found Grm.	Maximum deviation (±) from mean Grm.	Difference Grm.
4	Gutbier–Busch	0·1201*	0·1191	0·0001	−0·0010
6	Devarda alloy	0·1201*	0·1154	0·0004	−0·0047
5	Moore	0·1201*	0·1142	0·0007	−0·0059
4	Vasiliev–Busch	0·1200†	0·1194	0·0000	−0·0006
4	Treadwell–Hall	0·1200†	0·1201	0·0001	+0·0001(E)
		0·1200†	0·1183	0·0001	−0·0017(T)
4	Kolthoff	0·1200†	0·1193	0·0005	−0·0007

* Determined by calculation from the amount of sodium sulphate obtained from a portion of 25 ml. of the solution of sodium nitrate.
† Weighed directly as potassium nitrate.
(E) Using the empirical factor 0·1679.
(T) Using the theoretical factor 0·1653.

In the system studied, specific tests for the presence of entrained precipitant in the precipitate did not seem to be available. It was assumed that, if such entrainment does take place, the addition of the solution of nitrate to the nitron acetate would provide more favourable conditions, which would result in increased entrainment, and thus affect the weight of precipitate obtained. Two authors state that the method yields somewhat high results and attribute this to such entrainment. Since the weights of precipitate obtained in the present work did not vary appreciably with the different order of mixing the solutions, it was concluded that entrainment of precipitant is not a significant factor in affecting the errors involved in the method.

Assuming now that one may disregard entrainment of cations or precipitant as a source of appreciable error, there remains the question of the general reliability of the method, including both the reproducibility of individual determinations and the actual error of results obtained with the method. It has already been stated that the results of others show considerable variation in these items. Only Gutbier and Treadwell and Hall state definitely that the results are high. In the other cases some are high, some agree well, and some are definitely low, compared with the theoretical values. The latter quantity was determined in various ways, probably not all equally dependable.*

In considering the present work, the data in Table I show, by the maximum deviations from the mean, that the reproducibility of individual determinations may be taken as quite satisfactory, particularly in view of the restrictions necessary in washing the precipitate.

Much more disturbing is the disagreement between the average value actually found for sets of determinations and the amount of nitrate calculated to be in the

* See Hillebrand and Lundell, *loc. cit.*, p. 639, for a criticism of the method of determining nitrogen by means of a nitrometer, as used by Collins.[5]

sample. For the different sets the latter quantity, as already indicated, was calculated on the assumption that an amount of nitrate would be present equivalent to the metal determined. For any salt that could be so handled the solution was prepared by direct weighing of the solid and then, as a check on the concentration, the metal was determined by the procedure previously mentioned. In such cases standardisation by determining the metal agreed within 0·2 per cent. with the value calculated from direct weighing. In addition, some of the salts were tested and found to conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Admittedly such a determination of the content of nitrate was not as satisfying as a direct method would provide. Consequently, efforts were made to obtain more direct evidence. The results in Table II include the results secured by several such methods, two of them modifications of the familiar Kjeldahl method, and the third a procedure recently proposed by Kolthoff. In the Kjeldahl procedures it seems reasonable to assume that the reduction was not complete, but no higher results could be obtained. The method of Kolthoff was not available in time to check all the solutions. Applied to a solution of potassium nitrate it yielded results averaging about the same, but not as reproducible as those obtained on the same solution by the nitron nitrate method.

If one makes the assumption that direct weighing of the purified salt, supplemented by gravimetric standardisation of the solution and by demonstration of conformity to specifications for purity, is sufficient evidence on which to base a calculation of the content of nitrate in the salt, then the present work indicates that in no case were appreciably high results obtained by the gravimetric determination of the nitrate. For lead, the average for all determinations was close to the calculated value; for all others, the results were low, those for copper being the lowest. If the direct volumetric determinations are taken as a more nearly correct measure of the nitrate in solution, part of the results are high, and part low, depending upon the method used in making the comparison. We are inclined to accept the first alternative. This leaves without interpretation the variation in lowness for the different salts. The chief possibilities seem to be either some error in the determination of the cation or some variation from equivalent amounts of cation and anion in the solutions. No evidence for either of these possibilities was found.

As a final point it may be mentioned that the nitron nitrate forms as a white compound in the form of relatively large crystals which are easily handled, with the exception of the necessary limitations on temperature and amount of washing. Others[24] have called attention to the advantage of using the method in certain situations. At present the cost of nitron is a definite disadvantage.

SUMMARY.—As a result of a study of the precipitation of nitron nitrate from solutions of various salts under different conditions, the following conclusions were reached:—(i) Entrainment, either of metallic cations or of precipitant, did not occur to an extent sufficient to influence appreciably the precision of analytical results.

(ii) The reproducibility of individual determinations was satisfactory, considering the solubility of the precipitate.

(iii) The reliability of the method varies for the different systems studied, if one assumes that the nitrate present is equivalent to the amount of metal found by a direct determination.

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Finger-print Detection

BY HENRY L. BROSE, M.A., D.PHIL., D.SC.

IN cases where finger-prints have been left on multi-coloured objects, such as check-patterned cigarette cases, it has been found that the ordinary photographic methods give results that are not sufficiently clear to allow the imprint to be identified or used as evidence. The back-ground comes out far more clearly than the finger-print, and it is impossible to find the twelve characteristic features of the imprint which are considered the minimum number necessary to establish identity.

A brief report of two methods devised to overcome the difficulty caused by the intrusion of the back-ground into the photographs was given in a recent issue of *Nature* (**1933**, **132**, 208). The purpose of the present note is to give the technical details of the processes. In the first method the details of the finger-print were isolated from the object on which it had been imprinted by dusting phosphorescent zinc sulphide powder on to the finger-print, and photographing the powder pattern after it had been rendered luminous by a source of ultra-violet light (mercury-vapour lamp, tungsten arc or carbon arc). The excess of powder

between the ridges of the finger-print had to be carefully removed by gently blowing or by brushing with a soft camel's hair brush. The illumination and exposure were made to alternate with one another in the manner familiar from Becquerel's phosphoroscope. This intermittent illumination is necessary in order to separate the phosphorescent light from the ordinary visible light. If, however, a sheet of Wood's glass (obtained from Messrs. Chance Bros., Ltd.) is interposed between the source of ultra-violet light and the object bearing the finger-print, only the "dark radiation" falls on the object and excites phosphorescence. In this case it is found advisable to place a sheet of Chance's calorex glass in front of the Wood's glass to absorb the extreme red and the near infra-red rays, since the Wood's glass cracks very readily if unevenly heated. To photograph the phosphorescent finger-print it is now necessary to perform the reverse operation, that is, to eliminate all the ultra-violet light and to transmit only the visible light into the camera. This is accomplished by interposing a thick plate of Andrew's super-protex glass between the object and the camera.

It is commonly believed that the glass used for lenses of ordinary cameras transmits only light of the visible region of the spectrum. This is by no means the case. Ordinary glass does not cut off the ultra-violet light sharply, but transmits a not inconsiderable portion of the nearer ultra-violet. Super-protex glass contains a relatively high percentage of lead, and is therefore used to absorb *X*-rays. (The absorbing power of *X*-rays depends on the atomic number, and hence also on the atomic weight of the absorbent.) Investigation has shown that super-protex glass cuts off the ultra-violet light very sharply. Instead of protex glass we may use an aqueous solution of cerium ammonium nitrate contained in a rectangular cell with ordinary glass walls. It may be mentioned that the Wood's glass, referred to above, may likewise be replaced by a cell containing a solution of nitroso-dimethylaniline, but in this case the walls of the cell must be composed of quartz or of the much less expensive "vita glass." Vita glass transmits a considerable amount of ultra-violet light of the longer wave-length, and has rendered excellent service in the present investigation. A simple form of light-filter may be made by fixing a rubber ring with flat sides between two sheets of vita glass, the ring being left open at the top so as to provide an aperture through which the solution under examination or being used as a filter may be admitted. The glass walls may be clamped together by means of insulation tape tightly wound round the edges of the cell. We have used cells in which the rubber rings have had a diameter of eight inches. The "time" of exposure for these phosphorescent photographs is about twenty minutes if very fast Ilford hypersensitive panchromatic plates are used, but sharper contrasts are obtained with Ilford rapid process panchromatic plates, for which the exposure must be extended to forty minutes. The Wellington 450 plates are also very good for this purpose.

The second method of photographing finger-prints is by means of fluorescent light. In this case the illumination of the object is continuous. The arrangement of apparatus is the same as that used for continuous phosphorescence. The incident ultra-violet light passes through calorex glass and Wood's glass, and the resulting fluorescent light passes through protex glass into the camera. The accompanying figures are copies from photographs obtained with the fluorescent

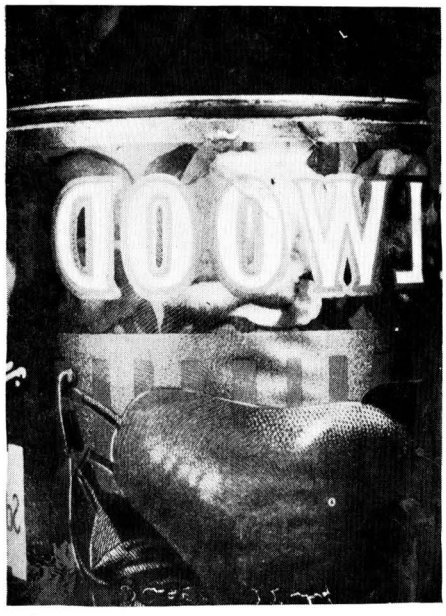

Fig. 1

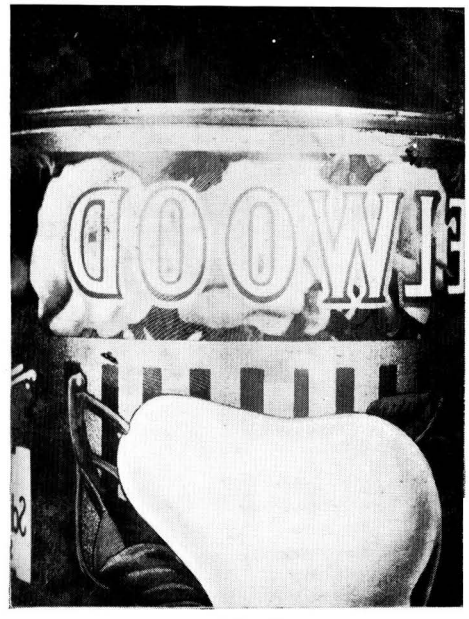

Fig. 2

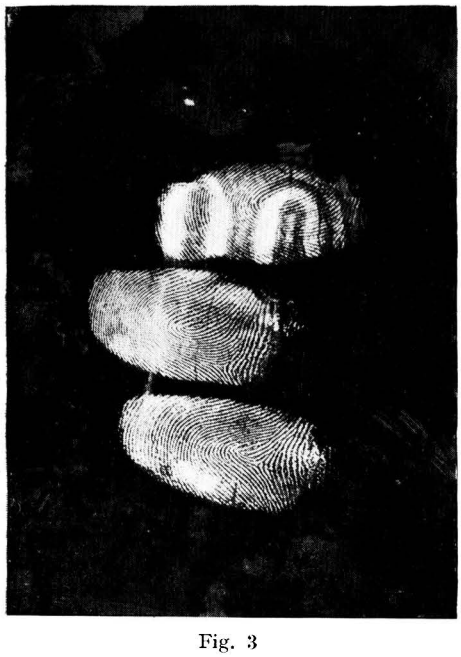

Fig. 3

Fig. 4

Photographs of finger-prints on the multi-coloured label of a fruit tin
(Taken by members of the Derby Criminal Investigation Department)

Fig. 1, with an ordinary camera.
Fig. 2, with Wood's glass interposed.
Fig. 3, with anthracene powder dusted on to the prints.
Fig. 4. A contact print from a reversed plate (Wellington 450) with protex glass filter between object and camera. Two minutes' exposure. Stop, F.32.

method by members of the Derby C.I.D. In place of the phosphorescent powder they used very pure finely powdered anthracene. Fig. 1 represents a photograph of a finger-print taken with an ordinary camera, a Hanovia Quartz Lamp being used as the illuminant. The impress had been made on the multi-coloured label of a fruit tin. In Fig. 2 Wood's glass had been interposed between the source and the label. The finger-print has come out slightly more clearly, but not sufficiently so to admit of identification. In Fig. 3 the photograph was taken with anthracene on the ridges of the finger-print, and Fig. 4 shows a contact print made from a lantern-slide of Fig. 3. In Fig. 4 the finger-print has been almost completely isolated from the back-ground, so that the task of identification has been made extremely simple. The phosphorescence method was worked out in conjunction with members of the Nottingham C.I.D.

It is important to ensure that no light enters the camera, except that from the fluorescent or phosphorescent object; this may be achieved by using a light-tight conical funnel blackened on the inside. Both the camera and the ultra-violet light source must be carefully screened. The technique described above may, of course, be used for the photography of any fluorescent object whatsoever, and the use of the glasses and photographic plates mentioned will be found to enable good photographs to be obtained with time of exposure much less than is usual (often many hours) when other materials are used. The interposition of calorex glass allows the source of light to be brought much nearer to the object than when Wood's glass is used alone; this again reduces the time of exposure.

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Notes

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

THE COMPOSITION AND CALORIFIC VALUE OF ENGLISH CIDER

Two kinds of cider can be differentiated and characterised:

I. SHARP CIDERS (*Cidres de pommes aigres. Apfelwein*).—In the fruit mixture sharp apples must preponderate. The juice is pale and thin, being low in tannin, but high in acidity and total nitrogen. The fermentation is rapid, rather tumultuous, and complete; the sugar disappears before the nitrogen is exhausted. The ciders are not naturally sweet, but they can be made sweet. A great loss of titratable acidity occurs during manufacture (Säureabbau; désacidification). The juice from the press has from 0·7 to 1·5 per cent. of acidity (calculated as tartaric acid), and half of this may be lost, malic acid being equi-molecularly transformed into lactic acid. Ciders A to F in the following table are sharp ciders, ranging from a sparkling apple wine to a still, diabetic cider. The first had 465 calories per pint, and the specially dry cider had 275, thus being equal to stout in food value. The manufacture of sharp cider provides an alternative market for the grower of table and culinary apples.

II. WEST-COUNTRY CIDER (*Cidres naturellement doux, sucrés par fermentation alcoolique incomplète*).—The fruit must include a suitable proportion of bitter-sweet, sharp, and sweet cider apples. The juice is coloured and darkens on contact with oxygen or alkali. The sp.gr., sugar, tannin and pectin are high, whilst the nitrogen and acidity (below 0·7 per cent.) are low. The fermentation is slow and incomplete, throwing up a brown head and depositing calcium pectate (*fermentation pectique*). Extraction of the juice by diffusion inevitably introduces some 20 per cent. of water. The composition and calorific values of G and H are typical. Chapman (1932) gives 275 calories for bottled cider and 228 for draught cider. Cider apples are useless for anything except cider-making.

The extract or total solids of cider includes mineral matter, sugar, tannin, pectin, glycerol, sorbitol, and organic acids, some of which have a doubtful *net* energy value. For the present purpose, however, the calorific value is taken to be: Calories, per pint = (extract per cent. × 22·4) + (alcohol Vol. per cent. × 32.0).

	A	B	C	D	E	F	G	H
Sp.gr.	1·0114	1·0222	1·0253	1·0098	1·0189	0·9979	1·0194	1·0218
Original gravity	1·0868	1·0784	1·0701	1·0677	1·0592	1·0529	1·0537	1·0395
Acidity (tartaric)	0·78	0·83	0·61	0·59	0·59	0·56	0·45	0·38
Alcohol (by vol.)	10·03	7·36	5·79	7·60	5·21	7·16	4·36	2·30
Extract ..	6·42	8·40	8·66	5·25	6·82	2·05	6·70	6·44
Sugars	4·12	6·16	6·91	3·17	5·32	0·12	5·13	5·35
Non-sugars ..	2·30	2·24	1·75	2·08	1·50	1·93	1·57	1·09
Ash	0·23	0·21	0·17	0·23	0·13	0·22	0·23	0·13
Calorific value ..	465	423	379	361	319	275	290	218*

* Saccharin present.

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THE DETERMINATION OF CARBON IN GRAPHITED CUP GREASES

I WAS recently asked to determine the amount of carbon in samples of graphited cup greases and to report on the quality of the carbon. The specification required that the greases should consist of a lime soap base with the addition of 5 per cent. of graphitic carbon. It was, therefore, necessary not only to determine the free carbon, but to isolate it in an unchanged form for further examination. The following method was found to be very satisfactory:

From 3 to 4 grms. of the sample are weighed into a small beaker, 30 to 40 ml. of glacial acetic acid are added, and the mixture is gently boiled for a few minutes. During this operation the lime soap base is first dispersed in the acetic acid in the form of small liquid globules, and subsequently dissolves completely, being decomposed into calcium acetate and higher fatty acids.

The mixture is filtered, with the aid of slight suction, through a weighed Jena-glass crucible with sintered glass disc of suitable porosity. The residue of carbon in the crucible is washed two or three times with hot glacial acetic acid, and then thoroughly with hot water, after which the crucible and contents are dried and weighed.

The above method is quick and reliable; a perfectly sharp separation is achieved, and the carbon can be further examined if required.

The disc of the crucible can be cleaned afterwards by the prolonged action of hot fuming nitric acid, to which a little potassium chlorate has been added, followed by extraction with dilute solution of alkali and washing.

F. HEATHCOAT

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AN AID TO THE READING OF GERBER MILK-FAT TUBES

OWING to the transparency of the fat separated in the Gerber method of determination, the reading of a large number of tubes in artificial light, or even in daylight, is tiring, especially when the graduations on the tubes are not widely separated. The meniscus is made more visible by the following device:

A light-tight box, of height greater than the length of a Gerber tube, and width not less than three inches, has one face removed and replaced by a sheet of glass, the inner side of which is completely covered by grease-proof paper. Inside the box an ordinary electric filament lamp is placed and connected with a plug or switch. The box is then fixed to the wall at a convenient height, forming a translucent window. The Gerber tube is held at a distance of about one inch from the glass, against which both the zero line and the upper meniscus of the fat layer stand out clearly. We have not tried ground-glass in place of the paper-covered glass but, no doubt, this would give equally good results.

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FREEZING-POINT OF MILK—HORTVET METHOD

I WISH to point out an omission in the instructions given in the *Methods of Analysis of the A.O.A.C.*, which I think might be worth recording in THE ANALYST.

No mention is made of the necessity of removing the freezing starter from the apparatus before tapping the thermometer, proof of which is shown in the following experiment. On one occasion the starter was accidentally left in while the zero was being determined, and a zero of +0·040° C. was obtained, as against +0·022°C. To test whether the starter had anything to do with the former figure, several determinations of the zero were made, with and without removal of the starter. When the starter was removed a constant zero of +0·022° C. was obtained, but when it was left in, the zero varied between +0·022° C. and +0·040° C. After a constant zero of +0·022° C. had been obtained, the starter, which had been kept in ice, was again inserted, and the thermometer tapped; the zero jumped up to +0·038° C. In every instance when the zero jumped, there was a distinct click, as though the starter had hit the thermometer during tapping. The above experiment has also been tried on samples of milk and with similar results.

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Official Appointments

THE Minister of Health has approved the following appointments:

FREDERICK WILLIAM EDWARDS as Public Analyst for the Metropolitan Borough of Westminster (City of), in place of P. A. Ellis Richards, resigned December 31st, 1933 (December 23rd, 1933).

ALBERT HOULBROOKE as a Public Analyst for the County Borough of Leeds, in addition to C. H. Manley (December 23rd, 1933).

Erratum:—January issue, p. 29: *For* "F. G. D. Chambers" *read* "F. G. D. Chalmers as Additional Public Analyst for Coventry.

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 THIRD QUARTER, 1933

OF the 1193 samples of food and drugs examined during the quarter, 11 were bought formally and 1182 informally. The total number returned as adulterated or incorrect was 65.

TEA "FREE FROM TANNIN."—A sample was labelled as being composed only of the tips of the leaves and therefore free from tannin. Analysis showed it to contain 14·1 per cent. of tannin. The packers agreed to amend their description, and circulars to this effect were sent to their customers.

LIQUID PARAFFIN.—A sample of liquid paraffin was not of the correct viscosity, the figure being 237 seconds, as against the minimum B.P. figure of 260 seconds. The sample was examined by the supplying firm, and they agreed that it was not of B.P. quality, and replaced the liquid paraffin remaining in stock by a new supply of the correct viscosity.

H. H. BAGNALL

BRISTOL

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1932

SIXTY-SIX of the 1400 samples of foods and drugs examined were adulterated.

TEA.—Seventeen samples gave the following mean analytical results: Total ash, 5·67; soluble ash, 3·44; alkalinity (as K_2O), 1·65 per cent. There was no evidence of spent leaves or foreign structures, but two samples contained excess of stalk and gave soluble ash, 2·7; and alkalinity, 1·3 per cent.

PRESERVATIVE IN WALNUTS.—Three samples of walnuts containing sulphurous acid were condemned, the amounts being 0·12, 0·04 and 0·01 per cent.

PORT SAMPLES.—One hundred and sixty-nine samples were examined, including dried fruits, fruit pulps, etc., mainly for the presence of preservative. A sample

of raisins alleged to be damaged contained 0·14 per cent. of combined chlorine, thus showing slight but definite evidence of contamination. Samples of white haricot beans and rice, alleged to be damaged, contained fungal hyphae, and the washings from the beans also contained excess of chlorine.

Arsenical Contamination of Frozen Meat.—Frozen liquid from cloth off two lambs' carcases contained 0·0004 and 0·004 per cent. of arsenious oxide, and a sample of frozen liquid and meat contained 0·0028 per cent. Thirteen other samples of meat, cloth or ice, suspected of containing arsenic, gave a negative result or contained mere traces in 5 cases; the remaining 8 samples gave amounts ranging from 0·00003 to 0·0025 per cent. of arsenious oxide.

An investigation was made by the Medical Officer of Health to discover the origin of the contamination. The carcases affected were for the most part in two tiers in the hold of the ship, and above them there was evidence of a leak in the deck having taken place. Samples of pelts and of pelt liquor which had been discharged at London from that deck were examined, but it was concluded that they were not the source of the arsenic. Every other effort to trace the origin of the contamination was unsuccessful.

Gas in Tinned Cherries.—Samples of cans of cherries having a blown appearance were opened by sterile puncture, and inoculation made into broth tubes; in every instance, except one, the contents were sterile, and had an agreeable taste. Gas collected from two of the tins measured 25 ml., and proved to be hydrogen. The interiors of the tins were slightly excoriated, but there was only 0·01 per cent. of tin in solution, or about half the amount corresponding with the hydrogen present. It was concluded that the cherries were perfectly sound.

EDWARD RUSSELL

LEICESTER

ANNUAL REPORT OF THE CITY ANALYST FOR 1932

THE number of samples examined was 2386, of which 1472 were of food and drugs. These included 900 milk samples and 43 of these were reported "not genuine."

ALKALINE LARD.—A sample, which was alkaline in reaction and yielded 0·13 per cent. of ash consisting of sodium carbonate, was condemned. It was not clear whether the alkali had been deliberately added to mask acidity, or whether its presence was accidental from a previous washing process.

POTTED MEAT.—Of 36 samples examined, 3 contained starchy matter equivalent to 8·8, 5·1 and 6·8 per cent. of dry starch, respectively. There is no provision in the Public Health (Preservatives, etc., in Food) Regulations for any cooked meat to contain preservative. Two of the samples containing starch also contained sulphur dioxide (162 and 135 parts per million). The maker had used a preservative preparation intended for use only with sausage meat.

One sample contained 28 parts of sulphur dioxide per million, but the maker emphatically denied that he had used any preservative, and submitted a further sample for examination. This was found to contain 9 parts of sulphur dioxide per million. Ten days later, when the sample was in a decomposing condition, the apparent sulphur dioxide content had risen to 55 parts per million. The inference was that the sample was exhibiting incipient decomposition, although no other indications of this had been observed. Potted beef, when made from corned beef, tends to give off traces of volatile sulphur compounds under the usual conditions of determination.

CELERY PILLS.—Samples were accompanied by a formula giving the composition of each pill, one item in which was "Phenolphthalein . . . gr. $\frac{1}{5}$." Analysis showed that none of this ingredient (the most expensive in the formula) was present. The manufacturer was cautioned.

Many compound drugs are now sold with the composition declared, the object being to avoid paying Stamp Duty, since no proprietary rights are claimed. In the case of such products, there seems good scope for sampling, since there can be no question of the fairness of judging an article by a standard volunteered by the manufacturer; however, the onus should be on the manufacturer and not on the retailer.

BATH WATERS.—The great amount of bacterial pollution which may occur in swimming baths has long been recognised, and continuous treatment is necessary to maintain the water in a safe condition. The most effective agent for this purpose is chlorine, following the processes of filtration and aeration.

One can only be sure of the safety of the water by making regular bacteriological examination; the treatment can then be adjusted accordingly. About one part of chlorine per million is the optimum amount. A certain threshold value is necessary to oxidise organic matter, nitrites, etc., before the residual chlorine has any bactericidal effect, while amounts much in excess of one part per million become self-evident and objectionable to bathers.

After some preliminary tests, the following standards were adopted, and regular sampling was carried out throughout the year.

Standards.—(i) The free chlorine shall not exceed 0·5 part per million. (ii) The bacterial count (24 hours on agar at blood heat) shall not exceed 1000 organisms per c.c.; (iii) *Bacillus coli* shall not be present in more than two out of five 10 c.c. tubes.

System of Sampling.—Each bath is sampled the first week it is open to the public for the year. If the water fails in any one of the above tests it is sampled again weekly until a satisfactory sample is obtained. It is then sampled again after a fortnight, and, if still satisfactory it is sampled thereafter once a month.

If the first sample from a bath is satisfactory it is sampled again after a fortnight, and thereafter monthly while it remains satisfactory.

Generally speaking, it has been found that so long as the water gives a good reaction for free chlorine the bacterial results are satisfactory, and *vice-versa.*

F. C. BULLOCK

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.

MINT ADULTERATED WITH AILANTHUS LEAVES

On November 27th three shopkeepers were summoned at Sheffield Police Court for selling packets of dried mint adulterated with ailanthus leaves in proportions ranging from 15 to 20 per cent.

Mr. John Evans, F.I.C., the City Analyst, said that the foreign leaves in the sample of dried mint examined by him were leaves of the ailanthus, or "tree of heaven" (*A. glandulosa*), a Chinese tree which had been acclimatised in Europe.* They did not possess the properties of mint, or of sage, marjoram or thyme, which belonged to the same order of herbs as mint. They were quite useless, and were not accidental impurities.

For the defence it was urged that technical and unavoidable offences had been committed. The mint in question was a blend of British and foreign mint leaf, and the foreign constituents had been adulterated before it reached this country. The mint had been supplied to the respective defendants in packets and had been sold in the same form. The London wholesalers, who had supplied the mint to one of the defendants, had heard of the adulteration earlier in the year, and, acting on the representation of the Ministry of Health, had attempted to get back all supplies; they had, in fact, recovered 309 lbs. of mint, representing from 6000 to 7000 packets, and it was extraordinarily unfortunate that the inspector should have got some of the packets that had not been returned.

Fines of 5s. and costs were imposed in each of the three cases.

A firm of Sheffield manufacturing chemists was then charged with "consigning certain food, to wit, dried mint, which was not of the nature, substance and quality demanded by the consignee, and contained foreign leaf."

* Structure of Ailanthus Leaves.—The accompanying diagrams and description of the microscopic structure of *Ailanthus* leaves are reproduced by permission of Messrs. G. Stafford Allen and H. Deane from their communication to the British Pharmaceutical Conference, 1914 (*Year Book of Pharmacy*, 1914, p. 337). Calcium oxalate crystals are distributed in lines along the veins, in some leaves occurring even in the smallest branches. Fig. I is an intermediate example. The epidermal cells are polygonal, and stomata occur only on the lower surface (Fig. II). The striations on the upper surface usually radiate from the hairs. These are characteristic, being

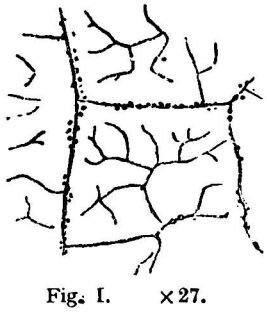

Fig. I. ×27.

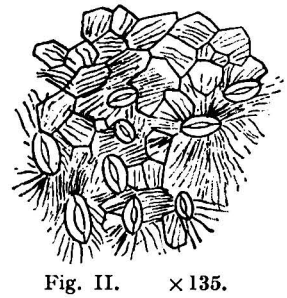

Fig. II. ×135.

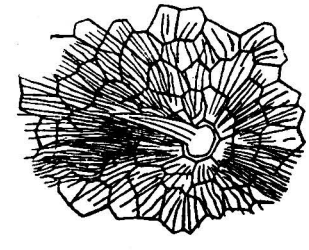

Fig. III. ×135.

slightly curved, unicellular, and usually thick, though occasionally thin-walled. Sometimes they attain a great length; the hair represented in Fig. III is rather short. The leaves were for a long time used as a substitute for sumach, which they resemble, but it was shown by A. G. Perkin (*J. Chem. Soc.*, 1898, **73**, 383) that they are valueless as a tanning agent. According to Mitlacher (*Z. allgem. Oest. Ap. Ver.*, 1911, **49**, 149) *Ailanthus* leaves were being used in 1911 in Italy as an adulterant of senna and of belladonna.

Mr. John Evans said that the sample in question contained not less than 12 per cent. of ailanthus leaves. He did not think that its therapeutic action had been worked out, but agreed that, so far as he knew, ailanthus was perfectly harmless. He would consider that he was prejudiced if he received mint sauce or savoury stuffing containing ailanthus, just as much as he would be if he received stuffing containing sawdust, which was also inert from the therapeutic point of view.

Mr. Okell submitted that there was no case for the defendants to answer, since the section of the Act under which the summons had been issued related to the purchase of goods from a retailer. The defendants were wholesalers, and, in his submission, there was no case against the wholesaler. The Act dealt in the first place with the person who originally mixed the herb. The firm was summoned as consignors, and he submitted that that form of summons did not allege an offence, but that the summons had been concocted under another section of the Act, which provided that the sampling officer might, when the retailer was delivering goods to the purchaser, take a sample at the place of delivery. The summons was formed under that section, but that section did not specify any offence; it simply described the powers of the sampling officer.

There could be no doubt that his clients were innocent victims who had been badly let down by their foreign supplier.

A fine of £20 and costs was imposed.

Mr. Okell said that notice of appeal would be given.

Department of Scientific and Industrial Research

REPORT OF THE FUEL RESEARCH BOARD FOR THE YEAR ENDED MARCH 31ST, 1933*

THE Report opens with a summary of the main investigations in progress at the Fuel Research Station and in the Survey Laboratories, and is followed by the more detailed report of the Director of Fuel Research, which is divided into an Introductory Section and nine other sections.

PHYSICAL AND CHEMICAL SURVEY OF THE NATIONAL COAL RESOURCES.—Survey committees are now at work with the co-operation of the mine owners and the Geological Survey in nine coal areas covering 96 per cent. of the present production of the country. Outlines of the results in the various areas are given, and reference is made to Survey Papers, Nos. 19 to 27.

EXAMINATION OF COAL AND COKE.—*Microscopical Examination of Coal.*—Mr. C. A. Seyler has continued his study of methods for the investigation of the micro-structure of coal. During the year, attention has been paid chiefly to the percentage of light reflected from polished surfaces by the various micro-petrological constituents of coal, a Berek slit photometer being used for the purpose. The brightness of the components is related to the "rank" (*i.e.* degree of coalification) or composition of the coal. As a rule, the brightness of the vitrain component increases with the rank, whilst the spore material is much less reflective than the vitrain in bituminous coal, but is nearly as bright as the vitrain in anthracite coal.

Significance of Spores in the Correlation of Coal Seams.—This has been dealt with in Survey Papers No. 17 and No. 23. It has been inferred that, in the absence of a characteristic spore, the microscopical method of correlation is only applicable where a full thickness of seam is available, and thin sections can be prepared, inch by inch. But if a fair sample of the seam is available, even though it be crushed,

* H.M. Stationery Office, Kingsway, W.C.2. pp. 135. Price 2/6 net.

the spore examination may still provide useful data, for if the numbers of individual spore types are recorded as a percentage of the total number of spores counted, percentages of similar magnitude are found in different sections of the same seam.

Examination of certain Durains and Clarains.—It has been found possible, by a method of gravity separation, to separate the durain of the Plessey seam of Northumberland into a number of fractions which show a progressive change of hydrogen-content. The fractions contain different amounts of spores, the highest spore-content being associated with the highest hydrogen-content and the lowest specific gravity.

CONSTITUTION OF COAL.—*Oxidation of Coal and Allied Substances.*—The work of Professor Bone at the Imperial College has been mainly concerned with a systematic examination of the alkaline permanganate oxidation of representative celluloses, lignins, peats, brown coals, bituminous coals and anthracites. So far the results indicate that the matured coal substance has mainly originated from lignin.

Action of Solvents on Coal.—The report on this part of the subject has been published in *Technical Paper* No. 37.

ANALYSIS OF COAL.—*Volatile Matter.*—The British Standards Specification (No. 420, 1931) suggests that the temperature at which the volatile matter test is carried out should be so adjusted that crystals of potassium chromate show incipient fusion when placed in the bottom of the crucible. Pure potassium chromate melts at 965° C., whereas the normal temperature for the test is 925° C. Attempts have been made to use other salts in the test, but each contained sufficient impurity to influence the test. Hence the thermo-couple method seems to be the most satisfactory for the purpose.

Nitrogen.—Experiments on the lines of Börnstein and Petrick (*Brennst. Chem.*, 1932, **13**, 41) have shown that the nitrogen loss in the Kjeldahl process is only about 0·04 per cent., after the occluded nitrogen has been drawn off.

Coal Ash.—A scheme, based on methods already recognised for the analysis of silicate rocks, has been published in Survey Paper No. 28 (*cf.* ANALYST, **1933**, **58**, 614). Spectroscopic methods are being applied at the National Physical Laboratory.

Phosphorus.—A new method of determining phosphorus in coal ash has been worked out in detail; it involves the precipitation of the phosphorus as magnesium ammonium phosphate, without removal of the metals of the iron group. Citric acid is added to a solution of the ash, and the resulting complex salts of iron, aluminium and titanium remain in solution throughout the analysis. This avoids the necessity for repeated fusion and extraction of insoluble residues; apparently the inhibiting influence of certain elements on the precipitation of the phosphorus is also checked.

Vitrain containing Titanium.—Samples of exceptionally pure vitrain obtained from fossilised tree trunks, known locally as "cauldron bottoms," have been examined in the Coal Survey Laboratory at Newcastle. The ash from the cleaned coal has been found to contain titanium (approx. 15 per cent.).

Chlorine in Coal.—Tentative methods for the determination of total and water-soluble chlorides have been evolved. These methods were used for the investigation of the horizontal and vertical distribution of chlorine in two N. Staffordshire coal seams.

The vertical distribution of total chlorine and the proportion of water-soluble to total chlorides were found to be approximately constant, but there were considerable variations in the horizontal distribution, the total chlorine in the seams varying from 0·02 to 0·66 per cent., and the water-soluble chlorides from 0·01 to 0·46 per cent. in different parts of the field. As a general rule, the chlorine-contents of the dirt bands, the floor and roof strata and other non-coal materials were substantially lower than those of the associated coal. Washing processes

removed only a small proportion of the water-soluble chlorides, and actually increased the percentage of both forms of chlorine by removing the strata, etc., containing the lower percentage of chlorine.

In commercial grades of the coals the chlorine was found to be concentrated to some extent in the fine grades. Removal of the finest grades of the slack slightly reduced the chlorine-content, but experimental work suggested that a steaming process at a temperature above 200° C. is probably the only method by which the chlorine-content of a coal could be appreciably reduced on a commercial scale.

Calorimeter Bombs.—Experiments with a certain stainless steel bomb showed that the steel was acted upon by the acids formed during combustion. Further search, and tests on several makes of British stainless steel, showed that two of these were suitable for this purpose, the action on the metal being very small. As an experiment the first-mentioned bomb was chromium-plated inside, and tests were carried out which showed that no chromium, and only a trace of iron, was present after several hours' exposure to acids. This bomb has now been used for about 500 determinations of calorific values, and the chromium plating appears to be still in good condition. Some further corrosion tests were made, and these showed no traces of either chromium or iron in solution. A monel metal bomb in which corrosion occurred has been similarly treated, with quite satisfactory results.

Errors of Sampling.—Parallel series of 64 determinations on laboratory samples of coal and on pure chemicals were made. The results have been analysed in accordance with the Law of Errors, and are being published as Survey Paper No. 29.

Reduction of Coal Samples for Analysis.—A simple type of sampler has been designed, constructed, and tested at the Fuel Research Station, and has been found to give satisfactory results, with a great saving of time and labour as compared with the usual method of "coning and quartering."

The apparatus consists of two concentric metal cones mounted together so as to enclose an annular space between them. On the outer surface of the inner cone two chutes are fixed diametrically opposite to one another, extending from a position near the base of the cone, and terminating at their lower ends in the sample offtakes. The top of the outer cone terminates in a short length of parallel tube, above which is fitted a special slide valve and hopper. The apex of the inner cone projects inside the short length of straight tube.

The gross sample of coal to be reduced is charged to the hopper, a slide at the base of the latter is withdrawn, and the coal flows in a solid column down the tube and streams over the apex of the inner cone. Two sections of the annular stream of coal flow into the chutes and are discharged through the sample offtakes. The remainder of the coal, or reject portion, is discharged at a central offtake.

The portions of the coal discharged from the sample offtakes are taken together to form the sample, further reduction of which may be done either in a smaller "cone" sampler or in a riffle.

Softening Points and Coking Properties of Coal.—Work by Mr. C. A. Seyler has been continued (*cf.* C. A. Seyler, Presidential Address, *Proc. South Wales Inst. of Engineers*, 1931). A precise definition of the "softening points" of coal and their relation to the plasticity has been formulated, and a practical method of determination of the plasticity at different temperatures, based upon the softening point under different loads, has been devised.

Structure and Reactivity of Coke.—An investigation on the structure and reactivity of coke has been carried out by Professor J. W. Cobb at Leeds University, and a resumé of his results is given in the Report (pp. 40–42).

CLEANING and DE-ASHING OF COAL AND ITS PREPARATION FOR THE MARKET.—Experiments have continued on the cleaning of coal by the vacuum-flotation process and on the improvement of slurry settling tanks. A new process for the

dry cleaning of coal designed in the South Yorkshire Coal Survey Laboratory is under investigation, and shows considerable promise.

CARBONISATION OF COAL.—Experiments on increasing the velocity of the heating gases in horizontal retorts have been continued, and show the advantages and limitations of this method of increasing the throughput of the retorts. An investigation of the possibility of increasing the yield of gas in horizontal retorts by steaming is in progress.

The new setting of vertical chamber ovens was completed and put to work in November, 1932; it will be used for experiments on the effect of blending coals on the coke, tar and gas produced.

The new setting of narrow vertical brick retorts, intended for use at lower temperatures than those normally used in gasworks to produce a free-burning coke and tar suitable for hydrogenation, has been at work since April, 1931. Experiments indicate that this design of retort may be suitable for use over a wide range of temperatures.

USE OF PULVERISED COAL, INCLUDING MIXTURES OF COAL AND OIL ("COLLOIDAL" FUEL).—The "Grid" burner designed at the Fuel Research Station has given promising results, and is being developed.

Progress has been made with the problem of stabilising dispersions of coal in oil.

HYDROGENATION OF TAR AND COAL.—Experiments have shown that the ease of hydrogenation of tar varies rapidly with the temperature of carbonisation over a critical range. Much of the plant of the larger shale unit has been erected, and experience with a unit dealing with 100 pounds of tar a day is being applied to the design of a unit with a daily throughput of one or two tons.

MISCELLANEOUS.—Other subjects dealt with in the Report include internal combustion engines, domestic heating, a description of a new lamp for the determination of sulphur in light spirits, an apparatus for the removal of fog from gases, and heat losses from surfaces.

There are three appendices: I, List of Fuel Research Staff; II, List of Committees and their Members; III, List of Publications, (*a*) official; and (*b*) other publications since March 31st, 1932, containing reports on work connected with the Board. The Index occupies four pages.

Government of Madras

REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1932

THE Chemical Examiner (Lt.-Col. Clive Newcomb, F.I.C.) reports that there was a small decrease in the cases and articles received for examination in 1932 (6136 articles as against 6360 in 1931).

HUMAN POISONING CASES.—Opium again heads the list as the poison of most frequent occurrence (33 cases), arsenic coming next (24 cases), then mercury (18 cases) and oleander (16 cases). Unidentifiable poisons were found in 12 cases; this shows the need for research on the indigenous vegetable poisons, so that suitable tests for identifying them may be found. The total number of poisoning cases investigated was 323, and in 168 of these poison was found.

Madar Juice Poisoning.—There were 7 cases of poisoning with the white juice of the poisonous weed, madar (*Calotropis gigantea*), which is commonly used as a poison by the mouth or as an abortifacient introduced into the uterus on a small stick. In addition to the identification tests previously described (ANALYST, 1931, **56**, 665), the following new test has been devised:—An alcoholic extract of

the juice, when hydrolysed with caustic potash and extracted with petroleum spirit, yielded a large amount of a white crystalline substance readily soluble in ether and chloroform. This substance gives a crimson colour with sulphuric acid. Even in the presence of fats, as in the examination of viscera, it can be readily extracted in cases of madar poisoning.

Poisoning with Oduvan Leaves.—The acidified ethereal extract of the leaves gives a green colour with strong hydrochloric acid and a purple colour with strong sulphuric acid, and causes paralysis and death when injected under the skin of a frog. The green colour with hydrochloric acid, however, often cannot be obtained with extracts of viscera, although the other reactions are obtainable. The oduvan leaf has the following microscopic characteristics: (i) an upper epidermis of polygonal cells with no stomata; (ii) a single layer of palisade cells; (iii) a spongy mesophyll with large prismatic crystals of calcium oxalate in abundance along the course of both sides of the vessels; (iv) a lower epidermis of wavy-walled cells with numerous stomata. The stomata are surrounded by two cells, each of which is parallel to the ostiole (*cf.* ANALYST, 1931, **56**, 665; 1932, **57**, 717). The root of this plant is also poisonous.

Oleander Poisoning.—Yellow oleander is one of the most commonly used poisons in Madras, the red variety being much less frequently used. Both varieties, when extracted with acidified ether, yield extracts fatal to frogs and giving a deep violet colour with sulphuric acid after the lapse of several hours. The fresh kernels of the yellow variety give a green colour when boiled with hydrochloric acid, but this reaction is not obtained with viscera. In an investigation of the poisonous constituent, Dr. R. Naydu has obtained the following results:—The expressed seed cake was extracted with a mixture of chloroform and ether (1: 2), and the extract was evaporated to dryness, freed from oil by means of petroleum spirit, and dried (Extract A). The kernels were next extracted with absolute alcohol, the extract was treated with ether, and the resulting precipitate was purified by re-precipitation and dried (Extract B). Extract A had an ultimate composition agreeing with that of thevetin. It gave a cherry-red and then violet colour with concentrated sulphuric acid, and, when painted in dilute solution on a frog's heart produced characteristic effects. Extract B was very poisonous when injected into frogs (vomiting, paralysis, asphyxial spasms and death), but was comparatively non-toxic to white rats. For guinea-pigs the minimum lethal dose was 10 mgrms. per kilo. of body weight. This extract gave a deep blue colour when boiled with dilute hydrochloric acid.

Eucalyptus Oil.—In two cases of suspected eucalyptus oil poisoning, in each of which about an ounce of the oil was drunk, eucalyptus oil was detected in the vomit. At the trial, medical evidence was given that eucalyptus oil was not ordinarily likely to cause death, and, on this evidence, the accused were acquitted of the charge of a mutual suicide pact. The doctor's opinion, that eucalyptus oil is non-poisonous, is generally accepted, though it is questionable whether it is correct. The comparative harmlessness of the eucalyptus oil ordinarily bought in the Madras bazaars may be due to its being heavily adulterated with other oil—probably arachis oil.

Betel Poisoning.—Cases of poisoning by chewing pan supari are reported from time to time. The substance chewed consists of betel leaves wrapped round areca nut and slaked lime. Which constituent is the occasionally poisonous one is uncertain. In a case sent in during the year under report a man, aged about 30, after chewing a roll of betel leaves began to sweat profusely and suffered from vomiting and diarrhoea. His symptoms rapidly got worse and he went into convulsions, became unconscious, and died within an hour. As is usual in such cases, no poison could be detected in the viscera. An investigation of the alkaloids of areca nut is in progress, with a view to discovering which of them may give rise to these symptoms.

INCENDIARISM IN MADRAS.—There were several cases of incendiarism during the year, and in every instance yellow phosphorus was probably used. In one house the bedding of the horses in the stables, a cloth over a tea tray, a towel over a cane chair, and several other articles were observed to be smouldering at different hours of day and night without any apparent cause. These strange happenings were attributed to black magic; but, as portions of the burnt articles all revealed traces of phosphoric acid, it is more probable that phosphorus (possibly in solution) and normal human spite were the cause of the phenomena.

There have been several attempts to set fire to the contents of postal letter boxes. In some cases yellow phosphorus was found rolled up in a moist cloth; and, in others, in which the articles were partly burnt, phosphoric acid was detected in the charred portions. In one of these attempts at arson a child's toy clockwork motor car had been used to convey the incendiary material through a hole too small for any larger apparatus.

IDENTIFICATION OF TYPEWRITERS.—An investigation was made in connection with certain anonymous typewritten letters to ascertain if it is possible to determine whether two specimens of typewriting, each typed on a new machine of the same make, with none of the letters distorted and with good alignment, originated from the same or from different machines. The problem is more difficult than in a case in which there are obvious defects in the face of the type; these settle the matter at once; there is, however, always the possibility that the writer of incriminating documents may have the cunning to use a new machine in good condition for typing them. The tests showed that, however good the machine, each letter has its own mean alignment, although the differences may be imperceptible to ordinary observation. This characteristic was found to be a more useful measurement than the spacing between the letters, which may vary according to the position of the letter in the typescript, the speed of typing, etc.

The procedure adopted was as follows:—A straight line is ruled just below the lines of type and the distance from the top of this line to the bottoms of the various letters is measured. Several measurements of the same letters (E, T, A, O, I, N, S, R, H) are made by means of a travelling microscope giving a magnification of about 25 diam., and having a vernier reading to 0·02 mm. From the measurements obtained for a given line the straight line which, as nearly as possible, touches the bottom of all the letters, is calculated (by the method described in any book on the theory of statistics), and the measured alignments of the letters are then adjusted as from this line. Then, after 200 to 300 letters in each specimen of typescript have been calculated, the mean alignment of each of the selected nine letters and the deviation of the letter about this alignment are calculated.

If it is found that the mean alignments of some of the letters differ in the two specimens of typescript by more than can be accounted for by the chance deviations in alignment, the specimens have been typed on different machines. If, on the other hand, the mean alignments of all the letters are within the allowable deviations, it is probable that the two specimens were typed on the same machine, but here it is more difficult to estimate the probability of this conclusion. Data are needed as to the variations in the alignment of the letters on different machines of the same model.

It should be borne in mind that on an old machine the deviations of the various impressions of some letter may be large, some being visibly out of alignment upwards and others downwards. A hasty conclusion from the naked eye observations of a few impressions of this letter might easily lead to error.

New Zealand

ANNUAL REPORT OF THE CHIEF CHEMIST, DEPARTMENT OF AGRICULTURE

THE Report of the Chief Chemist (Mr. B. C. Aston, F.I.C.), of the Department of Agriculture, is published as a section of the Annual Report of the Department. In addition to details of analyses of soils, fertilisers, etc., the Report gives particulars of certain special investigations.

USE OF LIMONITE IN "BUSH SICKNESS."—Perhaps the most remarkable and far-reaching aspect of animal nutrition ever experienced in the Dominion's history has been brought about by the widespread adoption of the advice given by the Chief Chemist in the use of limonite for the rectification of those stock conditions associated with iron deficiency and generally known as "bush sickness." The use of finely ground high-grade limonite can now be looked upon as a standard farm practice on all known bush-sick country, and is rapidly extending to the marginal areas where the condition is present in a modified form. The treatment is so well recognised that the distribution of the material has been taken up by commercial agencies, some operating on an extensive scale. Successful treatment of iron deficiency by such simple means is proving a godsend to farmers in affected country.

Air-deposited rhyolite pumice, which is the type of volcanic ash associated with bush sickness in the North Island, constitutes the chief soil-forming material over an area of about 8,000 square miles, or one-fifth of the total area of the North Island. Bush sickness has so far been found to occur over about half of this area, or more than two and a half million acres. Within the outer boundaries of this proved sick area, however, scattered portions, associated mainly with special topographical features, are relatively healthy. The occurrence of various degrees of pathogenicity is well established, and it is probable that much of the remaining subaerial-pumice country, on large areas of which stock-farming with modern methods has never been attempted, will be found eventually to be affected with bush sickness, either in the usual condition or to the extent that treatment with iron licks, such as limonite, will materially increase production.

Disappointing results obtained on several farms, as well as in one departmental experiment, were traced to the use of limonite which was found to be of inferior grade. This product was not from the Whangarei deposit, and on changing over to the previously tested material from that source the trouble was quickly rectified. It is thus evident that field trials should precede the general use of limonite from any new source, and that producers should take care that only stone of the highest quality is ground for stock lick. Grittiness in even a good grade may make the limonite distasteful to sheep. The fineness of an excellent sample of Whangarei limonite recently analysed showed that 83 per cent. of material passed a 200-mesh sieve and that gritty particles were practically absent, everything passing a 60-mesh sieve.

Control of Ragwort.—In a few cases where inconclusive results attended the use of limonite it was considered that the animals were suffering from ragwort poisoning. The importance of controlling ragwort is, therefore, even greater in the bush-sick area than elsewhere, owing to the possibility of confusion of symptoms leading to wrong treatment and incorrect reports of the value of limonite for bush sickness.

The usefulness of sodium chlorate for ragwort destruction is somewhat diminished by the fire hazards attending its use. Trials are therefore being made with other substances to which this objection does not apply, in particular

ammonium thiocyanate, which has given promising results in preliminary experiments.

IODINE INVESTIGATION.—The work has been actively prosecuted during the year. Several thousand thyroid glands, comprised in 760 samples, have been analysed for iodine-content. Lack of iodine is not shown in new-born calves except, possibly in cases of acute deficiency; the iodine is supplied from the body store of the mother. Analysis of samples of thyroids from sheep showed that the percentage of iodine increased with age, but no difference was observed either in size or iodine-content between male and female glands in 43 pairs of samples of lambs' thyroids.

The average weight of glands containing 0·03 per cent. iodine is 3·57 grm. Accepting this as a provisional standard, about 36 per cent. of the glands in Otago and Southland districts are enlarged above normal, while about 10 per cent. are grossly enlarged—*i.e.* weight over 6 grm.—the latter occurring at Mataura Island, Otama, Sterling, Milton, and Awamangu.

Experiments on the efficacy of iodised salt licks as a means of increasing the iodine-content of glands are at present being carried out in Southland under the supervision of the District Superintendent, glands from the various groups being forwarded as they become available.

BITTER VEGETABLE MARROW.—Two samples of vegetable marrow with an intensely bitter taste were received, one being grown in Wellington and the other imported from Australia. Both were immature and were regarded with apprehension by the purchasers, while vomiting had followed the eating of portions of one sample. The samples were too small for the identification of the bitter principle, which did not give any of the reactions for alkaloids. The family to which the vegetable marrow belongs (*Cucurbitaceae*) contains many poisonous species closely allied to the marrow, and under certain external conditions it is possible that even the cultivated species may produce poisonous fruits.

Cyprus

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1932

DR. S. G. WILLIMOTT, the Government Analyst, reports that 2428 samples were examined during the year, 2399 of these being official, including 969 of food and drugs and 278 relating to criminal cases.

FOOD AND DRUGS.—For the purposes of the administration of the Food and Drugs Law, the Island is divided into seven districts. Of the 299 samples from the Nicosia district, 155 were adulterated, the remaining 40 adulterated samples being distributed over the other six districts.

Milk.—The legal standards at present in vogue in Cyprus are 3 per cent. of fat, and 8·5 per cent. of solids-not-fat. Milk for human consumption is derived from the cow, sheep or goat, and, with the possible exception of cows' milk, is usually mixed. With an average fat-content of 5·0 per cent. for sheep's milk, and of 4·5 per cent. for goats' milk, it is obvious that the prevailing standards are too low, and the experience of the last three years has shown that the fat-limit might well be raised to 3·25 per cent.

The experimental findings of Baker and Taubes (ANALYST, 1932, **57**, 375) on the fluorescence of milk have been confirmed. The characteristic canary-yellow fluorescence of milk (cow, goat or sheep) cannot be attributed to the fat, as it is stated to be by Popp (ANALYST, 1926, **51**, 540).

Coffee.—Twenty-seven of the 183 samples examined were adulterated with starch in proportions ranging from 7 to 65 per cent.

Olive Oil.—Of 35 samples, one was found to be adulterated with soya bean oil; apparently this practice is on the increase in Cyprus.

Mineral Water.—Every one of the twelve samples examined was condemned; they had been carelessly prepared from unsuitable water under obviously unsatisfactory conditions.

CRIMINAL EXHIBITS.—Many uses have been found for the ultra-violet lamp, especially in the examination of dangerous drugs and of cancelled postage stamps which have been re-used on receipt vouchers.

Counterfeit Coins.—The coins examined were of three types. Eight consisted of silver and copper, 11 of lead and tin, and six of tin. Two counterfeit English silver coins, which, from their excellence of manufacture, were evidently stamped, proved to be of almost pure tin.

QUININE POISONING.—Since the case recorded in 1931 (*Lancet*, Nov. 21, 1931, p. 1133) several other cases have been described. A forest guard attempted to commit suicide by taking 32 five-grain tablets of quinine sulphate, but the large dose caused prompt and repeated vomiting which ejected most of the alkaloid. After stomach lavage and treatment he recovered in 24 hours.

In another case a woman (aged 18) took 20 five-grain tablets of sugar-coated quinine hydrochloride in an attempt to procure abortion. The usual symptoms came on, and about 12 intact tablets were vomited. The patient remained unconscious for 6 hours, but afterwards made an uneventful recovery.

In November, 1932, a girl (3 years old) swallowed 8 five-grain tablets of sugar-coated quinine sulphate in mistake for sweets. After vomiting and purging, the child became cyanosed, but, after treatment, she made a slow recovery. It is questionable whether the danger of sugar-coated quinine tablets being taken by children does not far outweigh their advantages.

British Pharmaceutical Codex

CODEX REVISION COMMITTEE

REPORT OF DRESSINGS SUB-COMMITTEE*

THE Dressings Sub-Committee has summarised in a Report the Principal Standards for Surgical Dressings recommended by them and accepted, provisionally, for inclusion in the British Pharmaceutical Codex, 1934.

The substances proposed for inclusion in the next issue of the Codex include: (1) Basic materials such as jute, silk and wool, for which the sub-committee have prepared monographs giving descriptions of the characters of these substances, (2) dressings such as phenol gauze, mercuric chloride gauze, euflavine gauze, and phenol tow, for which the sub-committee have not recommended the inclusion of a quantitative standard for the proportion of medicament present, and (3) the more important dressings for which revised requirements have been prepared. It is with the last group of substances that this summary deals.

The summary has been prepared in the hope that it will provide information useful to manufacturers and others. The Editor of the *British Pharmaceutical Codex* (17, Bloomsbury Square, W.C.1) will welcome comments on the standards proposed or suggestions for the improvement of the tests and will give careful consideration to all communications relating to them.

* Published by the Direction of the Council of the Pharmaceutical Society of Great Britain. The Pharmaceutical Press, 23, Bloomsbury Square, W.C. 1. Price 1/6.

Pharmacy and Poisons Act, 1933

POISONS BOARD

THE following members of the Poisons Board have been appointed under Section 16 of the Pharmacy and Poisons Act, 1933 (*cf.* ANALYST, 1933, **58**, 548):

	Appointing authority
Sir Gerald Bellhouse, C.B.E. (Chairman) ..	Secretary of State for the Home Department
Sir Walter Greaves-Lord, K.C., M.P.	Do. do.
Sir William George Lobjoit, O.B.E., J.P. ..	Do. do.
W. H. Whitelegge, Esq.	Do. do.
J. M. Johnstone, Esq., M.B., Ch.B., F.R.C.S.(Ed.) ..	Secretary of State for Scotland
J. N. Beckett, Esq.	Ministry of Health
F. McCleary, Esq., M.D.	Do.
H. E. Dale, Esq., C.B.	Do.
Sir Robert Robertson, K.B.E., D.Sc., LL.D., F.R.S. (or Deputy) ..	*Ex officio* as Government Chemist
J. H. Franklin, Esq.	Pharmaceutical Society of Great Britain
H. N. Linstead, Esq.	Do. do.
G. A. Mallinson, Esq.	Do. do.
E. T. Nethercoat, Esq.	Do. do.
P. Sparks, Esq., C.B.E., J.P.	Do. do.
Sir William Willcox, K.C.I.E., C.B., C.M.G., M.D., B.Sc.	Royal College of Physicians of London
R. Stockman, Esq., M.D., LL.D., F.R.C.P. ..	Royal College of Physicians of Edinburgh
S. A. Smith, Esq., M.D., M.R.C.P., D.P.H. ..	.. .. General Medical Council
Gerald Roche Lynch, Esq., O.B.E., M.B., F.I.C.	Council of the Institute of Chemistry of Great Britain and Ireland
J. W. Bone, Esq., M.D.	British Medical Association

The Board has appointed Mr. M. D. Perrins of the Home Office as Secretary, to whom any communications to the Board should be addressed.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Determination of Nitrogen in Yeast and Brewing Materials. W. A. Davis, J. G. Maltby, and F. E. Salt. (*J. Inst. Brewing*, 1933, **39**, 577–581.)—The authors confirm the conclusion of J. S. Ford *et al.* (ANALYST, 1933, **58**, 618), that almost identical results are obtained by the Kjeldahl–Gunning–Arnold method and by the Christensen and Fulmer modification for brewers' and bakers' yeasts sampled at different stages of manufacture or after undergoing different treatments, and for pure nucleic acid; the difference was about 0·5 per cent., and the latter method usually gave the higher results. The suggested explanation of the contradictory results of previous workers is the difficulty in determining the exact amount of nitrogen in the hydrogen peroxide used, as stabilisers of different types are used by different makers. Thus (*e.g.*) Merck's "perhydrol" contains uric or barbituric acid, and other manufacturers use urea, lecithin, casein, gelatin, etc., or even non-nitrogenous stabilisers, such as salicylic acid, resorcinol, phosphates, guaiacol,

etc. In order to obtain an accurate "blank" 0·5 grm. (in some cases 1 grm.) of sugar of known nitrogen-content should be added to ensure the complete conversion of the nitrogen into ammonia during the digestion with sulphuric acid; when this is omitted only one-tenth of the blank is obtained. It is also pointed out that the Dumas method may give high results owing to the presence of unburnt methane in the nitrogen measured (*cf.* Dunstan and Carr, *Proc. Chem. Soc.*, 1896, 48), and that the method of Haas (*J. Chem. Soc.*, 1906, 570), in which copper oxide is replaced by lead chromate, eliminates this error. Similarly, lead chromate may be used with advantage in the ordinary Liebig combustion process for carbon and hydrogen; it shortens the process, avoids low results due to unburned methane, and enables the method to be used when halogens and sulphur are present. Ter Meulen's hydrogenation method (ANALYST, 1932, **57**, 524) gave excellent results for glycine if care was taken to remove all nitrogenous matter from the nickel formate, but with yeast the results were always about 5 per cent. lower than those obtained by the Kjeldahl–Gunning–Arnold method. The evolution of ammonia was slow, being incomplete after 2 hours, but this might have been due to an inactive catalyst. J. G.

Detection of Ketoses by a Microscopic Method. M. Wagenaar. (*Pharm. Weekblad*, 1933, **70**, 1029–1034.)—One mgrm. of the sugar is suspended in a drop of a 2 per cent. solution of α-naphthol in glycerin (sp.gr. 1·26), which is then brought into contact with a drop of hydrochloric acid of equal size. With glucose, lactose, arabinose or maltose the drop remains colourless; with rhamnose or galactose a slight colour is developed; whilst fructose, sucrose or raffinose produces a deep blue or blue-violet colour. The sensitiveness is normally 1 per cent., but 0·1 per cent. of cane sugar in milk sugar is detectable. The reaction distinguishes ketose from aldose sugars (*cf.* the hydroxymethyl furfuraldehyde test, and L. Ekkert, *Z. anal. Chem.*, 1930, **80**, 229), but is not specific for individual sugars. J. G.

Californian Honeys. W. Bartels and A. Fauth. (*Z. Unters. Lebensm.*, 1933, **66**, 396–407.)—Many North American, especially Californian, honeys show abnormally low diastatic activities, although no evidence is available that such honeys have been heated or that the bees have been sugar-fed. The results now given for many of these honeys fail to reveal any relationship of either the floral origin or the number of pollen grains of the honey to the diastase-content. It is suggested that the high temperatures occurring in many districts of California may be answerable for the low enzymic content of the honey, this view being supported in some cases by examination of the pollen present. T. H. P.

Detection of Sorbitol in Presence of Dulcin and Saccharin. G. Reif. (*Z. Unters. Lebensm.*, 1933, **66**, 408–412.)—Adulteration of wine with cider or perry may be demonstrated by showing the presence of sorbitol (*cf.* Werder, ANALYST, 1929, **54**, 476), which may be detected (1) by the formation of its hexacetyl compound, or (2) by the colour reaction of its benzylidene derivative with acetone in presence of sulphuric acid; in this case it is the benzaldehyde liberated which gives the coloured compound with the acetone. Possible disturbance of

these reactions by the presence of "dulcin" (*p*-phenetole carbamide) or "saccharin" (*o*-benzoic sulphimide) is considered by the author. It is found that benzaldehyde and dilute sulphuric acid (1:1) act on dulcin, giving benzylidenedulcin, with formation of a red colour; that dulcin forms a crystalline acetyl compound, and that treatment of benzylidenedulcin with aqueous sulphuric acid and acetone results in the liberation of benzaldehyde and the appearance of a yellowish-red colour. Unlike sorbitol, dulcin is, however, completely adsorbed by the carbon used in Werder's test, and hence does not interfere with the tests. Saccharin behaves differently, as it yields no benzylidene derivative; moreover, it produces no coloration with acetone and sulphuric acid, it is completely adsorbed by carbon, and, if the acetylation test is used, is entirely removed during the procedure followed. The effect of mannitol on the tests is also considered, and the following methods of carrying out the test are recommended:

From 100 to 130 ml. of the wine are heated with carbon and filtered by suction through Seitz filtering material. Distillation and treatment with sulphuric acid (1:1) and benzaldehyde are effected as usual, and the product is left for 24 hours in a cold room (best 7° C.). The subsequent procedure is varied according to the amount of the benzylidene sorbitol formed. With a relatively large amount, the residue is washed from the flask with 100 ml. of cooled water into a beaker and left for 30 minutes. It is then filtered by suction on to a fritted glass crucible (grain size 1 G2), and washed, first with about 100 ml. of water (lumps being broken up with a glass rod), then with two portions (5 to 10 ml.) of an ice-cold mixture of 3 parts of absolute alcohol and 7 parts of petroleum spirit, and, finally, twice with at least 10-ml. quantities of petroleum spirit; before each addition of washing liquid, the suction is interrupted so that the precipitate may be thoroughly mixed with the added liquid. The precipitate is then dried in the crucible or on a watch-glass for 30 to 60 minutes at 75° to 80° C. To a small portion (0·01 to 0·03 grm.) of the dry precipitate—which should be practically colourless—in a test-tube, 0·9 ml. of water and 0·3 ml. of pure acetone are added, and the whole is mixed by swirling the tube; 0·52 ml. of concentrated sulphuric acid (sp.gr. 1·84) is then pipetted rapidly on to the middle of the liquid surface, and the swirling is repeated. If benzylidenesorbitol is present, the crystals dissolve, and the acid liquid assumes, either at once or after a few minutes, an orange-red colour, which reaches its full strength after about 15 minutes. If only benzylidenemannitol is present, the crystals dissolve, but the liquid either remains colourless or turns yellow. If less than 0·01 grm. of precipitate forms, it is best collected on a small filter-paper in a Gooch crucible, washed with 20 ml. of water, two 3-ml. quantities of the alcohol-petroleum spirit mixture, and two 10-ml. quantities of petroleum spirit, no interruption of the suction or stirring being necessary. After being dried for 30 minutes at about 75° C., the paper, folded with the precipitate inside, is transferred to a test-tube and 0·45 ml. of water and 0·15 ml. of acetone are added. The filter is pressed into the liquid with a rod, 0·26 ml. of sulphuric acid is added, and the tube is swirled. The orange-red colour may take an hour to develop. This procedure shows clearly the presence of 3 per cent. of cider in wine and gives a faint pink colour even with 2 per cent. T. H. P.

Detection and Determination of Diacetyl in Butter. W. L. Davies. (*Food Manufacture*, 1933, **8**, 346–348.)—To detect traces of diacetyl in butter, the diketone may be condensed with hydroxylamine to form dimethylglyoxime, which yields a red nickel compound. Also, the Voges-Proskauer reaction may be used; *viz.* in strong alkaline solution diacetyl gives a deep red colour with various compounds containing a guanidine nucleus, such as peptone solution or creatine. As little as 1/100 mgrm. of diacetyl may thus be detected, but the depth of colour is not proportional to the amount present. To determine the diacetyl, the nickel glyoxime method is used. From 0·5 to 1 kilo. of butter is distilled in the presence of 500 ml. of a mixture of 0·1 *N* sulphuric acid and 1 per cent. acetic acid, and a drop of oleic acid is added to oxidise any carbinol to diacetyl. The mixture is heated for 20 minutes in an all-glass apparatus beneath a reflux condenser, and 40 ml. of distillate are then collected and kept at 90° C. for 1 hour after being mixed with 10 ml. of a buffered nickel reagent (1 part of 20 per cent. hydroxylamine hydrochloride, 1 part of 10 per cent. nickel sulphate solution, 2 parts of 20 per cent. sodium acetate solution). After the liquid has been cooled and neutralised to a p_H of 7·2 the nickel compound is left to settle for 24 hours; the liquid is then filtered through a tared sintered Jena crucible (IG_3), the precipitate is dried at 110° C. and weighed, and the weight is multiplied by 0·596 to obtain the weight of diacetyl. Repeated determinations of known amounts of diacetyl gave results with 97 to 103 per cent. of theory. If the diacetyl is to be estimated from the intensity of the red colour on Gooch filter discs (*cf.* ANALYST, 1932, **57**, 389), 40 to 100 grms. of butter and 100 ml. of water are directly distilled, and no neutralisation is necessary. D. G. H.

Determination of the Insoluble Bromide Values of Oils [in Cans of preserved Fish]. R. Marcille. (*Ann. Falsif.*, 1933, **26**, 393–398.)—The amount of fish oil in the covering oil of preserved fish is calculated from the proportion of insoluble bromides yielded by the oil in the can. One grm. of the oil is weighed into a tared centrifuge tube, 30 c.c. of ether are added, and the tube is corked and placed in a little iron wire support in a crystallising apparatus filled with ice and water. After 10 minutes, bromine is gradually added, 0·20 to 0·25 c.c. at a time, with mixing, after each addition, at intervals of 10 to 15 seconds, until a distinct red colour is obtained, about 0·5 to 1·5 c.c. of bromine being required. The tube is left in the ice-water for at least 3 hours; any clear liquid is then poured off and the tube is centrifuged for a few minutes, after which decantation is easy. Three to 4 c.c. of ether (previously chilled in ice-water) are poured down the side of the tube, the precipitate is detached from the bottom with a small rod of hardwood or bone, and the contents are mixed with a circular movement. The tubes are again centrifuged, the precipitate is washed with a further 10 to 11 c.c. of chilled ether, and, after a final centrifuging, the solvent is driven off, the tube warmed to 90 to 100° C., and subsequently weighed. The insoluble bromide value is taken as the weight of the derivatives given by 100 grms. of oil. Five per cent. of fish oil in either olive or arachis oil gave a value of 60; 10 per cent. a value of 63; 20 per cent. a value of 68; 40 per cent., 77; 60 per cent., 80·5; and 100 per cent., a value of 85. It was found that the weight of bromine derivative was not proportional to the content

of the oil in the mixture. This applied to both linseed oil and fish oil, and no difference in this respect was observed whether the diluting oil was olive, or arachis. Linseed oil, either in China wood oil or in jequirity oil, gave the following values:

Linseed oil, per cent... ..	5	10	20	40	70	100
Insoluble bromide, per cent...	28	29	33·5	36	44·4	47

Commercially, pure linseed oils should always give a value exceeding 45. D. G. H.

Analysis of Oils in Cans containing preserved Fish. R. Marcille. (*Ann. Falsif.*, 1933, **26**, 398–403.)—To make use of the insoluble bromide values of the fish oils to determine the proportion of the oil in the vegetable covering oil in cans of preserved fish, it is necessary to know the constants of the pure fish oils, and these oils are not easy to procure. Authenticated samples of certain oils gave the following figures:—Two sardine oils (1930 and 1931) obtained from fish prepared for cooking and canning; $n_D^{20°}$, 1·4826, 1·4805; insoluble bromide value, 85, 71; iodine value, 185, 175. Oil recovered from fish waste, by boiling with water, $n_D^{20°}$, 1·4806, insoluble bromide value 71; iodine value 177. Sardine oil from Sablesdes Olonne (1932); fish and waste oil (August, 1932); sardine oil from Quiberon (October, 1932); and tunny fish oil from Tunis, $n_D^{20°}$ 1·4805, 1·4826, 1·4826, 1·4813; insoluble bromide value, 69, 84·4, 85, and 80, respectively. Probably the oils with the lower values are from immature fish. To determine the proportion of fish oil in the covering oil, the following table is used.

	Insoluble bromide values		
Percentage of fish oils	Small sardines	Ordinary sardines	Tunny fish
5	50	60	60
10	51	63	60
20	54	68	65
40	60·5	77	61
60	63	80·5	72·5
100	69	85	80

The refractive indices and iodine values are used as criteria of the purity of the vegetable oil used. The method was checked by applying it to a box of sardines in oil, accompanied by a sample of the olive oil used for preservation. The covering oils (originally olive oil) in boxes of sardines vary greatly in composition, some containing about 25 per cent. of fish oil and others as little as 5 per cent. Preserved tunny fish usually has but little fish oil in the covering oil. D. G. H.

Determination of Fish Fat in Sardines in Oil. G. Lunde and E. Mathiesen. (*Z. Unters. Lebensm.*, 1933, **66**, 435–444.)—Unsuccessful attempts have been made to determine fish oil when mixed with olive oil by means of the polybromide value (*cf.* Hehner and Mitchell, ANALYST, 1898, **23**, 310) and the iodine value. For quantitative purposes, Bull and Saether's method (*Chem.-Ztg.*, 1910, **34**, 733) is found useless. Approximately correct results are, however, obtainable by making use of the refractive index, which varies only from 1·4743 to 1·4764 (mean for 18 samples 1·4755) for the oil of *Clupea sprattus* at 25° C., and from 1·4672 to 1·4673 for Spanish olive oil, and from 1·4675 to 1·4677 for

French olive oil (mean for olive oil 1·4673). With mixtures of the olive and fish oils the refractive index is almost exactly additive.

After the gross weight of the tin has been determined, the oil is centrifuged, if necessary, to remove water, and is then filtered through a dry filter. The sardines are transferred to a porcelain basin, and the tin is rinsed out with ether, which is added to the fish in the basin. The ethereal solution is passed through the original filter into a weighed flask. The sardines are then intimately mixed with anhydrous sodium sulphate and the mixture extracted with ether in a Soxhlet apparatus. The ethereal extracts are evaporated *in vacuo* at 40° C., the dried oil is added to the filtered oil, and the total oil is weighed. The refractive index gives the proportions of sardine and olive oils present in the mixture, and the percentage of this in the contents of the tin can be calculated. If the fish have been subjected to preliminary drying by smoking, the oil-content is increased in proportion to the loss of water. A curve is given which shows the relationship between the percentages of oil in the fresh and smoked fish, so that results obtained with smoked fish may be converted into those for the fresh fish. T. H. P.

The Taffel and Revis Method for Estimating the Rancidity of Oils and Fats. J. K. Giles. (*J. Soc. Chem. Ind.*, 1933, **52**, 816–817.)—Practical experience of the Taffel and Revis 1(*b*) method (ANALYST, 1931, **56**, 323) for estimating the rancidity of fats that have become rancid at moderate temperatures, *i.e.* the method as applied to solid fats, shows that in dealing with fats of very slight rancidity, the variability of the blank limits the application of the test, and the following modification of the test has therefore been adopted: About 11 ml. of the melted fat are poured into a 10-ml. measuring cylinder (counterpoised to 0·05 grm.) and kept warm. Forty ml. of glacial acetic acid are placed in a 2-oz. bottle, which is clamped up to the neck in water at 95° to 100° C., and a stream of carbon dioxide is passed through by means of a tube drawn out to a fairly fine capillary. After 2 minutes, 2 ml. of 50 per cent. potassium iodide solution are run in without stopping the carbon dioxide; not more than a very light yellow tint should appear. After another minute the liquid fat is added (the cylinder being re-weighed), and the stream of carbon dioxide is continued for 4 minutes. The contents of the bottle are poured into 150 ml. of water in an 8-oz. wide-mouthed stoppered bottle, the tube and bottle being rinsed. Starch solution is added, and the liquid is titrated with 0·5 *N* thiosulphate solution. The final colour is yellow or gray, and the end-point is reached when 2 drops of thiosulphate solution fail to give a distinct brightening of the colour. A blank test is made. Volatilisation of iodine was found to be within the error of experiment. D. G. H.

Täufel and Thaler's Reaction for Ketone Rancidity. J. Pritzker and R. Jungkunz. (*Chem.-Ztg.*, 1933, **57**, 895–896.)—Fortner and Rotsch's observation (*ibid.*, 1933, **57**, 714) that undoubtedly fresh table butter sometimes gives Täufel and Thaler's reaction for ketone rancidity (ANALYST, 1932, **57**, 466) is confirmed, and it is found that the reaction is shown by acetylmethylcarbinol, but not by diacetyl. The presence of acetylmethylcarbinol in the distillate to be tested may be avoided by distillation with ferric chloride, which does not affect methyl ketones. The reaction is applicable to highly acid fats, since the volatile

fatty acids of butter-fat do not react. The following modification of Täufel and Thaler's procedure is recommended:

The fat is distilled in Pritzker and Jungkunz's apparatus for water determination (*Chem.-Ztg.*, 1929, 603), which is provided with a 200-ml. Erlenmeyer flask and a pendant condenser. The cock of the apparatus is adjusted so that the distillate collects in the upper part and no reflux to the flask occurs. No cork or rubber is used in the connections. Thirty grms. of the butter, 120 ml. of water, 30 ml. of ferric chloride solution (German Pharmacopoeia), and a few small pieces of glass tubing or porcelain are placed in the flask and 30 to 40 ml. are distilled over. The distillate is collected in a tube (about 50 ml.) with ground stopper, and 0·4 ml. of the salicylaldehyde reagent is added. The whole is shaken vigorously for 3 minutes and centrifuged, the water being then poured off carefully to leave about 4 ml. After further shaking for a short time, the emulsion is treated with 2 ml. of concentrated sulphuric acid, which is poured into the liquid and not down the wall of the tube. After thorough mixing, the aldehyde layer separating becomes yellow in absence of ketones, but shows a deepening pink or red colour if even traces of ketones are present. A faint coloration may be intensified by immersing the tube for 15 minutes in a boiling water-bath. T. H. P.

Production of Pseudomorphine from Morphine. C. C. Fulton. (*Amer. J. Pharm.*, 1933, **105**, 503–510.)—Although pseudomorphine may be produced from morphine by simple or catalytic oxidations, the oxidations are difficult to control. By dissolving morphine in dilute alkali, or a salt of morphine in water, and adding sodium hydroxide to slight excess with subsequent addition of potassium ferricyanide until no more is reduced, a yield of about 90 per cent. of pseudomorphine may be obtained. A similar yield may be obtained by heating morphine with a salt of mercury, *e.g.* mercurous chloride. A yield of about 75 per cent. may be obtained by catalytic oxidation with persulphate as oxidising agent, copper as catalyst, and pyridine as the substance with which copper forms an effective complex. The formation of pseudomorphine may be used as a characteristic and fairly simple test for morphine by making use of the strong green colour formed with Marquis' reagent. To 0·5 ml. of morphine solution is added 1 drop of 10 per cent. sodium carbonate solution (in addition to that required for neutralisation), and then, drop by drop, 1 per cent. potassium ferricyanide solution until the solution is distinctly yellow. From 1 to 2 ml. of concentrated sulphuric acid are introduced beneath the liquid, 1 drop of 37 to 40 per cent. formaldehyde solution is added, and the whole is mixed while being cooled with running water. The green colour produced will detect 1 part of morphine in 3000. If formed gradually, pseudomorphine will be precipitated as crystals of characteristic structure. D. G. H.

Properties of Pseudomorphine. C. C. Fulton. (*Amer. J. Pharm.*, 1933, **105**, 511–513.)—Pseudomorphine, the first oxidation product of morphine, is formed from 2 mols. of morphine by the removal of 2 hydrogen atoms, and oxidation may easily proceed further. It is a natural constituent of opium, to the extent of 0·02 to 0·04 per cent., but is physiologically inert. It contains 4 hydroxyl groups, and is a phenol of similar kind to morphine. Pseudomorphine

is a weak base, insoluble in water, and, when precipitated slowly, or from hot acid solution by ammonia, forms small square leaflets, silky needles, or occasionally diamond or 4-pointed star-shaped crystals. If formed rapidly it is amorphous. When the precipitate is washed with distilled water or alcohol it gradually forms a colloidal solution and passes through the filter, but this may be prevented by addition of an electrolyte. Although fairly soluble in most acids, the salts with mineral acids are less so than those of most alkaloids, the sulphate being insoluble. It is readily soluble in acetic acid, is precipitated by ammonia, but is soluble in excess of alkali. It is insoluble in ordinary solvents, and resembles other weak insoluble alkaloids of opium in its precipitation reactions with alkaloidal reagents. Its colour reactions are numerous. Although pseudomorphine may be formed in many oxidations of morphine, it is not a necessary stage. The formation of pseudomorphine from morphine can be made almost quantitative, and it may be used as a test for aldehydes. D. G. H.

Biochemical

Colorimetric Determination of Tryptophan in the Haemolymph of the Silkworm. L. Mamoli. (*Giorn. Chim. Ind. Appl.*, 1933, **15**, 437–438.)—The tryptophan was determined colorimetrically by Fürth and Nobel's modification (ANALYST, 1921, **46**, 293) of Voisenet's reaction: 1 ml. of the haemolymph, 1 drop of 2·5 per cent. formaldehyde solution and sufficient concentrated hydrochloric acid to make the volume up to 15 ml. were shaken in a ground-stoppered graduated 25-ml. cylinder; after addition of 10 drops of 0·05 per cent. sodium nitrite solution, the volume was made up to 20 ml. with concentrated hydrochloric acid. The violet colour, which reached its maximum intensity after 5 or 10 minutes, was compared in a Duboscq colorimeter with that given similarly by 0·1 per cent. tryptophan solution (containing 2 per cent. of sodium fluoride to prevent decomposition). Six samples of the haemolymph showed from 0·150 to 0·163 (mean 0·152) per cent. of tryptophan. It is suggested that, in the silkworm and possibly in other insects also, digestion of proteins proceeds as far as the liberation of free amino-acids. T. H. P.

Seasonal Variation in Butter-fat. I. Seasonal Variations in Carotene, Vitamin *A* and the Antimony Trichloride Reaction. R. G. Booth, S. K. Kon, W. J. Dann, and T. Moore. (*Biochem. J.*, 1933, **27**, 1189–1196.)—During an investigation of the seasonal variations in the vitamin-content of typical English milk several unexpected difficulties were encountered in accepted routine biological tests, and it was necessary to seek new explanations of the observed facts. This was the case when it was attempted to apply the well-known colorimetric and spectroscopic methods to the determination of carotene and vitamin *A* in butter-fats, and the report is concerned with attempts to overcome this difficulty. The seasonal variation in the carotene and vitamin *A* contents of typical English butter from shorthorn cows was followed by colorimetric methods. Determinations of the intensity of yellow colour were carried out on the untreated butter-fats.

Antimony trichloride blue values were determined both on the untreated fats and the corresponding non-saponifiable residues. Data obtained on yellow colour and blue value, as determined on the non-saponifiable residue, agreed well with the established variation of the carotene and vitamin *A* contents of the butter, corresponding with the quantity of grass or of green fodder available in the diet of the cow. Blue values determined on the untreated butter-fat were found to be valueless as a guide to vitamin *A* content, being 5 to 10 times lower than values determined on the non-saponifiable matter. Although blue values determined on the untreated fats showed no consistent quantitative variation, qualitative differences in the behaviour of the blue colours produced by "winter" and "summer" butter-fats were observed. These differences were connected with an inhibitory substance or substances, present in much larger concentration in "summer" than in "winter" butter-fats, whose presence could be detected from its inhibitory power on the blue colour given by vitamin *A* when added from an external source. It is pointed out that in the practical assay of the total vitamin *A* activity of butter-fats by colorimetric means both the vitamin *A* and carotene contents should be taken into account. A provisional formula for calculation of the total vitamin *A* activity is suggested. Assuming from recent work that 2 yellow units of carotene are roughly equivalent to 5 blue units of vitamin *A*, and accepting the international standard of vitamin *A* activity as referring to 1γ of pure carotene, the total activity of a given sample of butter-fat is calculated as follows:

$$\frac{\text{Y.U. per grm.}}{2} + \frac{\text{B.U. (non-sap)}}{5} = \text{international units per grm.}$$

The total vitamin *A* activity of summer butter-fat from shorthorn cows appears to be some 3 times greater than that of winter butter-fat. The fraction of the total activity due to carotene is also greater in summer butter-fat. The authors hope to deal with spectroscopic variations in winter and summer butter-fats in a subsequent communication. P. H. P.

Absorption Spectra of the Mixed Fatty Acids from Cod-liver Oil. W. J. Dann and T. Moore. (*Biochem. J.*, 1933, **27**, 1166–1169.)—Previous workers have shown that there is a surprising difference between the absorption spectrum of cod-liver oil itself and that of the mixed fatty acids derived from it. Cod-liver oil itself was found by Morton and Heilbron (ANALYST, 1928, **53**, 664) to have relatively low absorption ($E^{1\%}_{1\,\text{cm.}} = 1{\cdot}2$ for a good oil) in the ultra-violet, characterised by the broad unbroken band of vitamin *A* at 328$m\mu$. On the other hand, Gillam, Heilbron, Hilditch, and Morton (ANALYST, 1931, **56**, 471) found that the mixed acids and unsaponifiable matter, obtained by acidification and ether extraction of the hydrolysate, had so intense an absorption ($E^{1\%}_{1\,\text{cm.}}$ at 270$m\mu$ = 250, at 230$m\mu$ = 190) as to obscure the presence of the admixed vitamin *A*. The absorption, moreover, was characterised by fine structure, showing not only a band at 230$m\mu$, but also 9 other narrow absorption bands. The change was irreversible, and it was suggested that under the conditions of hydrolysis a substance (or substances) accompanying vitamin *A* gives rise to acid decomposition products which display intense selective absorption. The authors

have now discovered that the duration of the saponification process exerts such a profound influence upon the absorption spectrum as to make data obtained under uncontrolled conditions of saponification almost meaningless. They found that the mixed fatty acids prepared from a typical cod-liver oil by a brief saponification, removal of the non-saponifiable matter by ether, acidification, and ether extraction, showed only relatively low absorption in the ultra-violet region without fine structure ($E^{1\%}_{1\,cm.}$ 230$m\mu$ = 6·5). If, however, the time taken for the saponification was prolonged, or if the separated acids were boiled with a further supply of alcoholic potassium hydroxide, the absorption became much more intense ($E^{1\%}_{1\,cm.}$ 230$m\mu$ after 12 hours = 72), and definite signs of fine structure became evident. Whether this phenomenon can be regarded as a complete explanation of the observations of Gillam and his colleagues cannot be decided with certainty, since these workers have given no details of their technique in saponification.

P. H. P.

Regeneration of the Reducing Properties of Oxidised Lemon Juice. S. W. Johnson. (*Biochem. J.*, 1933, **27**, 1287–1289.)—The observation of Tillmans, Hirsch and Dick (*Z. Unters. Lebensm.*, 1932, **63**, 267), that lemon juice oxidised with indophenol, iodine or hydrogen peroxide can regain its reducing capacity when treated with hydrogen sulphide immediately after oxidation, is confirmed. Various difficulties were encountered in repeating the work. It was found necessary to use juices in which no traces of iron were present, as this vitiated the results. The major difficulty was the complete removal of the hydrogen sulphide. However, it was found that after passing nitrogen for about 3 hours, except in the case of oxidations with hydrogen peroxide, the persistent residuum of hydrogen sulphide was insufficient to affect appreciably the titrations. The juices were considered to be free from hydrogen sulphide when the issuing gas failed to decolorise a solution containing 1 ml. of N/1000 indophenol when bubbled through it for half-an-hour. The ratio between the capacity of lemon juice for reducing iodine in acid solution and indophenol in neutral solution was almost invariably constant, and the amounts of these reagents reduced were roughly equivalent. Good agreement between indophenol and iodine titrations of the oxidised and untreated juices, and the absence of hydrogen sulphide in the above test, were therefore regarded as criteria that regeneration had been effected. Experiments in which indophenols were used as oxidising agents gave rather low results after regeneration; in these experiments also no iodine titrations could be undertaken, as the indicator interfered. The experiments with iodine as oxidising agent gave the most satisfactory results, both with decitrated lemon juice and the raw juice. Since hydrogen peroxide functions most satisfactorily in an acid medium, oxidations with this reagent were carried out on the raw juice. Some typical experiments are described, and the results obtained are given. P. H. P.

Vitamin *C* in *Citrus* Juices. A. H. Bennett and D. J. Tarbert. (*Biochem. J.*, 1933, **27**, 1294–1301.)—The recent work of Svirbely and Szent-Györgyi (*Biochem. J.*, 1933, **27**, 279) has brought almost conclusive proof of the identity of vitamin *C* and the ascorbic acid which can be prepared from orange

juice, paprika, or suprarenal glands, and several workers have shown that there is a close connection between the amount of ascorbic acid as determined by titration with Tillmans' reagent, dichlorophenolindophenol, and the antiscorbutic value of the material examined. This method of titration has been applied to the examination of a number of samples of lemon and orange juices, both freshly prepared and preserved in various conditions, with the object of ascertaining the degree of natural variation in the content of ascorbic acid and the conditions which determine its preservation or disappearance in storage. It has been found that: (*a*) The reducing power of fresh lemon juice is subject to considerable variation; the lowest samples examined had only 60 per cent. of the reducing power of the highest. (*b*) The reducing power of orange juice is more constant and rather higher than that of lemon juice. (*c*) The reducing power of both juices does not diminish much in storage in the absence of preservatives, but the use of any preservative which is efficient in preventing fermentation is followed by the gradual diminution of the reducing power, which totally disappears in, at most, a few weeks. (*d*) The same result is brought about by strong acidification, pasteurisation, or boiling. It is concluded that in untreated juice the reducing factor is protected from atmospheric oxidation by the action of an enzyme, and that when this action is inhibited by any of the usual means the reducing power is rapidly lost. P. H. P.

Vitamin *D* Activity of Butter. I. Chemical Differentiation of the Anti-rachitic Factor of Autumn and Winter Butter from Irradiated Ergosterol and the Vitamin *D* of Cod-liver Oil. S. K. Kon and R. G. Booth. (*Biochem. J.*, 1933, **27**, 1302–1309.)—In a series of experiments to determine the vitamin *D* in butter in winter, summer and autumn by curative and protective experiments on rats, the butter-fat was administered to the experimental animals by pipette separately from the diet, and it was found almost impossible to give to the rats more than 1·5 grms. (or almost 2 ml.) of butter daily. When planning curative experiments it was decided to concentrate the anti-rachitic factor of butter by saponification and to feed to rats the non-saponifiable residue of larger quantities of butter, 3 and 6 grms. daily. In order to test the feasibility of such a method, the anti-rachitic effects of graded amounts of autumn butter have been compared in protective experiments with those of equivalent amounts of the non-saponifiable residue from this butter. It is shown that autumn and winter butters, either saponified in the usual way by boiling for 1 hour on the water-bath with alcoholic potassium hydroxide, or by heating with alkali for 2 minutes only, lose a large part (over 80 per cent.) of their anti-rachitic potency, as determined by prophylactic experiments on rats. Under exactly similar conditions irradiated ergosterol (the International Standard of vitamin *D*) or cod-liver oil can be subjected to saponification either alone or mixed with butter without loss of potency. The fact that the stability to saponification of the anti-rachitic factor of cod-liver oil and of irradiated ergosterol is not adversely influenced by the presence of butter speaks against the existence in butter of a specific destructive factor, and in favour of a true chemical difference between the anti-rachitic factor of butter and those of cod-liver oil and irradiated ergosterol. P. H. P.

Bacteriological

Use of some Micro-organisms in Sugar Analysis. V. J. Harding and T. F. Nicholson. (*Biochem. J.*, 1933, **27**, 1082–1094.)—A number of micro-organisms have been examined as possible analytical reagents for sugars. A close relationship between sugar-removal power and fermentation has been shown. Four of the organisms examined appear useful as biological reagents for sugars. A strain of *Proteus vulgaris* has been developed as an analytical reagent for glucose. *Proteus* is without removal action on fructose, mannose, maltose, lactose, sucrose, arabinose and xylose, but is variable towards galactose. *Proteus* can be applied to Folin-Wu blood-filtrates and to urines after treatment with sulphuric acid and Lloyd's reagent, and after treatment with mercuric sulphate and barium carbonate. Details of the analysis of mixtures of glucose, fructose, and sucrose are given. *Monilia tropicalis* is extremely active in removal of maltose. A method for the determination of maltose is given, which depends on the use of *Saccharomyces marxianus*, followed by *Monilia tropicalis*. Baker's and brewer's yeasts show variations in their removal power towards maltose, depending on the freshness of the organism. A method with the use of "aged" and "fresh" baker's yeast for the separation of glucose and maltose is suggested. *Monilia krusei* is a useful sugar reagent, as it removes only glucose, fructose and mannose. From these results and those of Harding, Nicholson and Grant (*J. Biol. Chem.*, **1932–33, 99,** 625), a system of carbohydrate analysis has been constructed and is outlined. A mixture of glucose, fructose or mannose, galactose, sucrose, maltose, and lactose can be analysed by the use of *Proteus vulgaris*, *M. krusei*, *S. marxianus*, and *M. tropicalis*, combined with acid hydrolysis at appropriate stages; the following steps are necessary: A. Determine *glucose, fructose, mannose* by *M. krusei*. B. Determine *galactose* on the residual fluid from A by *S. marxianus*. C. (In absence of galactose) determine *glucose* by *Proteus vulgaris*. A–C = *fructose-mannose*. D. (In presence of galactose) determine *fructose-mannose* on residual fluid from C by *M. krusei*. A–D = *glucose*. E. Determine *sucrose* on residual fluid from A or D by hydrolysis, followed by use of *Proteus vulgaris* and *M. krusei*. (In presence of galactose or maltose calculate the sucrose from the fructose value.) F. Determine *maltose* by *S. marxianus* followed by *M. tropicalis*. G. Determine *lactose* on fluid from F by hydrolysis. Calculate the lactose from the galactose value, assuming 72 per cent. hydrolysis. The determinations A, C, F are made on the original mixture. The details of analysis of the six sugars each present at a concentration of 10 mgrms./100 ml. have been given in a previous paper by Harding, Nicholson, Grant, Hern and Downs (*Trans. Roy. Soc. Can.*, 1932, **26**, (5), 33). The following table shows the percentage recovery of the sugars from mixtures analysed by the biological reagents:

	I	II
Glucose	97·6	95·4
Fructose	101·7	101·1
Galactose	96·7	100·8
Sucrose	103·0	103·0
Maltose	109·6	105·1
Lactose	98·8	106·2

Some precautions in the use of organisms as analytical reagents for sugars are suggested. P. H. P.

Bacterial Activity in the Hot Springs at Aachen and Aachen-Burtscheid. A. Brussoff, F. Reinartz and A. Schloemer. (*Z. Unters. Lebensm.*, 1933, **66**, 446–453.)—Stony and sandy lime deposits from these springs proved to be bacteriogenic in origin. Lime- and iron-storing bacteria, and also bacteria which deposit silicic acid, take part in their formation. T. H. P.

Bactericidal Efficiency of Menthol and Camphor. L. Gershenfeld and R. E. Miller. (*Amer. J. Pharm.*, 1933, **105**, 490–502.)—No bactericidal action could be attributed to either menthol or camphor when used as 1 per cent. solutions, either separately or mixed, but a saturated solution of menthol proved bactericidal against *B. typhosus* within 30 minutes (0·1 ml. of culture) and against *Staphylococcus aureus* (0·1 ml. of culture) within 24 hours in most instances, and bacteriostatic action was shown against *B. coli*. Saturated aqueous camphor solutions were less active and proved bacteriostatic only against *B. coli*, and neither bactericidal nor bacteriostatic against *B. typhosus* or *Staphylococcus aureus*. Solutions of menthol and camphor in a solvent composed of 31 parts each of alcohol, glycerin and water and 6·6 parts of soap, when tested against *B. typhosus* and *Staphylococcus aureus*, yielded the following phenol coefficients for menthol and camphor:—Average phenol coefficient with *S. aureus*: menthol, 1·2 at 37° C., compared with phenol at 20° C.; camphor, 0·5 at 20° C., compared with phenol at 20° C. With *B. typhosus*: menthol, 5·6 at 20° C., compared with phenol at 20° C.; camphor, 0·74 at 20° C., compared with phenol at 20° C. D. G. H.

Water Analysis

Occurrence of Hydrogen Phosphide in Well Waters. O. Lüning and K. Brohm. (*Z. Unters. Lebensm.*, 1933, **66**, 460.)—The occurrence of hydrogen phosphide in a well water was previously (*ibid.*, 1931, **61**, 443) attributed to the penetration of juice from sugar-beet slices or leaves into the sub-soil. Two similar cases have now been observed, but in these the odour soon disappeared. T. H. P.

Agricultural

Feeding Value of Tung-Seed Meal. W. Godden. (*Bull. Imp. Inst.*, 1933, **31**, 352–358.)—Tung-seed was extracted below 45° C. with petroleum spirit (b.pt. 90°–105° C.), and the meal washed, dried, steamed for 40 minutes, and dried for 24 hours at 20°–30° C., giving sample A. On expressing the seed 24 per cent. of oil still remained, and the cake was therefore treated with solvent as above, and sample B was produced. Analysis of samples A and B gave the following percentage figures:—Moisture, 9·53, 10·47; crude protein, 28·12, 32·19; ethereal extract, 1·58, 0·57; crude fibre, 19·93, 22·04; total ash, 5·07, 5·73; soluble carbohydrates (by diff.), 35·77, 29·00; acid-insoluble ash, 0·23, 0·27; lime (CaO), 1·70, 0·83; soda (Na_2O), 0·066, 0·066; potash (K_2O), 1·27, 1·50; phosphoric acid (P_2O_5), 1·51, 1·82; chlorine, 0·029, 0·035; iron, 0·019, 0·016. Palatability and feeding trials were carried out with sample A; rats on a diet consisting of 25 per cent. of tung meal and 75 per cent. of their ordinary ration had begun to lose condition in 21 days, and did not eat very freely; poultry would hardly touch a mash containing as little as 5 per cent. of tung meal; cows, after the first time, refused 10 per cent.

in their production concentrates. Extended experiments were carried out with pigs, but under no condition did the pigs receiving tung-seed meal do well. *Post-mortem* examination of slaughtered types of the feed groups showed that some irritant material is present in the meal which has a harmful effect on the mucous membranes of the intestine. D. G. H.

Organic Analysis

Acetamide as a Solvent. O. F. Stafford. (*J. Amer. Chem. Soc.*, 1933, **55**, 3987–3988.)—Acetamide fuses at about 80° C. to a fairly mobile liquid, which appears to have a wider range as a solvent than any other substance investigated. About 400 organic and 200 inorganic compounds were tested; of the former, only cellulose was apparently quite unaffected. Asparagin, barbituric acid, oxamide, and uric acid (all slightly soluble in water and insoluble in alcohol and ether) are sparingly soluble below 100° C. Other organic ammonia derivatives, carbohydrates, alcohols, nitro- and nitroso-compounds, hydrocarbons, and acids are quite soluble. The solubility of inorganic compounds in acetamide is strikingly similar to their solubility in water; potassium perchlorate, the halides of mercury and lead, and mercuric oxide are more soluble in acetamide. Sparingly soluble inorganic compounds were precipitated, as in water, by double decomposition reactions. Bismuth nitrate gives a "basic" salt as a white precipitate. Mercurous nitrate and halides undergo some alteration; chromic acid and chromates are rather slowly reduced. W. R. S.

Rapid Determination of Mercaptans. G. R. Bond. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 257–260.)—The method, which is applicable to impure gasoline, etc., involves titrating the sample with a solution of cupric oleate, when the mercaptans are precipitated according to the equation $4RSH + 2Cu(Ol)_2 = 2CuSR + R_2S_2 + 4H(Ol)$. Cupric oleate for the titrating solution was prepared by exactly neutralising "elaine" oil with sodium hydroxide, and treating it in warm dilute solution with the theoretical amount of cupric nitrate; the precipitated cupric oleate was dissolved in kerosene free from oxidation products, to give a solution containing about 4 grms. of copper per litre, and the solution was standardised by shaking a known amount with dilute hydrochloric acid to remove the copper, which was determined iodimetrically. The sample of gasoline to be tested, contained in a glass-stoppered cylinder, is titrated with the copper solution, with shaking. At the end-point a pale green colour of the solution, marking an excess of copper, becomes visible, and may be verified in the presence of much precipitate by filtering some of the liquid. The amount of copper solution required to produce a similar green colour with a sample of the gasoline, after extraction with alcoholic potash to remove mercaptans, should be deducted from that used in the mercaptan titration; 1 grm. of copper = 1·009 grm. of mercaptan sulphur. Hydrogen sulphide interferes, but may be removed, without seriously altering the mercaptan-content, by extraction with acidified cadmium chloride solution (Faragher, Morrell and Monroe, *Ind. Eng. Chem.*, 1927, **19**, 1281). The method was tested, with reasonably good results, on synthetic solutions of various mercaptans in naphtha. S. G. C.

Colorimetric Detection of Trichloroethylene, Carbon Tetrachloride and other Aliphatic Chlorinated Hydrocarbons in Technical Solvents. H. H. Weber. (*Chem.-Ztg.*, 1933, **57**, 836.)—The method is based on the use of carbon tetrachloride by Driver (*Z. anal. Chem.*, 1930, **81**, 62) for the distinction of α- and β-naphthols, and is more selective than existing reactions. Three tests are suggested, 1 drop of the sample being heated at the boiling point for 25 seconds with a small particle of sodium hydroxide (double quantity for ethylene dichloride) and (*a*) 2 ml. of a 2 per cent. solution of α-naphthol in cyclohexanol, or (*b*) cyclopentanol. The mixture is then transferred to another test-tube and cooled, the colour is noted, and an equal volume of (1) 85 per cent. sulphuric acid or (2) glacial acetic acid is added as a layer; after 1 minute the mixture is shaken and the colour is again noted. (*c*) In the neck of a test-tube (180 × 20 mm.) containing 2 drops of the sample, 2 ml. of a 2 per cent. solution of phenolphthalein in cyclohexanol, and a small particle of sodium hydroxide, is fitted an ordinary test-tube through which running water flows (to serve as a condenser), and the whole is immersed in a 200-ml. Erlenmeyer flask containing 30 ml. of boiling glycol. Exactly 5 minutes after the contents of the tube have started to boil the mixture is transferred to an ordinary test-tube and is cooled and shaken well with 1 ml. of glacial acetic acid and a few glass beads. The resulting colours are summarised as follows for solvents having b.pts. in °C. as shown:

Reaction	Methylene chloride (40 to 60° C.)	Tech. acetylene dichloride 48·5° C.	Tech. acetylene dichloride 60° C.	Chloroform (61° C.)	Carbon tetrachloride (77° C.)	Ethylene dichloride (81° to 87° C.)	Trichloroethylene (85° to 87° C.)	Tetrachloroethylene (119° to 120° C.)	Tetrachloroethane (144° C.)	Pentachloroethane (159° C.)
(*a*) Heated	Blue	Yellow-brown	Yellow-brown	Blue	Blue	Yellow-brown	Yellow-brown	Yellow-brown	Grey	Brown
(*a*1)	Green-blue	Reddish-violet	Violet	Intense blue	Intense blue	Colourless or very weak green	Intense green-blue	Green	Intense green-blue	Grey-green
(*a*2)	Yellow	Yellow	Colourless	Orange yellow	Red	Colourless	Yellow tinge	Colourless	Yellow tinge	Yellow
(*b*)	Yellow tinge	Yellow tinge	Yellow tinge	Yellow tinge	Light brown	Yellow tinge	Green	Yellow tinge	Green	Yellow tinge
(*c*)	Colourless	Almost colourless	Almost colourless	Reddish-brown	Reddish-brown	Lilac	Almost colourless	Almost colourless	Lilac-red	Colourless

The minimum percentage quantities detectable in petroleum spirit and in benzene, respectively, are:—Methylene chloride, 0·1, 0·5; acetylene dichloride (b.pt. 60° C.), 10·0, 10·0; chloroform, 0·1, 0·1; trichloroethylene, 1·0, 2·5; tetrachloroethane, 0·1, 5·0; carbon tetrachloride, 0·05, 0·1 [by reagent (*a*1)]. Chloroform, 0·5, 0·5; carbon tetrachloride, 0·1, 0·5 [reagent (*a*2)]. Trichloroethylene, 15, 15; tetrachloroethane, 20, 15 [reagent (*b*)]. Ethylene dichloride, 75, 75; tetrachloroethane, 75, 75 [reagent (*c*)]. J. G.

New Method for the Differentiation and Determination of Formaldehyde and Acetaldehyde in their Mixtures. M. V. Jonescu and H. Slusanschi (*Bull. Soc. Chim.*, 1933, **53**, 909–918.)—Investigation of the rates of reaction of

formaldehyde and acetaldehyde with dimedone (dimethyl dihydroresorcinol) affords a means of distinguishing between the two aldehydes and of determining them when mixed. With solutions of each aldehyde, the times which elapse before a precipitate is formed with dimedone depend on the concentration of the aldehyde, and these times have been determined for concentrations ranging from $N/5$ to $N/7500$. From the time-concentration curves the concentration of either aldehyde in its pure solution may be read off directly. This method is quicker and more exact than the titrimetric, gravimetric or colorimetric methods available.

The curves show that there is a definite concentration ($N/150$) below which the time necessary for the appearance of a precipitate with acetaldehyde exceeds the 75 minutes necessary for completion of the precipitation with formaldehyde. If, at this concentration of aldehyde, precipitation occurs 4 minutes 45 seconds after addition of the reagent, only formaldehyde is present, but if the time is between this and 75 minutes, the solution contains both aldehydes, and the proportions of the two are given by the time reading. If the time is 75 minutes, acetaldehyde only is present.

With the $N/150$ formaldehyde solution, the time of precipitation is short, and, to diminish the error involved in measuring the time, it is recommended that a concentration $N/225$ be used. As addition of the reagents dilutes the solution three-fold, the aldehyde solution tested is made of $N/75$ strength. The procedure is as follows:—

The total aldehyde concentration of the solution is determined by Ripper's iodimetric method (*Monatsh.*, 1900, **21**, 1079), the solution being treated with excess of standard potassium bisulphite solution, and the excess determined by titration with iodine solution. The aldehyde solution is then diluted to $N/75$ strength, and 5 ml. are placed in a test-tube with 10 ml. of dimedone solution (6 grms. per litre); the tube is inverted to effect mixing and the stop-watch started at once. As soon as crystalline precipitate appears, the watch is stopped. The percentage concentrations of the two aldehydes in the solution, as diluted by the reagent, are shown in the following table:

Time of precipitation		Grms. per 100 ml.	
Min.	Sec.	Formaldehyde	Acetaldehyde
5	40	0·0066	—
6	0	0·0060	0·00098
6	40	0·0050	0·00244
8	0	0·0040	0·00391
9	30	0·0030	0·00538
11	50	0·0020	0·00684
14	0	0·0015	0·00758
16	0	0·0012	0·00802
20	0	0·0010	0·00831
28	0	0·00075	0·00868
35	0	0·00060	0·00890
58	0	0·00030	0·00939
75	0	0·00020	0·00948

These values must be multiplied by 3 to obtain the contents of the aldehydes in the $N/75$ solution tested. The minimum percentage of formaldehyde thus determinable

accurately is 0·0006 (in the $N/225$ solution). If less than this is indicated, the test is repeated with a solution three times as strong, and the concentrations are then read off from the following table:

Time of precipitation Min.	Sec.	Grms. per 100 ml. Formaldehyde	Acetaldehyde
2	20	0·020	—
3	20	0·015	0·00733
4	10	0·012	0·01173
4	45	0·010	0·01466
5	20	0·0075	0·01833
5	40	0·0066	0·01965
6	0	0·0060	0·02053
6	40	0·0050	0·02200
8	0	0·0040	0·02346
9	30	0·0030	0·02493
11	50	0·0020	0·02640
14	0	0·0015	0·02713
16	0	0·0012	0·02757
20	0	0·0010	0·02786
28	0	0·00075	0·02823
35	0	0·00060	0·02845
58	0	0·00030	0·02889
75	0	0·00020	0·02904

The laboratory preparation of dimedone is described. T. H. P.

Determination of Higher Alcohols (Fusel Oil). B. Bleyer, W. Diemair and E. Frank. (*Z. Unters. Lebensm.*, 1933, **66**, 389–395.)—Of various aldehydes tested as substitutes for the salicylaldehyde usually employed in the colorimetric determination of fusel oil in alcohol by Komarowsky's reaction, *p*-dimethylaminobenzaldehyde has proved the most suitable, and offers certain advantages over salicylaldehyde. T. H. P.

Characterisation of Sansa [Olive] Oil. F. Bernardini and E. A. Gauthier. (*Giorn. Chim. Ind. Appl.*, 1933, **15**, 329–330.)—Morawski's reaction (with acetic anhydride and sulphuric acid) and Pettenkofer's reaction (with alcoholic furfural solution and sulphuric acid) are given, not only by the resins of sansa oil, but also by the phytosterols found in all vegetable oils. The sterols may be removed by the following procedure: Twenty ml. of the oil are heated to boiling with 20 ml. of 70 to 75 per cent. (by vol.) alcohol, and the cooled liquid is filtered through a paper moistened with alcohol. The filtrate is evaporated to dryness in a dish, and the residue is heated with 15 ml. of 2 *N* potassium hydroxide solution on a water-bath to saponify the resins. The alkaline liquid is then extracted with ether, which dissolves out the phytosterol. To ascertain when this extraction is complete, 3 ml. of concentrated sulphuric acid are poured carefully down the side of a test-tube containing 5 ml. of the separated ethereal solution, and 10 drops of a 0·25 per cent. solution of furfural in alcohol; when the acid is cautiously mixed into the solution, at most a faint pink colour should appear.

When this is the case, the alkaline solution, containing only the resins, is acidified with 3 ml. of concentrated hydrochloric acid, and the resin acids thus

liberated are extracted with about 20 ml. of ether. About 5 ml. of the ethereal solution are used for the furfural and sulphuric acid test, and the remainder is evaporated to give a residue to which the acetic anhydride (3 drops) and sulphuric acid (1 drop) test is applied; the latter test gives a violet-red, and the former an amethyst-violet, colour with resins. A fresh sample of olive oil gave no colour with either test, but two old oils (3 years and 1 year), containing respectively 13·54 and 3·95 per cent. of oleic acid, gave a deep violet colour changing to reddish-brown with the Morawski test and a deep reddish-brown changing to deep violet with the Pettenkofer test. Five sansa oils, some old and some fresh, were tested, and all showed a violet-red colour with the Morawski test, and an amethyst-violet colour with the Pettenkofer test. T. H. P.

Colour Reactions of Meta-dinitrobenzene in Alkaline Solution. R. Truhaut. (*J. Pharm. Chim.*, 1933, **125**, 339–353.)—The aldehydes and ketones examined gave a colour reaction with *m*-dinitrobenzene in alkaline solution, although in some cases it was necessary to apply heat. The reaction appears to be a general one, but no colour was formed with camphor. Acetone gives a positive reaction, and with denatured alcohol a pink colour turning brown was observed. This reaction might prove useful to detect (after distillation) adulteration of tinctures with denatured alcohol. The reactions of compounds containing a CO group were also examined, 1 ml. of a 1 per cent. alcoholic solution of *m*-dinitrobenzene and 2 ml. of 10 per cent. sodium hydroxide solution being used, and 0·1 grm. of the compounds added to the warmed mixture. Uric acid alone gave a positive reaction, yielding a very stable and characteristic violet colour. With certain amino acids (glycocoll, lysine and β-alanine) a violet ring is formed when 2 ml. of 1 per cent. alcoholic *m*-dinitrobenzene solution are poured, without mixing, on to a solution of 0·1 grm. of amino acid in 2 ml. of 10 per cent. soda solution, and the mixture is very lightly shaken. The reaction is most pronounced with glycocoll, and is enhanced if the glycocoll is dissolved in the *m*-dinitrobenzene and a few solid pieces of the alkali are added. Tryptophan gives a yellow colour, cystein and glutathione a yellow green colour, turning brown-black; phenyl β-alanine gives a brown colour, rapidly changing to an intense violet. D. G. H.

Inorganic Analysis

New Colour Reactions of Cuprous Salts. G. Tartarini. (*Gazz. Chim. Ital.*, 1933, **63**, 597–600.)—Cuprous salts give deep red colorations and orange precipitates with αα-dipyridyl, and violet colorations and blue precipitates with *o*-phenanthroline. In this preliminary paper the characteristics and compositions of four of the compounds thus formed are described. T. H. P.

Determination of Tin by Means of Phenylarsonic Acid. J. S. Knapper, K. A. Craig, and G. C. Chandlee. (*J. Amer. Chem. Soc.*, 1933, **55**, 3945–3947.)—Phenylarsonic acid (which is known to precipitate zirconium and thorium) can be used for the quantitative determination of tin. Metallic tin (about 0·1 grm.), or one of its alloys, is attacked with nitric acid, after which the excess acid is driven

off without dehydration of the stannic acid. Strong hydrochloric acid is then added, drop by drop, until the precipitate dissolves. The solution is diluted to 150 or 200 ml., which should provide for a maximum acidity of 5 volumes per cent. of strong hydrochloric acid. The hot solution is treated with 35 ml. of a saturated aqueous solution of the reagent. Under the proper conditions of acidity the precipitate can be collected after a very short time, but near the prescribed maximum acidity the solution should stand for several hours; a little pulp assists filtration. The precipitate is washed with 4 per cent. ammonium nitrate solution until free from chlorides or sulphates, and ignited gently until the paper is charred. It is then heated in an electric furnace at about 1100° C. to constant weight. None of the metals occurring in brass or bronze is occluded in the precipitate, with the exception of iron. If this is present, the washed precipitate is dissolved in about 5 ml. of strong hydrochloric acid, the solution is diluted to about 200 ml., and the precipitation is repeated. W. R. S.

Solubility of Lead Chromate. M. Huybrechts and C. Degard. (*Bull. Soc. Chim. Belge*, 1933, **42**, 331–346.)—The solubility of lead chromate in various reagents at 20° C. was determined. The figures below indicate grms. of $PbCrO_4$ per litre of solvent. Water dissolves 0·00017 grm.

Acetic acid	Ammonium acetate	Acetic acid (*a*) + amm. acetate (*b*)	Potassium chromate
0·025 *N* : 0·00130	0·05 *N* : 0·00093	(*a*) 0·1 *N* } 0·00175	0·1 *N* : *nil*
0·05 *N* : 0·00234	0·1 *N* : 0·00136	(*b*) 0·05 *N* }	0·01 *N* : *nil*
0·1 *N* : 0·00429	0·2 *N* : 0·00210	(*a*) 0·2 *N* } 0·00234	0·001 *N* : *nil*
0·2 *N* : 0·00468	0·5 *N* : 0·00936	(*b*) 0·05 *N* }	0·0002 *N* : 0·000,006
0·5 *N* : 0·00616			

The solubility in 0·1 to 0·04 *N* solutions of calcium chromate is so slight that it could not be determined. The presence of calcium ion favours the flocculation of lead chromate. The following solubilities were observed in 0·004 *N* calcium chromate solutions containing also:

Ammonium acetate	Acetic acid
0·2 *N* : 0·00004	0·2 *N* : 0·00004
0·1 *N* : 0·00002	0·1 *N* : 0·000015
0·05 *N* : 0·00002	0·05 *N* : 0·000015
	0·02 *N* : 0·000015

In solutions containing ammonium acetate, acetic acid, and calcium chromate at concentrations similar to the above, the solubility was of the order of 0·00002 grm. Neutral lead chromate may be precipitated from cold, neutral nitrate solution by potassium chromate in presence of 20 ml. of 0·01 *N* calcium nitrate solution. A measured excess of chromate being used, the excess may be determined in the filtrate by iodimetry. W. R. S.

Detection of Caesium, Rubidium and Thallium. P. Robin. (*J. Pharm. Chim.*, 1933, **12**, 384–387.)—The following process, which involves concentration of the rare metal salts and subsequent spectroscopic examination, has been used for mineral waters: Two litres or more of the water are concentrated to a small volume, and one-tenth each of this volume of acetic acid and of sodium cobaltinitrite reagent (28·6 grms. of anhydrous cobalt nitrate, 180 grms. of sodium nitrite,

1000 ml. of water, together with 50 grms. of glacial acetic acid) are added, in order to precipitate the potassium, caesium, rubidium, and thallium as triple nitrites. After being kept for 24 hours at a low temperature the precipitate is filtered off, washed with acetic acid (10 per cent.) and dried. The precipitate is decomposed by heating at 300° to 350° C. in a metal capsule, yielding cobalt oxide and the nitrites of sodium, potassium, etc. The residue is extracted with water, and the cobalt oxide is filtered off, washed, and rejected. The solution is acidified with hydrochloric acid and evaporated to dryness on a water-bath. The dry chlorides are dissolved in 4 parts (by weight) of water, and the solution is diluted with 2·5 volumes of alcoholic hydrochloric acid [1 vol. of hydrochloric acid (22° Bé.) and 2 vols. of alcohol (96 per cent.)] resulting in precipitation of the bulk of the sodium and potassium chlorides, which are removed by filtration and rejected. The filtrate is evaporated, and this separation process is again applied. The solution containing the rare metals is evaporated with an excess of nitric acid in order to convert the chlorides into nitrates. The dry nitrates are dissolved in 15 parts of water, and an equal volume of freshly prepared silver and bismuth nitrite reagent [5 ml. of sodium nitrite solution (50 per cent.), 1 ml. of bismuth nitrate solution (50 per cent.), 2 ml. of silver nitrate solution (10 per cent.)] is added; caesium, rubidium and thallium are precipitated (the limiting concentration for precipitation by the reagent is 6×10^{-2} for potassium, and 1×10^{-5} for caesium, indicating the necessity for removal of potassium as far as possible by the alcoholic hydrochloric acid process). The bismuthinitrites of caesium, rubidium and thallium crystallise in yellow rectangular plates. After the liquid has stood 24 hours at a low temperature the precipitate is filtered off on a sintered glass funnel and washed with alcohol. It is then dissolved in a few drops of nitric acid, which is evaporated off, and the residue is dissolved in 1 ml. of water. Spectroscopic tests are then made for the rare metals, a little of the solution absorbed in a cotton fibre wound around a platinum wire being used for introduction into the flame. S. G. C.

Analysis of Clays. R. C. Groves. (*J. Agric. Sci.*, 1933, **23**, 519–525.)—Alternatives to the sodium carbonate fusion method have been investigated. The following method, involving decomposition of the sample with "tri-acid" mixture, was found to be satisfactory for the determination of silica, alumina, iron oxide and titania in most soil clays: To 1 grm. of the clay are added 50 ml. of acid mixture [150 ml. of sulphuric acid (sp.gr. 1·84), 300 ml. of hydrochloric acid (sp.gr. 1·2), 100 ml. of nitric acid (sp.gr. 1·42), and 450 ml. of water]. The liquid is heated to boiling, and when nitrous fumes have ceased to be evolved, it is evaporated until fumes of sulphuric acid are given off. The residue is cooled, dissolved, as far as possible, in 100 ml. of water, and the silica is filtered off; traces of silica in the filtrate are recovered by a second evaporation process. The silica is ignited, weighed, and evaporated with hydrofluoric acid and sulphuric acid in the usual way; the residue is fused with potassium bisulphate, and the melt is dissolved in water and added to the main filtrate. Titania may be directly determined colorimetrically in the filtrate after addition of hydrogen peroxide. The liquid is subsequently boiled to decompose the peroxide, and divided into two equal parts. In one part of the solution, after the addition of 20 ml. of hydrochloric

acid, the "total sesquioxides" are precipitated by means of ammonia, filtered off, ignited and weighed. In the other part the iron and titanium are precipitated by the addition of sufficient sodium hydroxide to keep the aluminium in solution, the object being to remove the bulk of the aluminium. The precipitate is filtered off and dissolved in dilute sulphuric acid; the solution is neutralised with ammonia, and diluted to 300 ml., 30 ml. of hydrochloric acid are added, and the liquid is cooled. The iron and titanium are then precipitated by means of cupferron in the usual way, and the precipitate is ignited. The weight of iron oxide is obtained by deducting the corresponding amount of titania found from the colorimetric determination, and the weight of alumina is obtained by deducting the combined weight of iron oxide and titania from the weight of the "total sesquioxides." Some clays, notably those with a high silica : alumina ratio, or clays which have been ignited before analysis, are not completely decomposed by acid, and the sodium carbonate fusion process is necessary. Incomplete attack of the clay by the acid mixture is revealed by an abnormally high residue being left after the usual hydrofluoric acid volatilisation of the silica. S. G. C.

Microchemical

Quantitative Drop Analysis. (I) Apparatus and Technique. P. L. Kirk. (*Mikrochem.*, 1933–34, **14**, 1–14.)—Apparatus is described for micro-volumetric work suitable for volumes of 0·5 ml. down to a fraction of a drop. *Pipettes* of volumes ranging from 0·01 ml. to 0·2 ml. are made from glass capillaries, in the ends of which are sealed, with Krönig cement, fine hypodermic needles. The liquid measured is controlled by a 0·5-ml. tuberculin syringe. The same syringe may be used for a series of pipettes. *Vessels for titration and precipitation.*—For small volumes a microscope slide is used; for larger volumes a depression, which is preferably frosted, in a thick slide. When heating is necessary a conical glass vessel, about ¾ inch in diameter, is used, a small handle for this being made by sealing to the edge a thin glass rod. When the volume is very large, casserole-shaped vessels of 0·5 to 1·0-ml. capacity are used. *Stirrer.*—An electric stirrer is made from an electro-magnet, such as is used in a small electric buzzer; this is attached to the side of a small wooden block, and in the adjacent side of the block a glass tube is inserted and bent round to pass in front of the magnet cone, at a distance of about 2 mm. At the point nearest to the magnet a small piece of iron is sealed inside the glass tube. The glass tube is drawn out, and therefore made flexible between the place of insertion and the electro-magnet; it is wider at the point where the iron is placed, and then drawn out to a very fine tip, which is bent down slightly to form the stirrer. The current from a 110-volt alternating circuit is passed through the electro-magnet, an electric light bulb in circuit being used to give the necessary resistance. The stirrer vibrates according to the frequency of alternation (usually 60 cycle). Either a tapping switch (for momentary stirring) or an ordinary switch is used. *Burettes.*—Three types are used, all of which are made from thick-walled capillary tubing of about 0·5 mm. bore, and readings are accurate to about 0·02 to 0·03 c.mm. In the first type the titrating solution is on the top of a mercury thread which is raised by a steel screw.

The top of the burette is bent over in the form of an inverted U-tube. A small reservoir at the top of the U-tube facilitates refilling. There is a removable tip attached with rubber cement and fixed outside by means of 2 brass collars with an open-sided coupling between them to draw the collars together. The capacity is made 0·1 to 0·2 ml. The only disadvantage occurs when a titrating solution oxidises the mercury. The second burette is made in the same way as the pipettes, except that a screw is used to depress the plunger, and a coil spring is used to prevent backlash. The scale used is cut from graph paper. There is a slight lag due to compression or expansion of the air in the burette and syringe. The third burette is a combination of the two types, but a bubble of air in a small bulb in the capillary separates the titrating liquid from the mercury. The burettes are calibrated by measuring the length of a short thread of mercury over successive intervals to find the variation in bore of the tube, then the mercury-content of the burette is weighed, and finally the water-content, to find the drainage error, which is usually small. An adjustable titration table should be used for the work. *Heating equipment.*—An electric cigar lighter is a useful hot plate. A micro water-bath is made from a glass bulb of about 1½ in. diameter, heated with a small electric coil. *Filtration apparatus.*—Transfer of precipitate is generally impracticable. The filtrate can be transferred by filtering the liquid through a fine capillary with the end flared to hold either a 0·5-cm. sintered glass disc or a little asbestos. The filtrate is collected in a micro suction-flask of about 3-ml. capacity. *Centrifuge.*—A centrifuge is adapted or constructed to centrifuge the contents of tubes of about 0·5-ml. capacity. Titrations may be carried out with an accuracy of 0·2 to 0·3 per cent. The apparatus should be especially useful in chemical and biological work.

J. W. B.

Quantitative Drop Analysis. (II) Determination of Calcium. R. P. Mitler and P. L. Kirk. (*Mikrochem.*, 1933–34, **14**, 15–22.)—For simple solutions containing calcium the sample is measured with a syringe pipette into a conical glass vessel (see preceding abstract), and the pipette is rinsed once, the rinsing water being added to the sample. An equal volume of approximately saturated ammonium oxalate solution is then added, the mixture being stirred during the process. The vessel is heated over the micro hot plate until steam is evolved, ammonia is then added in slight excess, the digestion is continued for a few minutes, and the mixture is left for half an hour, after which it is filtered through the sintered glass filter. If this has been found not to retain the precipitate, it must be treated with a very small amount of asbestos suspension, prepared so as not to give a blank with permanganate. The precipitate is washed dropwise with dilute ammonia (1:6), which has been saturated with calcium oxalate before use. From 3 to 6 washings are sufficient. The precipitate is then dissolved in a drop of 2 *N* sulphuric acid, and another drop on the filter disc. The capillary burette (the second or third type described in preceding abstract) is filled with 0·01 or 0·05 *N* potassium permanganate solution, and the mixture is titrated while on the water-bath; a magnifying glass is useful to observe the end-point. When the end-point is nearly reached a minute crystal of diphenylamine is added, and the titration is continued until the appearance of the blue-violet colour. For blood

serum or plasma, about 20 c.mm. of the sample, containing about 5γ of calcium, is taken. It is usually necessary to clarify by centrifuging before taking the sample. The precipitation is carried out in the cold, and no ammonia is added. Immediately before filtration the mixture is diluted five times with water; this reduces the viscosity of the serum, rendering filtration less difficult. With serum it appears to be necessary to use asbestos on the filters. The method has been tested on known solutions of calcium chloride, on ox serum and on blood, with errors of less than 1 per cent. J. W. B.

Microchemical Soil Tests. M. F. Morgan. (*Conn. Agri. Exp. Station (New Haven) Bull.*, No. 333, 1932, 111–132.)—Simple soil tests for small samples, suitable for field or laboratory tests, include p_H, available phosphorus, nitrate nitrogen, ammoniacal nitrogen, replaceable calcium, and active aluminium. The tests are approximately quantitative. The small sample of soil for testing must be taken from a well-mixed field sample of ordinary-size, collected from 6 to 20 different points in the plot under examination. All the tests make use of the porcelain Morgan Soil-Test Block for washing a few drops of the soil solution out of the soil. The block is made for three separate samples of soil. The soil is placed in a small depression separated from a channel by a perforated section of porcelain through which the solution filters down and collects in a second depression at the other end of the block. The block is sloped so that the soil sample is higher than the depression in which the soil solution collects. To prevent the soil passing through the perforations, clean quartz sand may be placed at the other side, except for a sample to be used for the phosphate test. *Hydrogen ion test.*—The leaching liquid is a 0·3 per cent. (0·05 *N*) solution of sodium chloride. Three samples of soil are placed in the compartments of the Morgan block and a small drop of one of 3 different indicators is placed in each of the wells at the other end of the block. The leaching liquid is then dropped slowly on to the soil until it becomes saturated. From the colour-change of the indicators as the soil solution percolates into the different well depressions, the p_H may be determined. Indicators used were bromthymol blue (0·04 per cent.), 6·0–7·6 p_H range; chlorophenol red (0·04 per cent.), 5·0–6·6 p_H range; and bromcresol green (0·04 per cent.), 3·8–5·4 p_H range. For special work, bromphenol blue, cresol red and thymol blue are used. Colour charts are used.

Nitrate nitrogen.—The leaching liquid is distilled water. The reagent is made from 0·05 grm. of diphenylamine in 2·5 c.c. of concentrated sulphuric acid, and kept in a dark bottle at a low temperature. One drop of the extract-solution and 4 drops of the reagent solution are used, and the colour is compared with that of the chart (given in the Bulletin), or with that given by a standard nitrate solution. Nitrate in plant material may be similarly determined by leaching the sample with a few drops of water in the Morgan Block.

Ammoniacal nitrogen.—The leaching solution is a saturated solution of potassium chloride, and the reagent is Nessler's reagent. Four drops of the soil-extract are used in the spot plate with 1 drop of the reagent, and the colour is compared, as before, with a chart or a standard. J. W. B.

Reviews

A SHORT MANUAL OF SYSTEMATICAL QUALITATIVE ANALYSIS BY MEANS OF MODERN DROP REACTIONS. By Prof. Dr. C. J. VAN NIEUWENBURG and Miss IR. G. DULFER. Pp. 88. Amsterdam: D. B. Centen's Uitg. Maatschappij (N.V.).

The well-known linguistic capabilities of the Dutch are illustrated by the present volume, which has been written in English by two members of the chemical staff of the Technical University at Delft. The evidence for their independence of English assistance, which runs like a thread throughout the text, consists of unusual spelling, quaint phrases, in certain expressions a meticulous grammatical accuracy that appears strange to us who by long familiarity have grown careless, and finally a rather novel use of exclamation marks to emphasise sentences.

The volume is intended as a practical qualitative manual for the use of students and analysts, and the principle adopted throughout is semi-microchemical in character, and one in which the test-tube and filter are largely replaced by a porcelain drop-plate or microscopic slide and a centrifuge. By this means the expedition, certainty, and economy of material of the more recently developed method are attained, and a student is enabled to detect from 5 to 10 cations in a quantity of material between 100 and 300 milligrammes in weight.

After some general remarks containing much excellent advice, the analytical reactions of the commoner metals and acids are given, and these are followed by Chapter III, dealing with the so-called "rare" elements, which the authors rightly state are often common, but are deceptively kept in the background, since they give much trouble in analysis. In the next section the dry, and other preliminary tests, are given in full detail and, although these are decried by some teachers, they undoubtedly provide excellent training for the student, and are of considerable value in later work. The next 15 pages contain the separation scheme for practically the whole of the metals, and, although so comprehensive, it appears thoroughly reliable. In this connection it is of interest to notice that the authors have found none of the newer methods of separation equal in reliability to the old and well-tried hydrogen sulphide method, and most of us will agree with them. In Chapter VI, fuller details of manipulation of the drop reactions mentioned earlier in the text are given, the book being brought to a close with a bibliography of original papers, etc., and a list of the reagents required.

The volume is not intended for use in the detection of traces of elements, and contracted methods, often untrustworthy, are not suggested; it has, however, many merits as a manual for use in the more modern methods of analysis and, in spite of some minor defects, is an excellent production. The authors deserve commendation for their courage in the production of such a textbook in a language which to them is foreign, and still more for the undoubted success they have achieved. The suggestion may, however, be made that the proofs of future editions should be submitted to an English chemist for revision, in order to eliminate the continental spelling and modes of expression.

T. J. WARD

WATER PURIFICATION CONTROL. By EDWARD S. HOPKINS. Pp. ix+131. London: Baillière, Tindall & Cox. Price 10s.

This little book, by the principal sanitary chemist of the Bureau of Water Supply, Baltimore, Maryland, is evidently the fruit of much experience and shrewd observation. It should be useful to both waterworks engineers and chemists, and to those consultants who deal with problems of water purification. The writer of the foreword, Abel Wolman, described it as "designed, in simplicity of language and arrangement, to meet the needs of the rank and file." The arrangement is both good and simple, and, as the author usually uses short sentences, the language is, in a way, simple and, when dealing with practical matters, clear. The book, however, is full of inelegant sentences, such as:— "The $p_{H_2}^7$ test is very accurate, is not unduly influenced by atmospheric conditions and, upon addition of acid, alkali or buffer salts, becomes quickly stabilised." "The clarity of filtered water should not exceed 0·2 to 0·5 p.p.m. of turbidity." "Use of ammonia to form chloramines with chlorine has been extensively utilised." If the reader knows something about the subject, it is always possible to know what Mr. Hopkins means, and he is usually right, but more precise language would have been equally simple, and at least as attractive to the rank and file.

It is interesting to note that storage appears to play no part in water purification in the United States, as expounded by this author. The water supply in some of the western States is so uncertain that one has seen suggestions that highly purified sewage should be conserved, and yet only methods which are applicable to the rapid treatment and distribution of water are described in this work.

In discussing coagulation of matters causing turbidity and the removal of colour, the author rightly stresses the importance of p_H control. He shows that, whereas matters causing turbidity are best removed, when alum is used as precipitant, if the p_H is adjusted to from 5·7 to 7·4, colour can be removed best at a p_H well on the acid side of neutrality, lime being added after coagulation to reduce the corrosive action of the treated water. A new and favourite coagulant, which is attracting some attention in this country, is "chlorinated copperas"— $Fe_2(SO_4)_3$, $FeCl_3.7H_2O$. The discussion of coagulation is very good, and filtration, disinfection (chlorination), tastes and odours and corrective treatment to reduce corrosion, receive sufficient attention. Useful tables, graphs, report forms, and a nomogram for determining chlorine dosage add to the value of this work.

The book is well and clearly printed on good paper, but the price seems excessive. Should it reach a second edition, as it deserves, the author would be well advised to revise the text, after a course of, say, the Bible or Defoe, both examples of simple writing for the rank and file. J. H. COSTE

THE PHARMACY AND POISONS ACT EXPLAINED. By H. GLYN-JONES. With Introduction by H. P. LINSTEAD. Pp. 117. London: Eyre & Spottiswoode. 1933. Price 8s. 6d. net.

The passing of the Pharmacy and Poisons Act during this year is an important milestone in the history of pharmacy, and for all pharmacists and others, who in any way handle pharmaceutical products, a thorough understanding of this Act is essential. From both the pharmaceutical and the legal aspect, Mr. H. Glyn-Jones

possesses all the necessary qualifications for elucidating the official phraseology of the Act, and in this he has succeeded, in a volume of just over one hundred pages.

It must be remembered that, as it stands at present, the Act is merely the skeleton around which the edifice must be built. It is not a Consolidating Act, and how and when such an Act or Acts will be passed in order to complete the scheme, is a matter for the future; but already there is abundant evidence that the regulations governing the practice of pharmacy are to undergo far-reaching changes.

From the point of view of the pharmacist, probably the most important changes are that membership of the Pharmaceutical Society—up to now voluntary—becomes compulsory, and that the conduct of his business comes under official control to a greater extent than at present.

For the Public Analyst there is one important item, and that is, that if a prosecution results from a breach of the Act, and the defendant does not question the Analyst's certificate, the Analyst himself need not be summoned to attend the Court.

The book is attractively arranged and free from errors. It will be required by all who wish to understand the changes taking place in the laws relating to pharmacy and poisons. S. G. STEVENSON

ORGANIC AND BIO-CHEMISTRY. By R. H. A. PLIMMER, D.Sc. Fifth edition. Pp. x+624. London: Longmans, Green & Co., Ltd. 1933. Price 21s. net.

The fifth edition of Professor Plimmer's well-known hand-book of organic and bio-chemistry follows closely the lines of the previous editions, and the high standard which he has set hitherto is well maintained. Several additions have been made, and the subject-matter has been brought up to date. This book, as the author says in the preface, has become a fuller and more comprehensive course on the subjects dealt with, and for this reason the title has been changed from *Practical Organic and Bio-chemistry* to *Organic and Bio-chemistry*. The work is divided into fifty-seven chapters, and these deal with the chemistry of the aliphatic and aromatic compounds, proteins, colloids, milk, blood, metabolism, composition of foodstuffs, respiratory exchange, urine, faeces, hydrogen-ion concentration, etc.; a useful list of the commoner reagents is appended. As in previous editions, full details for the carrying out of suitable laboratory experiments are included.

Taken as a whole, the volume adequately fulfils the aims of the author, namely, to consider organic chemistry, not as a subject by itself, but as the basis of physiological chemistry. The author is to be congratulated on the way in which he has dealt with the material at his disposal. The volume may be thoroughly recommended and should meet the needs not only of the medical student, but also of first-year science students.

The book is well produced and is written in an interesting manner. The text is exceptionally free from mistakes, and the numerous diagrams and figures are clearly represented. The author, however, should never omit, as he almost invariably does, to place a zero before decimal fractions. Thus, for example, "·1*N*-H_2SO_4" should always read "0·1*N*-H_2SO_4." The book is well indexed.

R. H. SLATER