THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Obituary

FRANK GEORGE EDMED

FRANK GEORGE EDMED died at Southsea on January 22nd, at the age of 63, only three weeks after his retirement from the post of Admiralty Chemist, which he had held since 1926, when he succeeded Mr. Arnold Philip. Edmed was born at Brighton and educated at Brighton Grammar School. Later he was a student at the Royal College of Science, obtaining the Associateship in 1897, in which year he also graduated B.Sc. (Lond.) with honours in chemistry. After a short service on the research staff at the Jenner Institute, Edmed joined the staff of the War Department Chemist at Woolwich; later (1919) he became Superintending Chemist in the Inspection Department of the Royal Naval Cordite Factory, and continued in this post until his appointment as Admiralty Chemist.

Edmed's experience in analytical chemistry, gained during his many years' service under the War Office and the Admiralty, was very extensive; few chemists, indeed, could claim such wide experience. He served on numerous technical committees of the British Standards Institution and the Institute of Petroleum, and his wide knowledge and experience was of the greatest value. He was particularly devoted to the work of the Institute of Chemistry. He served on the Council for three periods: 1928–31; 1932–33 and 1937 to the time of his death, and from 1933–36 he was a Vice-President. In addition, he was for some years Chairman of the London and South-Eastern Counties Section. He was on the Council of this Society in 1935 and 1936.

In recognition of his services during the Great War he was appointed an Officer of the Most Excellent Order of the British Empire.

Edmed had a great sense of humour and a gift of ready repartee. His cheerful outlook on life endeared him to his many friends and associates. He leaves a widow and two daughters.

J. S. S. BRAME

THOMAS STANTIAL GLADDING

THOMAS STANTIAL GLADDING was born in Virginia in 1853 and, while he was still a child, his family moved to Providence, Rhode Island, so that his background was New England. He was educated in the public schools of Providence and at Brown University, where he graduated B.A. in 1875 and M.A. in 1878. He was a brilliant scholar, stood high in his class, and was elected to the honorary society of Phi Beta Kappa.

He taught chemistry for two years at Suffield Academy and for one year at Worcester Academy. In 1878 he went to New York City and formed with Charles M. Stillwell the partnership of Stillwell and Gladding, a professional firm for chemical consultation and analysis.

Gladding was active in his profession for many years until his retirement in 1932. He was especially able in the development of analytical methods, increasing their accuracy and availability for practical use. The two outstanding methods that he developed and improved were the neutral ammonium citrate method for the determination of the availability of the combined phosphoric acid in fertilisers, and the potassium platinic chloride method for the determination of potash. These methods have been adopted as official by the Association of Official Agricultural Chemists of the United States.

For many years Gladding had been a member of this Society, the American Chemical Society and the Society of Chemical Industry. In addition to his professional work he was active in the church, in the Young Men's Christian Association, and in civic matters in his home town of Montclair, New Jersey. He was fond of travel and travelled extensively before the World War. After his retirement from active work he lived in Easton, Maryland, until his death in December, 1939, in his 87th year.

He leaves a widow but no children. H. E. CUTTS

FRANK THOMAS SHUTT

FRANK THOMAS SHUTT was born in Stoke Newington, London, England, on September 15th, 1859, a son of Denis Shutt, C.E., and Charlotte Cawthorne Shutt. After receiving private tuition in England he came to Canada as a boy and was a pupil of Dr. William Hodgson Ellis at the School of Technology, Toronto. On removal of this school to Queen's Park to become the School of Practical Science of the University of Toronto, Dr. Ellis became Professor of Applied Chemistry and acted as Public Analyst. As his assistant for five years Shutt obtained valuable training and experience in analytical chemistry.

In 1885 he obtained his B.A. from the University of Toronto with first-class honours in chemistry, and he received his M.A. one year later. In 1914 he was awarded the D.Sc. (*honoris causa*). On the formation of the Dominion Experimental Farms System, with headquarters at Ottawa, he was chosen to be the first chemist in 1887. In 1912 he received the title of Dominion Chemist and was also appointed Assistant Director. He served in this dual capacity until his retirement in 1933.

During his forty-six years of service Shutt made many valuable contributions to agriculture. Always interested in the practical side of farming, his guiding thought was the application of chemistry to the everyday problems of the farmer. He was a pioneer in Canada in establishing on a firm scientific basis the manurial value of clover and legumes. His investigations with fertilisers have gone far to bring about their rational and judicious use. In 1901 he published results of an extensive study of the "soft pork" problem, which has proved a valuable guide to all who are interested in pork and bacon production. His investigations of the qualities of Canadian-grown wheats were extensive and had much to do with the permanent establishment of Marquis wheat. His publications in scientific journals were numerous, and he frequently contributed articles of practical value to the agricultural press.

Dr. Shutt's achievements in scientific agriculture have been widely recognised. In 1935 he received the honour of the C.B.E. The Royal Society of Canada awarded him the Sir Joseph Flavelle medal, and he received the prize of the American Society of Agronomy for outstanding research. The Canadian Institute of Chemistry recognised his services by electing him to an honorary fellowship. He was a Fellow of the Chemical Society, the Royal Society of Canada, and the Institute of Chemistry of Great Britain and Ireland. He was elected to our Society in 1916, and he was also a member of the Society of Chemical Industry, the American

Chemical Society and the American Association for the Advancement of Science, and an original member of the Association of Official Agricultural Chemists.

He passed peacefully to his rest at Ottawa on January 5, 1940, in his eighty-first year. His contributions to agriculture in Canada remain a lasting memorial.

Apart from his profession Dr. Shutt's main attachment was to his family. He remained a bachelor, and was devoted to his mother, a charming, stately old lady, who for many years was the head of his home. On her death his sister took her place. For her and his brothers, his nephews and nieces, "Uncle Frank" was the centre and chief tie of union of the family.

Next to his family, probably, the deepest current of his life set to his church. He was never a man who talked about his religious convictions, which by training and habit formed as natural and integral a part of his life as breathing. He had a great many acquaintances and a small circle of warm friends. Talks over a pipe before a grate fire, walks in the country, photographing expeditions, and little picnic parties with tea made over an outdoor fire were some of the ways in which he enjoyed comradeship.

His life was enriched by a number of hobbies. He was fond of music; indeed, for several years he played the organ in an Ottawa church. Latterly, he derived much pleasure from the gramophone and the radio. He was to the end an ardent photographer, and some of his work attained a high degree of excellence.

His was a thoroughly conservative nature. In politics he took no part, but in music, in art, in thought and in manners he held to the old ways. Fastidious in his habits, in his speech, and his writings, he would, we think, have liked the designation which might well be applied to him, "A gentleman of the old school."

C. H. ROBINSON
W. J. SYKES

Hair Dyes II. The Functions and Reactions of Phenols

BY H. E. COX, D.Sc., PH.D., F.I.C.

(*Read and illustrated by a cine-film in colour at the Meeting, April 3rd,* 1940)

IT is a commonplace to hear it said that a particular hair dye contains a certain diamine, just as though that were the whole of the story. Such is very far from the truth; tinctorial power is obviously important, but there are many other desiderata. For example, an ideal hair dye should (1) provide a silky lustre on the hair; (2) not make the hair brittle; (3) not irritate or stain the scalp; (4) not fade or produce "off" colours; (5) be unaffected by permanent waving or the application of heat or alkali. Moreover, it will be required to produce a wide range of colours to suit the particular individual. Such range of colours cannot be obtained by oxidation of any one diamine, aminophenol or other compound. It is probably true to say that the perfect hair dye which fulfils all these conditions does not yet exist. Those who have studied the subject and examined a number of types of hair dyes will know that a good hair dye of the oxidation class will contain, in addition to the diamine, buffer salts, wetting agents—soap or otherwise—perfume, perhaps alcohol or glycerin, and, most important, a quantity of polyhydric phenol such as resorcinol, catechol or pyrogallol. The range of colours is usually attained by the adjustment of the relative quantities of the base and the phenol. So far as I know, the functions and reactions of the phenol have not been examined, although the practical dyer or the manufacturer would say he could not get his shades without them.

There are certain factors which complicate the study of hair dyes. Hair has the general properties of wool so far as composition is concerned, but it has considerably less affinity for dyes. Living hair, too, is more resistant than non-living hair; it is apt to be protected by natural grease, not removed by shampooing, which resists the absorption of dyes just as do living yeast cells. So, while the use of wool or of dead hair is very useful for studying the reactions and general colours produced, precise results can only be ascertained by trial on living hair. In general, hair dyes have to be oxidised at temperatures below, say, 37° C., usually in weak alkaline solutions by the application of diluted hydrogen peroxide or solutions of urea peroxide. The oxidation must be neither too fast nor too slow. It is clear that direct oxidation methods involving the use of heat or of dichromate or ferric chloride will not be appropriate to the study of the chemical reactions; such reagents produce green or blue indamines or indophenols in presence of amines or phenols and would be most unwelcome on a lady's head.

It will be convenient to consider primarily the oxidation products of *p*-phenylenediamine under various conditions, since this substance, notwithstanding certain well-known disadvantages, is still the most efficient hair dye and is capable of producing the most natural shades. Excess of a solution containing about 2 per cent. will produce a black, and less quantity will give intermediate shades of grey when oxidised with hydrogen peroxide.

Experimental

Although the shades obtainable with living hair differ in certain respects from those obtainable with wool, it is convenient to use wool for experimental purposes, and it seems that the reactions are the same in kind. Preliminary experiments show that the colour obtainable from a given mixture depends upon three factors: the particular base and phenol present, the relative quantities of these substances, and the time of application. The rate of oxidation is comparatively slow at hair-dyeing temperatures; so, too, is the rate of absorption; it is slower with live hair than with dead hair, but more rapid with wool, and the normal duration of application of a hair dye is to be reckoned in minutes. It was found, for example, that 1 per cent. *p*-phenylenediamine dyed wool a blue-black colour in 15 minutes, the intensity of the colour being proportional to the time, but the result is always grey or black. When a half-molecular proportion of resorcinol is added the result in the same time is a brownish-black; when an equal molecular proportion of resorcinol is used the product is a rich brown and is not changed by further addition of resorcinol. This indicates that one molecule of the amine and phenol are jointly concerned in the reactions described later. In order to trace the course of the reactions more accurately and determine how much of the reactants was absorbed, each of the following experiments were made at room temperature on 10 g. of white wool; the mixtures were allowed to act for 24 hours, so that all reactions might be complete and colours fully developed.

A. p-*Phenylenediamine only.*—Dye bath:—*p*-phenylenediamine, 1·08 g.; sodium carbonate (dry), 1·0 g.; water, 150 ml.; hydrogen peroxide (20 vol.), 20 ml.

The dyed wool had a dull black colour, and the diamine had distributed itself thus:—*p*-phenylenediamine combined in the wool, 0·405; as insoluble (Bandrowski) base, 0·365; unoxidised remaining in the solution, 0·311; total, 1·081 g.

Examination of the black dyed wool showed that it contained free Bandrowski base (extractable by pyridine) and an azine combined in the fibre. Only this latter is the real dye; the whole of the Bandrowski base can be extracted, leaving an uninteresting dull black.

B. p-*Phenylenediamine and catechol.*—Dye bath:—*p*-phenylenediamine, 1·08 g.; sodium carbonate, 1·0 g.; catechol, 2·20 g.; water, 150 ml.; hydrogen peroxide, 20 ml.

Wool was dyed a dark brown colour and the distribution was:—*p*-phenylenediamine combined in the wool, 0·353 g.; as insoluble base, nil; unoxidised in the liquor, 0·727 g.

No Bandrowski base had been formed; there was no soluble dyestuff, but a brown-black dye of azine-type had been formed.

C. p-*Phenylenediamine and resorcinol.*—Dye bath:—*p*-phenylenediamine, 1·08 g.; sodium carbonate, 1·0 g.; resorcinol, 2·20 g.; water, 150 ml.; hydrogen peroxide, 20 ml.

The wool was dyed a deep brown colour and the base was distributed as follows:—combined in the wool, 0·322 g.; as insoluble base, 0·074 g.; incompletely oxidised in solution, 0·698 g.; total, 1·094 g.

The wool did not contain any Bandrowski base; it yielded nothing to pyridine and the dark brown dye gave the reactions of an azine or oxazine.

D. p-*Phenylenediamine and quinol.*—Dye bath:—*p*-phenylenediamine, 1·08 g.; sodium carbonate, 1·0 g.; quinol, 2·20 g.; water, 250 ml.; hydrogen peroxide, 20 ml.

The wool was dyed a cocoa-brown colour and contained the equivalent of 0·349 g. of diamine. There was no formation of Bandrowski base, but some insoluble matter was formed unless the mixture was well diluted. The explanation is that *p*-phenylenediamine forms a crystalline addition compound (m.p. 199–200° C.) with quinol; this contains 1 mol. of quinol and has low solubility, so that it is necessary to add more water.

E. p-*Phenylenediamine and pyrogallol.*—Dye bath:—*p*-phenylenediamine, 1·08 g.; sodium carbonate, 1·0 g.; pyrogallol, 2·52 g.; water, 150 ml.; hydrogen peroxide, 20 ml.

The wool was dyed a light brown colour; it contained the equivalent of 0·356 g. of diamine. There was no Bandrowski base.

F. p-*Phenylenediamine and phloroglucinol.*—Dye bath:—*p*-phenylenediamine, 1·08 g.; sodium carbonate, 1·0 g.; phloroglucinol, 2·52 g.; water, 150 ml.; hydrogen peroxide, 20 ml.

Wool was dyed a greyish-brown colour and contained the equivalent of 0·247 g. of the diamine. There was no insoluble base.

Examination of Dyed Wools.—The dyed wools were examined to ascertain, as far as possible, the chemical type of dye formed and the distribution of the diamine and phenol. With the *p*-phenylenediamine alone it is not difficult to identify Bandrowski's base and a complex azine in the fibres. With catechol and resorcinol two substances can be detected—an (oxazine) dye and a diamine-phenol addition product, loosely held in the fibres, which can be extracted. The dye can be reduced with formaldehyde sulphoxylate reagent, and quantitative extraction of the residual liquor in the dye bath shows that approximately equal molecular proportions of the phenol and the base have been absorbed and oxidised. The colour can also be dissolved out by conc. sulphuric acid in which it forms the characteristic green solution, becoming brown again on dilution; the solutions may be reduced with zinc dust and re-oxidised in the usual way.

With the trihydric phenols somewhat different reactions appear to take place. There is a marked difference in colour, as light browns are produced, although the fibre has absorbed approximately the same amount of diamine. This brown colour, however, can be further oxidised to dark brown and black by means of dichromate applied to the fibres; thus it seems that the trihydric phenols retard the oxidation of the diamine and form, in addition to the dyestuffs, some rather unstable quinones or hydroxyquinones which are capable of further oxidation to black or brown substances.

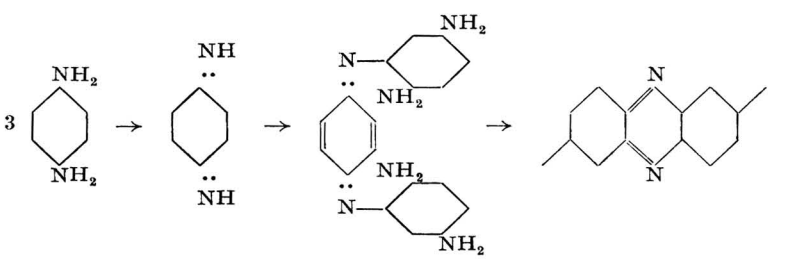
Behaviour of other Phenolic Compounds.—In order to observe whether these results are at all peculiar to *p*-phenylenediamine a similar set of experiments was made with *p*-*p*′diamino-diphenylamine. With resorcinol and catechol similar results were obtained—that is, good dark browns, but with trihydric phenols the

resulting colours were all comparatively light browns and, particularly with pyrogallol, the effect of the phenol was much greater than would appear from its chemical equivalent. Even one-tenth or one-fifth molecular proportion had quite a marked effect. It is evident that both dihydric and trihydric phenols prevent the formation of Bandrowski's base and that resorcinol and catechol facilitate the formation of oxazines or oxazones, which are the desirable and permanent colouring matters. Quinol also leads to the formation of an oxazine, but perhaps by a slightly different route.

The colours can be reduced with Formosul reagent and re-oxidised in air, and no phenol can be separated by processes of extraction, even after reduction.

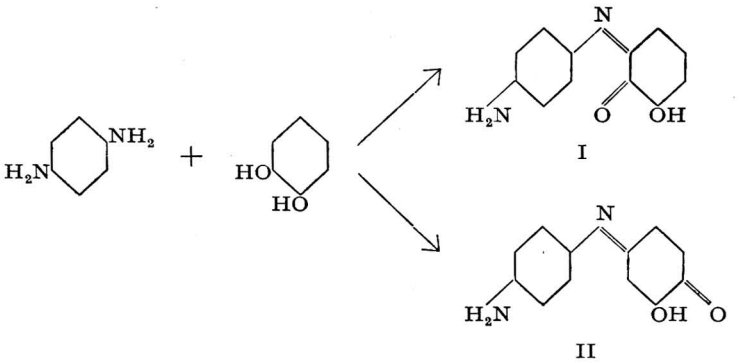
The Reactions Involved

As has been shown in a previous paper,[1] there is little doubt that when *p*-phenylenediamine is oxidised by hydrogen peroxide in alkaline solution in presence of animal fibres, the principal products are Bandrowski's base, an azine and a little quinone. I have shown too that the azine can be produced by direct oxidation of the Bandrowski base. These reactions are commonly represented thus:



The final product must have a molecular weight of at least 500, and may be reduced to a colourless leuco compound. In presence of catechol, resorcinol and the other phenols there is no formation of insoluble base, so that the reaction must proceed otherwise. This may be due in part to the fact that most of the phenols form double compounds with the diamines; some of these are of commercial importance. For example, *p*-phenylenediamine with catechol forms a white crystalline product containing two mols. of catechol and having m.p. 110° C.; similarly with quinol there is formed a well-defined compound with m.p. 200° C., containing one mol. of each constituent. Such compounds preclude the formation of Bandrowski's base, and the fact that they are stable enough to prevent the direct oxidation of the diamine is shown by the fact that hypochlorite produces no precipitate of dichlorimide, as it does with the diamine alone. Oxidation in this way of mixtures or of the double compound gives rise to red and violet dyes, which are not very stable but are rapidly oxidised or condensed to brown substances. It is commonly stated in textbooks that indophenols are blue, but all are not so; Hodgson and his collaborators[2] have described several red and brown ortho-indophenols.

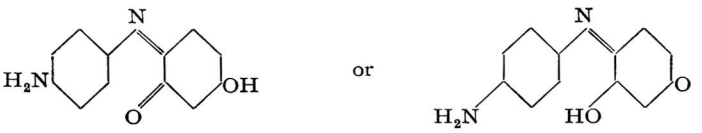
Further, the indophenols are unstable compounds which are easily oxidised or decomposed in various ways, although some of the ortho-compounds may even be acetylated in presence of a reducing agent. The essential factor determining the colour of an indophenol is that the ortho-compounds are red or brown, whereas the para-compounds are blue.[3] As these colours are observed in the course of the oxidation of mixtures, it appears that the reactions proceed *via* the indophenols. Thus, when a catechol is oxidised with a *p*-diamine or condensed with *p*-nitroso-dimethylaniline there are two possibilities:



I

II

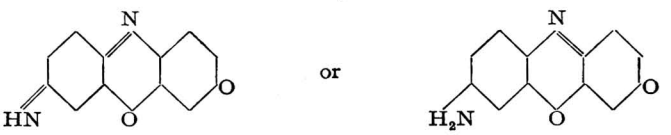
Of these, I will be brown and II blue; similar results may be expected from resorcinol. III will be red, and IV will be blue.



III

IV

If these red and brown indophenols remained unchanged, the problem would be fairly simple; but, although they are more stable than the blue para-compounds, they slowly change to insoluble brown and black substances of high molecular weight, which evidently must be formed by condensation of the ortho-quinonoid compounds, such as I and III. This may be accomplished by the elimination of hydrogen and the formation of oxazones; thus with resorcinol there will be formed

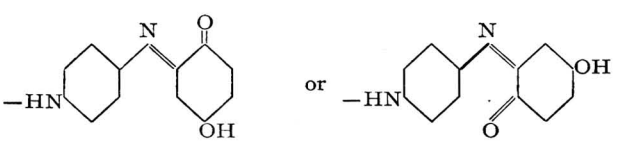


V

VI

and the molecule may be prolonged. Such a compound would be similar to the black produced on direct oxidation of Bandrowski's base, which is also a complex azine

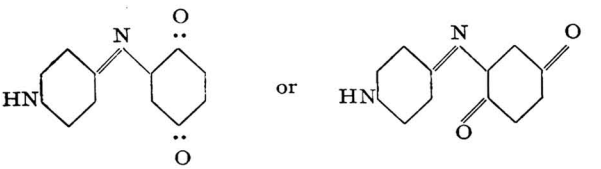
When quinol is used a blue indophenol does not seem possible, as the para-positions are occupied; there are two ways in which a brown compound may be formed:



VII

VIII

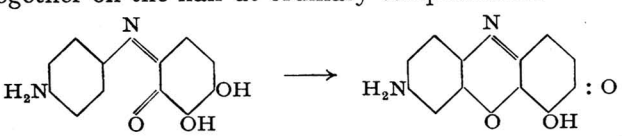
When the mixture is oxidised a brown compound is formed which quickly changes into an insoluble base. This base, when separated, washed and crystallised from benzene, showed no melting point, but had the ultimate composition $C_{12}H_8N_2O_2$ It is but slightly soluble in water, more so in alcohol, and has the characters of a complex quinone for which two tautomeric formulae are possible:



IX X

and as the final product is an oxazone dye, it seems certain that X is the correct formula.

Evidently such a compound is formed in the fibres of the hair; that this is so is also shown by the fact that hair may be dyed by boiling it in slightly alkaline solution with this brown substance, just as it is when the diamine and phenol are oxidised together on the hair at ordinary temperatures.



XI XII

Analogous brown compounds, XI and XII, can be formed from pyrogallol and phloroglucinol; for example, pyrogallol can form first a brown indophenol and then an oxazone by loss of one of the hydrogens from the hydroxyl groups. It is evident that there is room for much further study.

CONCLUSIONS.—It is concluded, therefore, that the functions of phenols in hair dye mixtures are:—(1) They promote the formation of fast colours particularly of brown shades. (2) They prevent the formation of Bandrowski's base. (3) They give a better colour for the same amount of diamine. (4) They promote the formation of *o*-indophenols and oxazones in the fibre. (5) The trihydric phenols retard the oxidation of the diamines, form complexes with the base, and promote the formation of light brown colours. (6) These results are brought about mainly by the formation of ortho-quinonoid indophenols which are further oxidised to oxazones.

I hope to describe methods of analysis applicable to some of these mixtures at a later date. In conclusion one debatable point may be mentioned; all the polyhydric phenols are capable of forming addition compounds with *p*-phenylenediamine, usually with one molecular proportion of the phenol. Such compounds have well-defined melting-points, but may be oxidised either in acid or alkaline solution to produce the same results as the oxidation of a simple mixture. Are such compounds salts of *p*-phenylenediamine within the meaning of Schedule 4 of the Poisons Rules, and is the irritant property of *p*-phenylenediamine lessened when it is so combined with a polyphenol?

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2. H. H. Hodgson and D. E. Nicholson, *J. Chem. Soc.*, 1939, 1405.
3. H. Kehrmann, *Helv. Chim. Acta*, 1921, **4**, 527.

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March, 1940

The Iodimetric Determination of Alkali: An Investigation of G. S. Smith's Method

By J. HASLAM, M.Sc., F.I.C., and R. F. ROBERTS

G. S. Smith[1] put forward a method for the determination of alkali, in which the alkali solution is heated under reflux with a solution of iodine in benzene for a given period of time, after which the excess of iodine and benzene are removed by boiling, and the solution is cooled. Potassium iodide and sulphuric acid are then added, and the liberated iodine is titrated with standard sodium thiosulphate solution. The method is based on the following reactions:—(i) $2NaOH + I_2 = NaI + NaIO + H_2O$; (ii) $3NaIO = 2NaI + NaIO_3$.

The complete reaction is represented by: $6NaOH+3I_2=5NaI+NaIO_3+3H_2O$. On the addition of acid in excess the iodine liberated is equivalent to the amount of alkali which has previously reacted with iodine.

$$5NaI + NaIO_3 + 3H_2SO_4 = 3I_2 + 3Na_2SO_4 + 3H_2O.$$

Smith's method is based, to a certain extent, on earlier work of Walker and Gillespie,[2] who claimed to obtain accurate results by treating the alkaline solution in a conical flask with an excess of $N/10$ iodine solution followed by gentle boiling until all the iodine not required by the alkali had been expelled; the solution was then cooled, and, after addition of dilute acid, titrated with $N/10$ sodium thiosulphate solution.

Smith found that the results obtained by the application of Walker and Gillespie's method were low, and our own experience confirms this. In one actual experiment 25 ml. of $N/10$ sodium hydroxide solution were boiled gently with 50 ml. of $N/10$ iodine solution until the excess iodine was removed; the solution was cooled and treated with acid, and the liberated iodine was titrated with $N/10$ sodium thiosulphate solution. A titration figure of 24·7 ml. of $N/10$ sodium thiosulphate solution was obtained.

This experiment was modified as follows:—Twenty-five ml. of $N/10$ sodium hydroxide solution were boiled with 50 ml. of $N/10$ iodine solution and 1 g. of solid iodine in an open conical flask of about 350-ml. capacity until almost the whole of the iodine had been volatilised, and further additions of iodine in 0·5-g. portions were made until the period of boiling had reached 30 minutes, after which no further iodine was added and the boiling was continued until the excess of iodine was removed. After cooling and treatment with excess of acid, a titration figure of 25·0 ml. of $N/10$ sodium thiosulphate solution was obtained. Although this modification gave an accurate result, it was realised that it would be of little practical use.

Attention should be drawn to the fact that in our application of Smith's method the alkali solutions used in the work have, in effect, been standardised against pure silver,[3] as is our usual custom.

Smith's method was applied to a known volume of standard sodium hydroxide solution as follows:—Twenty-five ml. of $N/10$ sodium hydroxide solution, 2 to 3 ml. of pure benzene, a definite weight of sublimed iodine and a known volume of water were placed in a flask of 150 to 250 ml. capacity, and the solution was heated under reflux for a definite time. The excess of iodine was then removed by continuing the boiling after removal of the water from the condenser. The contents of the flask were cooled, and the iodate was determined in the usual manner by means of $N/10$ sodium thiosulphate solution after addition of 2 g. of potassium iodide and 50 ml. of $3M$ sulphuric acid solution.

The results thus obtained under different conditions are given in Table I.

TABLE I

Expt. No.	Alkali	Volume of solution refluxed ml.	Iodine used g.	Duration of refluxing, minutes	Thiosulphate solution ($N/10$) required ml.	Notes
1	25·0 ml. $N/10$ NaOH	70	0·5	30	24·0	
2	25·0 ml. $N/10$ NaOH	70	0·5	30	24·0	
3	25·0 ml. $N/10$ NaOH	120–180	0·5	30	24·0	Benzene fractionated previous to use and fraction boiling at 80·5° C. used.
4	25·0 ml. $N/10$ NaOH	120–180	0·5	30	22·95	NaOH solution used was free from carbonate and contained a small proportion of barium chloride.
5	25·0 ml. $N/10$ NaOH	120–180	0·5	60	23·6	
6	25·0 ml. $N/10$ NaOH	120–180	0·5	60	23·9	NaOH solution used was free from carbonate and contained a small proportion of barium chloride.
7	25·0 ml. $N/10$ NaOH	120–180	0·5	120	23·6	
8	25·0 ml. $N/10$ NaOH	120–180	0·5	180	23·3	
9	25·0 ml. $N/10$ NaOH	120–180	1·0	30	23·55	
10	25·0 ml. $N/10$ NaOH	120–180	2·0	30	23·4	
11	25·0 ml. $N/10$ NaOH	120–180	0·5	30	23·8	Iodine and benzene were added to the boiling solution of the alkali.
12	25·0 ml. $N/10$ Na_2CO_3	70	0·5	150	23·45	
13	25·0 ml. $N/10$ Na_2CO_3	70	0·5	150	23·2	

It will be noted that the results are low in every instance, and it may be said that in our experience Smith's method has invariably given low results, either at the dilutions which he prescribes or at greater dilutions which we have used to facilitate manipulation. It therefore seemed possible either (1) that the iodine had reacted incompletely with the alkali in the test, or (2) that complete reaction of the iodine with the alkali had taken place, but that a certain amount of reduction of the resulting iodate had occurred, possibly owing to the presence of the benzene; in other words, that the iodate and iodide were not present in the reaction product strictly in the proportion $1NaIO_3 : 5NaI$.

The following experiments indicated that the second explanation was correct. Twenty-five ml. of $N/10$ sodium hydroxide solution, 0·5 g. of iodine, 2–3 ml. of benzene, and about 100 ml. of water were heated under reflux for 30 minutes, after which the excess of iodine was removed by boiling (after removal of the water from the condenser). After cooling, 2 g. of potassium iodide and 50 ml. of sulphuric acid solution were added, and the liberated iodine was titrated with $N/10$ sodium thiosulphate solution; 23·65 ml. of $N/10$ sodium thiosulphate were required.

In a duplicate experiment under the same conditions the liquid, after removal of the excess iodine by boiling, was transferred to the flask of an all-glass distillation apparatus having the delivery end of the condenser dipping into a 5 per cent. aqueous solution of potassium iodide. Ten ml. of sulphuric acid solution (6 N) were added through the funnel to the liquid in the distillation flask, and the liberated iodine was distilled over into the potassium iodide solution in the receiver. As the distillation proceeded $N/10$ sodium thiosulphate solution was added to the contents of the receiver, but a pale yellow colour, due to the presence of a little

iodine, was maintained. After the distillation and when the liquid in the distillation flask was perfectly colourless, the apparatus was disconnected, the condenser was washed down with a little potassium iodide solution, and the titration of the distillate was completed; a total of 23·52 ml. of $N/10$ sodium thiosulphate solution was recorded.

The iodine contained in the clear colourless liquid left in the distillation flask was then determined by the following modification of the method of Kolthoff and Yutzy.[4] The solution was neutralised with sodium hydroxide solution, methyl red being used as indicator, and then boiled down to 50 ml. and cooled. Fifteen g. of sodium chloride (AnalaR), 2 g. of sodium acid phosphate ($NaH_2PO_4.H_2O$, AnalaR), and finally 10 ml. of sodium hypochlorite solution (N in NaOCl-content and $N/10$ in NaOH) were added, and the liquid was heated to boiling. Ten ml. of sodium formate solution (30 g. of sodium hydroxide [pellets from sodium] and 32 ml. of formic acid solution [AnalaR, 90 per cent.] in 100 ml.) were added to the hot solution, precautions being taken to ensure that excess of sodium hypochlorite was decomposed by thorough washing of the sides of the beaker with water.

TABLE II

Expt. No.	Alkali used: Kind	Alkali used: Equiv. to $N/10$ ml.	Vol. of solution refluxed ml.	Iodine used g.	Duration of refluxing minutes	Result as $N/10$ alkali: Smith's method ml.	Result as $N/10$ alkali: Haslam and Roberts' method ml.
14	Sodium hydroxide	25·00	120–180	0·5	30	23·5	25·01
15	Sodium carbonate	25·00	,,	,,	120	22·95	24·97
16	Sodium bicarbonate	25·00	,,	,,	180	23·2	24·95
17	Sodium silicate	24·90	,,	,,	90	23·32	24·82
18	Sodium borate	25·07	,,	,,	30	23·7	25·01
19	Sodium aluminate	25·00	,,	,,	90	—	25·06
20	Trisodium phosphate	24·83	,,	,,	90	21·5	23·69
21	Disodium hydrogen phosphate	25·20	,,	,,	90	21·0	22·85

Notes.—The sodium aluminate was prepared by dissolving 0·05 gm. of pure aluminium in 25 ml. $N/10$ sodium hydroxide solution, filtering into a flask and boiling for 2 minutes to remove any dissolved hydrogen before proceeding with the determination.

In the experiments with the sodium phosphates, a clear colourless liquid was not obtained on removal of the excess iodine by boiling. A yellow colour persisted even after prolonged boiling.

After standing for 10 minutes the solution was cooled in running water, diluted to 300 ml. and treated with 2 g. of potassium iodide, 50 ml. of sulphuric acid ($3M$) and 1 drop of ammonium molybdate solution (2·9 g. of $[NH_4]_6Mo_7O_{24}.4H_2O$ in 100 ml.). The liberated iodine was then titrated with $N/10$ sodium thiosulphate solution. A titration figure of 7·82 ml. of $N/10$ sodium thiosulphate solution (after correction for the result of a control experiment) was obtained. This indicated that $\frac{7\cdot82}{6}$ ml., *i.e.* 1·30 ml., of $N/10$ iodine was still present in the clear colourless liquid in the distillation flask after complete removal by distillation of the iodine liberated on addition of sulphuric acid to the original alkali-iodine digestion product. The total amount of iodine found thus corresponded with 24·82 ml. of $N/10$ sodium hydroxide solution. The evidence also suggested that for every atom of sodium present as alkali in the original solution, one atom of iodine was present either in the form of sodium iodide or sodium iodate in the final reaction product. Hence it seemed that our difficulties in the application of Smith's method would be overcome by determining the total iodine in the final product of interaction of alkali and iodine, and not, as in Smith's method, the iodate alone.

Accordingly, various alkali solutions were taken and treated (*a*) by Smith's method, using 0·5 g. of iodine, the volume of solution refluxed being 120–180 ml., and (*b*) as in (*a*) up to the point where the excess of iodine not required in the reaction had been removed, after which the total iodine in the liquid remaining in the flask was determined as follows:—The solution in the flask was transferred to a graduated flask (200 ml.) and made to the mark with water. Fifty ml. of the solution were treated with 2 g. of sodium acid phosphate, and then immediately afterwards with 10 ml. of *N* sodium hypochlorite solution (see p. 401) and 15 g. of sodium chloride (Analar), and oxidised as described above, a final correction being applied as the result of a control experiment. The thiosulphate solution was standardised against potassium iodide; 50 ml. of a solution of potassium iodide containing 0·4151 g. of recrystallised potassium iodide per 200 ml. were oxidised to iodate by the hypochlorite procedure as a preliminary step.

The results in Table II are typical of those obtained.

The somewhat low results obtained with the sodium phosphates are not surprising; they are doubtless due to the influence of sodium acid phosphate, produced in the reaction, on the iodate-iodide mixture.

Our modification of Smith's method has proved to be of practical value in the determination of alkali in dark-coloured deposits and sludges containing appreciable proportions of sodium aluminate and silicate, *i.e.* for determinations in which ordinary titration methods with the use of indicators are not readily applicable.

Further, certain proprietary washing mixtures contain added dyestuff and, although as a rule interference due to dyestuff may be avoided by a preliminary treatment with sodium hypochlorite and hydrogen peroxide, followed by direct titration of alkali with the use of methyl orange as indicator, the alkali in such mixtures can invariably be determined by our modification, except when appreciable proportions of sodium phosphate are present.

Table III gives results obtained by Smith's method and by our modification of it in the analysis of solutions of other alkalis.

TABLE III

	Alkali used					Result as *N*/10 alkali	
Expt. No.	Kind	Equiv. to *N*/10 ml.	Vol. of solution refluxed ml.	Iodine used g.	Duration of refluxing minutes	Smith's method ml.	Haslam and Roberts' method ml.
22	Potassium hydroxide	24·14	120–180	0·5	30	22·9	24·12
23	Potassium carbonate	25·25	,,	,,	150	23·35	25·24
24	Calcium hydroxide	25·20	,,	,,	30	24·0	25·22
25	Barium hydroxide	24·75	,,	,,	30	20·12	24·3
26	Barium hydroxide	25·70	,,	,,	60	—	25·71
27	Calcium carbonate	24·85	,,	,,	150	22·25	24·53
28	Barium carbonate	24·93	,,	,,	150	21·9	24·29
29	Ammonium carbonate	24·45	,,	,,	30	13·63	19·36

Notes.—The low results with barium hydroxide are probably due to the difficulty of removing the very insoluble barium iodate from the reaction vessel.

In Expt. 26 the barium iodate was reduced to iodide by treatment with sulphurous acid prior to removal from the reaction vessel, in order to ensure that the whole of the combined iodine was determined in the subsequent hypochlorite oxidation.

In Expt. 29, after removal of most of the excess of iodine by boiling, a yellow colour remained and persisted even after prolonged boiling.

The results in Table III indicate that our modified method may be extended to the determination of alkali in solutions of potassium hydroxide, potassium carbonate, calcium hydroxide and barium hydroxide (provided that precautions are taken about the barium iodate produced in the reaction).

The results obtained with barium and calcium carbonates are not quite so trustworthy, and, as was to be expected, the reaction between iodine and ammonium carbonate does not proceed on the same lines as that between iodine and alkalis such as sodium hydroxide or potassium hydroxide.

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October, 1939

The Estimation of Lead in Drinking Water

BY C. H. MANLEY, M.A., F.I.C.

(*Read at the Meeting of the North of England Section, January 27th*, 1940)

THE tintometric estimation of lead in colourless waters presents no particular difficulties to the analyst. To a convenient quantity of the water, for example 25 or 50 ml., contained in a Nessler cylinder and made alkaline with ammonia, are added in succession ammonium citrate, potassium cyanide and sodium sulphide solution, and the colour produced is compared either with that given by a similarly treated standard lead solution or with a set of standard glass discs tinted to represent the colours yielded by different amounts of lead as lead sulphide.

On the other hand, waters which are naturally coloured present an obvious difficulty, especially when it is desired to exercise a close supervision of, say, a municipal supply containing very small concentrations of lead.

Examples of such waters are to be met with in many parts of the West Riding of Yorkshire, where, by reason of their peaty nature, they have a colour ranging from yellow to brown, and leave on evaporation a brown residue.

Thresh[1] called attention to the interference caused by the colour of moorland waters when he attempted to apply to them the method he had found successful for colourless waters, *viz.* addition of an acetic acid solution of gelatin followed by freshly prepared hydrogen sulphide[2] water.

Reith and de Beus[3] attempted to overcome the difficulty by evaporating 100 ml. of water to about 50 ml. with 5 ml. of 5 per cent. ammonium persulphate solution, and treating it at 50° C. with 4 drops of 10 per cent. potassium cyanide solution and 10 ml. of 20 per cent. Rochelle salt solution. There was awlays the possibility, however, that at this stage filtration might be necessary before a clear liquid could be obtained. If so, this involved subsequent washing of the filter-paper with dilute hydrochloric acid to remove any adsorbed lead, before the addition of ammoniacal ammonium chloride and sodium sulphide could be made. A method followed for some time in my laboratory consisted in sulphating the ignited residue from 200 ml. of the water previously evaporated in a platinum basin, heating the residue to expel the excess of sulphuric acid, and extracting it with 40 per cent. ammonium acetate solution, after which the liquid was filtered and treated with ammonia, potassium cyanide, and sodium sulphide.

There seemed reason, however, to suspect that some loss of lead by volatilisation of lead monoxide might be occurring during the ignition of the total dissolved solids. Consequently, a separate volume of 500 ml. of the water was acidified at the outset with dilute sulphuric acid, and evaporated for the lead test alone, so that the lead should be present as the non-volatile sulphate throughout. Even so, on occasion the final tint was not always truly characteristic of lead sulphide, and it was suspected that traces of platinum might be interfering.

It was obvious that either the Allport and Skrimshire method[4] or the S.P.A. method for the determination of lead in food-colouring materials[5] would have enabled an accurate estimation to have been carried out, but both methods are too lengthy for routine testing purposes.

Hence, about a year ago a short-cut modification of the S.P.A. method (*loc. cit.*) was tried with highly successful results, and this is the method in use to-day. It is really the Direct Sulphate Precipitation Method which the S.P.A. Sub-Committee found inapplicable to the determination of lead in food-colouring materials on account of the presence of appreciable amounts of inorganic salts (chiefly sodium and ammonium sulphates) and of the interference of ferric sulphate, frequently likely to be present. The principle involved is that of wet oxidation followed by alcoholic precipitation of lead sulphate and solution of the latter in ammonium acetate prior to tinting. The intermediate stage involving precipitation of the lead as sulphide is thus dispensed with. This indeed should be possible, because the peaty moorland waters dealt with rarely contain more than 10 parts of dissolved solids per 100,000. If 8 of these are considered present as $CaSO_4$ and 500 ml. of the water are taken, this is equivalent to a $CaSO_4$-content of 40 mg. in the 20 ml. of distilled water which is mixed with the alcohol used to complete the precipitation. This is the weight of $CaSO_4$ necessary to yield a saturated aqueous solution at 20° C.

METHOD.—A convenient quantity of the water (500 ml. when lead is likely either to be absent or at most present to the extent of 1/100 grain per gallon, *i.e.* 0·14 part per million) is mixed with 1 ml. of pure sulphuric acid and boiled down to a small bulk in a high-resistance globular glass flask. It is then transferred to a similar flask of 100-ml. capacity and the evaporation is continued until charring begins. The organic matter is then oxidised by heating with 1 ml. of conc. nitric acid, and the colourless solution resulting is twice evaporated with water until white fumes appear, before completing the precipitation of the lead sulphate overnight with a mixture of 20 ml. of water and 10 ml. of 95 per cent. alcohol. The precipitate is next transferred to a Gooch crucible containing prepared filter-paper pulp, and washed with two successive portions of 5 ml. of a mixture of water, alcohol and sulphuric acid in the proportions 20 : 10 : 1 by volume before being treated with two separate quantities of 10 ml. of hot 40 per cent. ammonium acetate solution. The pulp is washed twice with 5 ml. of hot water, and the filtrate is treated in a 50-ml. Nessler cylinder with 2 ml. of 8 per cent. ammonia, 0·02 g. of ammonium citrate, 0·02 g. of potassium cyanide, and 2 ml. of 10 per cent. sodium sulphide solution. The mixture is made up to 50 ml., and the lead is estimated either by comparison with a standard lead solution, each ml. of which contains 0·01 mg. of Pb, or in a B.D.H. Lovibond Nessleriser, using standard discs representing weights of lead ranging from 10γ–100γ. A blank estimation should also be carried out on the reagents. This is likely to give a correction of the order of 15γ.

With the foregoing method it has been found possible to recover quantitatively 50γ of lead added as nitrate both in absence and in presence of 500 ml. of Leeds City water, previously found free from lead.

I should like to express my thanks to Major A. Houlbrooke and Mr. H. Lobley for the assistance they have given me in connection with the present investigation.

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February 23rd, 1940

Micro-Tests for Elements in Organic Compounds, Part II. Phosphorus, Arsenic and Antimony

BY CECIL L. WILSON, M.Sc., PH.D., A.I.C.

THE detection of phosphorus, arsenic and antimony in organic compounds depends on the conversion of these elements into corresponding inorganic anions.

Fusions on the macro scale may be carried out with (i) sodium nitrate and potassium nitrate, or (ii) sodium peroxide. On the micro scale very small amounts of material may be lost when (i) is used, while (ii) gives too violent a reaction. The lime fusion method of Feigl[1] gives insoluble compounds, which are not very suitable for subsequent identification.

The most satisfactory fusion mixture tested was one part of sodium peroxide intimately mixed with two parts of potassium nitrate. A few crystals of the sample are mixed with about three times their weight of this, and the mixture is filled into a bulb (4 mm. in diameter), blown on the end of a thin-walled glass tube, 7 cm. × 2 mm. The fusion mixture alone is placed on top of this until the bulb is half full, and its contents are fused in such a way as to melt slowly. After the fusion, the bulb is heated strongly and dipped into a large drop of water on a microscope slide or a small watch-glass, or, preferably, in a 1-ml. crucible. The mass is ground and stirred thoroughly, and the resultant solution or suspension is tested for the appropriate anions.

PROCEDURE.—Antimony and arsenic are first tested for by a modified Gutzeit test. Of the many recommended methods for the separate identification of arsine and stibine, the only one that proved completely successful on the micro scale depended on reduction with tin and hydrochloric acid in presence of platinum.

A "couple" is made from a strip of platinum foil, 20 × 2 mm., and a strip of tin foil, 60 × 2 mm. The strip of tin is twisted loosely and then wound from one end of the platinum strip to the other in such a way as to leave a considerable area of bright platinum visible. The platinum strip is in turn wound about its short edge into a loose flat spiral of such a size as to drop into the reaction vessel of the gas detection apparatus described elsewhere (see p. 407). A drop (one-half) of the fusion *suspension* is transferred to the chamber. (Under the conditions of the fusion described, antimony appears to form an insoluble salt, probably sodium pyroantimoniate.) Five drops of 5 *N* hydrochloric acid are added, and heating is begun.

Arsenic.—By this treatment, arsenate is reduced to arsine, which rapidly blackens the silver nitrate test-paper. If antimony is present, it is retained. There may, under continued reduction, be a very faint yellowing of the test-paper if antimony is present and arsenic absent, but, since even minute traces of arsenic darken the paper appreciably, this may be neglected.

Antimony.—In the course of the reduction with the tin-platinum "couple," antimony is deposited as the metal, in the form of a black coating on both tin and platinum. This is sufficient verification of its presence (dulling of the platinum by small amounts of antimony is very easily seen) but, if desired, confirmation may be obtained by removing the "couple," separating the tin and platinum and washing the platinum strip thoroughly with air-free distilled water. The antimony is then dissolved off the platinum in the reaction chamber of the gas detection apparatus by heating gently with three drops of conc. hydrochloric acid. When the platinum is completely cleared it is removed by means of a fine glass rod. Several drops of water and a few chips of zinc are added, and the presence of antimony will be shown by the blackening of silver nitrate test-paper.

Phosphorus.—If arsenic is absent, a direct test for phosphorus is made in the remainder of the fusion liquid. The clear liquid is transferred to a slide and rendered just acid with sulphuric acid. The reagent solution is made up as follows: 3 g. of ammonium acetate and 10 ml. of ammonia (sp.gr. 0·88) are made up to 25 ml. with water. After complete solution has taken place, 1 g. of magnesium acetate is dissolved. A large drop of this reagent is added to the test drop, so that the whole has a *strong* odour of ammonia.*

The drop is allowed to stand for a few minutes, and if only small or poorly developed crystals have appeared by then, the whole is heated just to boiling, and allowed to cool. The presence of phosphorus (as phosphate) is indicated by the formation of characteristic crystals, as described by Chamot and Mason.[3]

If arsenic is present, it must first be removed. The test-drop is placed in the reaction chamber, and to it are added five drops of 5 *N* hydrochloric acid and a few chips of zinc. Reduction is continued until no arsine can be detected on addition of a further drop of acid and a small chip of zinc. A large drop of the liquid is then removed, and tested for phosphate as before. Under these conditions the forms of the phosphate crystals tend to be less feathery than those from an unreduced phosphate solution.

The following compounds were satisfactorily used for the tests: Sodium glycerophosphate, sodium phenyl phosphate, triphenyl phosphate, nucleic acid; sodium cacodylate, tryparsamide, *p*-arsanilic acid, sodium methyl arsonate; antimony strontium tartrate, antimony potassium tartrate, antimony oxalate.

The sensitivity of the tests varied with the compounds, but in general, in mixtures containing 5 to 20γ of phosphorus compound, 10 to 20γ of arsenic compound and 20 to 30γ of antimony compound, the elements could be detected correctly. Although these figures are not so low as those given by Feigl,[4] they apply to mixtures, for which his methods are not suitable.

SUMMARY.—The detection of phosphorus, arsenic and antimony microchemically in organic mixtures is preceded by oxidation to the corresponding inorganic anions. Phosphorus is detected by its characteristic double magnesium ammonium compound. To distinguish arsenic and antimony, reduction is effected by a tin-platinum "couple," and a modified Gutzeit test is applied.

I wish to express my indebtedness to The British Drug Houses, Ltd., who kindly supplied me with samples of organic compounds.

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February, 1940

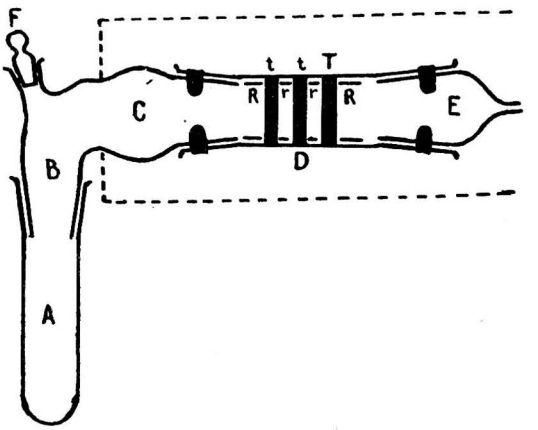
* Since it is essential to maintain the relative proportions of ammonia and the two acetates, particularly when small amounts are being tested for, it is preferable to use this compound reagent solution, rather than to add the reagents separately, as described by other authors.[2]

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.

A GAS DETECTION APPARATUS FOR QUALITATIVE MICROCHEMISTRY

THIS apparatus, originally devised for the detection of arsine or stibine in presence of hydrogen sulphide, *cf.* p. 405, should prove useful whenever it is necessary to filter off one gas before testing for another.



The reaction vessel, A, shown in the diagram, is a fusion tube or micro-test-tube, connected with an arm, B, which leads the gases to the testing chamber and through which reagents may be added. A bulb, C, in this arm contains cotton-wool or glass-wool, to retain spray. The testing chamber, D, is a length of straight tubing. Within this is a series of glass rings, R, *r*, which just slide in it; these may be prepared by cutting them from another piece of glass tubing of the appropriate size. These serve to hold apart and in position test-papers, *t*, T, impregnated with suitable reagents. The test-papers are discs cut from "spot" paper by a cork borer, and they should fit the walls of the testing chamber tightly at every point. A spare testing chamber is necessary when a blank test has to be applied to the reagents. At the end of the apparatus is a piece of tubing, E, drawn out to a fine aperture to avoid undue contamination of the test-papers with the atmosphere. The whole apparatus is mounted by means of two metal spring clips on to a piece of asbestos board, which may be held in a retort stand for the reaction vessel.

In testing *e.g.* for arsine in presence of hydrogen sulphide, the two testing chambers are fitted as follows:—The chamber is held vertically with the lower end blocked. The first stop ring, R, is placed in position, and a disc of paper, *t*, is pressed home with a plunger (conveniently a glass tube of the same diameter as the rings). A large drop of lead acetate solution is applied by means of a capillary tube to the disc, which must be completely wet by the liquid. One of the intermediate rings, *r*, is then inserted, followed by a second disc of paper. This is also impregnated with lead acetate solution, and followed by another intermediate ring and a third disc of paper, T. Unless a very small trace of arsine in presence of a very large amount of hydrogen sulphide is to be expected, no more filtering test-papers are required, and this third disc is impregnated with a small drop of dilute nitric acid and a drop of silver nitrate solution. The second stop ring is then added.

Two testing chambers are prepared in this way. One is fitted into the apparatus. The ends of the other are plugged until it is required.

Several small chips of zinc and then five drops of 5 *N* hydrochloric acid are introduced through the filling aperture, F, and the apparatus is heated so that vigorous effervescence takes place for a fixed time, say, two minutes. When very small traces of arsenic are being sought for, this period must be longer.

The testing chamber is replaced by the spare chamber, and the test material is introduced through F. Heating (and effervescence) are continued for the same length of time, after which the chamber is withdrawn, and the discs of paper are removed and examined.

Those from the blank test should, of course, be white, or nearly so. Of the discs in the second test chamber, No. 1 may be black or brown, showing the presence of hydrogen sulphide. No. 2 should be white, or nearly so. If No. 3 is darker in colour than No. 2, and also than No. 3

of the blank, then arsine (or stibine, when no other method of distinguishing between the two has been used) is present.

If disc No. 2 is appreciably darkened, the test must be repeated with more filtering discs present. The length of the testing chamber allows for the addition of more discs, and in the final test just sufficient should be present to ensure that the final one immediately preceding the actual test-disc is unaffected.

After considerable experience with the apparatus, it will be found that it allows not only of detection of the gases, but also of a rough estimation of the relative amounts present.

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October, 1939

THE DETERMINATION OF COCOA ALKALOIDS IN CONFECTIONERY

THE process here described is concerned with the final extraction of the alkaloids after treatment of the material according to the method of Moir and Hinks (ANALYST, 1935, **60**, 439). In that method 10 to 20 g. of confectionery are heated under reflux with 200 ml. of 80 per cent. alcohol and 2·5 g. of magnesia for 1½ hours and then filtered through a Buchner funnel. The residue is extracted with two further quantities of 80 per cent. alcohol, and the extract is filtered The filtrate is evaporated to low bulk, and water is added to bring the volume up to about 100 ml. This solution is slightly acidified, transferred to a 200-ml. flask, treated with 5 ml. of zinc acetate solution followed by 5 ml. of potassium ferrocyanide solution, mixed, made up to volume and filtered, and a suitable portion of the filtrate is concentrated to about 10 ml.

In the original method this concentrate is extracted with chloroform, and, if 20 to 30 mg. of alkaloids are present, as many as ten extractions are required to remove them completely (*cf.* A. E. and H. A. Parkes, ANALYST, 1937, **62**, 791), and the resulting alkaloids are invariably impure, thus necessitating a nitrogen determination. With the idea of avoiding this tedious extraction process I investigated the possibility of converting the small quantities of theobromine into caffeine (which is much more soluble) in the presence of many times its weight of sugar.

In a preliminary experiment 10 mg. of pure theobromine and 5 g. of sugar were dissolved in about 10 ml. of water, and the solution was transferred to a small separating funnel, and treated with 1 ml. of *N* sodium hydroxide solution, followed by 0·5 ml. of methyl sulphate, the separator being shaken occasionally during 5 minutes. One ml. of 50 per cent. sodium hydroxide solution was then added to decompose the excess of methyl sulphate and, after standing for 10 minutes, the mixture was extracted with three successive portions of 30 ml. of chloroform, and the chloroform extracts were washed once with water and run through a dry filter-paper into a weighed flask. The chloroform was evaporated and the residue was dried at 100° C. and weighed. It consisted of white crystals of caffeine weighing 10·6 mg.

Ten g. of home-made chocolate cake were treated according to the method of Moir and Hinks as described, the final concentrate was made up to 20 ml. and 10 ml. were extracted directly with chloroform.

	g.
Weight of alkaloid after 5 extractions, each with 30 ml. of chloroform	= 0·021
,, ,, ,, ,, 10 ,, ,, ,, ,,	= 0·024
Nitrogen calculated as caffeine	= 0·0156

The alkaloids recovered by this process were amorphous and darkened considerably when treated with sulphuric acid.

The other 10 ml. were treated with methyl sulphate as described above.

	g.
Weight of alkaloid after 3 extractions, each with 30 ml. of chloroform	= 0·015
,, ,, ,, ,, 5 ,, ,, ,, ,,	= 0·015

The residue from this chloroform extract was white and crystalline and melted at 234° C., which corresponds with pure caffeine.

CONCLUSION.—After treatment of cocoa confectionery according to the method of Moir and Hinks the alkaloids are most conveniently recovered and weighed as pure caffeine by treating the clarified extract with methyl sulphate as described above. The weight of caffeine multiplied by 0·928 corresponds with the weight of the original alkaloids as theobromine, and an average factor for converting caffeine into mixed alkaloids is 0·935.

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May, 1940

THE IODINE VALUE OF SOFT PARAFFINS

As the iodine value of a sample of soft paraffin may give some indication of its liability or otherwise to become overheated during the preparation of bleach ointment, and may also affect the rate of the loss of available chlorine (*cf.* Macmorran, p. 423), it is necessary to use a method of determining it that will give concordant results in the hands of different workers. The B.P. method, which is a modification of the Wijs method, is unsuitable because soft paraffins are largely insoluble at ordinary temperature in the mixture of carbon tetrachloride and reagent as ordinarily used. Iodine values of soft paraffins have been published by Bryant and Spence[1] and by Fishburn,[2] but the method used is not stated. It was found that Rosenmund and Kuhnhenn's pyridine sulphate bromide method did not offer any advantage over the more commonly used Wijs method.

A study of the conditions showed that solution of the paraffin was greatly improved by reducing the volumes of the paraffin and the reagent. By using 1 g. of the sample, 20 ml. of carbon tetrachloride and 10 ml. of the official Wijs reagent, a clear solution was obtained with 35 different samples of white and yellow soft paraffins, and only with 2 samples, probably containing cerasine, was there a very slight precipitate. By varying the time of standing and excess of reagent it was found that, after an initial fairly rapid absorption of iodine, combination continues slowly for a very long time. Thus the following iodine values were obtained with a typical sample of B.P. yellow soft paraffin (1 g. with 20 ml. of carbon tetrachloride and 10 ml. of Wijs reagent):—After half-an-hour, 9·8; 1 hour, 10·0; 1½ hours, 10·8; 2 hours, 11·26; 72 hours, 12·7. In further experiments with 0·5 g. of the sample and 5 ml. of Wijs reagent, similar, but slightly lower, results were obtained. Raising the temperature or increasing the excess of reagent resulted in higher values, as was to be expected.

The results of these experiments show that it is necessary to fix a suitable time of contact with the reagent. On plotting iodine absorption against time, the curve with some samples showed a somewhat sharp rise at 1 hour, but became considerably flatter before the 1½ hour period. For this reason it was considered preferable to increase the usual 1 hour to 1½ hours. The following procedure, based on experiments with 37 representative samples, is recommended. It gives results agreeing within ±1 per cent. (usually ±0·5 per cent.) in duplicate determinations.

METHOD.—An amount between 0·95 and 1·05 g. of the sample, accurately weighed, is dissolved with the aid of gentle heat in 20 ml. of carbon tetrachloride in a glass-stoppered flask. The solution is cooled to between 19° and 21° C., and treated with 10 ml. of Wijs solution. The flask is closed and left for 1½ hours at 19° to 21° C. Ten ml. of 10 per cent. potassium iodide solution and 100 ml. of water are then added, and the excess of iodine is titrated with *N*/10 thiosulphate solution. A blank test is made without the soft paraffin.

By this method 18 samples of yellow soft paraffin, obtained mainly from importers, and of as varied a character as possible, gave iodine values ranging from 2·5 to 12·3 with an average of 9·6. Thirteen samples gave results between 9·5 and 11·5.

With 19 samples of the white variety, of similar origin, the iodine values ranged from 0·9 to 11·4 with an average of 5·1. Seven samples gave figures between 4·5 and 5·5.

As a rule, there was a close relationship between the iodine values of soft paraffins and their liability to become over-heated in the preparation of bleach ointment, the higher the iodine value, the greater the tendency towards over-heating. There were, however, one or two anomalous samples; the thermal bromine method was tried to see if it would give an indication of abnormality, but the results were practically parallel with the iodine values.

Other characteristics of soft paraffins were described in a previous communication.[3]

H. BRINDLE

REFERENCES

1. E. G. Bryant and J. Spence, *Year Book of Pharmacy*, 1926, 445.
2. A. G. Fishburn, *Pharm. J.*, 1940, **144**, 35.
3. H. Brindle, *Quart. J. Pharm.*, 1939, **12**, 361.

PHARMACY DEPARTMENT
MANCHESTER UNIVERSITY

March 19th, 1940

DETERMINATION OF CHROMATES IN SEWAGE LIQUORS

OWING to the increased use of chromic acid and chromates in industry the presence of chromate in sewage liquors is now of fairly common occurrence. If any significant quantity is present, the usual determinations of organic matter and B.O.D. are materially affected, and it is necessary to make a correction for the iodine liberated by the chromate from the potassium iodide used in these tests. Jenkins and Hewitt[1] determined directly the chromate correction to be used when applying the 4-hours oxygen-absorbed test to crude sewage; they acidified the sample in the presence of excess of potassium iodide and titrated the iodine liberated by interaction of chromate and iodide. Although simple, this method is not very reliable, since the iodine liberated by nitrites is also included in the correction. Nitrites are occasionally present in crude sewage and are of frequent occurrence in purified sewage. I have also found that the result so obtained

may vary with the age of the sample. Spencer's method,[2] in which the organic matter is first oxidised by alkaline permanganate, has an indefinite end-point, and has also been found to give erratic results.

Illustrations of these defects became available when, owing to an accident, about 15 cwt. of sodium dichromate was discharged into a sewer. This was accompanied by a quantity of a lead solution which caused partial precipitation of the chromate in the sewer and subsequent removal in the settling tanks at the sewage works. The following results were obtained with 24-hour samples taken at the sewage works:

Sample of:	Chromium, parts per 100,000 found: By Spencer's method	By Jenkins and Hewitt's method
Crude sewage (believed to contain 0·4–0·5 part of Cr per 100,000)	0·83	0·65
Settled sewage	1·48	1·52
Partly purified sewage	0·96	1·22
Final effluent	2·08	1·39

These figures have not been corrected for the presence of nitrites. The sample of crude sewage was again examined by Spencer's method, but was left to stand overnight after the excess alcohol had been boiled off. When potassium iodide was added to the acidified solution, this appeared to contain 59·4 parts of chromium per 100,000.

The following method was then tried:—Fifty ml. of the sample were measured into a stoppered bottle and a few crystals of sodium azide were added. The mixture was acidified with a few ml. of conc. phosphoric acid, rotated, and left to stand for several minutes. Excess of potassium iodide was then added, followed by 5 ml. of 25 per cent. sulphuric acid, and the liberated iodine was titrated with $N/40$ thiosulphate solution.

Comparison of the results obtained by this method with those obtained by the direct method on two further samples gave:

Sample of:	Chromium,* parts per 100,000, found: Azide method	Direct method
Partly purified sewage	0·20	1·00
Final effluent	0·35	2·29
,, ,, (after 5 days' incubation at 80° F.)	0·35	0·87

* Exact chromium content of liquors unknown.

In order to test the effectiveness of this method for the destruction of nitrites, quantities of sodium nitrite solution were added to a number of portions of $N/4000$ sodium dichromate solution so as to give a range of concentration up to 0·04 part of nitrous nitrogen per 100,000. The chromium-content was determined by the direct method and by the azide method. It was found that the result obtained by the azide method was independent of the nitrite concentration and that good end-points were obtained. An amount of 0·35 part of chromium per 100,000 in the final effluent from the works, with a total flow for the period of 12 million gallons, is equivalent to a total of about 10½ cwt. of sodium dichromate. Having regard to the precipitation which must have taken place and the further "loss" in the settling tanks, this figure is in fairly good agreement with the 15 cwt. known to have been discharged.

The azide-iodine reaction of Feigl[3] does not interfere, owing to the high acidity of the mixture.

REFERENCES

1. S. H. Jenkins and C. H. Hewitt, *J. Soc. Chem. Ind.*, 1940, **49**, 41.
2. J. H. Spencer, Ann. Summer Conf., Inst. Sewage Purif., July, 1939 (see *Sewage Purification*, 1939, **1**, 356).
3. F. Feigl, *Z. anal. Chem.*, 1928, **74**, 369.

D. DICKINSON

THE LABORATORY
STOCKPORT SEWAGE WORKS

May, 1940

Official Appointments

THE following notification (dated June 6th, 1940) of Amendment of the List of Public Analysts appointed by Local Authorities with the approval of the Minister of Health has been made:

Authority	Public Analyst
Castleford Urban District	F. W. M. JAFFÉ
Halifax County Borough	R. MALLINDER
Stockton-on-Tees Borough	C. J. H. STOCK
Thurrock Urban District	A. W. STEWART
Hereford Borough	F. G. D. CHALMERS (Additional)
Burton-upon-Trent County Borough	R. MALLINDER
Morecambe and Heysham Borough	J. R. STUBBS
Kingston-upon-Thames Borough	E. HINKS
Batley Borough	F. W. M. JAFFÉ
Huddersfield County Borough	R. MALLINDER
Chislehurst and Sidcup Urban District	F. W. F. ARNAUD
Brierley Hill Urban District	E. V. JONES
,, ,, ,, ,,	F. DIXON (Deputy)
Mitcham Borough	E. HINKS
,, ,,	D. D. MOIR (Deputy)
Scarborough Borough	R. MALLINDER
Carshalton Urban District	E. HINKS
,, ,, ,,	D. D. MOIR (Deputy)
Crosby Borough	W. H. ROBERTS
Gosport Borough	R. P. PAGE
Westmorland County Council	W. H. ROBERTS
Kendal Borough	W. H. ROBERTS
Gillingham Borough	F. W. F. ARNAUD
Beddington and Wallington Borough	H. A. WILLIAMS
Mansfield Borough	W. W. TAYLOR
Darwen Borough	J. R. STUBBS
,, ,,	ARNOLD LEES (Deputy)
Ilford Borough	J. H. HAMENCE (Joint)

FERTILISERS AND FEEDING STUFFS ACT, 1926

THE Ministry of Agriculture and Fisheries has notified the Society of the following changes in the appointments of Agricultural Analysts and Deputy Agricultural Analysts which have taken place since June 28th, 1939.

ERIC VOELCKER, F.I.C., A.R.C.S., Agricultural Analyst for the County Council of the West Riding of Yorkshire, *vice* H. T. Lea, M.Sc., F.I.C., deceased.

R. MALLINDER, B.Sc., F.I.C., Agricultural Analyst for the County Boroughs of Burton-on-Trent, Halifax and Huddersfield, *vice* H. T. Lea.

F. G. D. CHALMERS, M.A., B.Sc., F.I.C., Agricultural Analyst for the County Council of Warwickshire, *vice* W. T. Rigby, F.I.C.

W. F. GREEVES, F.I.C., Deputy Agricultural Analyst to the County Council of East Suffolk.

June 28th, 1940

The Margarine (Addition of Borax) Order, 1940

WE are informed that the Ministry of Food has made it a condition of the licences issued to manufacturers under the Margarine (Addition of Borax) Order, 1940 (see p. 413), that the amount of borax added to margarine should not exceed 0·25 per cent. expressed as boric acid.

EDITOR

July 11th, 1940

Home Office

Poisons

STATUTORY RULES AND ORDERS. 1940. No. 452*

THE POISONS (AMENDMENT) RULES, 1940, DATED MARCH 29, 1940, MADE BY THE SECRETARY OF STATE UNDER SECTION 23 OF THE PHARMACY AND POISONS ACT, 1933 (23 & 24 GEO. 5. C. 25).

The following Rules have been made:

1. In the First Schedule to the Poisons Rules, 1935, as amended by the Poisons (Amendment) Rules, 1937, and the Poisons (Amendment) Rules, 1938:

(*a*) in the item "Arsenical poisons" there shall be inserted at the end the words "and except dentifrices containing less than 0·5 per cent. of acetarsol";

(*b*) in the item "Para-aminobenzenesulphonamide" for the words "derivatives of para-aminobenzenesulphonamide having one or both of the hydrogen atoms of the para-amino group substituted by other radicals" there shall be substituted the words "derivatives of para-aminobenzenesulphonamide having any of the hydrogen atoms of the para-amino group or of the sulphonamide group substituted by another radical"; and

(*c*) there shall be inserted the following substances:—Sulphonal; alkyl sulphonals.

2. In Group II in the Third Schedule to the said Rules there shall be inserted in the first column the poison "Antimony, chlorides of" and opposite those words there shall be inserted in the second column the word "Polishes."

3. In the Fourth Schedule to the said Rules, in the item "Para-aminobenzenesulphonamide" for the words "derivatives of para-aminobenzenesulphonamide having one or both of the hydrogen atoms of the para-amino group substituted by other radicals" there shall be substituted the words "derivatives of para-aminobenzenesulphonamide having any of the hydrogen atoms of the para-amino group or of the sulphonamide group substituted by another radical."

4.—(1) These Rules may be cited as the Poisons (Amendment) Rules, 1940, and the Poisons Rules, 1935, the Poisons (Amendment) Rules, 1937, the Poisons (Amendment) Rules, 1938, and these Rules may be cited together as the Poisons Rules, 1935 to 1940.

(2) These Rules shall come into operation on the first day of April, 1940.

HOME OFFICE,
WHITEHALL

JOHN ANDERSON,
One of His Majesty's Principal Secretaries of State.
29th March, 1940

STATUTORY RULES AND ORDERS. 1940. No. 453*

THE POISONS LIST (AMENDMENT) ORDER, 1940, DATED MARCH 29, 1940, MADE BY THE SECRETARY OF STATE UNDER SECTION 17 (5) OF THE PHARMACY AND POISONS ACT, 1933 (23 & 24 GEO. 5 C. 25), AMENDING THE LIST OF THE SUBSTANCES WHICH ARE TO BE TREATED AS POISONS FOR THE PURPOSES OF THAT ACT.

Whereas the Poisons Board has recommended to me that the list of the substances which are to be treated as poisons for the purposes of the Pharmacy and Poisons Act, 1933(*a*), should be amended so that certain additional substances should be included in Part I of the said list:

Now, therefore, in pursuance of Section 17 (5) of the Pharmacy and Poisons Act, 1933, I hereby order as follows:

1. In Part I of the Poisons List (*b*) in the item "Para-aminobenzenesulphonamide" for the words "derivatives of para-aminobenzenesulphonamide having one or both of the hydrogen atoms of the para-amino group substituted by other radicals" there shall be substituted the words "derivatives of para-aminobenzenesulphonamide having any of the hydrogen atoms of the para-amino group or of the sulphonamide group substituted by another radical."

2. This Order may be cited as the Poisons List (Amendment) Order, 1940, and shall come into operation on the first day of April, 1940.

HOME OFFICE
WHITEHALL

JOHN ANDERSON,
One of His Majesty's Principal Secretaries of State.
29th March, 1940

(*a*) 23 & 24 Geo. 5. c. 25.

(*b*) *See* Schedule to the Poisons List Confirmation Order, 1935 (S.R. & O. 1935 (No. 1238), p. 1383), as amended by the Poisons List (Amendment) Order, 1937 (S.R. & O. 1937 (No. 1029), p. 1917), and the Poisons List (Amendment) Order, 1938 (S.R. & O. 1938 (No. 1547), II, p. 2829).

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* H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1940 Price 1d. net.

Ministry of Food

STATUTORY RULES AND ORDERS. 1940. No. 982*

EMERGENCY POWERS (DEFENCE)

Food

THE MARGARINE (ADDITION OF BORAX) ORDER, 1940, DATED JUNE 14, 1940

IN exercise of the powers conferred on him by Regulation 55 of the Defence (General) Regulations, 1939(a), and of all other powers him enabling the Minister of Food (hereinafter referred to as "the Minister") hereby makes the following Order:

1. In this Order "Borax" includes Boric Acid and Borates.

2. Subject to any directions given or except under and in accordance with the terms of a licence granted by or on behalf of the Minister no person shall:

(*a*) produce or manufacture for sale any margarine which contains any added borax; or

(*b*) treat with borax or add borax to any margarine.

Provided that the provisions of this Article shall not apply to margarine which is intended to be exported or intended for use as ships' stores.

3. It shall be lawful for any person subject to the provisions of this Order and of any other Order made or directions given by the Minister:

(*a*) to produce or manufacture for sale or sell or offer or expose for sale or deposit in any place for the purposes of sale any margarine notwithstanding that such margarine contains added borax; and

(*b*) to produce or manufacture for sale or sell or offer or expose for sale any article of food other than margarine, which contains borax necessarily introduced by the use in the preparation of that article of margarine containing borax.

4. Infringements of this Order are offences against the Defence (General) Regulations, 1939

5. This Order may be cited as the Margarine (Addition of Borax) Order, 1940.

By Order of the Minister of Food.

H. L. FRENCH,
Secretary to the Ministry of Food.

Dated the 14th day of June, 1940.

Department of Scientific and Industrial Research

REPORT OF THE NATIONAL PHYSICAL LABORATORY FOR 1939†

IN the Report of the Executive Committee, the Director (Dr. C. G. Darwin) refers to the work of the Laboratory in war time. Although each of the three services has a strong research department, certain problems arising out of war conditions continue to be submitted, so that the Laboratory is again playing its part, although in less degree than in the last war. The policy of not dispersing the scientific staff has been fully justified, and has enabled the peace-time function of tendering advice and help to industry on scientific and technical problems to be fully maintained. Subjects of special interest to which reference is made in the Reports of the Superintendents of the Physics Department and Engineering Department include the following:

SPECIFIC HEAT AND MELTING-POINT OF VERY PURE IRON.—A specimen of iron (purity 99·99 per cent.), prepared in the Metallurgy Department, had a specific heat of 0·11 at 50° C., and melted at 1533° ± 5° C.

INTERNATIONAL TEMPERATURE SCALE.—In order to obtain a "fixed" point between the b.p. of sulphur (444·60° C.) and the freezing-point of gold (1063·0° C.), the b.p. of selenium (684·8 ± 0·1° C. for normal atmospheric pressure) was determined by means of calibrated platinum thermo-couples.

INTERNAL STRAIN IN METALS.—It was found by X-ray measurements that the atomic lattices of copper, silver, nickel, iron and molybdenum expand when the metal is subjected to stress or cold-worked; this represents an unstable condition, since, on continuing the cold-working, there may be a reversion to normal dimensions. It was also found that the breakdown of metallic grains into finer components proceeds to a limit which depends on the metal and the temperature. This lower limit, which is a new physical constant, was determined for each of the above-mentioned metals.

TOOTH STRUCTURE.—Earlier X-ray investigation showed that tooth enamel contains two oriented groups of apatite crystals, the hexagonal axes of which make angles of about 5° and 40° respectively with the prism direction. Further work has indicated that the 5° group usually

(a) S.R. & O. 1939, No. 927.

* H.M. Stationery Office, York House, Kingsway, London, W.C.2. Price 1d. net.

† H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1940. Price 2s. 6d. net.

predominates within the prism, and the 40° group in the interprismatic substance. The degree of calcification may be indicated by the interference colours shown by enamel in polarised light. This method has confirmed the X-ray result that in the human tooth calcification diminishes inwards from the outer enamel surface. A method of determining the proportion of calcified matter in the enamel or dentine from point to point in a tooth section has been based on microphotometric measurements of radiographs.

HAEMOGLOBINOMETER STANDARDISATION.—Colorimetric estimation of carboxyhaemoglobin in a haemoglobinometer tube has hitherto been based on comparison with a standard solution of carboxyhaemoglobin defined in terms of the oxygen-content of the haemoglobin. Haldane found that the blood of an average healthy person contained 18·5 ml. of oxygen per 100 ml., and this value was adopted in preparing colour tubes. A special Committee of the British Standards Institution decided that it would be preferable to define the standard solution colorimetrically. In order that there should be agreement with existing colour tubes, carboxyhaemoglobin, prepared by Haldane's method, was colorimetrically measured, and the result was taken as defining the standard solution. A sensitive colour comparator has also been devised to enable colour tubes to be accurately calibrated.

SURFACE FINISH OF METALS.—In a photoelectric instrument, designed in the Laboratory, the ratio of the regularly reflected light to the scattered light is measured; a high value denotes a high quality of surface finish. This instrument, which has been tested on numerous materials, could be constructed and used in industrial laboratories.

ELECTRICAL STANDARDS.—It has been proposed to change from international units to absolute units in 1940, and, with this end in view, standards of resistance and standard cells were calibrated in both systems and sent to the International Bureau of Weights and Measures for comparison with standards from other countries. It was found that all the values for the ohm (absolute) agreed within 2 parts per 100,000, and it was agreed that the most probable value is:

1 international ohm = 1·00049 ohm (absolute).

With regard to the ampere and volt, only the National Physical Laboratory and the National Bureau of Standards agreed within about 1 part in 100,000. The Consultative Committee was therefore unable to recommend a value with limits closer than 1 or 2 parts per 10,000, and therefore proposed the adoption for the present, of the values:

1 international ohm = 1·0005 ohm (absolute)
1 international ampere = 0·9999 ampere (absolute)
1 international volt = 1·0004 volt (absolute)

Owing to the outbreak of war, no action is being taken at present to introduce the absolute units.

DIELECTRICS.—Previous work on the properties of plastics as electrical insulating materials had been mainly confined to synthetic resins of the phenolic type. A similar investigation of aniline resins and of pure hydrocarbon resins, including polystyrene and polyethylene, has shown that these materials have advantages for certain classes of electrical work. Experiments have also been made on the properties of laminated boards made from paper and the various resins.

INTERNATIONAL VISIBILITY CURVE.—Further work has been done on the curve relating the energy for each wavelength of light with its effect as perceived in the normal eye. It was agreed at the meeting of the International Commission in Illumination in July that no change should be made. A review of the work of the past few years has shown that changes in the conditions of observation, particularly field size and brightness, may cause considerable variations in the curve. There is even some evidence of variation with the season, possibly owing to differences in the vitamin A content of the normal diet.

INVESTIGATIONS RELATING TO AIR RAID PRECAUTIONS LIGHTING RESTRICTIONS.—The problem of measuring the intensities of very faint lights has been studied. For many purposes it is sufficient to ascertain if a light falls below some fixed standard, and a simple portable gauge to do this has been designed. The comparison field is provided by radium luminous compound, which does not require frequent renewal. By suitable modification the instrument can be used for measurement instead of gauging.

A simple photometer has been designed for measuring the brightness of materials intended to be luminescent after exposure to daylight or ultra-violet light.

In connection with the "black-out," the opacity of black textiles has been studied, and "complementary lighting" has been investigated. This method consists, for example, in using red or yellow light in a building and preventing it being visible by night by having windows of blue glass of sufficient transparency to allow enough daylight to enter during the day time. Delicate adjustment of the pairs of colours is necessary.

LUBRICATION RESEARCH.—An investigation of the comparative lubrication value of animal, vegetable and mineral oils has been completed by the Engineering Department. It was found that under all conditions, other than a complete fluid film, animal and vegetable oils are superior to mineral oils from the purely mechanical point of view. As a rule, no serious effects were caused by the chemical instability of fatty oils, and the temperature of journal bearings could be raised to 200° C. several times without apparent loss of lubricating quality of the oil. Advantages that fatty oils have over mineral oils are reduction of friction at high load and low speed, and, under extreme conditions, reduction of wear and increase in the breakdown load. Little difference was observed in the behaviour of vegetable and animal oils.

International Union of Chemistry

TENTH REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS*

THE Report covers the period from September 30th, 1938, to September 30th, 1939, and the Committee, whose members are the same as before (*cf.* ANALYST, 1939, **64**, 352), has been able to complete it, notwithstanding the outbreak of war.

TABLE OF ATOMIC WEIGHTS.—There are three changes in the International Table. The atomic weight of hydrogen is now 1·0080 (previously 1·0081), that of iron 55·85 (previously 55·84), and that of lutecium 174·99 (previously 175·0).

Hydrogen.—The work of different investigators, the most recent of which is that of Swartout and Dole (*J. Amer. Chem. Soc.*, 1939, **61**, 2025), on the ratio of the isotopes $_1H$ and $_2H$ in certain waters of natural occurrence, has indicated that that value is higher than the one hitherto used for calculating the atomic weight of hydrogen; with the value 1·00785 for $_1H$, calculated on the chemical basis, and with the value 6000 for the ratio $_1H/_2H$, the atomic weight of hydrogen in natural waters becomes 1·0080.

Iron.—The change in the atomic weight of iron has been based on the work of Hönigschmid and Liang (*Z. anorg. Chem.*, 1939, **241**, 361), who prepared spectroscopically-pure metallic iron, converted it into ferrous bromide by heating it in a current of bromine and nitrogen and purified the product by re-sublimation in pure nitrogen. The pure salt, weighed with all precautions, was dissolved in water acidified with sulphuric acid, the solution, which contained no trace of ferric salt, was oxidised with somewhat less than the calculated amount of dichromate, and a nephelometric comparison with silver was made. In 8 experiments the precipitated silver bromide was also weighed. The mean of all the determinations was 55·850, which is slightly higher than the value (55·838) previously found by Baxter, Thorvaldson and Cobb. The Committee attributed this discrepancy to the presence of traces of carbon, and possibly also of ferric salt, in the ferrous bromide used by Baxter *et al.*

Baxter and Hoover (*J. Amer. Chem. Soc.*, 1912, **34**, 1857) obtained the value 55·847 by reduction of ferric oxide, and Hönigschmid, Birckenbach and Zeiss (*Ber.*, 1923, **56**, 1473), basing their results on the analysis of ferric chloride, found the value to be 55·853.

The most recent investigations of the quantitative ratios of the isotopes of iron have given the values 55·853 and 55·851. The Committee therefore adopted the value 55·85 for the Table of Atomic Weights, since, although the maximum value obtained by the reduction of ferric oxide is 55·847, the possibility of the reduction not being quite complete cannot be excluded.

Lutecium.—The decision to change the atomic weight of lutecium was based on the work of Hönigschmid and Wittner (*Z. anorg. Chem.*, 1939, **240**, 284), who prepared pure lutecium trichloride and titrated it nephelometrically; in some of the experiments the precipitated silver chloride was also weighed. The resulting value, 174·996, agrees well with the value obtained spectrographically by Mattauch and Lichtblau (*Z. Physik.*, 1939, **111**, 514), 174·994. The Committee therefore adopted the value 174·99 for the Table.

Other Elements.—Among other atomic weight investigations reviewed by the Committee were those on chlorine by Hönigschmid and Wittner (*Z. anorg. Chem.*, 1939, **242**, 222), on molybdenum by Mattauch and Lichtblau (*Z. physik. Chem.*, 1939, **42**, B, 288), on europium by Lichtblau (*Naturwiss.*, 1939, **27**, 260), and on lead by Nier (*Physical Rev.*, 1939, **55**, 193). The results did not indicate the necessity for any immediate changes in the respective values in the Table.

Union of South Africa

FERTILISER PROBLEMS IN VEGETABLE PRODUCTION†

QUESTIONS of industrial development and of local markets are surveyed, and an outline is given of oversea practices in the period before the war. From the records of the experience gained the general conclusion is drawn that if vegetable growing is to be profitable, an artificial fertiliser should be applied, if necessary, only as a supplement to, or partial substitute for, natural manure. Green manuring as a method of building up soil organic matter in South Africa is not to be recommended, since the humus is being oxidised too rapidly. Vegetable gardeners near inland towns make use of sewage sludge to a limited extent, but some of the coastal municipalities in South Africa have their sewage pipes running into the sea, so that this source of manure supply is not available in those areas. Composting is being practised on an ever-increasing scale, and gives results as good as those obtained with manure.

*p*H OF SOILS.—The Virginia Truck Station of U.S.A. had drawn up the following table for

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* *J. Chem. Soc.*, 1940, 475.

† Reprint No. 19, 1940. By E. J. Greenstein, Division of Chemical Services, Pretoria.

soils in coastal plains, vegetable crops being grouped according to ranges of soil reaction for *optimum* growth:

*p*H 5·0 *to* 5·5.—Potatoes, sweet potatoes, water melons.

*p*H 5·5 *to* 6·5.—Beans, broccoli, cabbage, carrots, cauliflower, cucumber, parsley, parsnips, pumpkins, radishes, sweet corn, squash, tomatoes.

*p*H 6·0 *to* 6·5.—Asparagus, beets, celery, leeks, lettuce, onions, peas, spinach.

In South Africa the *p*H values can be raised somewhat. For example, in certain northern Transvaal areas tomatoes grow well at a *p*H range of 6·2 to 7·0.

There are definite signs that some of the soils in the Johannesburg and Pretoria districts are very acid, the *p*H values ranging from 4·5 to 6·5 in the vegetable-producing areas.

General Recommendations.—The use of acid-forming fertilisers must be avoided on acid soils; conversely, alkaline fertilisers should not be used on limy soils. For acid soils and for vegetable crops, it is generally considered that the fertiliser should contain a relatively large proportion of phosphorus, the ratios between the nitrogen, phosphoric oxide and potassium oxide being somewhat as follows:—4 : 12 : 4; 4 : 16 : 4; 4 : 10 : 6; 3 : 12 : 6. For potatoes and root crops, especially on sandy soil, fertilisers containing a large proportion of potash are preferred (4 : 8 : 8; 5 : 10 : 10).

In general, a heavy dressing of slow organic material, such as manure or compost, plus a good dressing of phosphate and potash at planting time is advocated, together with top dressings of sulphate of ammonia (or nitrate of soda or nitro chalk in very acid soils) when necessary.

COMPOST: ITS PREPARATION AND USE*

This pamphlet describes the nature and object of compost making, and discusses briefly the relative merits of organic manures and inorganic fertilisers.

Fate of Organic Matter in the Soil.—The following table shows how the organic matter content (both carbon and nitrogen) of the soil is a fairly reliable guide to its state of fertility, and also demonstrates the rapid loss of organic matter under arable conditions:

		Carbon Per Cent.	Nitrogen Per Cent.
No. 1.	Virgin land (veld)	1·20	0·098
No. 2.	Abandoned land, previously cultivated	0·55	0·050
No. 3.	Land from same slope as No. 2, but still under cultivation	0·89	0·071

It is difficult to build up the organic matter of soil by green manuring; normally, at least 75 per cent. of carbon added in that form will be lost by the oxidising action of the soil within 4 months of ploughing in the green crop.

Methods of Making Compost.—The essential conditions for the making of synthetic manure or compost include air supply, suitable temperature, adequate moisture supply, addition of suitable mineral nutrients, maintenance of a suitable reaction in the fermenting heap, and the presence of living micro-organisms. Each of these factors is discussed in detail.

In the ADCO process a patent nutrient mineral mixture is used to induce and maintain decomposition of the plant residues, whilst in the INDORE process a suitable proportion of inoculum, usually containing a good supply of available nitrogen (*e.g.* from manure or urine earth from the floor of cattle sheds), together with wood ashes, is used. Directions as to the factors necessary for the successful working of each process are given. Modifications suitable for special local conditions or material are also described.

Manurial Value of Compost.—Well-made compost should have a nitrogen-content closely approximating that of good farmyard manure. The phosphate-content is nearly always low, unless that constituent is specially added, as in the ADCO process. The potash-content also tends to be low, although that is not so important as the nitrogen and phosphate contents in South Africa, where the soils contain a fair proportion of potash. One of the main factors influencing the final composition is the amount of soil that has been allowed to mix with the compost. In the INDORE system, soil may amount to 50 per cent. of the dry weight of the compost. The lowering of nitrogen, phosphate and potash contents, as revealed by a chemical analysis, will not necessarily reflect the efficiency of the composting process unless total weights are supplied, so that a balance sheet may be made out. The presence of an unduly high proportion of soil will naturally increase the cost of carting and handling.

The following Table shows the composition of various types of compost and manure:

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* Science Bull. No. 201. Department of Agriculture and Forestry (*Chemistry Series No.* 157). By E. R. Orchard, Ph.D., Division of Chemical Services, Pretoria.

Description	Moisture	Composition on air-dry basis: Organic matter	N	Available P_2O_5	Available K_2O
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Well conserved cattle manure	80·5	78·5	2·2	1·0	2·2
ADCO from wheat straw (England)	75·0	56·0	2·4	1·7	0·8
ADCO from grass cuttings (England)	82·7	58·4	4·9	3·6	5·9
ADCO from garden refuse (England)	63·7	44·9	1·5	2·6	3·4
ADCO from wheat straw (South Africa)	79·6	69·5	2·4	1·7	3·1
ADCO from fresh veld grass (Rhodesia)	72·9	57·1	2·0	1·7	1·1
ADCO from maize stalks (Rhodesia)	72·4	58·9	2·2	1·3	1·0
ADCO from sugar-cane trash (South Africa)	62·4	56·7	1·9	1·6	1·4
Kraal refuse (South Africa)	—	48·4	1·5	0·2	1·8
Farm wastes put through kraal	—	29·4	0·8	0·2	1·3
INDORE compost from maize and sunflower stalks	60·8	39·5	1·1	0·2	0·7
INDORE compost, mean of 12 samples made largely from kraal wastes	—	32·5	0·9	0·1	0·5
Guano, cull oranges, veld grass and pine needles	—	37·5	1·6	1·4	1·2

The variable nature of compost and its low phosphate-content used are clearly brought out. The age of the vegetable residues has a pronounced influence on composition.

Over-mature compost closely resembles a garden soil and will not repay its cost of manufacture. Various chemical methods of judging the state of maturity have been suggested, but these are not of practical value on the farm. Usually compost is regarded as suitable for carting when 80 to 90 per cent. is fine enough to pass through a ½-inch mesh and when the coarsest constituents have rotted so that they can be pulverised easily by rubbing.

Steps must be taken to minimise the loss, by excessively rapid or unnecessary oxidation, of organic matter both from the soil and from the compost heap.

The pamphlet concludes with sections on crop response to compost applications and on composting from the economic aspect, and a bibliography of 19 references.

Norwegian Canning Industry

SIGNIFICANCE OF THE BACTERIAL COUNT IN DETERMINING THE FRESHNESS OF HERRING AND BRISLING, THE RAW MATERIALS OF KIPPERED HERRINGS AND CANNED BRISLING*

Bacterial Decomposition of Winter Herring.—To establish a standard for the quality of fresh winter herring, the raw material of kippered herrings, the fish were stored at temperatures ranging from −3° to +13° C., and samples were taken daily for bacterial count, organoleptic examination and smoking. Bacterial invasion of the flesh was investigated by aseptically taking portions of the back after removal of the skin. The fish, clipped with sterile scissors, were shaken with sterile saline and plating out was done on agar and gelatin. The results of the bacterial counts, which are given in tables, show good correlation with the degree of freshness. When the fish give a count of 500,000 per g. their flavour is "strong"; stale fish contain 1 to 2 million bacteria per g. and may be considered unmarketable. The examination of a mixed sample of 6 lots of fish from different factories showed that 1000 to 100,000 bacteria per g. is the average number for herring of good quality. The bacterial count of smoked herring clearly shows the bactericidal efficacy of the smoking, the average count being about 1000 per g.

Sanitary Quality of Brisling used in the Norwegian Canning Industry.—Brisling, which are packed during the summer, are very subject to invasions of decomposing bacteria, and precautions are taken to guard against this during transport. Samples from four factories were examined, an average of ten fish being used for each sample. The whole fish, including intestines and surface slime, were clipped with sterile scissors and shaken with sterile saline, and dilutions were made for plating; the counts are therefore not comparable with those obtained with herring, and the average for fish of good quality one day old was found to be about 100,000 per g.

* Bull. No. 57, Norwegian Canning Industry. E. Aschehoug and R. Vesterhus. *Tidsskrift for Hermetikindustri*, 1940, 17–26; 49–53.

PROCESSING STUDIES OF KIPPERED HERRING.—It was found that "high-short" processing impaired the quality of the smoked fish. Processing at 6 lbs. pressure for 70 minutes in half-oval tins is recommended. For smoked brisling packed in tomato sauce, processing at even lower temperature for a longer time is recommended (*e.g.* at 4 to 6 lbs. pressure for 60 minutes), the colour and taste of the tomato sauce being easily impaired; but for packing in olive oil, processing at 6 to 8 lbs. pressure for 50 minutes is permissible. D. R. W.

British Standards Institution

THE following Standard Specification has been issued*

NO. 894—1940. THE DETERMINATION OF THE FLOW AND DROP POINTS OF FATS AND ALLIED SUBSTANCES

(APPARATUS AND METHOD OF USE)

The apparatus, which is of the Ubbelohde type, is shown in diagrams. A glass cup of specified dimensions, with an orifice at the bottom, is filled with the fat to be tested and attached to a metal fitting which is fixed to a standard thermometer, the bulb of which is situated centrally in the cup. The thermometer, with the cup attached, is fitted through the cork of a boiling tube at a specified level, and the boiling tube is fixed vertically in a beaker containing a suitable liquid heating medium which is kept stirred. The temperature of the outer bath is adjusted so that the temperature of the fat rises at the rate of 1° C. per minute over a range of about 10°C. immediately below the flow-point.

The *flow-point* is defined as the temperature at which the substance under examination forms an approximately hemispherical protuberance at the orifice of the glass cup. The *drop-point* is the temperature at which the first drop falls from the glass cup.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection by Walkiewiecz's Method of the Decomposition of Meat. H. Keller and H. Möller. (*Z. Fleisch- u. Milch-hyg.*, 1939, **49**, 141–143; *Z. Unters. Lebensm.*, 1940, **79**, 298–299.)—Walkiewiecz's method, which consists in adding 2 or 3 drops of extract from the meat to 3 or 4 ml. of mercuric chloride solution (1 : 1000), and to the same volume of the mercuric solution containing acetic acid (0·05 : 1000), is modified by using an extract prepared by shaking 5 g. of meat with 50 ml. of water. At *p*H values not lower than 6·2 there forms immediately a grey-violet precipitate, which settles in a few seconds and, on stirring, yields an opalescence. With acidified sublimate solution this reaction is positive only with meat in which the acid-forming stage of decomposition is past. The authors' results, which do not agree entirely with previous work, are as follows:—(1) Muscular tissue containing much connective tissue, fat and blood always gives a positive reaction with both sublimate solutions, so that decomposition of such meat cannot be detected by this method. (2) With beef and calf muscle from healthy animals with a normal meat acidity Walkiewiecz's reaction detects decomposition 1 or 2 days earlier than the Eber (hydrogen-sulphide) test. The *p*H at which the precipitate forms is 6·0. (3) Beef and veal from unhealthy animals give a positive reaction with both sublimate solutions, indicating very slight decomposition. (4) Pig muscle and slightly acid horse muscle, from both healthy and unhealthy animals, give a positive reaction with both sublimate solutions, so that the test is not applicable to pork or horseflesh. E. M. P.

Estimation of Sulphur Compounds in Vegetables. W. Diemair and J. Koch. (*Z. anal. Chem.*, 1940, **119**, 94–108.)—Conversion of the loosely combined sulphur in the proteins of vegetable substances into thiosulphate by treatment with alkali, with subsequent transformation into ferric thiocyanate, was found to be an unsuitable method for colorimetric estimation. The following modification of the method of Diemair, Strohecker and Keller (*Z. anal. Chem.*, 1939, **116**, 385) proved more satisfactory. The material (20 g.) is mixed with 50 ml. of sodium hydroxide solution (0·1 *N* or 0·01 *N*) and distilled in a pear-shaped 500-ml. flask over a naked flame at such a rate that distillation begins in 4 minutes and 18 ml. of distillate are collected in the next 6 minutes. The distillate is received in a cylinder containing 1 ml. of a 0·5 per cent. solution of dimethyl-*p*-phenylenediamine in conc. hydrochloric acid and 1 ml. of 10 per cent. ferric chloride solution.

* Obtainable from the Publications Department, 28, Victoria Street, London, S.W.1. Price 2s. net; post free 2s. 2d.

The methylene blue formed is estimated colorimetrically in a Pulfrich photometer. Strict adherence to the experimental conditions is necessary, especially to the ratio of material to alkali, the time of distillation and the volume of distillate. The sample must be so prepared that it forms a thin broth with the alkali. As it was found that, of the vegetables investigated, peas produced much frothing, the quantity of sample and alkali used were reduced to 10 g. and 25 ml. respectively, and the vegetable was not pulped before distillation. With canned vegetables the maximum separation of sulphur occurred when the alkali solution was 0·01 *N*, but with fresh vegetables 0·1 *N* alkali was required. A number of fresh and preserved vegetables were examined by the process described, and the amount of loosely combined sulphur found was compared with the total sulphur determined by the method of Denis (*J. Biol. Chem.*, 1910, **8**, 401). With spinach, asparagus, carrot, pea, mushroom, bean, kohlrabi and celery the relation between the loosely combined sulphur and the total sulphur was not the same, but the experimental results indicated a division of these vegetables into three groups. In the first group (asparagus, pea and kohlrabi) the loosely combined sulphur is greater in the conserve than in the fresh vegetable, and in the second group (spinach and bean) there is less in the conserve than in the fresh substance. In the third group (carrot, mushroom and celery) no sulphur was obtained by distillation. This grouping can be explained by a consideration of the processes of manufacture of the conserves. Examination of peas in different stages of ripeness showed that, although the total sulphur increased with advancing ripeness, the sulphur obtained by distillation diminished. In order to determine the relation of the loosely combined sulphur to the cystine, cysteine and glutathione in the plant, the proteins of spinach, asparagus and pea were hydrolysed and the cystine and cysteine were separated by means of 9-phosphotungstic acid and estimated colorimetrically by the methods of Schöberl and Ludwig (*Ber.*, 1937, **70**, 1422) and Hornung (Dissertation, Würzburg, 1938). The ratio of sulphur derived from cystine to that derived from cysteine, although subject to variation, was found to approach 1 to 6 in the vegetables investigated. In asparagus and peas the sulphur was entirely in the organic form. In beans 85·9 per cent., in kohlrabi 81·3 per cent., in carrot 79·3 per cent. and in spinach 63·8 per cent. of the sulphur was in the organic form. These results suggest that in those portions of the plant where there is meristematic tissue and active growth (asparagus tips) or nutritional material for the embryo (pea) the sulphur is in the easily assimilated organic form. In leaf (spinach), root (carrot) and stem (kohlrabi), where growth is not active, a smaller proportion of the sulphur is in the organic form. A. O. J.

Component Glycerides of Vegetable Fatty Oils. Niger-seed Oil. N. L. Vidyarthi and M. V. Mallya. (*J. Indian Chem. Soc.*, 1940, **17**, 87–95.)—The component fatty acids are estimated by the usual methods of lead salt separation, ester fractionation and hexabromide determination. The neutral oil is then dissolved in 6 times its weight of dry acetone and crystallised at 0° C., when any fully saturated or di-saturated glycerides will crystallise. Successive oxidation of the neutralised oil in acetone solution affords a measure of the quantity of fully-saturated glycerides. The remaining oil, after removal of the saturated and disaturated glycerides, is dissolved in light petroleum spirit and brominated at 0° C., and the solid and liquid bromo-glycerides are further resolved into a number of fractions by treatment with benzene, acetone, alcohol and acetone-alcohol (1:1 mixture). The fractions are all brominated, the component fatty acids are determined, and the amounts of the different glycerides in the fractions are calculated. This method has been used for niger-seed oil (*Guizotia abyssinica*) which was extracted from the seed with carbon tetrachloride. The sample examined had the following characteristics: n_D^{25}, 1·472; saponification value, 189·7; iodine value, 129·2; acetyl value, 19·8; free fatty acids (oleic), 4·27. The percentages of glycerides in the oil are given as tri-linolin, 2; myristo-di-linolin, 2; myristo-oleo-linolin, 3; palmito-di-linolin, 6; stearo-di-linolin, 2; palmito-oleo-linolin, 11; stearo-oleo-linolin, 4; di-oleo-linolin, 30; and oleo-di-linolin, 40. Palmito-glycerides contain the small quantity of lauric, and other lower acids present, and stearo-glycerides contain the arachidic, lignoceric and behenic acids. By hydrogenating the oil to iodine values of 1·8 and 27·2 respectively the amount of C_{18} glycerides was calculated to be about 77·3 per cent. and the remaining 20·8 per cent. of glycerides to contain at least one acid with less than 18 carbon atoms. This agrees fairly well with results obtained from the brominated glycerides. The major component acids—oleic and linolic—are evenly distributed in the glycerides. D. G. H.

Carbohydrate Characterisation. I. Oxidation of Aldoses by Hypoiodite in Methanol II. Identification of Seven Aldo-Monosaccharides as Benzimidazole Derivatives. S. Moore and K. P. Link. (*J. Biol. Chem.*, 1940, **133**, 293–311.)—A very satisfactory method of identifying aldoses consists in oxidation to the corresponding acids by means of potassium hypoiodite and methylalcohol, and condensation of the acid so obtained with *o*-phenylenediamine to give the benzimidazole derivative. I.—A sample of the solution or syrup equivalent to 2 g. of aldo-hexose is concentrated or diluted, as required, to a volume of 4 ml. Into a 500-ml. 3-necked flask equipped with a stirrer, thermometer and dropping-funnel are introduced 5·7 g. of iodine and 80 ml. of methyl alcohol. After being stirred for a few minutes the solution is warmed on the water-bath to about 40° C., and the aldo-hexose solution, dissolved in 25 ml. of methyl alcohol (filtered and decolorised with charcoal if necessary), is added. Stirring is at once resumed, and 4 per cent. potassium hydroxide solution is added dropwise, 65 ml. over a period of 10 to 15 minutes, and, after 10 minutes' further stirring, 50 ml. more, also dropwise; the colour

should then be pale straw yellow, and if it is darker a few more ml. of the alkali may be added. Finally the liquid is stirred for 10 minutes and allowed to cool, and any precipitate that separates is filtered off, washed twice with methyl alcohol and once with water, and dried. The solid consists of the potassium salts of the acids derived from glucose, galactose and arabinose. The filtrate is returned to the reaction flask, and a solution of 5 g. of barium iodide (dihydrate) in 25 ml. of methyl alcohol is added to it dropwise with stirring. The barium salts corresponding to any other aldoses present (except xylose) separate out and are centrifuged off and washed with methyl alcohol and ether.

II.—The mixed potassium or barium salts are condensed with *o*-phenylenediamine in presence of acid catalysts at 135° C., except the salt of xylonic acid, which requires zinc chloride and a temperature of 180° C. The benzimidazoles crystallise readily, have sharp melting-points, and yield derivatives that crystallise well. They possess many advantages over osazones for characterising sugars. Moreover, benzimidazoles can be precipitated as copper salts from aqueous solution, thereby facilitating the isolation of small amounts of derivatives which might otherwise escape detection; the benzimidazole is regenerated from the copper salt by the use of hydrogen sulphide. The following is a summary of the properties of the benzimidazole derivatives from seven aldomonosaccharides:

Carbohydrate	Benzimidazole		Hydrochloride	Picrate
	m.p. °C.	$[\alpha]_D^{25}$	m.p. °C.	m.p. °C.
l-Arabinose	235 (decomp.)	+ 49·2	230	158
d-Galactose	245 (decomp.)	+ 43·3	202–204	217 (decomp.)
d-Glucose	215	+ 9·6	180	203 (decomp.)
d-Lyxose	189	− 12·8	191	95–99
d-Mannose	227 (decomp.)	− 22·0	101–150	205 (decomp.)
l-Rhamnose	207	+ 27·4	173–174	168
d-Xylose	224	+ 64·8	200–202	191

The rotations were measured in 5 per cent. citric acid solution at $C = 2$. The method of carrying out the condensation is best illustrated by the use of calcium gluconate. To 2 g. of calcium gluconate (hydrate), (0·009 mole of gluconic acid), in a test-tube, 1·1 g. (0·01 mole) of *o*-phenylenediamine, 4 ml. of water, 1 ml. of ethyl alcohol, and 1·7 ml. (0·02 mole) of conc. hydrochloric acid are added. The mixture is heated for 2 hours in an oil-bath at 135° ± 5° C. The syrup that remains is dissolved in 10 ml. of water, charcoal is added, and the suspension is filtered. On making the filtrate (diluted to about 30 ml.) alkaline with ammonium hydroxide, crystals of gluco-benzimidazole separate out. The treatment of the potassium salt fraction from the oxidation of aldoses is carried out in a similar manner, but with the addition of 0·8 ml. of syrupy phosphoric acid. The working up of the barium salt fraction is carried out in a slightly different manner. The equivalent of 1 g. of aldo-hexose is suspended in 10 ml. of water in a centrifuge tube, and the solution is neutralised to phenolphthalein with dilute hydrochloric acid. To the neutral solution 0·8 ml. of conc. hydrochloric acid is added and sufficient of a mixture of sulphuric acid and water (1:1) to precipitate the barium ion. The solution is filtered, the filtrate is evaporated to 4 ml., and the concentrate is transferred to a test-tube containing 0·7 g. of *o*-phenylenediamine. After the addition of 0·5 ml. of phosphoric acid the condensation is continued as described above. To the filtrate from the potassium or barium salt fraction, from which excess ammonia has been removed by evaporation, a cupric ammonia solution is added, 20 ml. for each g. of benzimidazole present. This solution is prepared by suspending 10 g. of cupric acetate (monohydrate) in water, adding sufficient ammonia to give a clear solution, and diluting to 100 ml. The precipitate of copper salt is filtered off and suspended in a mixture (3:1) of water and alcohol. The suspension is decomposed with hydrogen sulphide, and the filtrate usually crystallises on being concentrated. Xylonic acid, if present, does not yield a benzimidazole under these conditions, but an intermediate reaction product is formed which is contained in the filtrate obtained by decomposing the copper salt with hydrogen sulphide. Accordingly, the residue left after the removal of any benzimidazoles is concentrated to a syrup, and for each 0·5 g. of xylose estimated to be present, 0·5 ml. of conc. hydrochloric acid and 0·3 g. of zinc chloride are added. The mixture is placed in an oil-bath at 135° C., and the temperature is raised to 180° C. over a period of 45 minutes and maintained at that point for an hour. The syrup is taken up in water and decolorised. Ammonia is added to the solution and excess removed by evaporation. The precipitate of zinc benzimidazole and zinc hydroxide is filtered off, suspended in water and decomposed with hydrogen sulphide. The filtrate yields crystals of xylo-benzimidazole on concentration. The presence of fructose does not interfere with the isolation of aldobenzimidazoles, but a small amount of *d*-arabo-benzimidazole (m.p. 235–236° C., $[\alpha]_D^{25} = -51°$; hydrochloride, m.p. 229° C.; picrate, m.p. 158° C.) is obtained from the barium salt fraction. Care should therefore be exercised in drawing conclusions from the formation of this compound, and tests for pentoses and ketoses should be carried out on the original material to determine whether fructose or *d*-arabinose is the source of this derivative. F. A. R.

Behaviour of Olive Oil and other Oils with Antimony Trichloride. W. H. Dickhart. (*Amer. J. Pharm.*, 1940, **112**, 131–133.)—Antimony trichloride produces a blue colour with vitamin A, synthetic vitamin A, and various carotenoids and other sterols. A standardised procedure was applied to a large number of olive and other oils. A 33·33 per cent. solution of antimony trichloride was made with C.P. chloroform, and to 1 ml. of this solution 2 g. (approx. 50 drops) of oil were added, the mixture was shaken and left for 1 hour, and the colour reading was taken in a Lovibond tintometer. Of 9 virgin olive oils from various sources, 7 gave an emerald-green colour, one ("Greek, extra") a pea-green, and one (from California) a blue-green colour. Five samples of refined olive oils (Greek, Spanish, Italian, Tunisian and Californian) gave blue colours, and one extracted refined foots oil an olive-green colour. The unsaponifiable matter from virgin oil gave a red colour changing to blue, and that from refined olive oil a red colour. A refined olive oil giving a blue colour was heated to 220° C. for 20 minutes, and then gave an amber colour. It is suggested that olive oil contains one or more of the lipochromes, as they are destroyed by oxidation, reduction, high temperatures and excessive exposure to light; and thus olive oil would presumably contain vitamin A, or a substance converted into vitamin A by the liver. The green colour is regarded as probably due to β-carotene or a mixture of a yellow pigment with the blue colour from α-carotene, γ-carotene or squalene. A list is given of the colours produced with a large number of oils, normal and hydrogenated, and it is suggested that the method may be of value in distinguishing normal olive oil from teaseed oil (orange with fluorescence); hydrogenated fish oil (deep purple) from hydrogenated cottonseed oil (light pink); oiticica and China wood oils (red) from those of lumbang (yellow to dark red), perilla (yellow to pale pea-green) and linseed (brown); cottonseed oil (pink) from kapok oil (yellow). D. G. H.

Fatty Oil from the Seeds of *Bauhinia variegata*. S. V. Puntambeka and S. Krishna. (*J. Indian Chem. Soc.*, 1940, **17**, 96–100.)—*Bauhinia variegata*, Linn. (N.O. *Leguminoseae*) is a deciduous tree found in the sub-Himalayan tract from the Indus eastward, and known in Hindi as Kachnar; its flowers are eaten as a vegetable. It produces pods, 6–12 inches by ¾ to 1 inch, containing 10 to 15 seeds. The seeds consist of 20 per cent. endocarp and 80 per cent. of kernels, which yield about 16·5 per cent. of a pale fatty oil on extraction with petroleum spirit, and about 6 per cent. when expressed. The oil examined had the following characteristics:—sp.gr. at 30°C., 0·9206; n_D^{30}, 1·4603; iodine value (Hanus), 91·3; Hehner value, 92·0; acid value, 2·8; unsaponifiable matter, 1·6 per cent. The mixed acids had mean molecular equiv. 294 and iodine value (Hanus) 93·2; they consisted of 32·3 per cent. of saturated and 67·7 per cent. of unsaturated acids. The mixed fatty acids were separated by the lead salt method, and the methyl esters of the solid acids were distilled into 5 fractions, which were analysed. The liquid acids were oxidised in cold alkaline solution with potassium permanganate, and the freshly prepared mixed acids were also brominated. The unsaponifiable matter appeared to contain sitosterol, and the residue was probably mostly hydrocarbons. The proportions of the constituent acids are given as: myristic, 1; palmitic, 17; stearic, 13·4; lignoceric, 1; oleic, 31·8; linolenic, 35·9 per cent. D. G. H.

Oil from the Fruit of *Ferula alliacea*. P. K. Bose and S. N. Dutt. (*J. Indian Chem. Soc.*, 1940, **17**, 49–52.)—The mature fruit of the umbelliferous plant, *Ferula alliacea*, Biss, has a pronounced aromatic odour when crushed. A petroleum spirit extract yields on steam distillation about 0·9 per cent. of a colourless sweet-smelling volatile oil. The fruit, which also contains some natural coumarins, yielded on extraction with petroleum spirit 19 per cent. of a yellow, bitter-tasting oil with the following constants:—sp.gr. at 31·5/31·5° C., 0·9156; n_D^{40}, 1·4691; solubility in alcohol at 25° C., 2·55 per cent.; saponification value, 189·62; iodine value (Wijs), 90·73; acetyl value, 23·56; Reichert value, 1·81; Polenske value, 0·25; acid value, 16·6; unsaponifiable matter, 1·96 per cent.; bromide test, nil; total saturated acids (corr.) 14·02 per cent. with iodine value, 19·9; unsaturated acids, 78·08 per cent. with iodine value, 100·6. The solid saturated acids contained some unsaturated acids, such as erucic or petroselinic acid, the lead salts of which are insoluble in ether. Five fractions were obtained after alcoholysis. The first consisted mainly of essential oil. Myristic and palmitic acids were apparently absent, and fraction V (b.p. 210–220° C.), which constituted the bulk of the distillate, had iodine value 86·16, and its separated fatty acids did not yield a solid product on bromination. D. G. H.

Quantitative Determination of Powdered Cinnamon and Cassia. A. H. Saber. (*Quart. J. Pharm.*, 1940, **13**, 7–13.)—The phloem fibres of cinnamon and cassia bark occur isolated or in rows of single files. From the areas of fibres per g. of the powdered bark, these drugs may be quantitatively determined in powders (*cf.* Saber, *Quart. J. Pharm.*, 1934, **7**, 645; Abst., ANALYST, 1935, **60**, 258). Twenty g. of cinnamon quills were reduced to No. 60 powder, 5 g. of this were reduced to No. 85 powder and dried at 100° C., and 0·1 g. of the dried powder was thoroughly mixed with 0·05 g. of lycopodium. The mixture was cleared in a small glass tube with 3 to 3·5 ml. of chloral hydrate solution (5 : 2), and the preparation was made up to 10 ml. with a suspending liquid (2 vols. of glycerin, 1 vol. of tragacanth mucilage and 2 vols. of water). From this suspension mounts were made in which the areas of fibres were determined (for details see Wallis and Saber, *Quart. J. Pharm.*, 1933, **6**, 655, or B.P. Codex, 1934, Appendix IX, 1592). The

minimum area representative of each mount was about 30 sq.mm. (actually 33·152 sq.mm.), consisting of 7 strips across the counting square separated by 2-mm. intervals. Commercial cinnamons of various qualities and grades were similarly examined. Mean results for 6 samples were: Good quality commercial (A) 92·5, Grade 0000 (B) 98·0, Grade 00 (C) 87·0, Quillings (D) 110·0, Featherlings 70·0, Chips 40·0 sq.cm. per g. The high result for (D) was due to the presence of an unknown bark. When unground, the ungraded sample (A) was less fine than (B) but better than (C). The relation between the results and the qualities and grades of the powders is due to the presence of the outer bark, which is fibreless, in increasing amounts as the quality of the sample deteriorates. It is not necessary to remove the small amount of oil in the bark before examination. Cassia bark or Chinese cinnamon is the partly decorticated dried bark of *Cinnamomum Cassia* Blume, and is very closely related to *Cinnamomum zeylanicum*, from which cinnamon is obtained. When examined by the method above, the average result for 2 cassia samples was 13·1 sq.cm. per g.; this is so different from that of good quality cinnamon—*e.g.* 92·5 on 3 preparations of (A)—that the relative amounts of cassia and cinnamon in a mixture of both may be determined by this count. In an experimental cassia-cinnamon mixture the cassia found by this calculation was 33·4 per cent. (actual, 35·38 per cent.). When the grade of cinnamon is not known the calculation should be based on results for quills, because lower grades are not permitted in medicine. If the cassia is powdered by a disintegrator instead of an iron hand-mortar, results are higher—*e.g.* 15 sq. cm. per g. E. B. D.

Determination of Piperazine. A. Castiglioni. (*Z. anal. Chem.*, 1940, **119**, 118–120.)—Pratt and Young (*J. Amer. Chem. Soc.*, 1918, **40**, 1428) have shown that piperazine yields a characteristic crystalline precipitate with Dragendorff's reagent, and other authors have suggested that this extremely insoluble substance might be used for quantitative purposes. It was found, however, that under ordinary conditions, the piperazine is not completely precipitated. Good results have been obtained by the use of the reaction of piperazine with carbon disulphide in which the addition compound, $C_4H_{10}N_2CS_2$, is formed. The precipitation must be made with an excess of carbon disulphide in absence of water. In the application of the reaction to the determination of carbon disulphide (Castiglioni, *Z. anal. Chem.*, 1939, **115**, 257; Abst., ANALYST, 1939, **64**, 230) 95 per cent. alcohol or mixtures of other solvents may be used, but in the determination of piperazine only chloroform or mixtures of other solvents (alcohol-ether, alcohol-acetone) give satisfactory results, the reason being the limited solubility of carbon disulphide in alcohol containing water. Chloroform is recommended as solvent because it promotes the formation of a coarse precipitate, which settles rapidly. The procedure is as follows:—If the piperazine is dissolved in 95 per cent. alcohol, an excess of a mixture of equal parts of carbon disulphide and ether is added and the mixture is warmed slightly and allowed to stand. If the piperazine is in chloroform solution it is sufficient to add an excess of carbon disulphide, warm slightly and allow the mixture to stand. When the supernatant liquid has become clear, the precipitate is collected, washed with small amounts of alcohol-ether or chloroform (according to the solvent used), dried at 105° C. and weighed. Each molecule of the addition compound contains a molecule of piperazine. Hexamethylene tetramine gives no precipitate with carbon disulphide; consequently, the method may be used for the determination of piperazine in the presence of that substance. A. O. J.

New Solanaceous Alkaloids from *Duboisia myoporoides*. W. Mitchell. (*Pharm. J.*, 1940, **144**, 137.)—As previously reported (*J. Chem. Soc.*, 1937, 1820; 1938, 1685), the alkaloids in this drug are hyoscine and the four new alkaloids: tigloidine, valeroidine, poroidine and *iso*-poroidine, but no trace of hyoscyamine or other similar alkaloid reported by earlier workers was found. It is therefore recommended that the official description of "duboisine" sulphate as a mixture of hyoscine and hyoscyamine sulphates be discontinued. Tigloidine has now been synthesised and shown to be tiglyl-ψ-tropëine; valeroidine is the mono*iso*valeryl ester of a dihydroxytropane previously isolated from Peruvian coca leaves as the dibenzoyl ester, and has also been synthesised. Poroidine and *iso*poroidine have been isolated as a mixture originally called base Z; the former is now shown to be *iso*valerylnortropëine, and the latter *d*-α-methylbutyrylnortropëine, and both have been synthesised. A partial separation of base Z, which closely resembles a mixture of 10 parts of poroidine and 1 part of *iso*poroidine, has been made by an indirect method, and *iso*valerylnortropëine has been isolated. The Codex indicates that duboisine is a mydriatic drug and much more powerful than atropine. D. G. H.

Pelletierine of Commerce. J. A. Goodson. (*Quart. J. Pharm.*, 1940, **13**, 57–63.)—In the B.P., 1932, pelletierine means the total alkaloids of the pomegranate stem and root bark; the French Codex drug is a more basic fraction of the total alkaloids of the bark. In this article pelletierine means Tanret's pure, optically active base, isolated from pomegranate root bark, and "pelletierine" is used for the alkaloids liberated from pomegranate root bark by sodium hydroxide but not by sodium bicarbonate. The weaker bases of the alkaloids (pseudo-pelletierine and methyl pelletierine) are probably valueless as vermicides, and the anthelmintic properties of the bark appear to be due to the presence of *l*-pelletierine and its racemic isomer. It is therefore considered desirable that some quantitative test, such as the determination of the bases liberated by sodium hydroxide but not by sodium bicarbonate, should be introduced into the B.P., especially

as commercial sulphates and tannates recently examined have frequently been deficient in "pelletierine." Ewers' method gives fairly accurate results. The inactive pseudo-pelletierine may be separated from the total alkaloids by treatment of the hydrochlorides with acetone, in which pseudo-pelletierine hydrochloride is insoluble. F. B. D.

Volumetric Determination of Acridines with Methylene Blue. A. Bolliger. (*Quart. J. Pharm.*, 1940, **13**, 1–6).—2:8-Diamino-acridine (A) and 2:8-diamino-10-methyl-acridinium chloride (B) and their commercial forms (proflavine, euflavine and acriflavine) are determined by precipitation as picrates and subsequent determination of the excess of picric acid with methylene blue. A solution of 0·1 g. in 30 ml. of 0·5 per cent. acetic acid is precipitated with a measured excess of *N*/100 (2·29 g. per litre) picric acid, diluted to 200 ml., and filtered after precipitation is complete (*i.e.* after at least 1 hour in a refrigerator). Twenty ml. of the solution are then titrated with *N*/1000 methylene blue by Bolliger's method (*cf.* ANALYST, 1939, **64**, 416). The determinations of (A) sulphate, of (B), and of mixtures of the hydrochlorides of (A) and (B) are as described above, except that acetic acid is replaced by water as solvent and that at least 4 hours in the refrigerator are required for complete precipitation. (A), (A) sulphate and (B) are equivalent to 47·85, 32·56 and 38·46 ml. of *N*/100 picric acid solution, respectively, per 0·1 g. The methylene blue solution is standardised on *N*/1000 picric acid solution prepared by dilution of the *N*/100 acid (*cf.* Bolliger, *loc. cit.*). The monopicrates of (A) and (B) have been isolated and analysed. (A) picrate is obtained as a yellow, partly crystalline precipitate, insoluble in dilute picric acid solution, sparingly soluble in water, alcohol, ether, benzene and chloroform, readily soluble in pyridine; it crystallises from a pyridine-water mixture (1 : 3) in yellowish-orange needles which decompose, without melting, at about 250° C. Its solubility in water at room temperature is less than 0·2 mg. per 100 ml. but if it is recrystallised from hot water its solution remains supersaturated (0·5 to 0·6 mg. per 100 ml.) after standing overnight at room temperature. (B) is obtained as an amorphous orange precipitate, insoluble in dilute picric acid, sparingly soluble in most solvents, soluble in pyridine; it crystallises from dilute pyridine in deep orange-red needles, m.p. 244° C. (with decomposition). Admixture with small amounts (1 : 9) of (A) picrate depresses the m.p. by at least 20° C. Its solubility in water is less than 0·3 mg. per 100 ml. E. B. D.

Bleach Ointment. G. H. Macmorran. (*Pharm. J.*, 1940, **144**, 213–214.)—The A.R.P. Handbook No. 3 prescribes a mixture of equal parts by weight of supertropical bleach and white soft paraffin for the preparation of bleach ointment. According to the B.P. Codex, tropical bleach is ordinary bleach mixed with unslaked lime,. Two ointments were prepared on a small scale, and their available chlorine contents were determined over a period, with the following results:

Time Weeks	Tropical bleach ointment		B.P. bleach ointment	
	Available chlorine Per Cent.	Percentage loss in chlorine	Available chlorine Per Cent.	Percentage loss in chlorine
0	16·72	—	19·21	—
2	15·49	7·36	17·31	9·89
4	15·36	8·13	16·47	14·27
6	15·09	9·75	15·65	18·53
8	14·73	11·90	15·10	21·40
10	14·50	13·28	14·57	24·15
12	14·31	14·41	14·12	26·50

Eight lb. of each ointment were then made in a granite end runner mill, the bleach being passed through a No. 40 sieve before mixing. No difference was observed during milling, the temperature of each ointment remaining about 20° C. Both ointments were left overnight in earthenware jars on a stone floor. In the morning the B.P. bleach ointment had overflowed as the result of vigorous chemical reaction and a "witness-tube" containing phenazone placed in the ointment had melted, showing that the temperature had reached at least 111° C. The ointment had become yellowish and contained only 1·05 per cent. of available chlorine; the tropical bleach ointment contained 16·8 per cent. The effect of the degree of saturation of the base was indicated by the following experiments:—An ointment was made with a vegetable fat having an iodine value of 63, and chlorinated lime containing 39·1 per cent. of available chlorine. At first the chlorine-content was 19·36, but after 2 weeks it had fallen to 11·40 per cent., showing a loss of 41·12 per cent. of the available chlorine. The B.P. ointment in the preceding table, made with chlorinated lime (available chlorine, 39·2 per cent.), was prepared with soft paraffin (iodine value, 5). This ointment lost 9·89 per cent. of its available chlorine in 2 weeks. A third ointment made with hydrogenated fat (iodine value, 1·6) and chlorinated lime (39·1 per cent. of available chlorine) contained 19·04 per cent. of available chlorine, and after 2 weeks showed a loss of only 1·21 per cent. These results confirm those of Fishburn (*Pharm. J.*, 1940, 35), who found that the higher the iodine value of the soft paraffin used, the more rapid the decrease in the available chlorine content. The general conclusions drawn from the experiments are that the use of supertropical bleach is to be recommended, that a soft white paraffin of low iodine value should be used, but that consideration should be given to the possible use of hydrogenated fats.

A tube is the most suitable container for bleach ointment. In the author's opinion the figure of 15 per cent. of available chlorine suggested (see Moir, ANALYST, 1940, 154) is too high, and a more reasonable figure would be 10 or 12 per cent.

Tests for Tannic Acid. D. B. Dott. (*Pharm. J.*, 1940, **144**, 137.)—Samples of tannic acid which have passed the B.P. test may still be unsatisfactory in practice. Four samples were dissolved in collodion (0·5 g. in 10 ml.). Sample A gave a very turbid solution; B a nearly clear solution in which a deposit slowly formed; C a clear straw-coloured solution; D a clear solution of the usual brownish tint which soon changed to green, although there was no evidence of metallic contamination. Tannic acid should dissolve readily in acetone giving a syrupy 1 in 2 solution, but with 0·5 g. in 10 ml. of acetone, sample A showed a considerable amount of insoluble matter; B dissolved to a nearly clear solution, but gradually deposited a brown sediment, and C gave a nearly colourless clear solution. The cupric acetate precipitation test was carried out by dissolving 1 g. of the tannic acid in 20 ml. of water and adding 1·5 g. of cupric sulphate dissolved in 40 ml. of water, then 1·7 g. of crystalline sodium acetate in 10 ml. of water, and lastly 0·5 ml. of acetic acid. After 3 or 4 hours the precipitate was collected, washed, dried and weighed. Sample A gave 1·143 g.; B, 1·179 g.; C, 1·163 g. A larger number of samples would have to be examined before deciding on maximum and minimum figures. D. G. H.

Determination of Cobalt in Foods. N. D. Sylvester and L. H. Lampitt. (*J. Soc Chem. Ind.*, 1940, **59**, 57–60.)—Since most existing methods have usually been concerned with materials of low ash-content, so that separation of cobalt from the ash has been unnecessary, the following procedure is recommended for other types of material:—The sample, which should contain 0·001 to 0·01 mg. of cobalt, is ignited at 500° to 550° C. in a platinum or new silica dish, small quantities of sulphuric and nitric acids being used to aid the process. The residue left after evaporation of a solution of the ash in 15 ml. of 50 per cent. hydrochloric acid is dissolved in a mixture of 5 ml. of the hydrochloric acid and 20 ml. of water, the filtered solution and washings are made up to 20 ml. with water, and 10 ml. of a 1 per cent. solution of α-nitroso-β-naphthol in glacial acetic acid are added. The mixture is boiled, left overnight and filtered on a Gooch crucible, the residue is washed with 10 ml. of 5 per cent. acetic acid and transferred (with the filter-pad) to a Pyrex boiling-tube with the aid first of 2 ml. of warm sulphuric acid and then of 2 ml. of warm 60 per cent. perchloric acid. The contents of the tube are heated to destroy organic matter, *i.e.* until a yellow colour (due to chlorine dioxide) is formed and then disappears; 30 ml. of water are then added, and the solution is extracted with 5-ml. portions of a 0·15 per cent. solution of dithizone in chloroform (*cf.* ANALYST, 1935, **60**, 378) until the absence of colour in the last extract indicates that all the copper has been removed. Ten ml. of a reagent prepared by making a solution of 250 g. of citric acid in water just alkaline with ammonia and diluting to 1 litre, are then added, followed by sufficient ammonia to produce an orange colour with the residual dithizone, and the solution is then re-extracted in succession with 5 ml. portions each of dithizone reagent and chloroform. The combined extracts, which contain the cobalt, are evaporated to remove the chloroform, and the residue is heated on a hot-plate in a Pyrex beaker with 0·5 ml. of sulphuric acid and sufficient perchloric acid (*e.g.* 5 drops) to destroy the organic matter; most of the residual acid is removed by heating until violent fuming ceases, and the colourless residue is used for the colorimetric determination of cobalt by a modification of McNaught's method (*id.*, 1939, **64**, 23). Thus, 6 ml. of water, 1 drop of phenolphthalein indicator, sufficient of a 50 per cent. sodium hydroxide solution to make the solution alkaline, and of 50 per cent. hydrochloric acid to make it just acid, are added in this order to the residue, followed by 1 g. of sodium acetate and 2 ml. of a filtered 0·2 per cent. solution of nitroso-R-salt. The solution is boiled gently for 2 minutes, and again, after the slow addition of 1 ml. of nitric acid, for a further 1 minute. It is then cooled, diluted to 10 ml. and filtered through a No. 42 Whatman paper, and its colour evaluated, *e.g.* in the Lovibond tintometer (1-inch cell), or by means of its extinction-coefficient as determined in the Pulfrich photometer against water (2-cm. cell, S. 53 filter). The results may be read from a graph compiled from data obtained with a standard solution of cobalt (0·001 mg. per ml.); thus, 0 (blank), 0·002, 0·006 and 0·010 mg. of cobalt correspond, respectively, with 0·25, 1·30, 3·60 and 5·80 Lovibond red units, and with extinction-coefficients of 0·066, 0·152, 0·326 and 0·505. The latter method is the more accurate, but the sensitiveness of both methods may be increased by the use of a cell which gives a greater depth of colour for the 10 ml. of solution available. If the colour obtained differs only slightly from that due to the blank, the presence of cobalt is not proved conclusively, and it is therefore suggested that the solution should be passed through a column of alumina which adsorbs the red colour but allows the excess of reagent to pass through; this provides a qualitative test for cobalt (sensitiveness, 0·0002 mg.). Merck's alumina was used; it was made slightly greasy by immersion in a solution of a vegetable oil in acetone, and then washed almost free from the oil with acetone. When known quantities of cobalt (0·005 to 0·10 p.p.m.) were added to tea, milk, fruit pulp and coffee, and when 0·01 mg. was added to a solution containing 3·5 mg. of iron and 1 mg. of copper, the recovery was satisfactory. The cobalt-contents of 19 food samples are recorded, *viz.* gooseberry pulp, 0·004; 5 packet teas, 0·12 to 0·19; green leaf tea, 0·13; China tea, 0·15; straight-grade flour, 0·003; wholemeal flour, 0·010; 4 coffee beans, 0·028 to 0·049; 3 shelled cacao beans, 0·33 to 0·41 (Javanese, 0·03); milk, 0·001 p.p.m. The method was also used for the determination of small amounts of cobalt in commercial copper sulphate, after removal of the copper by electrolysis. J. G.

Biochemical

Respiration of Animal Tissue after Freezing in Liquid Air. F. Lynen. (*Z. physiol. Chem.*, 1940, **264**, 146–152.)—In an earlier paper it was shown that cooling in liquid air almost completely inhibited the respiration and fermentative power of yeast. Similar results are now reported concerning the effect of liquid air on the respiration of animal tissues, the uptake of oxygen being very considerably reduced after freezing. The reason for this appears to be that at such low temperatures, the cell-structure is destroyed and some of the soluble constituents of the respiratory system suffer excessive dilution. On the other hand, certain enzyme systems that consist entirely of insoluble components are not affected when the tissues are frozen in liquid air. An example of such a system is that responsible for the dehydrogenation of succinic acid to fumaric acid, with atmospheric oxygen as hydrogen acceptor. The components of this system are succino-dehydrogenase, cytochromes *a*, *b* and *c*, cytochrome oxidase and another factor not yet characterised, and none of these is soluble in water. When sodium succinate was added to the tissue suspension, a marked increase in the oxygen uptake was observed. With heart, liver and kidney, the oxygen uptake was the same whether the tissue was fresh or frozen, whereas with testicle, lung, spleen and Jensen sarcoma, the frozen tissue gave a considerably smaller value than the fresh tissue. This is attributed to a deficiency of these organs in one or other of the components of the enzyme system, but the nature of the limiting factor in each instance is not yet known.

F. A. R.

Determination of Reducing Groups with Porphyrindin, with Special Reference to Egg Albumin. E. Brand and B. Kassell. (*J. Biol. Chem.*, 1940, **133**, 437–444.)—The blue dye, porphyrindin, was introduced by Kuhn and Desnuelle (*cf.* ANALYST, 1938, **63**, 200), for the determination of sulphydryl groups in proteins. As solutions of the dye are relatively unstable above 0° C., all estimations were carried out at 0° C. Porphyrindin (5 to 7 mg. per ml.) was dissolved in 0·2 *M* phosphate buffer solution, *p*H 7·2, at 0° C., and the solution was filtered. It was standardised by titrating 2 ml., in a test-tube kept at 0° C., with an aqueous solution of metal-free cysteine hydrochloride (about 50 mg. per 100 ml.) to the disappearance of the blue colour. The concentration of the cysteine hydrochloride solution is established photometrically or iodometrically; 1 mg. of cysteine is equivalent to 1·16 mg. of porphyrindin. Alternatively, porphyrindin solutions can be standardised iodimetrically, 2 ml. being added to 3 ml. of a solution of 0·3 g. of potassium iodide in 0·5 *N* hydrochloric acid, and the liberated iodine titrated with 0·01 *N* sodium thiosulphate solution. One ml. of 0·01 *N* sodium thiosulphate solution is equivalent to 1·40 mg. of porphyrindin. Cysteine and glutathione are quantitatively oxidised to the corresponding -S-S- compound by the dye solution, and guanidine hydrochloride has no effect on the reaction. The *l*-forms of cystine, cysteic acid, tryptophane, hydroxyproline and histidine, and the *dl*-forms of methionine, serine, phenylalanine and threonine do not reduce porphyrindin. Tyrosine is oxidised by porphyrindin at 0° C. and *p*H 7·2, with the formation of a pink oxidation product, the reaction being unaffected by guanidine hydrochloride. Native egg albumin does not decolorise the dye, but in heat denatured egg albumin, –SH groups (but not tyrosine) are oxidised. In egg albumin dispersed by guanidine hydrochloride, –SH groups and phenolic groups are oxidised.

F. A. R.

Determination of Neutral Fat Glycerol in Blood with Periodate. L. Voris, G. Ellis and L. A. Maynard. (*J. Biol. Chem.*, 1940, **133**, 491–498.)—The principle of the method consists in the isolation of the neutral fat glycerol from the saponified acetone-soluble blood lipids and oxidation of the acidified aqueous solution of glycerol with potassium periodate solution (to give 2 mols. of formaldehyde and 1 mol. of formic acid). *Determination of glycerol with periodate.*—The reagent consists of a solution of 0·625 g. of pure potassium periodate in 500 ml. of 0·1 *N* sulphuric acid. Ten ml. of this solution are added to the aqueous glycerol solution (containing not more than 2·5 mg.), and the mixture is allowed to stand for 20 to 30 minutes. The excess of reagent is determined by titrating the iodine liberated on addition of potassium iodide at *p*H 4·4 to 7. The mixture is first neutralised, after addition of 3 drops of 15 per cent. magnesium sulphate solution, by adding dilute sodium hydroxide solution dropwise until a faint cloudiness appears, followed by 0·1 *N* sulphuric acid until the turbidity disappears. The reaction mixture is then treated with 10 ml. of a phosphate buffer solution (12 g. of disodium phosphate (hydrate) and 4·2 ml. of 10 *N* sulphuric acid in 100 ml.). Two ml. of 5 per cent. potassium iodide solution are added, and the liberated iodine is titrated with 0·00435 *N* sodium thiosulphate solution, with starch solution as indicator. One ml. of 0·00435 *N* sodium thiosulphate solution is equivalent to 0·5 mg. of potassium periodate or 0·1 mg. of glycerol. *Determination of neutral fat glycerol in bovine blood.*—The phospholipids are precipitated from 100 to 200 ml. of the alcohol-ether extract of plasma by the method of Ellis and Maynard (*J. Biol. Chem.*, 1937, **118**, 702), and the acetone solution is evaporated. The residue is saponified, and the solution is acidified with sulphuric acid to liberate the fatty acids, which are removed by extraction with petroleum spirit. The aqueous solution is used for the estimation of glycerol. Alternatively, 5 to 15 ml. of blood plasma are pipetted into 30 ml. of acetone, and 10 g. of anhydrous sodium sulphate are added. The acetone solution is removed, and the residue is re-extracted several times. The combined acetone extracts are evaporated, and the residue is saponified as described above. Good recoveries from added triolein were obtained.

F. A. R.

Stabilisation and Determination of Pyruvic Acid in Blood. E. Bueding and H. Wortis. (*J. Biol. Chem.*, 1940, **133**, 585–591.)—A significant decrease in the pyruvic acid content of blood occurs on standing, even for a minute, at room temperature. Sodium monoiodoacetate in a concentration of 0·2 per cent. prevents this loss, but produces an increase of 3 to 20 per cent. if the mixture is allowed to stand for 30 minutes; no significant change, however, occurs, in 3 minutes. A 50 per cent. solution of iodoacetic acid in water is adjusted with sodium hydroxide solution to *p*H 7·8, and a measured volume, corresponding to 25 mg. of iodoacetic acid, is transferred to a bottle containing 20 mg. of dried potassium oxalate. About 5 ml. of blood obtained by venipuncture are caught directly in this bottle. Three ml. of this mixture are transferred dropwise into a flask containing 12 ml. of 10 per cent. trichloroacetic acid solution constantly shaken. After standing for 30 minutes the solution is filtered, and 3 ml. of the filtrate are transferred to a test-tube and treated with 1 ml. of 0·1 per cent. 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. The mixture is allowed to stand at room temperature for at least 10 minutes and then extracted with 4 ml. of ethyl acetate, the layers being mixed with a capillary pipette through which a slow current of nitrogen is blown. The solution is re-extracted twice with 2-ml. portions of ethyl acetate, and the combined extracts are extracted with three 2-ml. portions of sodium carbonate solution. The combined sodium carbonate extracts are extracted with 1 ml. of ethyl acetate, transferred to the cell of an Evelyn colorimeter, and mixed with 4 ml. of 2 *N* sodium hydroxide solution. After 10 minutes the colour, due to pyruvic acid 2,4-dinitrophenylhydrazone, is measured with filter 520. The amount of pyruvic acid is calculated by reference to a standard curve prepared with pure pyruvic acid. F. A. R.

Chlorophyllase. C. A. Weast and G. Mackinney. (*J. Biol. Chem.*, 1940, **133**, 551–558.)—Chlorophyllase is an enzyme concerned with the hydrolysis of the phytyl ester linkage in chlorophyll, and is capable of operating in high concentrations of alcohol and acetone. An alcohol concentration of 80 per cent. was found to be optimal, whilst the concentration of acetone may be varied from 40 to 70 per cent. The optimal temperature in both instances is 25° C. Water is most effective at 75° C. The activity of the enzyme varies with its source. No activity was found with wild oats (*Avena fatua*); spinach showed high activity in water, but little in acetone or alcohol; figwort (*Scrophularia californica*) showed extremely high activity in alcohol, but none in water; whilst other plants investigated showed intermediate activities. Activity was detected by the formation of characteristic crystals of ethyl chlorophyllide when a leaf section was exposed to the vapour of ethyl alcohol, but the method was found to be of limited value. Two quantitative methods were therefore devised. In the first, 80 per cent. acetone extracts were prepared, and the pigments were partitioned between 80 per cent. acetone and petroleum spirit. The percentage hydrolysed was calculated by spectrophotometric measurement of the original solution and of the acetone solution after partition. In the second method, the pigments were partitioned between 80 per cent. acetone and petroleum spirit, and the pigments in the acetone extract were transferred to ether. Both fractions were evaporated, the residues were saponified with methyl alcoholic potassium hydroxide solution, and ethereal solutions of the unsaponified matter were extracted with 5 per cent. hydrochloric acid. The chlorin *e* and rhodin *g* thus formed were estimated spectrophotometrically. The evidence indicates that the enzyme acts on extracted chlorophyll in 80 per cent. alcohol, but on a denatured chloroplastin in hot water. F. A. R.

Experimental Avitaminosis A in Man. K. H. Wagner. (*Z. physiol. Chem.*, 1940, **264**, 153–188.)—Ten volunteers lived for a period of 6 months on a diet almost completely free from vitamin A and carotene, though otherwise adequate. A steady increase in weight was observed in every individual during the first four months of the test, but afterwards all (with one exception) showed a striking decrease in weight. Similarly, at the end of 6 months, marked symptoms of night-blindness were revealed in tests with a Nagel adaptometer; whereas normal persons give readings of about 130,000, the individuals receiving the diet free from vitamin A gave readings between 3500 and 6000, indicating that they were 20 to 30 times less sensitive than normal individuals to the same amount of light. Attention was directed by Jess to a difference between the field of vision of normal persons and of those suffering from night-blindness. Normally, the field of vision for the different colours decreases in the order—blue, yellow, red, green, but in those suffering from night-blindness the order is—blue, red, yellow, green. This same order was also found at the end of 6 months for all 10 persons undergoing test, except that the yellow field tended to fall within the green in one or other half of the eye, and in certain instances even lay wholly within it. This is regarded as a very characteristic sign of vitamin A deficiency in humans, since on administration of vitamin A, the yellow field gradually expanded to its original position between the blue and the red. An examination of the blood of the persons under test was also carried out. Decreased values were found for haemoglobin content, erythrocytes, colour index, thrombocytes and leucocytes, whilst the clotting time was abnormally high. At the end of 6 months, 5 of the individuals were given a supplement of β-carotene, and the other 5 a supplement of vitamin A (vogan). In both instances, the initial doses were too small to effect an improvement in the clinical symptoms (adaptometer reading and blood picture), and the doses were therefore progressively increased until improvement took place. The minimum daily dose of vitamin A required to effect this improvement was 2000 I.U., the average dose being 2500 I.U. Similarly, the average daily dose of β-carotene was found to be 5000 I.U. With these supplements the condition of all 10 persons gradually improved, the weight increased,

and adaptation, field of vision and blood picture all became normal. Estimations were then made of the amounts of vitamin A and carotene in the blood (the former by the Carr–Price reaction on the unsaponifiable matter of the blood serum, and the latter colorimetrically after chromatographing the unsaponifiable matter). In this way, a correlation was found between the intake on the one hand of vitamin A and its concentration in the blood, and on the other hand of β-carotene and the concentration of β-carotene and vitamin A in the blood; the vitamin A was found to make its appearance some 3 weeks after the β-carotene. From estimations of the vitamin A and carotene contents of faeces, it was concluded that about 50 per cent. of the carotene ingested is excreted unchanged, thereby confirming the finding that twice as much β-carotene as vitamin A is required for humans. The results establish the fact that, apart from the effect of absorption, β-carotene and vitamin A are utilised equally efficiently. F. A. R.

Estimation of Tocopherol in Animal Organs. P. Karrer, W. Jaeger and H. Keller. (*Helv. Chim. Acta*, 1940, **23**, 464–465.)—The finely minced tissue was twice extracted with 4 volumes of cold alcohol, the first extraction being for 3 hours and the second overnight. The dehydrated tissue was pressed to remove solvent and was then extracted twice with 4 volumes of a mixture (1:1) of alcohol and benzene, using the same extraction times as before. The four extracts were combined, and the solvent was removed by distillation under reduced pressure in an atmosphere of nitrogen. The residue thus obtained was saponified by heating with 8 volumes of 10 per cent. methyl alcoholic potassium hydroxide solution for 1 hour in nitrogen, and the unsaponifiable matter was extracted with peroxide-free ether. The combined extracts were washed with dilute acid and water, dried over sodium sulphate and then distilled under reduced pressure in nitrogen. The vitamin E content of the unsaponifiable matter was estimated potentiometrically by titration with gold chloride solution (*cf.* ANALYST, 1938, **63**, 835), and colorimetrically by the method of Emmerie and Engel (*cf.* ANALYST, 1939, **64**, 216). The following values were obtained for the α-tocopherol contents in mg. per kg. of tissue:

	Potentiometrically	Colorimetrically
Horse muscle ..	5·308	—
,, heart	4·892	6·17
,, liver	13·155	14·88
,, kidney ..	6·25	—
Ox-muscle	5·852	6·21
Ox-liver	9·540	10·55
Pig-fat	2·185	1·97

F. A. R.

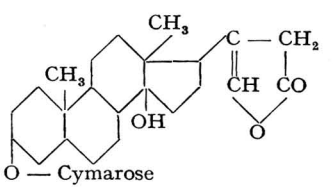
Toxicological

Action of Mustard Gas on Foods. A. Hasskó. (*Tierärztl. Rdsch.*, **1939**, pp. 131–133; *Z. Unters. Lebensm.*, 1940, **79**, 296.)—Foodstuffs impregnated with mustard gas lose their poisonous qualities the more rapidly the higher the temperature. Bread, bacon, and other dry foods treated with 0·1 ml. of mustard gas are poisonous for at least 20 days at 12° C., and for only 6 to 8 days at 20° C. Flour only moderately impregnated may remain poisonous for more than a month at 16° C. Sausages in "Cellophane" skins withstand the action of the gas for many days, but sausages with skins made from intestines absorb the gas rapidly and lose it only slowly in air. Milk treated with 0·01 ml. of the gas is poisonous after being boiled several times, whereas water treated with 2 ml. of the gas per 10 ml. of water is drinkable after several filtrations through active carbon. The detection of mustard gas poisoning is difficult with dry foods, but with moist foods brown spots or surface changes are soon visible, cucumber and marrow being particularly sensitive. Green peppers, green beans, peas, pears, gooseberries, apples, lemons, and oranges show visible changes only after 24 hours, beets and radishes only after 3 days. Some types of grapes turn brown. Meat from animals which had been given oral doses of mustard gas was not poisonous. E. M. P.

Toxicological Detection of Cocaine. A. Brüning. (*Z. Unters. Lebensm.*, **1940**, **79**, 93–99.)—The micro-reactions of cocaine and its decomposition product, ecgonine, were examined to discover the most suitable for extracts obtained by the Stas–Otto procedure. The formation of large crystals is promoted by placing a small grain of sand between the cover-glass and the microscope slide and introducing the reacting liquids from opposite sides of the cover-glass, the mingling of the liquids being observed through a binocular microscope. Control reactions should be made with a 1 per cent. cocaine hydrochloride solution. With aqueous 1 per cent. picric acid solution cocaine forms small crystals in 5 to 10 minutes, and these develop into feathery clusters on standing. With a 3 per cent. gold chloride solution typical fern-like aggregates form very quickly. Unlike the picric acid reaction, this reaction is influenced by the state of purity of the extract, and subsequent ethereal extracts give larger and finer crystals than the first. With Martini's reagent (*Mikrochem.*, 1932, **6**, 11; Abst., ANALYST, 1933, **58**, 57) a 1 per cent. cocaine hydrochloride solution gives a dense precipitate, but with a 0·001 per cent. solution characteristic needle-shaped crystals form in a few minutes. Wagenaar's reagent (5 per cent. of lead iodide dissolved in a 30 per cent. aqueous solution of potassium acetate), which has the advantage over

Martini's reagent that lead iodide does not separate on dilution, is less sensitive but yields similar crystals more readily and from concentrated solutions. After a short time these assemble into tree-like formations. In highly decomposed toxicological material much of the cocaine may have been transformed into ecgonine, which is not extracted by the Stas-Otto procedure. De Jong (*Rec. Trav. Pays-Bas*, 1937, **56**, 186, 198) has shown that ecgonine forms with barium chloride a double salt soluble with difficulty in water, but readily soluble in hot alcohol. This property was used to detect ecgonine in somewhat putrid material from a cadaver which had originally contained cocaine. The material was acidified with tartaric acid and extracted with hot alcohol. The usual purification of this extract by evaporation with water and alcohol was repeated several times until, after evaporation of the purifying agents, a colourless solution was obtained. This was acidified, made faintly alkaline with sodium hydroxide solution, repeatedly extracted with ether, and, after evaporation to a quarter of its bulk, again extracted with ether. The aqueous residue was evaporated almost to dryness and treated with 10 per cent. barium chloride solution until no further precipitation occurred. The mixture was evaporated to dryness, and the residue was powdered and exhaustively extracted with hot alcohol. The alcoholic solution was filtered, reduced to a quarter of its original bulk by evaporation, and treated with absolute alcohol containing a little sulphuric acid until no further precipitation occurred. It was then filtered, and the filtrate was neutralised with a drop of dilute ammonia and evaporated to dryness. The ecgonine was extracted from the residue with water. Amelink (*Pharm. Weekbl.*, 1938, **75**, 861; Abst., ANALYST, 1938, **63**, 740) has described the reactions of ecgonine with platinic chloride solution followed by sodium iodide solution, with gold chloride solution followed by sodium bromide solution, with mercuric chloride solution, and with a modified form of Dragendorff's reagent. Picric acid gives no crystals with ecgonine solutions; gold chloride forms rectangular plates. Martini's reagent treated with a crystal of ecgonine gives thick needles which dissolve after a time. With Wagenaar's reagent the crystals form more slowly and are larger. Reinecke's salt was found to be a good reagent for the identification of ecgonine, the best procedure being the introduction of a crystal of the salt into a drop of a 1 per cent. solution of ecgonine or its hydrochloride. Crossed crystals are formed first, and these gradually develop through star-like formations into rhombic plates. During their formation these plates often have serrated edges. To determine the effect of impurity on the reaction, a little impure extract obtained from the Stas-Otto procedure was used. Unlike most of the other reactions, the reaction with Reinecke's salt was quite unaffected by the presence of impurity. With cocaine the reagent gives a precipitate consisting of small spherical particles, but, in spite of its sensitivity, the reaction does not give characteristic crystals. A. O. J.

African Arrow-poisons. I. *Adenium somalense* Balf. fil. M. Hartmann and E. Schlitter. (*Helv. Chim. Acta*, 1940, **23**, 548–558.)—A new heart glucoside, to which the name somalin has been given, was isolated from the root of *Adenium somalense* (Fam. *Apocynaceae*). In spite of its close chemical affinity to digitoxin, pharmacologically it more nearly resembles strophanthin. It comprises a molecule of digitoxigenin and a molecule of cymarose, and has the formula:



F. A. R.

Bacteriological

Action of Sulphanilamide. (*Brit. Med. J.*, 1940, I, 775–6.)—There have been several conceptions of the possible mode of action of sulphanilamide on *Streptococcus pyogenes*, including that of the neutralisation of toxins, the stimulation of leucocytic activity, and antibody formation. What appears to be a complete solution of the problem has now emerged from the work of Paul Fildes and his collaborators. This was preceded by a search by D. D. Woods for a substance that would antagonise the bacteriostatic action of sulphanilamide in vitro—*i.e.* would furnish the bacterial cell with something, essential for its growth, of which sulphanilamide deprived it; he found that such a substance was contained in yeast. T. C. Stamp and H. N. Green found that it was also contained in an extract of *S. pyogenes* and *Brucella abortus*. By using completely synthetic media, every constituent of which was known, the chemical constitution of this substance was deduced step by step, and the conclusion reached that it is *p*-aminobenzoic acid. Confirmation of this is afforded by the fact that pure *p*-aminobenzoic acid neutralises the antibacterial action of sulphanilamide and sulphapyridine, so that mice inoculated with *S. pyogenes* and given *p*-aminobenzoic acid are not protected by sulphanilamide. *S. pyogenes* is capable of elaborating this substance from media which do not contain it, provided that the inoculum is sufficiently large; it is presumed that the effect of sulphanilamide is to inhibit the

enzyme action by which further utilisation is made of this substance and thus arrest growth. Fildes has shown that an exact parallel is to be found in the bacteriostatic action of low concentrations of mercuric chloride. In all but low concentrations mercuric chloride is of course bactericidal, but in low concentrations inhibition of growth is due to the removal of –SH compounds that are essential for bacterial metabolism. This is proved by the fact that growth can be restored by adding glutathione, a quantitative relation existing between the amount required and the amount of mercuric chloride present. D. R. W.

Water

Application of Hydrogen Ion Concentration to Boiler Water Treatment. G. W. Bond. (*J. Chem. Met. and Mining Soc., S. Africa*, 1939, **40**, 59–68.)—The following *p*H values for different solutions of commercial chemicals used for the treatment of water throw light on their behaviour in the process:

	*p*H		
	10 per cent.	0·4 per cent.	0·04 per cent.
Ferrous sulphate (copperas)	3·0	3·8	—
Alumina, ferric (local)	2·0	3·2	—
Filter alum (imported)	2·8–3·0	—	—
Soda ash (sodium carbonate)	11·6	11·6	11·6
Sodium aluminate (Alfloc brand) ..	11·6	—	—
Caustic soda	12·0	12+	12+
Trisodium phosphate (crystalline) ..	12·0	12·0	12·0
Disodium phosphate (crystalline) ..	9·5	9·4	—
Monosodium phosphate (crystalline) ..	4·4	4·53	—
Sodium hexa-metaphosphate ("Calgon")	5·8	6·25	7·0
Lime water (saturated solution) ..		over 12	

Generally speaking, and within strict limits, the higher the *p*H the greater the amount of oxygen that can be tolerated in feed-water. The solvent action of acids on iron may be represented as: $Fe + 2H^{\cdot} \rightleftharpoons Fe^{\cdot\cdot} + H_2$. The direction taken by this reaction will be determined by the *p*H of the water and the electrode potential of iron, together with its hydrogen overvoltage. The more easily the hydrogen film is removed from the surface the more readily will the reaction proceed to the right, *i.e.* the more easily will the metal be corroded, and any hydrated oxide film deposited on the surface will have a protective action and thus inhibit corrosion. In absence of oxygen corrosion of iron is proportional to the hydrogen ion concentration to *p*H 8·4, beyond which evolution of hydrogen almost ceases. In actual practice it is difficult to work up to this figure without getting excessive alkalinity in the boiler water. The acids that act in boiler feed waters are carbonic acid and, possibly, hydrochloric acid derived from the hydrolysis of magnesium chloride. Decomposition of sodium carbonate in high-pressure boilers is a source of carbon dioxide and may lead to corrosion of turbine blades and to formation of an acid condensate. To counteract this, alkali must be added in the form of lime, caustic soda or trisodium phosphate; the use of lime, however, may lead to scale problems. It is also necessary to add alkali to counteract the potential corrosiveness of sea water, or waters rich in magnesium chloride or nitrate. In coastal stations there may be small leakage of sea water used in the cooling system into the boilers. With regard to the controversial problem of caustic embrittlement, many chemists doubt very much if this is really due to excessive causticity, and the recent work of Straub himself (*Mechan. Engineering*, 1938, **60**, 371), the originator of the now famous A.S.M.E. ratio of $\frac{Na_2SO_4}{Na_2CO_3}$, throws doubt on the efficacy of that ratio. In any event, a large excess of alkali is undesirable for other reasons. When testing the *p*H of feed water it is essential to fill the sample bottle completely with the water from the sampling cock, and to make the determination as soon as the stopper is removed. Even a comparatively short exposure to air may cause a discrepancy in *p*H of as much as 0·5.

Practical Methods for Sterilisation of Water consumed by Evacuated Populations. R. D. de la Rivière. (*Mouvement Sanitaire*, 1939, **16**, 455–465; *Bull. Hyg.*, 1940, **15**, 117–8.)—Evacuated populations (of France), communities which shelter them, and troops in the neighbourhood are in danger of contracting infectious, and especially water-borne diseases. Where there is a reliable system of distribution (and all "concessionaires" are responsible by law for the purity of the water they supply) increased vigilance only is necessary. Where new distributing installations are adopted it will probably be simpler and cheaper to depend on chlorination rather than ozonisation for sterilisation. Two methods are successfully employed in various French towns:—"*Javelisation*" and "*Verdunisation.*" The Conseil Superieur d'Hygiène points out that for the former the water must be limpid and contain not more than 3 mg. of organic matter per litre with no appreciable amounts of ammonia, urea, nitrites or iron salts. The importance of adequate control of the amount of chlorine and time of treatment is emphasised. Where there

is no supply of pure water by main three means of dealing with the problem are available:—(1) Water sterilised elsewhere may be imported by tank-wagons and stored, as in 1914, in reservoirs of reinforced concrete. According to Manceau the water should not be used until 2½ hours after chlorination or stored for more than 12 hours. (2) Water available locally may be drawn and treated, as, for instance, by motor pumps fitted with an automatic Verdunising system, such as were successfully employed by Bunau-Varilla on the Verdun front in 1915. There are also at present on trial sterilisation plants mounted on trailers with capacity of 500 litres and possible daily output of 8000 litres. In these the "carbo-chlore" method of Gambier is adopted, in which the water is treated for 10 to 30 minutes with 10 mg. of chlorine per litre and filtered through activated charcoal. In addition, there are pinnaces with sterilising plants and storage for treating river water. (3) Disinfection of drinking water may be carried out by the consumers; boiling is simple and effective, or, alternatively, one drop of *eau-de-Javel* may be added to a litre of water and, ten minutes later, a tablespoonful of wine or cider to neutralise excess of chlorine and mask any taste. In general, the use, by the layman, of filters and chemical agents on the market, is inadvisable, but Tanon's method may be used. For this, two solutions are employed:—(A) Iodine, 1 g.; potassium iodide,2 g.; water, 200 ml.; and (B) Sodium thiosulphate, 10 g.; water, 50 g. To a litre of the water to be tested solution A is added, drop by drop, until a faint brownish tint is obtained; if this fades before 20 minutes, 2 more drops are added. After 20 minutes one drop of solution B is added. D. R. W.

The Presence of Sulphide in (Harrogate) Mineral Water and its Oxidation by Air. A. Woodmansey. (*Harrogate Spa Medical J.*, 1940, **2**, [ii], 8.)—The freshly-drawn water contained 9 parts per 100,000 of sulphide sulphur. When kept in a partly-filled stoppered bottle for 1 to 2 weeks, the content of sulphide sulphur gradually dropped to nil, the sulphide becoming oxidised by air to sulphur, thiosulphate and sulphate, and a little being lost as hydrogen sulphide. The loss of hydrogen sulphide is more pronounced when the water is poured from one vessel to another. The oxidation of the sulphide is promoted by the water being slightly alkaline; the oxidation was much less rapid when the water was slightly acidified. The probable source of the sulphide in Harrogate water is a deep-seated mass of igneous rock, and no evidence exists of any connection with the surface of a volcanic vent. S. G. C.

Agricultural

Selenium in Canadian Wheat. J. G. Malloch. (*Food Manufacture*, 1940, **15**, 160.)—The Director of the National Research Council of Canada points out that previous work of Byers and Laken may have caused apprehension that selenium may be present in dangerous amounts in some parcels of wheat exported from Canada. An extensive investigation by Thorvaldson and Johnson (to be published in the *Canad. J. Research*) has shown that the plants analysed by Byers and Laken were mostly of the so-called "indicator" species, which requires selenium for proper development. Only 4 samples of seedling wheat plants and none of grain were included. In Thorvaldson's investigation 2230 samples of wheat grain were examined, sufficient to show the conditions in the main wheat-producing area of Western Canada. The growth of rats is adversely affected by 6 p.p.m. of selenium, but not by diets containing less than 3 p.p.m. In the wheat samples examined the highest concentration was 4 p.p.m., but this was the only sample containing more than 3 p.p.m. The average amount was less than 0·5 p.p.m. It is highly probable that the selenium content of the wheat exported approximates to this figure because of the great amount of mixing with wheat from different areas that occurs before the grain reaches the seaboard.

Organic

Identification and Determination of Phenolic Compounds. L. F. Levy. (*J. South African Chem. Inst.*, July, 1939, 1–8.)—The following reagents are used:—(i) A 0·03 per cent. solution of 2 : 6-dibromo-4-aminophenol chlorostannate in 95 per cent. alcohol (*cf.* "*Organic Synthesis*," **15**, 8). This is permanently stable in a brown bottle. It contains a small amount of hydrochloric acid, for which the stock buffer must be compensated by addition of alkali. (ii) Neutral sodium hypochlorite solution (Dakin).—A mixture of 100 ml. of 10 per cent. (w/v) calcium hypochlorite solution and 100 ml. of a solution of sodium carbonate (4·5 g.) and sodium bicarbonate (4·8 g.) is filtered after a few hours. Immediately before use, the solution is diluted to 0·05 per cent. of sodium hypochlorite (strength found by titration with $N/10$ sodium thiosulphate solution). (iii) *Stock solutions.*—(0·1 per cent.) of phenol, *o*-cresol and *m*-cresol. These are diluted to 0·001 per cent. immediately before use. *Buffer solutions.*—(iv) (Clark and Lubs) *p*H 9·8—Fifty ml. of a solution of boric acid (12·4 g. per litre) and potassium chloride (14·9 g. per litre) are mixed with 16·3 ml. of $N/2$ sodium hydroxide solution and diluted to 200 ml. v)—(Sørensen) *p*H 10·5—Boric acid (12·4 g.) is dissolved in 196 ml. of N sodium hydroxide

solution and diluted to 1 litre. (Tested with aniline yellow GG, at *p*K assumed to be 11·0.) *Identification.*—To a buffered solution of phenols (*p*H 9·2 to 10·5) mixed with a little (i) is added (ii) in the ratio of 2 mols. to 1 of (i). The indophenol blue colour develops in ½ to 3 minutes (*o*-cresol), 1 to 3 minutes (*m*-cresol), or 5 minutes (phenol). Acidification with acetic acid to *p*H 3–4 produces a colour characteristic of the phenol present, *e.g.* phenol, deep reddish-violet; *o*-cresol, light brown; *m*-cresol, reddish-violet; *p*-cresol, no reaction; xylenols, deep bluish-violet. In a distillate containing cresols colour development after 3 minutes indicates the presence of phenol. *Determination.*—Interfering substances in the test solution must be removed by steam distillation. The distillate is buffered to approximately *p*H 9·8 (indicator, thymol-phthalein), and the phenols are determined colorimetrically in Nessler tubes (100 ml.). Five ml. of (iv), the test solution, containing approximately 0·1 mg. of cresol, and 1 ml. of (i) are diluted to a definite volume; a comparison solution similarly prepared, and 1 ml. of (ii) are mixed with each, and the colours are compared after 3 minutes.

For mixtures of *o*- and *m*-cresols a comparison solution similarly mixed is required. The method must be modified for phenol, which is oxidised rapidly at *p*H 10·5. Beakers (250 ml.) replace the Nessler tubes, the mixtures are made up to 110 ml., and the hypochlorite solution is added (from watch-glasses) simultaneously to each beaker. After mixing, 100-ml. Nessler tubes are filled to the mark with the solutions, and the colours are compared in the fifth minute (it is essential that comparison shall be made within 6 minutes, and the *p*H of the solutions must be as close as possible). When adjustment is difficult, a modification of the Houghton and Pelly method enables a large number of determinations of phenol to be made with the same reagent, as follows:—0·1 g. of *p*-nitrosodimethylaniline is dissolved in 2 ml. of 95 per cent. alcohol, diluted to 100 ml. with water and reduced by excess of zinc dust followed by constant shaking with hydrochloric acid, added drop by drop, until the colour disappears. After precipitation of the dissolved zinc by sodium bicarbonate, the reagent is stable for hours if kept in an atmosphere of carbon dioxide. (For determination, *cf.* ANALYST, 1937, **62**, 117). In a mixture of cresols only, the *o*/*m* ratio may be found as in *p*H determinations with two colour indicators, the *o*- and *m*-cresols as described above, and the total (*o*-, *m*-, and *p*-) cresols by Chapin's method (*cf. J. Biol. Chem.*, 1927, **72**, 649); hence each cresol may be determined.

Detection of phenols.—To 10 ml. of a solution, slightly alkaline to litmus, are added successively 5 ml. of 2 per cent. borax solution, 3 drops of (i) and a small drop of stock (undiluted) hypochlorite solution; the blue colour forms immediately. On addition of 2 drops of acetic acid the characteristic phenol or cresol colour appears. E. B. D.

Identification of Groups of Dyestuffs by their Reaction with Ferrous Hydroxide. H. Eichler. (*Z. anal. Chem.*, 1940, **119**, 91–94.)—Solutions of azo or triphenylmethane dyes are decolorised on addition of ferrous hydroxide, which is converted into ferric hydroxide. The azo dyes are decomposed into their component primary amines, the course of the reaction being

$$4Fe(OH)_2 + R.N{:}N.R' + 4H_2O \rightarrow R.NH_2 + R'.NH_2 + 4Fe(OH)_3.$$

With triphenylmethane dyes the reaction is more complex, and has not yet been elucidated. The reaction is carried out as follows:—Insoluble matter is removed from the dye solution by filtration and leuco bodies are oxidised by means of a current of air. The solution is then treated with a 30 per cent. solution of sodium, potassium or ammonium hydroxide and with saturated ferrous sulphate solution. The mixture may be boiled for a short time to promote settling of the precipitate, after which the clear liquid is decanted. Mono- and poly-azo dyes containing sulpho and carboxyl groups are completely destroyed, precipitate and solution being free from dye. In this group the following dyes were tested:—Methyl orange, methyl red, cochineal scarlet PS, cloth red 3B, crocein scarlet 7B, fast red A, toluylene orange R and N, Congo red, azo blue, orange R, palatine red A, rosazurine G, benzo brown, cloth red Bo, benzo fast scarlet SBS, azo-grenadine S, oxamine blue B, trona red 3B, mikado orange R, "Plutoschwarz A," toluylene brown BBo, "Plutoschwarz R and F," cloth red 3G, and azofuchsin GN. With the following azo dyes containing neither sulpho nor carboxyl groups the colour was either not destroyed or incompletely destroyed and was present in the solution and in the precipitate:—Chrysoidine G and T, Vesuvine OOO extra, Bismarck brown GOOO, and aniline yellow. With the following triphenylmethane dyes the solution and precipitate were free from colour:—New patent blue B conc., brilliant green O, methyl green, fuchsin, methyl violet 3RO and 5B conc., new Victoria blue B, new patent blue R, brilliant green extra, wool green BS, new green RS, eosin GO, new green extra, acid fuchsin NS, night blue, light green, rosolic acid, phenolphthalein, turquoise blue G, cyanol, Victoria blue R. With the following triphenylmethane dyes containing sulpho groups the solution was colourless, but the colour reappeared in the solution of the precipitate in dilute mineral or acetic acid:—acid fuchsin, alkali blue 7B, water blue, rhodamine 6G, new fuchsin, Poirrier's blue C4B. With the triphenylmethane dye auramine O, the precipitate contained dye and the colour reappeared in the filtrate when it was acidified and exposed to air. Iron lakes were formed with gallein and the oxyanthraquinone dyes. Acid anthraquinone dyes (alizarin, cyanine green K, anthracyanine FLA, alizarin saphirole A) formed lakes, and the colour reappeared in the alkaline solution when it was exposed to air. With the phenosafranin dyes (safranin G, indoine blue R and azo carmine G) the colour reappeared in the alkaline or acidified solution when it was exposed to the air, and the precipitate contained dye. With rosinduline dyes (phenyl rosinduline and Magdala red) the solution had no colour even on oxidation, but

the dye reappeared when the precipitate was dissolved in dilute acid. With thiazine dyes (methylene blue and methylene green) the colour reappeared in both acid and alkaline solutions and was present in the precipitate. With the oxazines (new blue R and celestine blue R) the colour returned to the solution and was present in the precipitate. With the oxazones (resorufin, resazurin, iris blue and tetrachlororesorufin) the colour returned to the alkaline solution exposed to air and was present in the precipitate. With the indophenols (resorcin indophenol) the colour reappeared in the alkaline solution exposed to air. Acridine dyes (benzoflavin, phosphine and rheonine A) gave a colourless solution and dye in the precipitate. Quinoline yellow occurred unchanged in the precipitate and solution. Nigrosine B and other nigrosines gave a colourless solution and dye in the precipitate. The pyrazolone dye tartrazine gave a sparingly soluble lake in acid solution. Nitro dyes (picric acid) gave metallic lakes. Oxyketone dyes (gallo-flavine) gave iron lakes decomposed by acids with liberation of the original dye. With fluorindines the colour reappeared on exposure of the alkaline solution to the air. A. O. J.

Estimation of Viscose Rayon. R. W. McKay. (*Amer. Dyestuff Rep.*, **1940**, **29**, 25–28; *J. Soc. Dyers and Col.*, **1940**, **56**, 243.)—For the estimation of viscose rayon in admixture with cotton, wool or silk, the fabric is cut into small pieces not exceeding 0·2 cm. in diameter and treated for an hour at −3° C. with 2*N* sodium hydroxide solution. The viscose rayon dissolves whilst cotton, wool and silk are hardly affected. The residue is washed with chilled 2*N* sodium hydroxide solution, then with water and finally with a little 0·2*N* hydrochloric acid, after which it is dried and weighed. The results are accurate to the nearest unit per cent. Resin finishes may interfere with the analysis.

Inorganic

Colorimetric Determination of Small Amounts of Lead by means of Dithizone. H. Fischer and G. Leopoldi. (*Z. anal. Chem.*, **1940**, **119**, 161–188.)—Recent work on the subject is reviewed and various investigations by the authors are discussed. *Extraction of Lead.*—The preferred method for amounts of lead of the order of 1 to 25γ involves treating the solution with dilute ammonia until it is just alkaline to litmus paper. When elements precipitated by ammonia are present, sufficient alkali citrate or tartrate should previously be added to prevent this. Potassium cyanide is added to convert interfering metals into complex cyanides; usually 3 to 5 ml. of 5 per cent. potassium cyanide solution to 10 ml. of the test-solution are sufficient, but, where justified by the presence of appreciable amounts of, for example, zinc, copper, silver or mercury, considerably increased amounts of potassium cyanide may be introduced without detriment. To overcome the interfering effect of oxidising substances which may be present, such as ferricyanide, a little hydroxylamine hydrochloride or sodium hydrosulphite is added, and the solution is boiled for a short time and then cooled to room temperature. It was found that small amounts of copper catalyse the oxidising action of various substances on lead dithizonate, but the treatment just mentioned eliminates this. Special adjustment of the *p*H of the solution between 8 and 10 is unnecessary, as the degree of alkalinity provided by the excess potassium cyanide allows of complete extraction of the lead. The solution, contained in a separating funnel, is well shaken with 3 to 5 ml. of green dithizone solution (about 6 mg. of dithizone in 100 ml. of carbon tetrachloride); the carbon tetrachloride layer containing the red lead dithizonate is drawn off, and the process is repeated until the non-aqueous portion is no longer red. *Colorimetric Determination of Lead.*—Advantages are offered by the following "mixed-colour" process. The combined extracts, obtained as described above, are shaken with 5 ml. of 1 per cent. hydrochloric acid. The green non-aqueous layer containing the dithizone is separated and rejected. The aqueous portion, containing the lead as chloride, is washed free from dithizone by shaking with a little carbon tetrachloride, and then transferred to a 25-ml. stoppered measuring cylinder and diluted to 10 ml. with 1 per cent. hydrochloric acid; 2 ml. of ammoniacal cyanide solution (75 ml. of ammonia, sp.gr. 0·9, with 100 ml. of 10 per cent. potassium cyanide, diluted to 1 litre) are added. Dithizone solution is added little by little from a burette, with occasional shaking, until there is an excess over that required to give the full red colour with the lead present, a "mixed-colour" between red and green being produced. (If the amount of lead is unexpectedly high, and a "mixed colour" cannot therefore be obtained, a fresh start should be made with a smaller sample). Into another similar stoppered cylinder are introduced 10 ml. of 1 per cent. hydrochloric acid, 2 ml. of the ammoniacal cyanide solution and the same volume of dithizone solution as was added to the sample solution. The liquid is titrated with standard lead solution, with shaking, until the colour matches that of the sample; the amounts of lead in the two liquids are then the same. The process is suited to amounts of lead from 1 to 25γ. *Determination of Lead in presence of Bismuth.*—The test-solution, containing not more than 5 mg. of bismuth, is treated with citrate and made slightly ammoniacal. An equal volume of 10 per cent. potassium cyanide solution and 2 ml. of dithizone solution are added, the liquid is well shaken mechanically for 5 minutes and the red carbon tetrachloride layer is separated. The extraction is repeated until the extract shows a pure orange colour. This indicates that lead dithizonate, which forms in preference to bismuth dithizonate (orange colour), has been completely extracted. To verify the completeness of extraction of lead, the last extract is shaken with 1 per cent. potassium cyanide solution, which discharges the colour due to bismuth. The

combined extracts are well shaken with 5 ml. of 1 per cent. hydrochloric acid, the metals passing into the aqueous phase. The small amount of bismuth accompanying the lead is separated by adjusting the *p*H to 2·8–3·0 (Congo-red indicator paper changing to a bluish tint) and extracting the bismuth by repeated mechanical shaking with small portions of dithizone solution; the solution remains green when extraction is complete. After a final shaking with pure carbon tetrachloride, the aqueous solution is rendered slightly ammoniacal, 5 ml. of 5 per cent. potassium cyanide solution and 1 ml. of 10 per cent. hydroxylamine hydrochloride solution are added, and the lead is extracted and determined as indicated above. Good, but slightly low, results were obtained in tests with 7·4 to 24·6γ of lead and 5 mg. of bismuth. *Determination of Lead in presence of Thallium.*—Lead is extractable in preference to thallous thallium, but it is not possible to judge the progress of the separation by colour alone, as both lead and thallium dithizonates are red. The expedient of shaking each extract with 0·5 per cent. potassium cyanide solution is suggested; lead dithizonate is unaffected, whilst thallium dithizonate is decomposed. The combined extracts, showing the red colour of the lead compound, are tested colorimetrically for lead-content by the usual "single-colour" process. Slightly high results were obtained in tests with 5 to 19γ of lead in presence of up to 500γ of thallium. *Qualitative Tests.*—Stannic tin does not interfere with the detection of lead with dithizone. Stannous tin gives a red colour like that with lead. The interference is partly suppressed by the presence of an excess of 10 per cent. potassium cyanide solution during the extraction process; if a red extract is obtained, it should be shaken with several separate portions of 1 per cent. potassium cyanide solution; any red colour due to stannous dithizonate is discharged. The colour of bismuth dithizonate is similarly discharged by 1 per cent. potassium cyanide solution. It is possible to detect 0·5γ of lead in presence of 1 mg. of bismuth and 2·5 mg. of stannous tin. An extensive bibliography is appended to the paper.

S. G. C.

Colorimetric Determination of Lead as Chromate with the aid of Diphenylcarbazide. T. V. Letonoff and J. G. Reinhold. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 280–284.)—The process is applicable to a few hundredths of a milligram of lead. The solution, containing hydrochloric acid, is treated with 2 ml. of 20 per cent. sodium citrate solution and sufficient ammonia to give a pink colour with phenol red indicator. Acetic acid is added to produce an orange-yellow colour with the indicator, followed by 1 ml. of 40 per cent. ammonium acetate solution and 1 ml. of 30 per cent. potassium chromate solution. The liquid is kept overnight and centrifuged. The precipitate is washed by centrifuging with several 10-ml. portions of 0·4 per cent. ammonium acetate solution. The precipitate is dissolved in 3 ml. of 10 per cent. hydrochloric acid, 10 ml. of 0·02 per cent. aqueous diphenylcarbazide solution are added, and the red colour is compared colorimetrically with standards prepared similarly by suitable dilution of a solution of lead chromate in 10 per cent. hydrochloric acid (39 mg. of lead chromate in 100 ml.; 1 ml. = 0·25 mg. of lead). The novelty of the method consists in the nature of the precipitate, which, when formed under the conditions stated, producing a *p*H of 6·6 to 7·4, was proved to be a double chromate of lead. The intensity of colour produced is double that shown by a standard solution of lead chromate containing the same amount of lead. At lower *p*H values of precipitation, normal lead chromate is precipitated. The method was applied to the determination of lead in biological materials after dry ashing.

S. G. C.

Volumetric Determination of Manganese and Lead Dioxides. C. Mahr and H. Ohle. (*Z. angew. Chem.*, 1939, **52**, 618.)—The determination is based upon the oxidation of thiourea by the metallic oxide (*cf.* ANALYST, 1940, 189). *Manganese dioxide* (0·07 to 0·08 g.) is added to a mixture of 5 ml. of syrupy phosphoric acid, 25 ml. of sulphuric acid (1:1), 5 ml. of 1 per cent. potassium iodide solution and 20 to 25 ml. of 0·1 *N* thiourea solution, and the whole is diluted to 75 ml. The solution is gently heated on a water-bath and shaken until the oxide is dissolved, after which it is cooled to 35° C. and the excess of thiourea is titrated with 0·1 *N* bromide-bromate solution and starch indicator until the blue end-point appears. It is then diluted to 250 ml. with water (35° C.) and the titration is resumed until the blue colour returns (ANALYST, 1939, **64**, 622).—*Lead peroxide* is determined similarly, the weighed quantity being added to a mixture of 15 to 20 ml. of 60 per cent. perchloric acid, 5 ml. of 1 per cent. iodide solution, and a measured excess of thiourea reagent; the operation is otherwise conducted as described above.

W. R. S.

Volumetric Determination of Ferric Iron by Means of Mercurous Nitrate. F. R. Bradbury and E. G. Edwards. (*J. Soc. Chem. Ind.*, 1940, **59**, 96–98.)—The advantage of the method is that it utilises a standard solution unaffected by atmospheric oxygen, *viz.* a 0·1 *M* solution of mercurous nitrate in 5 per cent. nitric acid. The titre remains unchanged for two weeks. The neutral or slightly acid solution of ferric sulphate is treated with 40 per cent. ammonium thiocyanate solution, and titrated with the mercury solution until the red colour just disappears. Towards the end the liquid is titrated, drop by drop, during constant agitation, but the whole operation should be conducted with dispatch, as the colour slowly returns on standing. Dilute sulphuric acid has no effect on the titration, but the concentration of hydrochloric acid, if present, should be below 0·1 *N* otherwise a positive error is introduced. The quantity of thiocyanate added should be at least ten equivalents per equivalent of ferric iron. The method is stated to be accurate within 0·1 per cent. Further investigation into the mechanism of the reaction and its practical application is proceeding; so far it is proved that the ferric iron must be present as the thiocyanate complex for reduction to take place.

W. R. S.

Estimation of Cerium in Cerous Salts. J. Plank. (*Magyar Chem. Foly*, 1939, **45**, 100–103; *Chem. Age*, 1940, **42**, 294.)—When a concentrated solution of potassium carbonate is added to a solution of a cerous salt it gives a white precipitate of cerous carbonate, which is soluble in excess of the carbonate solution, forming a double salt. The colour of the solution changes to yellow by oxidation of the potassium cerous carbonate to the perceric salt, and the intensity of the resulting colour affords a measure of the amount of cerium present. As other ions interfere with the reaction, the method is applicable only to solutions of pure cerium salts.

Modified Iodate Method for the Determination of Barium. F. C. Guthrie. (*J. Soc. Chem. Ind.*, 1940, **59**, 98.)—The solution of barium chloride (0·06 to 0·3 g.) in 20 ml. of water is heated to boiling, stirred, and treated with 25 ml. of a solution of potassium iodate (32 g. per litre) through a dropping tube, which is finally rinsed with small quantities of water. The mixture is boiled for about a minute, allowed to cool, transferred to a 100-ml. graduated flask, made up to volume, mixed, set aside for an hour, and filtered. Aliquot parts of the filtrate are treated with 2 g. of potassium iodide, 5 ml. of 2 *N* sulphuric acid, and 100 ml. of water, and the liberated iodine is titrated with 0·1 *N* thiosulphate solution standardised against potassium iodate. Calcium, if present, causes positive errors. The above procedure of partial filtration and indirect titration avoids the washing of the iodate precipitate in the direct titration method (the washed precipitate being treated with sulphuric acid and iodide solution), which gives somewhat low results owing to solubility losses. W. R. S.

Determination of Tellurium in Tin-Rich Alloys by Volatilisation. W. T. Pell-Walpole. (*Publ. No.* 96, *Int. Tin Research and Dev. Council*, 1940, pp. 3.)—The sample is heated for 1 hour at 1000° C. at 0·02 to 0·03 mm. pressure. Tellurium is lost quantitatively as the compound TeSn, permitting determination by loss in weight. Other volatile elements, such as cadmium, must be absent. S. G. C.

Volumetric Determination of Sulphate. A. Krüger. (*Z. anal. Chem.*, 1940, **119**, 216–221.)—The possibility of adapting the reaction $Na_2SO_4 + BaCO_3 = BaSO_4 + Na_2CO_3$ has been investigated. For various reasons it was only found possible to obtain practically theoretical results by adopting a detailed, lengthy and rigid technique. The amounts of sodium sulphate employed were of the order of 1·0 g. S. G. C.

Interference of Sulphite with the Determination of Sulphate by the Tetrahydroxyquinone Method. H. L. Kahler. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 266–267.)—Sulphite interferes, producing high results. Approximately 85 per cent. of the sulphite present is recorded as sulphate. The sulphite should, therefore, be removed by acidifying and boiling the solution. S. G. C.

Determination of Silicon in Fluorspar and Cryolite. T. Nakamura. (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 33B.)—The silicon is converted into potassium fluosilicate which is ultimately titrated with alkali. *Fusion process.*—A 1-g. sample is fused with 5 g. of fusion mixture. The cooled melt is dissolved, as far as possible, in water; the liquid is transferred to an Erlenmeyer flask fitted with a 2-holed stopper carrying (1) a tap funnel, the stem of which dips below the liquid, (2) two absorption bulbs of the "potash bulb" type, in series containing respectively 1:1 hydrochloric acid and water. The liquid in the flask is neutralised to methyl orange by admitting hydrochloric acid from the tap funnel. A current of air is passed through the apparatus for 15 minutes to remove carbon dioxide, which passes through the washing bulbs. The contents of the bulbs are then transferred to the solution in the flask, an equal volume of alcohol is added, and the solution is rendered distinctly acid. After 2 hours the precipitate of potassium fluosilicate is filtered off, washed with a 2 per cent. solution of potassium chloride, and titrated with *N*/10 sodium hydroxide solution, methyl red being used as indicator (Travers, ANALYST, 1921, **46**, 522). *Hydrofluoric acid process.*—A 1-g. sample, contained in a platinum dish, is allowed to remain in contact with 1 to 2 ml. of hydrofluoric acid reagent for 15 to 30 minutes. (The reagent consists of a mixture of equal volumes of conc. hydrofluoric acid and alcohol, with 2 per cent. of potassium chloride; any precipitate of potassium fluosilicate is filtered off.) The liquid is neutralised with 30 per cent. potassium hydroxide solution, phenolphthalein being used as indicator, and cooled. Equal volumes of alcohol and of 2 per cent. of potassium chloride solution are added, the liquid is acidified, and the precipitated potassium fluosilicate is filtered off and titrated as before. It is noted that cryolite precipitated during the titration adsorbs fluosilicate, rendering it necessary to digest the liquid on a water-bath and to continue the titration until a permanent yellow colour is obtained. S. G. C.

Microchemical

Micro-potentiometric Method of Formol Titration. A. Janke and E. Mikschik. (*Mikrochem.*, 1939, **27**, 176–179.)—Formol titration (Sörensen, *Biochem. Z.*, 1908, **7**, 45; Abst., ANALYST, 1908, **33**, 19) is now widely used for the determination of amino nitrogen in amino acids and peptides or the indirect determination of nitrogen in ammonium salts. Potentiometric titration, which has many advantages, especially with coloured liquids, may be applied to as little

as 0·1 ml. of the sample by using a special micro glass electrode as the titration vessel. The electrode is silvered on the outside to make electrical contact with the terminal and packed with cotton-wool in a cardboard holder to prevent damage to the delicate glass membrane. The electrode, which is bulb-shaped, is supported by the neck, and this is protected by a collar of asbestos paper, so that it can be shaken without risk. For the titration 0·1 *N* sodium hydroxide solution is used with a tapless micro-burette (Schwarz, *Mikrochem.*, 1933, **13**, 1; 1935, **18**, 106, 309; Abst., ANALYST, 1933, **58**, 422) or similar type of burette. The method has been applied to the determination of amino nitrogen in sugar beet. J. W. M.

Micro-gravimetric Separation of Zinc and Uranium. E. Kroupa. (*Mikrochem.*, 1939, **27**, 1–7.)—A method of separating zinc from uranium has been worked out in connection with the determination of the lead, thorium and uranium contents of feebly radioactive minerals in the measurement of geological time by the so-called "lead method"; the elements to be determined constitute a few hundredths of 1 per cent. of the minerals. The chloride or nitrate solution containing the zinc and uranium is buffered with monochloroacetic acid and sodium acetate as in Mayr's macro-procedure, the zinc is precipitated as zinc sulphide, the precipitate is dissolved in hydrochloric acid, and the zinc is determined as zinc ammonium phosphate. The filtrate containing the uranium is evaporated and treated with hydrochloric acid and bromine water. The uranium is then determined by precipitation in the usual way with 8-hydroxyquinoline in acetic acid solution containing ammonium acetate. In 11 determinations of uranium in amounts ranging from 0·5 to 12 mg. and of zinc ranging from 0·5 to 8 mg. the differences between the calculated and determined values never exceeded 1 per cent. J. W. M.

Quinaldinic Acid as a Micro-Reagent. IV. Determination of Zinc in presence of Copper, Silver and Mercury. P. R. Rây and T. C. Sarkar. (*Mikrochem.*, 1939, **27**, 64–66.)—Zinc may be determined as quinaldinate in presence of copper by masking the reaction of the copper with thiourea, with which it forms a complex cation stable in acid solutions. Thiourea has been used for the determination of zinc as quinaldinate in presence of silver and mercury on the macro-scale (Ray and Dutt, *Z. anal. Chem.*, 1939, **115**, 265; Abst., ANALYST, 1939, **64**, 229), and may also be used on the micro-scale. For the determination of 0·15 to 1 mg. of zinc in presence of copper in aqueous solution, 0·3 to 0·5 ml. of a freshly prepared 20 per cent. sodium bisulphite solution is added to reduce any cupric copper to the cuprous state. This is followed by the dropwise addition of 0·05 ml. of acetic acid and 1–1·5 ml. of a 10 per cent. solution of thiourea. The beaker is heated on the water-bath, and the zinc is precipitated with an excess (0·2–1 ml.) of sodium quinaldinate solution (1 per cent. quinaldinic acid). After settling, the precipitate is filtered off, washed 5 or 6 times with 0·5 to 1 ml. of hot water, and dried in a current of air at 125° C. The same procedure is used in presence of mercury and silver, except that the sodium bisulphite may be omitted. When silver, mercury and copper are present together, a little potassium iodide must be added before the sodium bisulphite, but the separation is less satisfactory than from the individual elements. The Emich filter-stick procedure is used throughout. J. W. M.

Physical Methods, Apparatus, etc.

New Cell for Electrodialysis, especially of Soils. A. W. Marsden. (*J. Soc. Chem. Ind.*, 1940, **59**, 60–62T.)—Electrodialysis is preferable to leaching methods for the determination of exchangeable bases in soils, because the bases are exchanged for hydrogen ions and appear as hydroxides in the cathode chamber, and there is no need to evaporate large volumes of solution and to remove the leaching agent before analysis. Existing cells are reviewed and criticised, and arguments are put forward in favour of a 3-chamber cell of the following design:—The central chamber is spherical in shape (to avoid "dead" spaces) and has a capacity of 30 ml. It is provided with a rotating stirrer which is inserted through a neck 7 cm. long in the top of the sphere, and on each side are interchangeable end-chambers which are separated from the sphere by means of small disc-shaped membranes of cellophane or other suitable material. The end-chambers are horizontal cylinders and have outlets, at the top to facilitate washing and the escape of electrolytic gases, and at the bottom to enable the liberated acids and bases to be withdrawn for analysis. The outer ends are closed with rubber stoppers, through which pass the glass tubes which hold the stout platinum wires supporting the disc-shaped vertical platinum electrodes (thickness 0·006 in., diameter 19 to 20 mm.). These electrodes are 4 cm. apart and each is drilled with 4 holes (diameter, 3 mm.) so as to facilitate the escape of gas bubbles, the accumulation of which would increase the internal resistance of the cell. Since the 3 chambers are held together by springs attached to the collars of the end-chambers, dismantling, cleaning and assembly are greatly facilitated. The procedure is to place 10 g. of air-dry soil in the central chamber, to fill the end-chambers with distilled water, and, after the current (D.C., 220 volts) has been switched on, to add 30 ml. of water to the central chamber and start the stirrer. As a rule the current does not rise above 60 to 100 milliamp. during electrodialysis, but should it do so, a 25-watt lamp may be included in the circuit. The temperature may be kept at 30° to 40° C. by changing the anode and cathode liquids hourly for the first few hours. This, however, may

also increase the resistance of the cell, although if advantage is taken of the fact that more base is liberated than acid and the cathode liquid only is changed, this effect is minimised. As a rule, 8 to 10 hours are required for complete electrodialysis, and the current is then about 5 milliamp. The results obtained are satisfactorily reproducible, and the cell appears to be suitable for the examination of other colloidal substances. The high electro-osmotic flow to the cathode, which is typical of 2-chamber cells, necessitating also the evaporation of a large volume of dialysate before analysis, is avoided; the possibility of any action of the liberated acids on the soil is eliminated, and these liberated acids may be removed for analysis. J. G.

Reviews

PRACTICAL PHARMACEUTICAL CHEMISTRY. By F. N. APPLEYARD, B.Sc., F.I.C., Ph.C., and C. G. LYONS, M.A., Ph.D., A.I.C. 4th Edition. Pp. 174 + vii. London: Sir Isaac Pitman & Sons. 1939. Price 6s. 6d.

The appearance of a fourth edition of this useful little manual is in itself a sufficient recommendation of its value in the training of pharmacists. The previous edition was made necessary by certain alterations in the syllabus for the Chemist and Druggist Qualifying Examination, for which the book is specially written, and in this edition the new material, chiefly concerned with qualitative organic analysis, has been extended.

Nearly half the book is devoted to exercises on volumetric analysis, some of which could possibly be omitted in a future edition without detracting from the book's usefulness. In addition, there are short chapters, presumably adequate for their purpose, on gravimetric analysis, official limit tests, alkaloidal assay processes and, rather unexpectedly, the preparation of organic compounds. All the exercises are carefully selected, both for their value as a means of learning chemistry and for their interest to the future pharmacist as being carried out on substances that are of importance pharmaceutically. The final chapter, on qualitative organic analysis, contains the most recent additions and is a bold attempt to compress a difficult subject into a small space. Again the examples given are substances of pharmaceutical importance.

The book is carefully written and the instructions are clear and precise. Indeed, the only fault that can be found with the book is that it is a little too precise. Its instructions do not allow of any initiative—or of any mistakes even—and are reminiscent of the official methods of assay in the British Pharmacopoeia, to which, in a way, the book serves as an introduction. One feels that the student may finish his course with the impression that he now knows all there is to know about analytical and organic chemistry, when in effect he has learned a little about the behaviour of a few of the more important compounds that have applications in pharmacy.

F. A. ROBINSON

ANNUAL REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY. Vol. XXIV for 1939. Issued by the Society of Chemical Industry. Pp. 756. Price to members, 7s. 6d.; to non-members, 12s. 6d.

In praise of the current volume of this well-known annual series of reports it is sufficient to say that it has all the virtues accorded by reviewers to its predecessors. The reports are arranged under the now familiar headings, and each contains the detailed account of progress in the past year required by the specialist, skilfully presented so as to form a lucid survey intelligible to the general reader.

In some of the reports progress in analytical work in a particular field is made the subject of a special section, in others it is not separated from the general subject-matter. Although there are no recorded advances in analytical procedure so outstanding as to merit special mention, the analytical chemist will find much that is applicable, either directly or with modification, to his own problems.

There are indications that many of the reports were cast into their final form some three months after the outbreak of war, and numerous references to our national needs are scattered throughout the volume. The reader will find comforting assurances that our chemical industries are fully prepared to deal with the demands that are, and will be, placed upon them.

Reports such as these must of necessity contain much highly specialised technical language. This has been used judiciously and never leads to obscurity, although there are a few brief instances of its degeneration into the cacophonous jargon associated with some industrial operations. Of the very few typographical errors (the phrase "substitutes to petrol" on p. 56 is presumably one of these), the only serious one is the appearance of "cistine" instead of "cystine" in the subject index. In one report the phrase "substituted by" affords an example of the use of "substitute" as if it were synonymous with "replace"—an error occurring with irritating frequency in contemporary scientific literature. These, however, are minor faults in a volume that presents a comprehensive survey of the work of the past year in a concise, interesting and often entertaining manner. A. O. JONES