THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, May 3rd, the President, Mr. F. W. F. Arnaud, in the chair.

Certificates were read in favour of Lionel Harry James, M.Sc., A.I.C., and Arthur Jones, M.Sc.

The following were elected Members of the Society:—George Vincent Hall, M.Sc., A.I.C., Geoffrey Holland, B.Sc., A.I.C., Herbert Stanley Howes, B.Sc., F.I.C., Frederick William Moore Jaffé, B.Sc., A.I.C., and Malcolm McFarlane Love, F.I.C.

The following papers were read and discussed:—"An Investigation of Solanine Poisoning," by S. G. Willimott, Ph.D., B.Sc.; "The Examination of Leather for the Presence of Extractable Chromium Compounds," by F. E. Humphreys, Ph.D., A.R.C.S., A.I.C., and H. Phillips, D.Sc., F.I.C.; "Barium as a Normal Constituent of Brazil Nuts," by W. M. Seaber, B.Sc., F.I.C.; "The Use of the Phytosteryl Acetate Test in the Routine Examination of Butter Fats," by Herbert Hawley, M.Sc., F.I.C.

Obituary

JOHN MILLAR THOMSON

By the death of Professor John Millar Thomson, the Society has lost a much esteemed Honorary Member—one who will be held in affectionate remembrance by many members of the Society, including not a few who, as old students, will recall their early training in King's College, London, with which he was associated for over half a century.

The son of Dr. Allen Thomson, F.R.S., Professor of Anatomy in the University of Glasgow, and grandson of Dr. John Thomson, F.R.S., Professor of Military Surgery and Pathology in the University of Edinburgh, he was born in the Old College, Glasgow, and educated at the High School and at the University of Glasgow.

In 1871 he was appointed an assistant demonstrator of Chemistry in King's College, London, where he became senior demonstrator in 1879, and Daniell Professor and Head of the Department of Chemistry in 1887. From 1880 to 1887 he also held the appointment of Professor of Chemistry at Queen's College, London. From 1905 he was Vice-Principal of King's College until his retirement in 1914, when he was appointed Emeritus Professor. He was an Honorary Fellow of King's and Queen's Colleges, and, in recognition of his services to chemical education, a medal—presented by Professors Smiles and Allmand—has been instituted in his honour to be awarded annually to the student of King's College who most distinguishes himself in the final year of the special honours course in the Department of Chemistry.

He was naturally less known to the post-war generation of chemists, because advancing years prevented his frequent attendance at meetings; but it should be clearly recognised that, in his younger days, he gave freely of his time and exceptional organising ability, for many years, to the interests of chemistry and of chemists.

He was Secretary of the Chemical Section of the (Royal) Society of Arts from 1879 to 1886, a Member of Council of the Society for four periods, Honorary Treasurer for five years, and Vice-President in 1913. He served on the Council of the Chemical Society for four periods, as Honorary Secretary of the Society from 1883 to 1897, and Vice-President for two periods.

He served as a Member of the Council of the Institute of Chemistry for four periods, as a Vice-President for three periods, as an Examiner for five years, as Honorary Secretary for one year, as Honorary Registrar for six years, as a Censor for twelve years, and as President for three years (1900–1903).

He was author of many contributions to scientific and technical journals—the Composition and Properties of Ancient Glasses, the Chemistry of Pigments, Putrefaction and Antisepsis, the Chemistry of Building Materials, the Composition and Optical Properties of Double Salts of Nickel and Cobalt, the Action of Nuclei on the Crystallisation of Supersaturated Solutions, and on Photography, etc. He edited, jointly with Mr. A. G. Bloxam, several editions of *Bloxam's Chemistry, Inorganic and Organic*, of which the original, published in 1867, was produced by C. L. Bloxam, his predecessor in the Chair of Chemistry at King's College. He was elected F.R.S. in 1897, and received the degree of LL.D. from the University of Glasgow in 1898.

He was possessed of fine physique and of a striking and dignified character and personality. In a small company of friends or students he was charming; in the class room he was absolute master—he expected discipline and had no difficulty in maintaining it. At a college ceremony or other public function he was always an attractive speaker and, on occasions, positively great.

A fluent and lucid lecturer, no one could better impart a knowledge of the general principles of chemistry, such as is covered by the editions of *Bloxam* for which he was jointly responsible, before the character of the work was changed in order to meet the more exacting requirements of the chemical student of the present day.

He could recall the time when what was called "practical chemistry" was taught by demonstration alone, and individual work was but little encouraged. As the profession of chemistry became established and better recognised, he was one of the first professors to realise that it was necessary for teachers to maintain their touch with practitioners and technologists, in order that they should keep abreast with the latest applications of their subject. While ready to acknowledge the educational value of research, he emphasised the necessity for sound fundamental training and experience, in order that such work should be of real value.

He died at Douro Place, Kensington, on 22nd March, aged 84 years. At the funeral at Hampstead Cemetery, Fortune Green, the Society was represented by Dr. Bernard Dyer and Mr. Patrick H. Kirkaldy.

RICHARD B. PILCHER

JAMES WOOD

BY the death of James Wood, which took place on April 4th, 1933, the Society has lost a member who was deeply interested in its welfare and who very rarely missed a meeting of the North of England Section.

He was born in 1878 on a farm in the county of Aberdeen. His parents removed to a suburb of the city of that name when he was at an early age, and he attended the Grammar School there. He subsequently entered Aberdeen University, and graduated as Master of Arts with honours in Mathematics and Natural Philosophy, and as Bachelor of Science with honours in Chemistry. He passed the examination for the Fellowship of the Institute of Chemistry in 1916. He joined our Society in 1920, and was elected a Member of Council in 1927. For two periods he served on the Committee of the North of England Section, and was the first Vice-Chairman.

On leaving the University he joined the staff of Robert Gordon's College as a lecturer in Chemistry, but he soon terminated the appointment in order to undertake research as a Carnegie Scholar under Prof. F. R. Japp, the results of this work being published in two papers (*Chem. Soc. Trans.*, 1905, **87**, 707, 712).

He then went to Liverpool to act as an assistant to the late Professor J. Campbell Brown in the Laboratory of the Lancashire County Council, where he worked for twelve years. It was during this time that a friendship, which lasted for the remainder of his life, was begun with the present writer. In 1917 he joined the newly-formed Research Department of the Co-operative Wholesale Society, Manchester, and three years later he was appointed chief analyst—a responsible post which he held until his death. There can be no doubt that the long training he had had in a Public Analyst's laboratory proved of great value when he was called upon to face, from the side of the manufacturer, problems connected with foodstuffs, and that it was also largely responsible for the disposition he showed, at all times, to confer, in a frank and helpful spirit, with Public Analysts.

Until a few weeks before the end he enjoyed good health, and it appeared likely that he had many years before him. From his early days he took great interest in various forms of sport; in later life he became increasingly devoted to

golf. He held the office of Chairman of the Greens Committee of the North Manchester Golf Club, and won a number of its trophies.

Speaking from an association with Wood extending over a period of twenty-eight years, it is a pleasure to the writer to testify to the strict integrity of his character, his great enthusiasm for his work, and, along with a hearty detestation of anything in the nature of make-believe or pretence, a genial and sane outlook on life. He had, as becomes a good Scotsman, an intense admiration for all things Scottish, but never obtruded his preferences to the annoyance of those whose fortune or misfortune it was to be born further south. His sense of humour was keen, never-failing and infectious; he had the enviable quality of being able to laugh at himself and his own peculiarities. Another characteristic of Wood was an equanimity which was very seldom, if indeed ever, disturbed by the vicissitudes and troubles of life.

He loved the company of his fellows, and especially that of members of our Society. Proof of this is shown by the fact that he generally formed one at those valuable informal talks which often follow our formal meetings; while at our Summer Meetings he was the embodiment of that feeling expressed by his favourite poet, Burns, in the lines:

"The luntin pipe, an' sneeshin mill,
Are handed round wi' right guid will."

He was a man who inspired friendships of the most delightful and enduring kind, for whether the interval of meeting was one of weeks, months or even years, the thread was taken up at the same point at which it had last been dropped.

At the funeral the Society was represented by Messrs. S. E. Melling and G. D. Elsdon, and the North of England Section by Mr. H. Heap and the Hon. Secretary; the Institute of Chemistry was represented by Prof. W. H. Roberts.

He has left a widow and three sons, to whom letters of sympathy have been sent by the Council of the Society and by the North of England Section.

J. R. STUBBS

The Freezing Point of Milk

THE Council of the Society has had under consideration the freezing point of milk and the use of this test for administrative purposes, such, for example, as proceedings under the Food and Drugs (Adulteration) Act, the Milk and Dairies (Amendment) Act, etc.

Investigations in this country and abroad have fully established that the freezing point of genuine milk varies only within narrow limits, and the Council approves the freezing-point determination as a means for the detection, and quantitative determination, of added water in milk.

The accurate determination of freezing points requires a refined technique, and, for the foundation of a proper judgment upon the results of the test, it is essential that the conditions under which the test is performed should be definitely

fixed and strictly adhered to, and that thermometers only of the highest degree of accuracy should be employed.

Confusion has in the past arisen owing to the publication of data obtained by different methods embodying different conditions of test. As a result, figures for the freezing point of genuine milk have been recorded by some observers which are not comparable with those obtained by others. It is thus of major importance that all analysts should use precisely the same procedure and record the freezing point in the same manner.

The Council has reviewed the merits of the various forms of apparatus at present available and the procedures employed therewith, and recommends

(1) That for administrative purposes the freezing point of samples of milk should be determined in accordance with the Hortvet technique exactly as described in "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Third Edition, 1930.

No correction, other than those directed therein, should be applied.

(2) That the freezing point thus obtained should be recorded, for example, as:

Freezing point (Hortvet) .. −0·550° C.

(*Signed on behalf of the Council*)

F. W. F. ARNAUD (*President*)

G. ROCHE LYNCH (*Hon. Sec.*)

The Characteristics of Millet Oil

BY WINIFRED E. SMITH, B.Sc., A.I.C., AND EDITH K. WALLER, B.Sc.

(WORK DONE UNDER THE SOCIETY'S ANALYTICAL INVESTIGATION SCHEME)

(*Read at the Meeting, December* 7, 1932)

MILLET (*Panicum miliaceum*, L.) has been cultivated for centuries in various parts of the world, and, although in this country its use as a food is restricted to animals and cage birds, it is used extensively for human consumption in the countries to which it is indigenous, notably China, India and, to a less extent, in Europe and in American countries.

Although millet has been the subject of a number of investigations, comparatively few have included details concerning the oil. Bersch, in 1895 (*Land. Vers. Stat.*, **46**, 103), examined the fat of various products and by-products of millet, and for rough millet found the saponification value to be 216 and the iodine value 60.

Kassner, in 1887–8, published a series of papers dealing with the composition of millet oil. In one of these he referred to a hydroxy acid to which he assigned the formula $C_{18}H_{32}O_3$, stating that this was probably an oxidation product of an acid

$C_{18}H_{32}O_2$ existing in millet. Lewkowitsch (*Oils, Fats and Waxes*, 5th Ed., I, 200) throws doubt upon the individuality of this acid.

Fabris and Settimj (*Atti del VI Congresso Internaz. di Chim. Appl., Roma*, 1907) obtained from *Panicum italicum*, by extraction of the powdered grains with ether, 3·5 per cent. of a turbid oil, which was brownish-yellow when filtered. Some of the characteristics which they determined, quoted by Lewkowitsch, are included in tables with our own results to facilitate comparison.

Dunbar and Binnewies (*J. Amer. Chem. Soc.*, 1920, **42**, 658) carried out, in 1920, an extraction of ground hulled "proso" (proso being a name used in the United States to designate common millet). They obtained a light golden-yellow oil which, on standing, deposited crystals of an unknown substance which they called "prosol."

From their results, which are included in the following table, they concluded that the saturated acids include a large amount of palmitic acid and smaller amounts of other acids, and that the unsaturated acids consist of oleic, linolic and *iso*-linolic acids.

In 1930 S. Ueno and N. Kuzei (*J.S.C.I., Japan*, 1930, **33**, 452B) published a description of koryo oil, extracted from a different species of millet (*Andropogon sorghum vulgare*). Some of the figures they obtained are in close agreement with those obtained for the oil of common millet.

In the present investigation a product sold as Italian white millet was used. A preliminary trial was made on a small amount of material obtained from a 1930 crop, and two further batches of oil were extracted from millet of a 1931 crop. These batches are referred to as I, II and III, respectively. The differences between II and III are attributed to a slightly different method of extraction, more heating being employed with II. The ground millet, including the husk, was extracted with warm petroleum spirit of b.pt. 40–60° C., and a yield of 4·7 per cent. of oil was obtained. After removal of most of the solvent the solution was of a golden-yellow colour, and showed a tendency to deposit a small amount of crystalline material. This was not removed from batch I, but, by decantation and partial filtration, was removed for separate examination from II and III.

The final traces of solvent were removed by heating the oil to a maximum temperature of 80° C., in a vacuum desiccator in the presence of alkaline pyrogallol. Heating caused the oil to darken in colour. Throughout the whole treatment and analysis great care was taken to avoid undue exposure of the oil to air, and the material was stored in the dark *in vacuo*. Some difficulty was experienced, especially with batch I, in maintaining the oil in a completely liquid condition while removing portions for analysis, owing to the separation of traces of crystalline material of high melting point. Characteristics of the solvent-free oil and of the fatty acids obtained from it are shown in the tables.

It was thought that the low saponification value of batch I, which could not be repeated owing to lack of material, might be explained by the presence of hydroxy acids capable of forming lactones. A number of saponification values were, therefore, determined on II and III with varying times of heating. No significant difference in results was obtained, however, since, on heating for ½, 1, 1½, and 2 hours, the values obtained varied only between 181·4 and 185·6, the average of these being 183·8. It may, therefore, be assumed that no lactones were present.

NATURE OF THE FATTY ACIDS.—Attempts were made to separate the saturated and unsaturated fatty acids by Twitchell's lead salt and alcohol method, with due regard to the conditions stated by Hilditch and Priestman (ANALYST, **1931, 56, 354**) in the matter of concentration of reactants, but under the conditions of this work it was not found possible to ensure a uniform temperature, and slight deviations from the minimum of 15–16° C. were observed. For this reason we suspect that these figures for solid acids are too low. The solid acids obtained by two precipitations from dilute acetic acid consisted of cream-coloured crystals, and amounted to 6·5 per cent. A second determination gave an even lower figure (5·3 per cent.).

TABLE I

PHYSICAL AND CHEMICAL CHARACTERISTICS OF MILLET OIL

	I	II	III		Fabris & Settimj,	Dunbar & Binnewies,	Koryo oil
	1930 crop	1931 crop		Bersch 1895	1907	1920	Japan, 1930
Sp.gr. at 25°/25° C.	0·9076	0·9194	0·9120		0·9275 (15° C.)	0·9228 (22·5° C.)	0·9206 (20° C.)
Refractive index, n_D^{40} ..	1·4620	1·4664	1·4648				1·4649
Saponification value ..	166·8	182·8	183·8	216	183·8	181·5	183·0
Acidity (as oleic), per cent. ..	31·9	36·6	43·1			11·9	20
Acetyl value	18·0					39·2	
Unsap. matter, per cent. ..	4·9	3·1	4·4			2·5	5·4
Iodine value (Wijs) ..	132·2	129·1	130·5	60	130·4	92·3 (Hübl)	114
Bromine value		85·5	80·2				
Calculated iodine value ..		134·9	127·2			195·5	
Neutralisation value of fatty acids	197·8	198·6	198·6				
Iodine value of unsaponifiable matter			143·4				

A separate estimation was made in order to discover the degree of purity of the solid acids obtained by one precipitation only, without re-precipitation from acetic acid. The yield of solid acids was 6·7 per cent., but that this product was probably contaminated with unsaturated acids is indicated by the fact that the iodine value was found to be 17·8, as compared with 4·1 for the acids obtained by two precipitations.

The unsaturated fatty acids amounted to 85·3 per cent., which is identical with the figure obtained by Dunbar and Binnewies, and corresponds closely with that obtained by Fabris and Settimj.

The unsaturated acids consisted of a dark brown oil which had an iodine value of 115·3. It was concluded that some oxidation had occurred. The chief characteristics of the fatty acids were as follows:

In the case of II and III the temperature did not fall below 25° C. during the first precipitation and 18° C. during the second precipitation. The solid acids obtained after reprecipitation from dilute acetic acid consisted of cream-coloured crystals and amounted to 7·0 and 6·6 per cent., respectively, for II and III. The iodine values of these acids were 2·6 and 2·7, respectively.

The unsaturated acids amounted to 93·3 and 93·4 per cent. This figure is higher than that obtained by other workers, but is consistent with the percentage

of solid acids found. The unsaturated acids consisted of dark brown oils, which had iodine values of 128·1 and 127·6 for batches II and III, respectively. These values are slightly low compared with those found for the mixed acids, but, since the acids had darkened in colour, it is probable that some oxidation had taken place. The chief characteristics of the fatty acids are given in Table II.

TABLE II

FATTY ACIDS EXTRACTED FROM MILLET OIL

	I	II	III	Fabris &	Dunbar &	
	1930	1931 crop		Settimj,	Binnewies,	Koryo
	crop			1907	1920	oil
	—	—	—	—	—	—
Appearance		Liquid with slight crystalline deposit				
M.pt. (capillary tube method) ..		23°–24°C.	22–23°C.	26°–27°C.		
Iodine value		136·8	96·6			
Bromine value		85·9	87·2			
Calculated iodine value ..		136·3	138·4			
Thiocyanogen value (15 hrs.) ..		78·6	77			
Calculated composition, per cent.:						
Oleic acid		22·7	17·4			
Linolic acid		64·2	67·8			
Saturated acids		13·0	14·0			
Lead salt and alcohol separation:						
Solid acids, per cent. ..		7·0	6·6	15·5	14·7	28·4
Iodine value		2·6	2·7	—	24·4	13·1
Liquid acids, per cent. ..		93·3	93·4	84·5	85·3	71·6
Iodine value		128·1	127·6	146·3	123·8	120·0

For the determination of the iodine value, bromine value and thiocyanogen value the fatty acids were isolated by extraction with ether after removal of the unsaponifiable matter, all the operations being carried out in an atmosphere of carbon dioxide. The iodine values calculated from the bromine values, which were obtained by the direct bromine vapour method described by Toms (ANALYST, **1928, 53, 69**), agreed fairly closely with those obtained by the Wijs method, particularly with batch II (Wijs 136·8, calculated 136·3). We therefore conclude that millet oil contains fatty acids with only non-conjugated double bonds, and is free from acids of the elaeostearic type.

The figure obtained for stearic acid, as ascertained by Hehner and Mitchell's method, was only 0·5 per cent., and a qualitative test on the oil showed that not more than traces of linolenic and the more highly unsaturated acids were present. The solubilities of the bromine addition compounds of the fatty acids were examined, and from the fact that these were completely soluble in ether and sparingly soluble in petroleum spirit it is evident that the main constituents of the unsaturated acids are of the oleic and linolic type. This conclusion is supported by a consideration of the thiocyanogen value, which was determined by Kaufmann's method on batch II of acids. It was found that the iodine value corresponding with the thiocyanogen absorbed was very much less than the amount absorbed in the Wijs method (thiocyanogen value, 78·6; Wijs, 136·8), indicating the presence of an acid having two double bonds. From these results, calculating the amounts of the acids in terms of oleic, linolic and saturated acids, the following composition is deduced:—Oleic acid, 22·7; linolic, 64·3; saturated fatty acids, 13·0 per cent.

An attempt was made to discover something of the nature of the solid fatty acids present. The solid acids obtained from a lead salt and ether separation were recrystallised from absolute alcohol. The first crop of crystals was cream coloured and melted at 63·5° C. The iodine value, however, was 33·6, so that they were probably still contaminated with unsaturated acids. Repeated recrystallisation of this mixture from 96 per cent. alcohol resulted in a very small amount of pure white crystals of m.pt. 74–75° C. Further concentration of the mother liquors yielded an acid of m.pt. 69–70° C. This seems to agree with the results of Dunbar and Binnewies, who suggested that the saturated acids might consist of a large amount of palmitic acid, with smaller amounts of carnaubic acid (m.pt. 74° C.) and daturic acid (m.pt. 72·5°–74° C.). We did not obtain sufficient of these acids, however, to make an accurate determination of the neutralisation value or the molecular weight.

TEST FOR VITAMIN *A*.—The antimony trichloride test for vitamin *A* was carried out on the oil from both crops, and only a greenish coloration was obtained. A similar test upon the unsaponifiable matter also gave a negative result.

UNSAPONIFIABLE MATTER.—It is interesting to note that Louis Rappaport (*Ber.*, 1887) mentions a method for the extraction of "passicol" from millet oil, by which large colourless rhombic crystals melting at 285° C. are obtainable.

G. Kassner, in 1887, extracted from the meal of millet an oil which deposited crystals of an optically inactive body of m.pt. 285°, which he called "panicol," and to which he assigns the formula $C_{13}H_{20}O$. In 1888 Kassner gave a further description of panicol, and concluded that it is the methyl ether of a phenolic body. Dunbar and Binnewies obtained a similar product, which melted sharply at 279° C. (corr.), and assigned to it the formula $C_{24}H_{36}O_2$, naming the substance "prosol." They state that their product gave the reactions of a ketone alcohol, but the evidence on which they base this assumption is somewhat vague. From the description of the manner of separation, crystalline form and solubilities it is evident that prosol is similar to, if not identical with, panicol. Since these workers carried out the extraction on hulled millet it is evident that the crystals are from the interior of the grain, and not merely a waxy covering of the husk, an observation which we have confirmed. In the present investigation, the crystals which separated from the concentrated solution of the oil in petroleum spirit formed approximately 1·2 per cent. of the whole oil. A further quantity of the same substance was also present in the unsaponifiable matter obtained in the usual way. The unsaponifiable matter extracted by petroleum spirit was a deep yellow, waxy solid containing well-defined crystals. It was soluble in benzene, and it was possible to recrystallise it from a mixture of benzene and alcohol. Acetone only partly dissolved the material, the yellow colouring matter being left as an oil after evaporation of the acetone extract. The freshly isolated crystals, after being washed with petroleum spirit, were white lustrous leaflets of m.pt. 275–276°C. Attempts to saponify with alcoholic potash did not alter the m.pt. of the crystalline extract. The crystals were soluble in hot acetic anhydride, but were precipitated unchanged on cooling. After recrystallisation from glacial acetic acid, followed by thorough washing and crystallisation from petroleum spirit, crystals were

obtained with m.pt. 285° C., a value which we later found to be identical with that noted by Kassner. (*Arch. Pharm.*, 1887, **25**, 395; *Arch. Pharm.*, 1888, **26**, 536.)

TABLE III

CRYSTALS OF UNSAPONIFIABLE MATTER

	Present work	Kassner, 1888	Dunbar & Binnewies, 1920
Name:	—	"Panicol"	"Prosol"
M.pt.	285° C.	285° C.	279° C.
Carbon, per cent.	84·5	—	80·8
Hydrogen, per cent.	11·8	—	9·1
Oxygen, per cent.	3·7	—	—
Formula	—	$C_{13}H_{20}O$	$C_{24}H_{36}O_2$
Rotatory power	None	None	

The purified substance was optically inactive. The Bolton and Williams test showed a value of 143·6. A micro-combustion, carried out on our behalf, showed:— Carbon, 84·5; hydrogen, 11·8; and oxygen, 3·7 per cent. If it be assumed that there is one oxygen atom in the molecule, the analysis corresponds with a compound of much higher molecular weight than was assigned to it by previous workers.

It was thought that some light might be thrown upon the nature of the crystals by the application of colour tests. Sulphuric acid, when added to a chloroform solution of the crystals, gave no coloration. The Liebermann–Burchard test resulted in the slow development of a violet tint, which was definite but not as intense as that produced in a control test with known sterols. From the depth of colour produced it was not possible to decide whether the positive result was due to the material itself or to traces of impurity in the form of sterol. Thus, although we are able to confirm the general physical properties recorded by Kassner, in view of the conflicting results obtained in the examination of "panicol," we prefer not to give a formula until satisfactory evidence has been obtained that our material is a chemical entity and not a mixture. This involves work on a larger scale than hitherto, and a separate investigation is now in progress.

It is possible that sitosterol is also present in the unsaponifiable matter, since, on boiling with acetic anhydride, cooling, and filtering off the unchanged panicol, a white crystalline substance can be obtained, which, after recrystallisation from alcohol, melts at 125° C. (sitosteryl acetate, m.pt. above 125° C.) These crystals gave a positive Liebermann-Burchard reaction. It was not easy, however, to get rid of the colouring matter and an oily substance, difficultly soluble in alcohol, which made the isolation of any sterols present very difficult.

We wish to express thanks to Dr. Ainsworth Mitchell, at whose suggestion this subject was investigated, for his interest in the work, and also to Mr. R. H. Coysh. We also acknowledge our indebtedness to the Director of the Royal Botanic Gardens for identification of the samples.

BATTERSEA POLYTECHNIC
S.W.11

A New Form of the Filter Stick: Its Use in Gravimetric Analysis

By EARL J. KING

(*Read at the Meeting, November* 2, 1932)

One of the greatest aids to filtering in analytical procedures is the filter stick (*Filtrierstäbchen*), introduced in recent years by the Emich[1] school of micro-analysts.[2] By this means the final precipitate to be determined gravimetrically is not transferred to a filter, but is left in the beaker or crucible, whilst the soluble material is filtered off with the washings, leaving the residue behind. This is accomplished by means of a short tube of narrow bore flared at the end and closed by a small plate of sintered quartz or glass or unglazed porcelain, or by a plug of asbestos, platinum sponge or filter paper.[3] These filter sticks are weighed, each with its own crucible or beaker, at the commencement of an analytical procedure, and finally with crucible or beaker plus the residue. The gain in weight is taken as the weight of the precipitate.

The filter-stick method of filtration avoids the possibilities of error commonly involved in the transference of a precipitate from one vessel to another, and, since the filter stick can be used as a stirring rod and the precipitate can be sucked almost dry, washing is greatly facilitated. Filtration by sucking off the filtrate and washings is, moreover, faster than filtration by gravity, and the amount of liquid required to wash the precipitate thoroughly is considerably less.

The use of the filter stick in silica determinations, however, presents a difficulty. Silica is determined by weighing the platinum crucible containing the silica residue before and after treatment with hydrofluoric acid. It is obviously impossible to use a filter stick of glass or other siliceous material where this operation is involved, since it would be necessary to leave it in the crucible during the treatment with hydrofluoric acid, which would attack not only the silica, but also the filter stick. This difficulty can be overcome by wrapping a small piece of filter paper around the end of a porcelain filter stick, detaching this and ashing after the filtration,[4] or by withdrawing the rolled filter paper plug from the end of a glass filter stick with the aid of a piece of platinum wire.[3] A new form of the filter stick, which has been used with considerable success in this laboratory, and which is illustrated in Fig. 1, makes this operation simpler and easier to carry out.

A thick-walled capillary tube, of about 0·5 cm. diameter and with a bore of about 1 mm., is pulled out slightly at one end and cut off smoothly at the other end at a length of about 10 cm. A piece of ordinary glass tubing of 5 or 6 cm. length is selected to fit snugly around the first tube. The glass tubes are held telescoped together by a piece of rubber tubing fitted around the inner tube 3 or 4 cm. below the pull-out end and over the end of the outer tube. The inner tube can now be pushed back and forth within the outer tube while they remain held together by the rubber collar. The inner tube is so adjusted that its broad

end is about 2 mm. within the opening of the outer tube. In the shallow cavity thus formed is inserted a roll of ashless filter paper, made by rolling up 2 or 3 strips of paper about 7 cm. long, or a disc of filter paper fibre, which can be made very conveniently by cutting out a circle from a Fisher's ashless filter paper "accelerator"* with a cork-borer of the correct diameter. Any crevices in the filter paper roll or at the edge of the disc can be filled by sucking in a little filter paper fibre suspended in water.

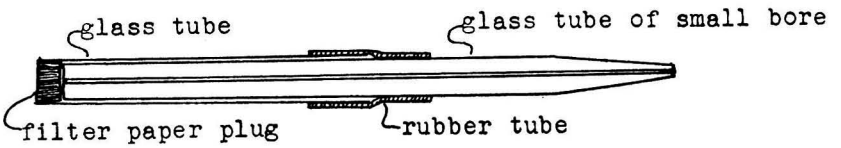

Fig. 1.

An analysis of a sample of commercial silicic acid and of "C.P." barium chloride will illustrate the use of the filter stick in ordinary macro-gravimetric analytical procedures, where it is felt that this method of filtration warrants considerably wider application than it has so far received.

Two samples of silicic acid were heated in platinum crucibles for an hour in the electric muffle at red heat. They were cooled in a desiccator and weighed to determine the percentage moisture. Four c.c. of 60 per cent. perchloric acid were added to each crucible and, after the mixture had been boiled gently for 20 minutes on a hot plate, the crucibles were cooled and the contents diluted with distilled water. Filtration was carried out as illustrated in Fig. 2. A filter stick was

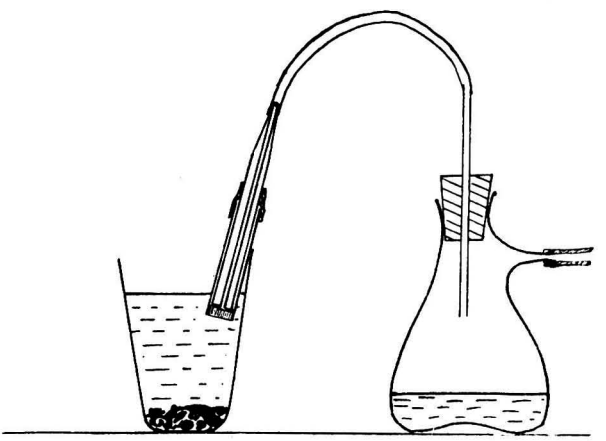

Fig. 2.

fitted with a plug of filter paper and the narrow end was inserted in a rubber tube fitted to a stopper in a filter flask. The filter stick was placed in a suspension of filter paper fibre in water and the suction pump turned on. The filtrate came over perfectly clear. The filter stick was now transferred to one of the platinum

* Fisher's "accelerators" are small squares of pressed filter paper fibre of approximately 1 mm. thickness. When shaken with water these disintegrate and form a uniform suspension of paper fibre.

crucibles and the solution sucked off. The residue of silica was washed five times with distilled water by blowing in a fine stream from the wash-bottle so as to stir up the precipitate of silica on the bottom of the crucible. Finally, the plug of filter paper was pushed out into the crucible by moving down the inner tube through the rubber collar of the filter stick. Any particles of silica adhering to the glass were washed into the crucible with the aid of the wash-bottle.

When filtration was complete the crucibles were dried in the oven, ignited in the muffle, cooled and weighed. Five c.c. of hydrofluoric acid were added with a few drops of sulphuric acid, and the crucibles heated on a hot plate in the fume closet. After ignition and cooling, the crucibles were found to contain an appreciable amount of residue. The treatment was repeated with 2 c.c. of hydrofluoric acid, but the residue persisted. The results are given in Table I.

TABLE I

ANALYSIS OF SILICIC ACID

	(i) Grm.	(ii) Grm.
Weight of sample	0·2020	0·3597
Loss in weight on heating	0·0241	0·0424
Loss in weight on HF treatment (=SiO_2)	0·1620	0·2893
Moisture	11·93 per cent.	11·79 per cent.
SiO_2 in sample	80·19 ,,	80·42 ,,

Three samples of crystalline barium chloride were weighed into 100-c.c. beakers of Jena glass. Water was added to about 70 c.c., and the beakers were placed on the water-bath until hot. Sulphuric acid (25 c.c. of 0·5 *N*) was slowly added to each beaker from a pipette capped with a piece of rubber tubing, and provided with a pinch-cock so adjusted that 10 to 20 drops were delivered per minute. The mixtures were kept stirred during the addition of the sulphuric acid. After having been kept hot for an hour, the beakers were allowed to cool and the solutions filtered off with filter sticks fitted with filter paper rolls into which had been sucked a little fibre. The residues of barium sulphate were washed by stirring up the precipitate with a stream of water from the wash-bottle, the sides of the beaker being washed down at the same time. Washing was repeated four times. The filter paper rolls were pushed out into the beakers and the filter sticks washed clean of barium sulphate. The beakers were wiped clean on the outside, first with a damp and then with a dry towel, dried in the oven and then heated in the muffle at a heat sufficient to burn off the rolls of filter paper. A few drops of sulphuric acid were added to re-convert into sulphate any sulphide which had been formed through the reducing action of the carbon from the paper. After being heated to drive off the sulphuric acid, the beakers were cooled in a desiccator and weighed. The results are given in Table II.

TABLE II

ANALYSIS OF BARIUM CHLORIDE

	(i)	(ii)	(iii)
Weight of barium chloride, grm.	0·2343	0·5873	0·9563
Weight of barium sulphate, grm. ..	0·2242	0·5598	0·9135
Barium found, per cent.	56·31	56·10	56·22
Barium calculated for $BaCl_2.2H_2O$, per cent.	56·23		

SUMMARY.—A new form of the filter stick has been described. Typical results are given to show that gravimetric analyses can be carried out simply and accurately by this method of filtering.

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Citric Acid and Its Detection

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(*Read at the Meeting of the North of England Section, February* 1, 1933)

SOME little time ago it became necessary to establish the absence of citric acid from a mixture which contained large quantities of tartaric acid. During the search for a suitable method we have studied some of the properties and many of the tests which have been suggested for detecting citric acid. The results obtained appeared to be of sufficient interest to place on record. They may be conveniently divided into two parts:—(i) The properties of citric acid; (ii) The detection of citric acid.

(i) THE PROPERTIES OF CITRIC ACID.—Crystallised citric acid is usually stated to contain one molecule of water of crystallisation. Thorpe's Dictionary states that crystals obtained from boiling saturated solutions contain half a molecule, whilst those obtained from a solution after long boiling are anhydrous. It is also stated that the m.pt. of the hydrated acid is 135°–152° C., that of the anhydrous acid 153° C., and that different batches of crystals may have dissimilar properties. Many text-books state that the acid begins to lose water at 75° C., and that it becomes anhydrous at 135° C. We have examined a sample of pure crystallised citric acid obtained from a commercial house. The crystallised acid was found to melt (in part) at 97° C., and to remain in this condition to 110° C., when solidification took place.

Elimination of water (from powdered acid).—On subjecting the pure crystallised acid to the following treatment the results indicated below were obtained.

1. Heated at 100° C. until no further loss took place.	Loss in weight 8·49 per cent. Theory for 1 mol. of water gives 8·58 per cent., and it would appear that the acid can be dehydrated in about 5 hours at 100° C.
2. Left in an efficient desiccator (ordinary pattern) for 7 days.	Loss in weight 8·36 per cent.
3. Heated in an oven at 69° C. for 17 hours.	,, ,, 8·40 ,,
4. Heated in an oven at 47° C. for 16 hours.	,, ,, 6·72 ,,
5. Exposed on a bench in the laboratory for 7 days.	Slight gain in weight of 0·08 per cent., the acid then containing 8·57 per cent. of moisture (theory 8·58 per cent.).

Experiments without first powdering the acid.

1.	Heated 14 hours at 100° C.	Loss in weight 7·22 per cent.
2.	Left in desiccator for 5 days.	,, ,, 4·05 ,,
3.	Heated at 70° C. for 5 days.	,, ,, 3·51 ,,
4.	Exposed on the bench in the laboratory for 5 days.	No change in weight.

From these results it would appear that, whilst crystallised citric acid is stable in air of ordinary humidity at the ordinary temperatures, it rapidly loses water in dry air or on warming. It can be completely dehydrated at 100° C. in the powdered condition in a few hours.

(ii) THE DETECTION OF CITRIC ACID.—The detection of citric acid depends chiefly upon one of two main principles: first, the insolubility of some of its metallic salts, such as the calcium salt (A. Klinger and A. Buzard, ANALYST, 1891, **16**, 210; R. Kunz, ANALYST, 1900, **25**, 40), the barium salt (T. C. N. Broecksmit, ANALYST, 1917, **42**, 357; *J. Soc. Chem. Ind.*, 1920, **39**, 173A; J. J. Willaman, ANALYST, 1917, **42**, 20), or the lead salt (W. Fresenius and L. Grünhut, ANALYST, 1913, **38**, 55), and, secondly, upon the fact that it can be oxidised fairly readily to acetone dicarboxylic acid, which, at the moment of its production, is precipitated as a very sparingly soluble mercuric double salt. (Denigès, ANALYST, 1898, **23**, 161; Gowing-Scopes, ANALYST, 1913, **38**, 12.)

$$\begin{array}{l} CH_2.COOH \\ | \\ C.(OH).COOH \\ | \\ CH_2.COOH \\ \text{Citric acid} \end{array} + O = \begin{array}{l} CH_2.COOH \\ | \\ CO \\ | \\ CH_2.COOH \\ \text{Acetone dicarboxylic acid} \end{array} + CO_2 + H_2O$$

or by conversion into insoluble pentabromacetone by the action of potassium permanganate and bromine (Stahre, ANALYST, 1895, **20**, 188).

$$\begin{array}{l} CH_2.COOH \\ | \\ CO \\ | \\ CH_2.COOH \\ \text{Acetone dicarboxylic acid.} \end{array} + 5Br_2 = \begin{array}{l} CBr_3 \\ | \\ CO \\ | \\ CHBr_2 \\ \text{Pentabromacetone.} \end{array} + 5HBr + 2CO_2$$

By neither of these methods, as originally suggested, is it easy to obtain concordant results. The precipitation of its metallic salts fails to distinguish the acid unless it can be obtained fairly pure and in comparatively large quantities, whilst the unstable nature of the acetone dicarboxylic acid makes this process liable to give erratic results, as it varies widely in delicacy according to the modification of the test employed.

Other methods have been proposed from time to time:

(*a*) By heating with ammonia in a closed tube at 110° C. a deep blue compound is produced (M. Sarandinaki, *Ber.*, 1872, **5**, 1100). Also used by A. Sabanin and N. Laskowsky (*Z. anal. Chem.*, 1878, **17**, 73; ANALYST, 1878, **2**, 182).

(*b*) By condensation with β-naphthol in the presence of sulphuric acid. This is not specific for citric acid, and is not very satisfactory (E. Pinerua, *Ann. chim. anal.*, ii, (4), 66).

(*c*) A colour reaction with vanillin and sulphuric acid, which is not very sensitive in the presence of tartaric acid (E. P. Häussler, *Chem.-Ztg.*, 1914, **38**, 937; ANALYST, 1914, **39**, 395).

(*d*) A colour reaction with sodium nitroprusside (J. A. Sanchez, *Anal. Assoc. Quim. Argentina*, 1926, **14**, 356–365; ANALYST, 1927, **52**, 358).

(*e*) Colour reactions with cobalt nitrate in the presence of caustic alkali (J. F. Tocher, *P.J.*, 1906, **77**, 87; *J. Soc. Chem. Ind.*, 1906, **25**, 829).

(*f*) The behaviour on heating (H. Stevens, *Ind. Eng. Chem.*, 1924, **16**, 155; *J. Soc. Chem. Ind.*, 1924, **43**, 277B).

(*g*) The use of ammonium metavanadate and vanadic acid (L. Rossi, *B.C.A.*, 1928, **3**, 873B).

(*h*) The use of an aqueous extract of cucumber seeds and the methylene-blue technique. This has been stated to be capable of detecting less than 0·01 mgrm. of citric acid (T. Thunberg, *Biochem. Z.*, 1929, **206**, 109–119; *B.C.A.*, 1929, **4**, 602A; O. Östberg, *Biochem. Z.*, 1929, **208**, 352–353; *ibid.*, 1929, **4**, 840A; H. Grönvall, *Biochem. Z.*, 1930, **220**, 82; *ibid.*, 1930, **5**, 946A; I. Nitzescu and I. D. Georgescu, *Compt. rend.*, 1930, **190**, 1325; *ibid.*, *B.C.A.*, 1930, **5**, 946; A. and M. Adams, *Proc. Staff Meetings Mayo Clinic*, 1931, **6**, 252; *ibid.*, 1931, **6**, 1455A).

Our experience would suggest that of these tests, the most satisfactory are those which depend upon the oxidation of the acid to acetone dicarboxylic acid or, preferably, the formation of pentabromacetone as, where the correct technique is used, these are both delicate and specific. We have given particular attention to the acetone dicarboxylic acid method of Gowing-Scopes and to a modification of Stahre's pentabromacetone method.

(1) *Gowing-Scopes' Method.*—The reagent (ANALYST, 1913, **38**, 12) used in this test consists of 51 grms. each of mercuric and manganous nitrates dissolved in 68 c.c. of concentrated nitric acid and diluted to 250 c.c. The test is carried out by neutralising the citric acid to phenolphthalein, adding 10 c.c. of the reagent, diluting to about 200 c.c. with water, and boiling for 3 hours. In the presence of citric acid a grey-white turbidity or precipitate is obtained depending on the amount of acid present. In our experiments we boiled for half-an-hour, at the end of which time any qualitative indication was evident. With 10 mgrms. of citric acid there was a distinct opalescence in two minutes. With 1 mgrm. of citric acid there was a faint opalescence after ten minutes' boiling. Under the above conditions the limit of delicacy of the test was about 0·5 mgrm. of citric acid.

Using tartaric acid we found that 0·5 grm. gave a positive reaction, whilst 0·1 grm. gave no reaction. With 0·1 grm. of tartaric acid, together with 1 mgrm. of citric acid, there was a positive reaction. One grm. of sucrose gave a considerable greyish precipitate, but 0·1 grm. gave a negative reaction.

By the Gowing-Scopes method it is thus possible to detect the presence of about 1 per cent. of citric acid in the presence of sugar or of tartaric acid. The fact, however, that both these materials, when present in larger amounts, give positive results with this test tends to make it of minor value.

(2) *The Pentabromacetone Method.*—The reaction was originally proposed by L. Stahre (*Nordisk pharm. Tidskrift*, 1895, ii, 141; ANALYST, 1895, **20**, 188). It has been modified by various workers, among whom may be mentioned A. Wöhlk

(*Z. anal. Chem.*, 1902, **41**, 77; ANALYST, 1902, **27**, 196), R. Kunz (*Arch. Chem. Mikrosk*, 1914; ANALYST, 1915, **40**, 464; 1916, **41**, 378; *J. Soc. Chem. Ind.*, 1919, **38**, 435A), D. W. Steuart (ANALYST, 1924, **49**, 465), Polonovski (*J. Pharm. Chim.*, 1921, **24**, 167; ANALYST, 1921, **46**, 464), W. B. McClure (*J. Biol. Chem.*, 1922, **53**, 357; ANALYST, 1922, **47**, 486), and B. G. Hartmann and F. Hillig (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 264; 1928, **11**, 257; 1930, **13**, 103; ANALYST, 1927, **52**, 549; 1928, **53**, 443; 1930, **55**, 396).

We have used the modification of Kunz and proceed as follows:—Ten c.c. of the solution to be tested are treated with 1 c.c. of sulphuric acid (1 : 1) and 0·3 c.c. of 37·5 per cent. potassium bromide solution. One c.c. of 5 per cent. potassium permanganate solution is then added, the mixture heated for 5 minutes at 45° C., and then any trace of manganese dioxide is removed by the addition of ferrous sulphate solution containing sulphuric acid.

Under the above conditions a very distinct turbidity is obtained with 1 mgrm. of citric acid. One grm. of tartaric acid or 1 grm. of sucrose, or both together, give negative results with the test, but in the presence of similar quantities of these substances the test with citric acid becomes less sensitive. It was, however, just possible to detect the presence of 10 mgrms. of citric acid in the presence of 1 grm. of tartaric acid and 1 grm. of sugar—a sufficiently delicate test for ordinary circumstances. It was found, however, that the test could be made considerably more sensitive by a preliminary extraction of such a mixture with ether. Thus, a mixture of 100 grms. of tartaric acid, 100 grms. of sucrose and 0·1 grm. of citric acid was carefully prepared. Ten grms. of the finely-ground mixture were treated for about 20 hours in a stoppered bottle with 50 c.c. of ether. The ethereal solution was removed and evaporated to dryness, and the residue dissolved in 10 c.c. of water. On applying the pentabromacetone test to the residue a definite precipitate was obtained. By this modification, therefore, and by taking suitable quantities of material, it is possible to detect as little as 0·01 per cent. of citric acid when present in so-called lemonade powders.

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Further Examples of the Use of Adsorption Indicators in Volumetric Analysis*

BY A. W. WELLINGS, B.Sc.

A. THE DETERMINATION OF ALKALI CYANIDES.—*Diphenyl carbazide* may be used as an adsorption indicator in Liebig's original method for the determination of alkali cyanides by direct titration with standard silver nitrate solution.

The colour change, *pink → violet*, occurs on the particles of silver cyanide, precipitation of which begins as soon as silver ions are present in excess of the concentrations required by the equation

$$2\overset{-}{C}N + \overset{+}{A}g \rightleftharpoons Ag(CN)_2^{-}.$$

* Cf. Berry and Durrant, *Analyst*, 1930, **55**, 613; Berry, *ibid.*, 1932, **57**, 511.

A few drops of a 0·1 per cent. alcoholic solution of diphenyl carbazide are added to aliquot portions of the cyanide solution, thus producing a pink coloration ; the liquid is then titrated with standard silver nitrate solution until a permanent violet colour is produced.

When $M/10$ solutions of the reactants are employed, the colour change can be observed on the precipitated particles of silver cyanide. In $M/100$ concentrations the colour change occurs on the colloidal particles of silver cyanide before any precipitated particles can be detected. Very accurate results are thus possible. In fact, $M/1000$ solutions of cyanide may be used, but it is inadvisable to employ solutions of silver nitrate more dilute than $M/250$. Two or three drops of 0·1 per cent. alcoholic solution of diphenyl carbazide are sufficient to give a satisfactory colour change in titrating 25 ml. of cyanide solution. The silver nitrate solution must be free from acid.

B. The Determination of Soluble Lead Salts.—Burstein (*Z. anorg. Chem.*, **1927**, **164**, 219) has determined lead salts by titrating potassium ferrocyanide (not stronger than $M/200$) with lead nitrate (not stronger than $M/100$), using *alizarin S* as an adsorption indicator. The colour change at the end-point is yellow → red, but it is very slow in making its appearance, and it is also generally necessary to make a duplicate titration in which most of the lead salt is added before the indicator is introduced.

Lead nitrate and lead acetate may be determined very rapidly in $M/10$ and $M/100$ concentrations by titrating standard sodium hydroxide solution with the lead solution. *Fluorescein*, *dichlorofluorescein*, and *dibromofluorescein* may be used as adsorption indicators. The end-point is indicated by the permanence of a *pink colour* on the precipitate of lead hydroxide; the colour change is more vivid for lead nitrate than for lead acetate. A few drops of a 0·1 per cent. alcoholic solution of the indicator are sufficient in each titration, and the low solubility of the lead hydroxide produced in the titration permits reasonably accurate results to be obtained. It is important to note that, in the titration, the lead salt must be run into the standard caustic soda solution ; the reason for this is that the anions of fluorescein are not adsorbed by the colloidal particles of lead hydroxide as long as hydroxyl ions are present in excess ; when, however, the hydroxyl ions have all been removed as lead hydroxide, the fluorescein anions are also adsorbed. The colour change is therefore visible when there is one drop of the lead solution in excess.

C. The Determination of Borates.—Borax, sodium metaborate, and sodium "perborate" may be determined in aqueous solution by direct titration with standard lead acetate solution, with *dichlorofluorescein* as an adsorption indicator. The colour change, *yellow→pink*, occurs on the particles of lead metaborate precipitated in the titrations.

For very accurate results the borate solutions, which are alkaline owing to hydrolysis, must be carefully neutralised before titration with the lead acetate ; a portion of the borate solution is exactly neutralised by the addition of nitric acid, with methyl red as the indicator ; acids, such as hydrochloric and sulphuric, which form insoluble lead salts must not be used in the neutralisation. Further aliquot

portions of the borate solution are then neutralised by the addition of the required amounts of nitric acid without adding the methyl red, the colour of which would mask the colour change in the subsequent titration with lead acetate. Care must be taken not to add hydrogen ions in excess of the hydrogen ion concentration of water, since preferential adsorption of hydrogen ions prevents the colour change with dichlorofluorescein. The neutral borate solution is then titrated with the standard lead acetate, five drops of a 0·1 per cent. solution of dichlorofluorescein to 25 ml. of borate solution being used. Reasonably accurate results, however, can be obtained in $M/10$ and $M/100$ concentrations of borax, and in $M/100$ concentrations of metaborate and "perborate," without preliminary neutralisation, since the concentration of hydroxyl ions is barely high enough to remove a large number of lead ions as lead hydroxide. The lead acetate solution used as the precipitant may be standardised by means of standard oxalate solution, using fluorescein as an adsorption indicator (Wellings, *Trans. Faraday Soc.*, **1932**, **28**, 565).

The metaborate used in the determinations was prepared from orthoboric acid and sodium carbonate, and the "perborate" by the action of hydrogen peroxide on cooled borax solution. Both salts were purified by repeated recrystallisation.

It is interesting to note that, in the titration of sodium "perborate," a precipitate of lead metaborate is obtained; this is in agreement with the view that the former salt is not a true perborate, $NaBO_3,4H_2O$, but a metaborate containing hydrogen peroxide of crystallisation, $NaBO_2$, $3H_2O$, H_2O_2. During the titration the "perborate" solution was kept at 0° C. in order to avoid the possibility of error due to liberation, from the hydrogen peroxide, of oxygen which might have oxidised the lead acetate.

The reactions of the borates are probably represented by the equations:

1. $Na_2B_4O_7+(CH_3COO)_2Pb+3H_2O = Pb(BO_2)_2+2H_3BO_3+2CH_3COONa.$

The orthoboric acid formed in the titration is so weak an acid that it has no appreciable effect on the colour change at the end-point.

2. $2NaBO_2+(CH_3COO)_2Pb = Pb(BO_2)_2+2CH_3COONa.$
3. $2NaBO_2,3H_2O,H_2O_2+(CH_3COO)_2Pb = Pb(BO_2)_2+2CH_3COONa+3H_2O+H_2O_2.$

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Notes

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

THE DETERMINATION OF MILK-SOLIDS BY DRYING *IN VACUO* ON ASBESTOS

IN tropical countries it is impossible at certain times of the year to obtain satisfactory weighings of milk-solids without the inconvenience of weighing all dishes with covers, which are used while the dishes are on the balance pans.

In Madras both temperature and humidity are high for a large part of the year, and to get over the difficulty, vacuum drying on asbestos was adopted as a routine process some eight years ago. A technique has now been developed which appears to give more trustworthy results than those obtained by the usual method, even in cold climates. The manipulations involved are simple and the results are obtained more quickly.

Two or three dozen flat-bottomed tube weighing bottles, $2\frac{1}{2}$ in. by $1\frac{1}{2}$ in. are half-filled with blue asbestos fibre (commercial quality) which has been washed with dilute acid, wrung out by hand with water until free from acid, and dried above 100° C. The weighing bottles are then placed in a 10-inch vacuum desiccator with a well-greased lid over concentrated sulphuric acid, each bottle having its stopper lying edgeways on the rim. The desiccator is then exhausted to about 2 mm. vacuum by means of an electric high-vacuum pump, a three-way stop-cock, a manometer, and a calcium chloride tower being placed in series between the pump and the desiccator.* After standing over-night, the pump is again connected with the desiccator, and worked until the manometer shows a maximum vacuum, after which the desiccator tap is opened; there should then be no change in the reading of the manometer, showing that the vacuum has been maintained. Air is now admitted by way of the three-way cock and the calcium chloride tower. The lid of the desiccator is removed, and the lids of as many tubes as are required are quickly tipped into position. The stoppered tubes containing dry asbestos are now ready for use. The large desiccator is then again exhausted, leaving a further supply of tubes ready for use as required.

The tubes are now weighed, the stoppers removed for a moment to enable approximately 5 grms. of milk to be introduced from a quick-delivery pipette, and the tubes again weighed to give the weight of milk taken.

The stoppers are next replaced edgeways on the tubes, which are placed in a 6-inch Hempel desiccator. These desiccators have the sulphuric acid in an annular glass tray supported on an iron tripod. Twenty c.c. of fresh concentrated acid are placed in the tray for each milk tube.† The desiccator is exhausted to full vacuum and allowed to stand overnight. The state of the vacuum is tested in the morning, as was done with the empty tubes, by exhausting the connecting line before opening the desiccator tap. Air is then admitted through the calcium chloride tower, the lid is removed, and the glass stoppers are tipped into position as rapidly as possible. The tubes can now be weighed at leisure.

The process has been found to have the following advantages over drying in an open dish:

(1) Agreement between duplicate samples is practically perfect. The differences never exceed 0·5 mgrm. on 5 grms. of milk, so that figures for total solids are accurate to the second decimal place.

(2) No charring occurs.

(3) No further dehydration is obtainable by prolonged drying of the open tubes at 100° C. On every occasion on which I have tried further heating in a steam-oven there has been a slight increase in weight. In an electric oven at 102–3° C. there is a small loss (about 2 mgrms.), probably due to dehydration of lactose.

(4) The results agree with those obtained by drying in an open dish if very strict precautions are taken to ensure that, in the latter case, no moisture is absorbed on the balance pan.

* In a circuit containing damp calcium chloride it has not been found possible to obtain a vacuum below 2 to 3 mm. at Madras temperatures. Probably this represents the vapour pressure of a saturated solution of calcium chloride. A higher vacuum would probably be obtainable in England.

† The amount of acid necessary has been investigated. If 15 c.c. are used, variations up to 1 mgrm. occur.

(5) The results for milks put on in the afternoon are available next morning without the necessity of running a steam-oven during the night.

(6) The process works equally well for condensed milks, but with sweetened condensed milk (5 grms. of a 20 per cent. solution) it is necessary to extend the time of desiccation for a further 24 hours. Samples dried overnight lose only a further 3 to 4 mgrms. if left for another 24 hours *in vacuo*.

The above conclusions are based on experience gained in Madras, where the normal night temperature is between 20 and 25° C. In more temperate climates it is possible that the lower rate of evaporation from the milk tubes would be compensated for by the greater desiccating power of sulphuric acid at a lower temperature. If this is not so and an inconveniently long period of drying is necessary, the difficulty could easily be overcome by placing the Hempel desiccator in an incubator overnight.

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A SIMPLE AND RAPID PROCEDURE FOR THE PURIFICATION OF ETHER AND OF ACETONE

THE several impurities which arise in ether under the ordinary conditions of usage have been the subject of numerous investigations. Up to the present time the following substances have been definitely identified: Acetic acid, formic acid, acetaldehyde, hydrogen peroxide, di-ethyl peroxide $(C_2H_5)_2O_2$, mono-acetaldehyde hydrogen peroxide, $CH_3CHOH.O.OH$, di-acetaldehyde hydrogen peroxide, $CH_3.CHOH.O.O.CHOH.CH_3$, vinyl ethyl ether, $CH_2 : CH.O.C_2H_5$, and probably vinyl alcohol, $CH_2 : CHOH$.

The combined action of air, light, and moisture is responsible for their origin. According to Wieland and Wingler (*Annalen*, 1923, **431**, 301, and King, *J. Chem. Soc.*, 1929, 738) vinyl ethyl ether is generated, whether the ether is exposed to light or not. The impurities, it will be noticed, are comprised under four types of substances: (1) Acids, (2) aldehydic bodies, (3) peroxides, and (4) unsaturated compounds.

Their presence leads to objectionable results in the use of ether in analytical operations, and in research work. Explosions have been known to occur during the evaporation of ethereal extracts on the water-bath, due to the unstable peroxides. Certain impurities in anaesthetic ether are decidedly toxic. According to Mita (*Arch. Exp. Path. Pharm.*, 1924, 276), dihydroxyethyl peroxide (now called di-acetaldehyde hydrogen peroxide), isolated as a water-soluble viscous liquid from a very toxic sample of ether, produced fatal results when injected into the blood-stream of some lower animals. As regards the detection of the impurities, aldehyde may be easily recognised by aid of the well-known Schiff's reagent; the peroxides are best revealed by shaking about 20 c.c. of ether in a separating funnel with 10 c.c. of a 5 per cent. solution of vanadic acid (Jorissen's test), when the lemon yellow colour of the reagent will be changed to a port wine shade. This reaction is capable of detecting 1 part of "peroxide" in 400,000 parts of ether. With particularly bad specimens of ether the reagent will assume a deep burgundy-red colour. The presence of unsaturated compounds may be recognised by shaking 10 c.c. of ether with 2 c.c. of dilute bromine water (about 0·2 per cent. of bromine), which will be *immediately* decolorised. While the acidity of impure ether can be readily shown, formic acid can be detected by its characteristic reducing action on mercuric chloride solution, as recommended by King (*loc. cit.*).

Various substances have been proposed, with more or less success, for removing one or other of the impurities, but a single reagent which will effectually remove

all the impurities in a few minutes is obviously desirable. It was noticed that when impure ether was shaken with silver hydroxide precipitated *in situ* by an excess of sodium hydroxide, the mud-grey colour of the silver hydroxide was rapidly changed to an intense black deposit of metallic silver, whereas pure ether had no such effect.

This observation has led to a simple procedure for the purification of ether, the efficiency of which is shown by the results of the following experiment:

A sample of ether which gave marked positive results for the four types of impurities was selected. To 500 c.c. of the sample, contained in a litre bottle, 4 grms. of silver nitrate, dissolved in 30 c.c. of water, were added; 50 c.c. of a 4 per cent. solution of sodium hydroxide were then introduced, and the mixture was vigorously shaken for about five or six minutes. When the ether so treated was poured off from the aqueous layer it was found to give negative results with each one of the tests already mentioned for the respective impurities. The "peroxides" were destroyed, while the aldehydic bodies and unsaturated compounds were oxidised to acids which were "fixed" by the excess of alkali.

Experiments with many samples of commercial ether have shown that the above amount of silver nitrate will generally be sufficient. A preliminary experiment with 25 or 50 c.c. of a particular sample will give an indication of the quantity of silver nitrate required for the purification of a larger volume of the ether. If the precipitate of silver hydroxide is completely blackened, a further addition of the silver salt will be necessary. It is remarkable how efficient this simple procedure has proved, and for ether required for anaesthetic purposes it is not necessary to purify the liquid any further by drying and subsequent distillation. This is an important point where the materials and apparatus required for this purpose are not at hand.

The Purification of Acetone

Commercial acetone, in addition to its contamination with traces of acetaldehyde and acetic acid, invariably contains an obscure impurity, the nature of which has not yet been determined. It originates in the process of manufacture and is responsible for the heavy unpleasant odour of the commercial product. It undoubtedly belongs to the group of unsaturated compounds and must be removed before acetone can be used in the manufacture of explosives, for which a highly purified product is essential.

Distillation alone has little effect in removing this impurity, and hence rather tedious methods have been found necessary in order to obtain acetone of a high degree of purity. The efficacy of the silver hydroxide method of purification is shown by the results here recorded.

The sample of acetone treated boiled at 56–57° C. and had a density of 0·7976 at 15° C.; it gave a very marked colour with Schiff's reagent after a few minutes, and when 10 c.c. were shaken with 2 c.c. of a 0·1 per cent. solution of potassium permanganate, there was rapid reduction of the permanganate—a result due mainly to the "unsaturated" impurity present. To 700 c.c. of the sample, contained in a litre bottle, 3 grms. of silver nitrate, dissolved in 20 c.c. of water, were added; 20 c.c. of *N* sodium hydroxide solution were then introduced, and the mixture was well shaken for about ten minutes. During this process the sides of the bottle became coated with a brilliant layer of metallic silver. In order to remove the water introduced, the acetone was dried over anhydrous calcium chloride and subsequently distilled. The product had a density of 0·7965 at 15° C., and the boiling point at 758 mm. was 56·1° C.

The test for aldehyde was negative, even after 10 c.c. of the acetone had remained in contact with an equal volume of Schiff's reagent for 40 minutes; the critical permanganate test also gave a negative result up to a period of 30 minutes, after which there was slight decolorisation of the reagent. Unlike ether, acetone,

when once purified, remains tolerably pure, even when exposed to light for a long time in a partly filled bottle.

A portion of the above purified sample, tested after fourteen months' exposure to light, including a fair amount of direct sunlight, was still found to conform to the standards required of pure acetone, with the exception that it showed a slight acidity.

I am indebted to Miss M. Black, M.Sc., for making a considerable number of experiments with various specimens of ether and acetone and so helping to establish the practical value of the method of purification.

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MAGNESIUM AMMONIUM PHOSPHATE IN CANNED SALMON

WITH reference to the note of Mr. L. H. James (ANALYST, 1933, **58**, 222) to the effect that crystals of magnesium ammonium phosphate (struvite) have not been previously reported as occurring in salmon, may I draw his attention to the paragraph dealing with this matter in my annual report for 1930 (ANALYST, 1931, **56**, 808). On identification of these crystals (noticed by a Leeds resident in a tin of salmon), I sought the opinion of a physiologist as to their probable origin.

He suggests that local decomposition, not necessarily of a harmful character, may have provoked the formation of the crystals, and states that microscopic crystals of this salt are occasionally found under abnormal conditions in the human digestive tract.

Following the publication of my report, Mr. John Allan wrote to me that several years previously he had found in two parcels of ambergris of different origin considerable quantities of struvite; he kindly sent me specimens, and pointed out that ambergris is probably an intestinal calculus or aggregation which is, on occasion, voided by one or more species of whale, though certain quantities of it are found in the intestines of whales caught in the ordinary way.

C. H. MANLEY

CITY ANALYST'S LABORATORY
LEEDS

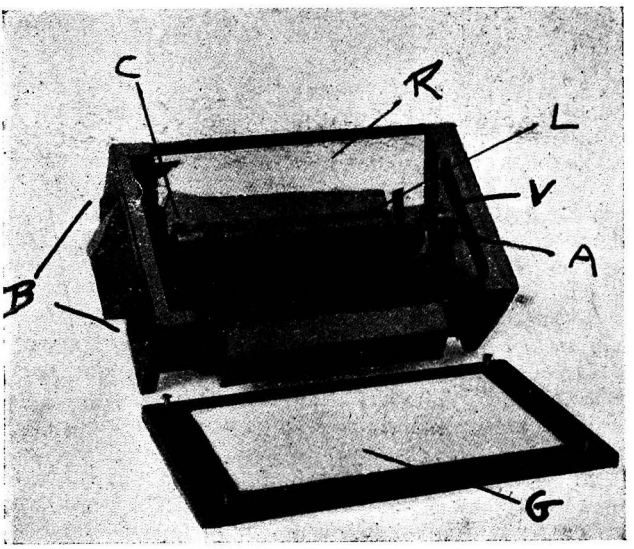
AN ARTIFICIAL DAYLIGHT ILLUMINATOR

ROUTINE work involving observation of titration "end-points" and colour matches frequently demands an excessive number of individual determinations per diem, and may, in consequence, give rise to prolonged eye strain, especially whenever a series of delicate colour changes has to be observed continuously under adverse lighting conditions. At the suggestion of the Advisory Chemist's Department of this College I have developed a special type of illuminator, designed to provide a convenient artificial source of daylight quality, and it was thought that a description of this apparatus might be of general interest.

The apparatus, as depicted in the figure, consists of a rectangular box structure of American whitewood, which houses the projector lamp, L, and its reflector, R. The external dimensions of the box are $35 \times 20 \times 9$ cm. Light, of daylight quality, is supplied by a Philips 150 volt, 40 watt double-ended tubular lamp with a blue glass envelope, the overall dimensions being 28·5 cm. long by 3·5 cm. diameter. The lamp is mounted in the focal line of a cylindrico-parabolic reflector, 28×18 cm., chromium-plated copper, and it is supported by two spring clips, C, cut from sheet brass and soldered to the bent arms, A, which are adjustable in a vertical plane.

This provision is necessary, since a very small displacement of the filament about the focal line will materially decrease the effective candle power available.

In order to secure a uniform intensity and quality of illumination when the apparatus is operated from a supply whose voltage fluctuates with varying load, the illuminator is wired internally in such a manner that the projector lamp may be connected externally with a sliding series resistance, this being adjusted to a value appropriate to the operating voltage of the lamp filament. Two rubber-



insulated leads are soldered directly to the lamp contacts, and external connection to the 200 volt D.C. supply mains and to the sliding resistance, is provided through a pair of standard double-contact bayonet sockets, B. A rectangular sheet of flashed opal glass, G, 29 cm. long by 16 cm. wide, covers a rebated aperture in the detachable box lid. This glazing diffuses the vertically projected beam and provides a uniformly illuminated flush-fitting panel for the working surface, adequate space being provided for two 600-c.c. titration beakers. Four slotted apertures, V, cut in the walls, ventilate the lamphouse, and these are protected by copper cowls which also act as light traps.

The entire structure is raised 4 cm. above the bench level, so as to permit of the bases of burette stands being slid under the illuminator.

Although the apparatus has been designed for use as a portable titration bench, orientation of the illuminated panel in a vertical plane provides a very convenient standard background in general colorimetric work; as, for example, the accurate matching of test samples with buffer solutions.

I am indebted to the aforementioned Department for defraying the expenses incidental to the construction of an experimental apparatus.

D. R. BARBER

PHYSICS DEPARTMENT
SEALE HAYNE AGRICULTURAL COLLEGE
NEWTON ABBOT

AN IMPROVED CRUCIBLE SUPPORT

PIPECLAY triangles have the drawbacks that any one of them can be used only for crucibles of about the same size, and that the supporting wires frequently break; platinum triangles, apart from the expense, sometimes adhere to the crucible when a blowpipe is used. Quartz, which has the advantage of high melting point, has been used for triangles or for rods projecting from triangles, but quartz triangles are readily broken, and will only take crucibles of one size, and quartz rods are either brittle if thin, or deprive the crucible of heat if thick. In any case, varying the distance between the ends of the rods in order to accommodate various crucibles, necessitates untying and retying each rod.

These disadvantages are overcome in the apparatus here described and illustrated (Fig. 1). It consists of a retort stand ring, 5 inches in diameter, provided at each angle with a block, drilled to receive a tube which can be advanced or withdrawn at will, and with locking screws fitted into the blocks. The three tubes, when advanced, meet at a common centre.

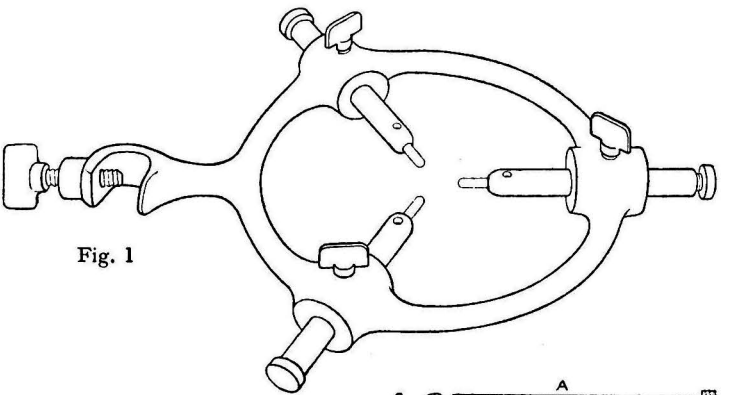


Fig. 1

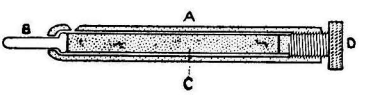


Fig. 2

Each tube is "choked" at one end and thereby reduced to such dimensions that the hole will only just take a quartz rod 1/8th inch in diameter, this rod being flattened into a button at one end to prevent it slipping out of the tube.

The rod having been introduced into the wider end of the tube, and projecting through the hole at the other end, a brass rod follows, to prevent any retreat of the quartz rod, and the tube is closed by a screw which ensures that the various portions act as one. The expansion of metal being different from that of quartz, a small hole is bored in the brass tube, quite close to the quartz rod. As thus constructed, the support will accommodate crucibles from "thimble" to about three-inch size, and, as the tubes are in the same plane as the ring, the risk of loss by spilling is greatly reduced.

The tubes, as depicted in Fig. 2, are 3 inches long and $\frac{3}{8}$ inch in diameter, and $\frac{3}{4}$ inch long and $\frac{1}{8}$ inch in diameter, respectively. The diagram shows the tube (A), the quartz rod (B), the brass rod (C), and the screw (D) used to retain these in position.

This apparatus has been tested for over three years under drastic conditions, and, although at fairly long intervals breakage required a renewal of the rods, the tubes showed no sign of undue deterioration.

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(From the beginning of the year 1921 *to date)*

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T. H. P.

Notes from the Reports of Public Analysts

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

COUNTY PALATINE OF LANCASTER

Annual Report of the County Analyst for the Year 1932

Of the 5531 samples examined, 5245 were submitted under the Food and Drugs Act, and 164 of these were returned as adulterated.

Formalin in Milk.—One sample was found to contain 75 parts of formaldehyde per million. Since 1925 no other milk submitted in the County has been found to contain this preservative. In that year three samples, all from the same source, were found to contain from 10 to 25 parts per million. The vendor of the 1932 sample was prosecuted, but the case was dismissed on payment of 4s. costs, the magistrates remarking that it was a proper case to bring before them.

Pearl Barley.—During the year, 21 samples of pearl barley have been examined, of which two were coated with maize starch to the extent of 1·2 and 0·9 per cent. respectively, and were returned as adulterated. It is suggested that the addition of coating to pearl barley has the effect of concealing the inferior quality thereof, even if it is not intended to do so. The main section of the Food and Drugs (Adulteration) Act allows the addition of any ingredient or material to any article if it is required for the preparation thereof, but it is definitely laid down that such additions must not be used to conceal the inferior quality of the article being prepared.

There is apparently an increase in the sale of coated pearl barley. During the years 1912–1925, 139 samples of pearl barley were examined, of which two were coated. During the years 1926–1930, 130 samples were examined, of which four were coated, whilst during the year 1931 seven of the 32 samples examined were coated. There is apparently no justification for such methods, and the practice should be prohibited.

Artificial Cream.—"Artificial Cream" is defined in the Artificial Cream Act, 1929, as an article of food resembling cream and containing no ingredient which is not derived from milk except water or any ingredient or material which by virtue of the proviso to sub-section (2) of section 2 of the Food and Drugs (Adulteration) Act, 1928, may lawfully be contained in an article sold as cream.

A sample, which was contained in a carton on which the words "Artificial Cream" were printed, was found to contain 23 per cent. of fat foreign to milk, 21 per cent. of sucrose and 14 per cent. of glucose syrup, none of which ingredients is contained in milk. The substance, therefore, did not comply with the sections quoted above. This sample was an informal sample. Endeavours were made to obtain a formal sample from the same vendor, but without success.

Jam.—Whilst it cannot be seriously contended that the suggested standards are either perfect or incapable of improvement, it must be admitted that they have done good. The best type of jam has not suffered in any way, whilst the grossly inferior jams which were becoming so prevalent a few years ago, have almost entirely disappeared from the market. It is to be hoped that these unofficial standards may, before long, form the basis of legal enactments.

During the year 1932, sixty-three samples of jam have been examined, of which four, or 6·3 per cent., have been returned as adulterated.

Since the beginning of the year 1931 the percentage of total soluble solids has been determined in 126 samples of commercial jam. The amount found by the refractometer has varied between 63·7 and 75·4 per cent., but of the 126 samples only 10 have been materially under the standard of 68·5 per cent. Only 6 of the 126 samples contained less than 67 per cent. of total soluble solids, whilst only one sample has contained less than 65 per cent.

There is a difficulty in keeping the jam so well mixed during manufacture on a commercial scale that each jar will contain the same amount of fruit. The same difficulty, however, does not occur in the case of total soluble solids. The deficiency probably arises from the fact that too little sugar has been used in the preparation, or that the jam has not been boiled for a sufficient length of time.

In all cases the amount of insoluble solids has also been determined; the results obtained, together with others obtained during the years 1930–31, are given in the following table:

Insoluble Solids in Jam, per cent., 1930–32

	Number.	Average.	Highest.	Lowest.
Blackcurrant ..	25	2·26	2·98	1·29
Strawberry ..	61	1·22	2·28	0·52
Raspberry	39	2·17	3·00	0·72
Apricot	11	1·02	2·76	0·44
Damson*	23	0·97	2·45	0·40
Red Plum	4	0·52	0·54	0·48

* Without stones.

LEMONADE POWDER.—One sample, described as "Lemonade Crystals," consisted of a mixture of ordinary sugar and tartaric acid. Another, also described as "Lemonade Crystals," was labelled "These Crystals are Manufactured from the finest Oil of Lemon, the natural acid of the Grape, and Sugar." The only constituent of the lemon found in the sample was the essential oil. A sample, submitted as "Lemonade Tablets," had a label with a proprietary name, together with the words "Lemon cubes," and "The lemon drink with creamy foam." These tablets might roughly be described as the effervescent portion of a seidlitz powder flavoured with oil of lemon and sweetened with sugar.

Apparently lemonade was originally lemon juice diluted with water, flavoured with lemon peel, and sweetened with sugar. It would appear not unreasonable for a purchaser to think that "Lemonade Crystals" or "Lemonade Tablets" are substances from which such a solution may be made. In earlier years it was not possible to produce a concentrated lemon juice from which a true lemonade could be obtained by dilution, but such preparations are now actually on the market, in which a considerable proportion of the original properties of the fruit juice is retained. Apart from the natural sugars, lemon juice contains a considerable proportion of citric acid, a natural flavouring agent, and vitamins. A liquid prepared from the samples in question would contain no citric acid, no vitamins, and no natural sugars of the lemon. Tartaric acid is only about two-thirds the price of citric acid; but, apart from this, it is used because it is thought not to be so liable to take up moisture from the atmosphere as citric acid.

GINGER WINE ESSENCE.—A sample, described as "Ginger Wine Essence," consisted of an aqueous solution containing about 1 per cent. of alcohol, together with extracts of ginger and capsicum, probably prepared by the dilution of a mixture of tinctures of ginger and capsicum. The flavouring of the sample was due more to the capsicum than to the ginger, but it appears that many commercial formulas for the preparation of substances known as "ginger wine essence" contain capsicum as an ingredient, and the sample was therefore classified as genuine.

G. D. ELSDON

Legal Notes

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

LABELLING OF GRADED MILK

ON April 18th a dairy company was summoned before the Petty Sessional Court at Kensington Town Hall, for failing to comply with the terms of a licence for the sale of Grade "A" tuberculin tested milk.

Mr. Gilbert Paul, appearing for the Chelsea Borough Council, said that the three summonses were taken out under the Milk and Dairies (Amendment) Act, 1922, according to which Grade "A" might not be sold or advertised for sale except in accordance with a licence granted by the Minister of Health or someone authorised by him. Under the Act an Order, called the Milk (Special Designations) Order, 1923 (Statutory Rules and Order, 1923, No. 601),* had been made, which prescribed that each licensing authority should set forth upon the licence the conditions upon which it was issued. On January 1st, 1933, the Chelsea Borough Council issued a licence to the defending company to sell Grade "A" tuberculin-tested milk, and also a licence to sell Grade "A" pasteurised milk, under specified conditions.

On March 2nd a representative of the Council's sanitary inspector bought a pint bottle of milk, which was labelled with the name of the dairy company and named the farms, but did not state that the milk was Grade "A" or of what type it was.

On March 7th a bottle of milk was ordered from a retailer and, when supplied, was labelled as before. On March 10th an advertisement was published in a West London newspaper, referring to "Grade 'A' T.T. Pasteurised Milk"; there was no such milk described in the Order.†

For the defence, Mr. J. D. Cassells, K.C., submitted that the company was entitled to sell any kind of milk. They had not sold as "Grade 'A' T.T." milk something called "Superity Farms" milk. In their advertisement they had used the expression "Grade 'A' T.T." milk, because that was the foundation of the milk which was called "Superity Farms" milk, and to which cream had been added. When a local authority granted a licence it did not mean that the licensee was bound hand and foot and obliged to sell milk with that particular name. He could always add cream to it provided that it was always of the same quality and always had the same amount of butter-fat. In this case, the milk sold was superior to "Grade 'A' T.T." milk. He contended that only a technical offence had been committed.

The dairy company was fined £5 on each of the first and second summonses, and £1 on the third, with £9 9s. total costs.

* *Cf.* Memo 77/Foods, on the Earlier (1922) Order (ANALYST, 1923, **48**, 120), and Circular 408 (ANALYST, 1923, **48**, 330).

† At no stage must Grade "A," TT milk be subjected to heat.

Commonwealth of Australia

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH
DIVISION OF FOREST PRODUCTS*

THE CHEMICAL COMPOSITION OF WOODS OF THE IRONBARK GROUP. PART II

THE present studies (*cf.* ANALYST, 1932, **57**, 101) have been applied to 65 samples of the 4 ironbarks *Eucalyptus sideroxylon* (red or mugga ironbark), *E. siderophloia* (broad-leaved ironbark), *E. crebra* (narrow-leaved ironbark), and *E. paniculata* (grey ironbark), and to some less-important related species. These occur mainly in Queensland, New South Wales and Victoria, and, on account of their strength and durability, are in great demand for all types of heavy structural work.

It is shown that the standard methods of wood analysis (L. F. Hawley and L. E. Wise, *The Chemistry of Wood*, 1926; A. W. Schorger, *The Chemistry of Cellulose and Wood*, 1926; ANALYST, *loc. cit.*; *Allen's Commercial Organic Analysis*, Vol. X) are not really applicable to the eucalypts on account of the presence of brittle extraneous substances which resist hydrolysis and are insoluble in organic solvents (*vide infra*). The methods have, therefore, been modified considerably, and it is suggested that, as these modifications give very consistent results for samples taken in various localities and from various parts of the tree, they should be applied to wood analysis in general.

METHODS.—*Sampling.*—The piece of unweathered sound truewood (*i.e.* from between the pith and the sapwood) was disintegrated in an impact mill (instead of by rasping or sawing followed by grinding) until it all passed through a 100-mesh sieve; of a sample weighing 200 grms., not more than 4 grms. should be rejected. A suitable mill is described.

Alkalinity of the Ash.—A sample weighing up to 15 grms. was ignited in a muffle-furnace at a temperature below 600° C., and the ash was boiled with an excess of 0·1 *N* hydrochloric acid, which was then cooled and back-titrated to phenolphthalein with 0·1 *N* sodium hydroxide solution.

Cellulose.—The Cross and Bevan method was used, except that for complete de-lignification at least 9 (and sometimes 13) chlorinations, with subsequent sulphite treatments, were required. This was due to the extraneous matter and to the presence of relatively short and fine fibres which are not severed in the impact mill. The hydration produced by these processes rendered filtration difficult.

Lignin.—The extraneous matter was found to be insoluble in the usual mixture of benzene and alcohol, and a hot 0·125 *N* sodium hydroxide solution was used instead (*vide infra*). The residual lignin was separated after hydrolysis, first with 72 per cent., and then with boiling 3 per cent. sulphuric acid for 2 hours (*cf.* ANALYST, *loc. cit.*).

Extractives.—The methods for solubilities in hot and cold water were standardised by washing to a definite volume (as in the analysis of tanning materials), and it was usually necessary to extend the periods of extraction with alcohol and with mixtures of benzene and alcohol to 13 hours. Solubility in 0·125 *N* sodium hydroxide solution (cf. *supra*) was determined on 3 grms. of sample in 100 c.c. of the alkali for a period of 80 minutes on the water-bath.

RESULTS AND CONCLUSIONS.—The full results are tabulated in the paper, and enable the following conclusions to be drawn:

(1) The solubility in 0·125 *N* sodium hydroxide solution is an approximate indication of the amount of so-called extraneous matters present. These are

* Technical Papers, Nos. 4 and 5, 1932. No. 4 by W. E. Cohen, A. L. Baldock and A. G. Charles, pp. 36. No. 5 by H. E. Dadswell and M. Burnall, pp. 34.

actually brittle, dark-coloured, gum-like substances, similar to the kinos, and are exuded from the bark. They are distributed throughout the rays, vessels and fibres of the wood, and impart to it the characteristic red sheen.

(2) Comparison with analyses of the N. American hardwoods (*cf.* Schorger, *loc. cit.*) indicate that the Australian eucalypts are characterised by (*a*) the presence of the above-mentioned extraneous matter; (*b*) lower cellulose-contents; (*c*) lower total pentosan-contents. If allowance is made for differences in the method of analysis used the lignin-contents are almost identical.

DIAGNOSTIC VALUE OF THE RESULTS.—It is considered that the chemical results can supplement division into groups by macroscopical and microscopical methods, by providing a means of sub-classification into species. The significant ratios are provided by the solubility values, viz. (1) hot water/(2 benzene : 1 alcohol), and (2) sodium hydroxide solution/alcohol, and these are shown in the table; a fuller schematic plan of identification is given in the original paper.

Species	1			2		
	Average	Maximum	Minimum	Average	Maximum	Minimum
E. sideroxylon ..	1·32	1·61	1·00	1·84	2·70	1·42
E. siderophloia	2·63	4·00	2·17	3·70	5·29	2·44
E. crebra ..	2·27	3·45	1·89	2·56	5·13	1·82
E. paniculata ..	2·78	3·85	1·82	2·74	3·86	1·35
E. fergusoni ..	2·22	2·78	1·89	2·9	3·7	2·44
E. propinqua ..	2·33	4·00	1·61	2·73	3·77	1·93
E. punctata ..	1·47	2·38	0·87	2·06	2·30	1·68

METHODS FOR THE IDENTIFICATION OF THE COLOURED WOODS OF THE GENUS EUCALYPTUS*

This preliminary investigation has been applied to at least 10 samples of each of 37 species of coloured Australian eucalypts included in the botanical groupings (after Baker), ironbark gums, boxes, bloodwoods, and mahoganies. The geographical distribution of the groups is shown in a number of maps.

EXPERIMENTAL PROCEDURE.—*Basic Density* was determined by the method described by Dadswell (ANALYST, *loc. cit.*), and the results were divided into 4 classes, ranging from above 62·5 to below 40 lbs. per cb. foot.

Colour.—A freshly-cut longitudinal face was examined in each case, and the results were placed in one of 2 categories, *viz.*:—(*a*) Dark red, red, dark brown, chocolate or pink, and (*b*) light brown, yellow, faintly-coloured or white.

Fissibility.—This term was applied to indicate the readiness with which the wood splits when tested parallel and at right angles to the medullary rays. The appearance of the fibres was also noted.

Burning-splinters Test,—Splinters having the size of a match were taken from at least 4 different positions in the truewood and were burnt. Three types of residue are distinguished and are illustrated by photographs, viz.:—(*a*) A blackened and charred whole splinter, due to slow burning. (*b*) A shrunk and charred stump from which particles of ash become detached. (*c*) A complete ash, which retains the shape of the original splinter.

Pores.—The number was determined microscopically (×20) in a circle, 5 mm. in diameter, made by impressing a steel die on the transverse section of the sample. The sizes were classified into 5 groups ranging from below 100μ to over 400μ.

Microscopical Examination.—Transverse, radial and tangential sections (20μ in thickness) were mounted, unstained, in Canada balsam. Features of which special notes were made are the shape of the pores (double, multiple or

* Technical Paper, No. 5.

"touching"), the sizes and cell-numbers of the rays, and the amount of the parenchyma and location of the cells (*i.e.* near to or surrounding the pores, distributed indiscriminately, or linking up the pores).

The above variations in structure are illustrated by means of photographs. The average results are tabulated and discussed for each of the 37 types of sample, and a tentative key for their identification has thence been evolved. This is given in schematic form, but the following points may be noted:

(1) *E. sideroxylon* is distinguishable from all other ironbarks by the slightly-fluorescent turbidity obtained on dilution with water of an extract of the wood in alcohol.

(2) *E. crebra* normally gives an ash of type (*b*), but a few abnormal cases are recorded where the appearance of the ash might lead to confusion with *E. siderophloia*, which gives an ash of type (*a*).

(3) If 12 drops of 5 per cent. solution of sodium hydroxide are added to 2 c.c. of the extract obtained by boiling 2 grms. of sawdust with 20 c.c. of alcohol, the colour deepens from wine-red to dark blood-red in the case of *E. robusta* and *E. rostrata*, whilst with *E. marginata* (jarrah), which gives an orange extract, there is little or no change.

(4) It is impossible as yet to differentiate between *E. paniculata* and *E. fergusoni*, *E. propinqua* and *E. punctata*, *E. accedens* and *E. redunca* var. *elata*, *E. haemastoma* and *E. micrantha*, and between *E. grandis* and *E. saligna*.

J. G.

Philippine Islands

ANNUAL REPORT OF THE BUREAU OF SCIENCE FOR THE YEAR 1931

THE Bureau of Science does work and manufactures supplies, mostly free of cost, for practically all the Government Departments of the Philippine Islands. It manufactures vaccines and serums and serves as a laboratory for the Health Service. During the year there were examined 46,793 samples of faeces, 21,479 samples of foods and beverages, 4953 samples of water, and 49,232 rats for plague. All analyses and examinations made in connection with the Pure-Food Law are conducted by the Bureau for the Philippine Health Service. The Bureau also serves as a laboratory for the Board of Pharmaceutical Examiners and Inspectors, and makes all analyses for them in connection with the Enforcement of the Drug Law.

A considerable proportion of the funds of the Bureau is expended in ways that are of direct value to the people of the Philippine Islands, such as the development of home canning and food preservation, prevention of rabies, identification of minerals, plants and animals, and research on the medicinal constituents of plants, commercial uses of various Philippine products, nature of soils, etc.

RICE BRAN.—Among the practical researches was one on the utilisation of rice bran, which was found to contain 20 per cent. of digestible fat and 15 per cent. of protein. Recipes were devised for preparing from the bran food products, such as cakes and bread, and it has been shown that these products will prevent or cure beri-beri in pigeons, and should therefore prevent or cure human beri-beri.

INVESTIGATION OF PLANTS.—The study of the sclerotium disease of rice is nearing completion, and it has been found that some of the best and most prolific varieties of rice are resistant, so that the disease can be easily controlled.

Coriaria intermedia.—This plant, which is common in pasture in Mountain Province, has caused the death of cattle. A poisonous principle has been isolated from it.

ARTESIAN WATERS.—The chemical properties of artesian waters in and near Manila have been studied, and the waters have been classified in accordance with their predominating constituent. None of the waters contained abnormal quantities of radium emanation, and these findings conform with the findings of investigators in foreign countries with respect to natural waters. Four of the artesian waters examined contain as much radium emanation as the waters of the famous springs at Sibul, which is a well-known vacation resort.

In view of the considerable value of the use of chemicals for disinfecting drinking waters in the Philippines, an investigation was made of the keeping qualities of the various hypochlorites under different conditions. It was found that calcium hypochlorite, properly sealed, keeps well.

MOSQUITO LARVICIDES.—Paris green, diluted with road dust, has long been used as a larvicide for mosquitoes. Investigations have shown that powdered charcoal is an equally good diluent. Also, it has been found that if, instead of making a mixture of charcoal and Paris green, Paris green is absorbed by the charcoal, lower concentrations of Paris green may be used with good effect. An automatic distributor of Paris green has been devised; also a method of controlling larvæ by damming streams. It has been found that if a stream is dammed and the water from the dam is periodically released, the larvae above the dam are stranded, while those below are flushed out. An attempt to find where the malaria mosquitoes stay during the day has shown that they may be found along old stone walls, under bridges, and along undercut banks of streams.

ULTRA-VIOLET RAYS IN THE TROPICS.—The question of ultra-violet rays in the Tropics has long been one of great interest. It has often been claimed that in the Tropics there is excessive ultra-violet radiation which is deleterious to health. The Board has spent much effort along this line, and the results indicate that in Manila the ultra-violet rays are not excessive, as has often been believed (see p. 373).

The Grading of Milk in the United States

THE systems for the distribution of milk in the United States of America are described and discussed by Professor G. S. Wilson, of the London School of Hygiene and Tropical Medicine, in a communication to the Health Organisation of the League of Nations.* The two principal systems are the permit system and the milk ordinance system, the former being in force in various towns and States which have not decided to adopt the other system. The permit system, the regulations of which vary in different localities, requires that milk may be sold only by those who have complied with the regulations and have received a permit from the health officer. In the more efficient areas there is also a system of milk grading, which is enforced by inspection and by chemical and bacteriological examinations in the State or municipal laboratories.

The milk ordinance is the system recommended by the public health service of the Federal Government, which, however, has no executive power over the control of milk, but acts merely in an advisory capacity. There are eight grades of milk, namely, Certified,† Grade A Raw, Grade B Raw, Grade C Raw, Grade D

* *Quart. Bull. Health Organisation League of Nations*, 1932, i., 664–712.

† Certified milk shall contain an average of 4 per cent. of butter fat, with a minimum of 3·5 per cent., the average being based on a period of not more than ninety days. It shall contain not more than 10,000 bacteria per c.c. when examined by the methods of the American Public Health Association. In case a count exceeding 10,000 per c.c. is found, daily counts shall be made, and, if normal counts are not restored within ten days, certification may be suspended. It is also advised that the milk be examined at frequent intervals for the presence of *Streptococcus epidemicus* (Davis) and for *B. coli*.

Raw, Grade A Pasteurised, Grade B Pasteurised, and Grade C Pasteurised. These are all defined in terms of the conditions on the farm or in the dairy, and have definite bacteriological standards. There is, however, no uniform system of grading milk bacteriologically in the United States. Many towns have laid down their own individual standards, other towns have accepted the standards laid down by the Federal Government in the Milk Ordinance and Code, but there are no compulsory standards laid down for milk throughout the country. The number of grades to be adopted by any community is optional, but must be sufficient for the particular local conditions. The health officer of each area is required to announce every six months, and preferably every three months, the grades of milk and cream delivered by all producers and distributors. These grades are determined by inspection, analysis and bacteriological examination, and failure to comply with the requirements may result in reduction to a lower grade, or, in extreme cases, in revocation of the permit. Provision is made, however, for a de-graded vendor to be restored to his grade on proof that the unsatisfactory conditions have been altered.

In both systems of distribution it is ensured that all the milk sold within a given area is appropriately labelled, and the public demand for the better grades of milk tends to eliminate the lower grades. The permit system, without grading, is difficult to enforce, and the principle of de-grading, which is an essential feature of the ordinance system, is more effective, convictions for breach of the regulations being readily obtained. On the other hand, the ordinance system is more expensive to work, and it demands a high standard of technical knowledge and vigilance on the part of the officials. In Professor Wilson's opinion it is not likely to be uniformly adopted in the near future.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Detection of Goat's Milk in Cow's Milk. J. Krenn. (*Z. Unters. Lebensm.*, 1933, **65**, 297–304.)—According to Grosbüsch (*Schweiz. Milchztg.*, 1930, **56**, 221; *Milchw. Literaturber.*, 1930, No. 37, 231) if 5 c.c. of milk are shaken with 15 c.c. of a solution of ammonium sulphate (sp.gr. 1·134) and 10 c.c. of ether for 1 minute, the layer of serum which separates after a further 15 minutes is turbid with goat's milk and clear with cow's milk. The method has been confirmed for 10 and 30 samples of the respective milks, and is shown to be capable of detecting with certainty 5 per cent. (and in some cases 2 per cent.) of the former in the latter. It is unaffected if the milk is 24 hours old, or has a high acid value or is preserved with up to 1 per cent. of formalin, or if it is obtained from ill or otherwise abnormal animals. A less satisfactory reaction, which is affected by these factors, is due to Steinegger (*Molkerei-Ztg.*, 1903, **13**, 398, 410), and depends on the selective coagulation of the proteins in the milk by ammonia. A mixture of 20 c.c. of the sample and 2 c.c. of 25 per cent. ammonia is maintained for 30 minutes at 50° C. and shaken well. The presence of a sharp layer of separation on standing indicates that the presence of goat's milk is probable; 20 per cent. of such milk produces a visible modification in this appearance, and 50 per cent. produces a definite turbidity. J. G.

Determination of the Age of Eggs in the Summer Months. A. Schrempf and G. Weidlich. (*Z. Unters. Lebensm.*, 1933, **65**, 325–328.)—Grossfeld's plumb-line method (not described) depends on the progressive drying which occurs as an egg ages, the apparatus being calibrated so as to give the weight of the egg under water directly in terms of its age in weeks. Trustworthy results are usually obtained, but the accelerated rate of drying during the hot summer months may give high results. Thus, on storage at 15·3 to 24·5° C. the means of the ages obtained from daily tests on 9 new-laid eggs were 0·3 to 1·85, 2·1 to 3·05, and 3·2 to 4·7 weeks during the first, second and third weeks, respectively. J. G.

Determination of Amino Acids and Related Compounds in Honey. R. E. Lothrop and S. I. Gertler. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 103–105.)—Twenty-five grms. of the honey are dissolved in 25 c.c. of water, proteins are removed by treatment with bentonite (*cf.* ANALYST, 1931, **56**, 402), and the amino acids are precipitated by alternate additions of *N* sodium carbonate solution and *N* mercuric acetate solution. The final mixture should have a slightly alkaline reaction to bromothymol blue paper. The precipitate is separated and washed (with alcohol) by centrifugal action, then suspended in dilute hydrochloric acid, heated, and treated with hydrogen sulphide, the mercuric sulphide is separated by filtration, and the filtrate is concentrated under reduced pressure to a volume of 15 c.c. This liquid is rendered slightly alkaline with sodium hydroxide solution, neutralised with hydrochloric acid, diluted to 25 c.c., and 2 c.c. of the solution are used for the determination of the amino acids by means of the ninhydrin method. Various honeys examined yielded from 0·0024 to 0·0066 per cent. of amino nitrogen. W. P. S.

Distinction between Malt and Barley Substitutes for Coffee. H. Barsch. (*Chem.-Ztg.*, 1933, **57**, 242–243.)—The method of distinguishing unground malt-coffee from barley-coffee by observation of the acrospire is not regarded as satisfactory, although more reliable conclusions are possible if the corns are first steeped and then cut lengthwise. A more rapid and more certain test consists in placing 5 grms. of the unground material in 100 c.c. of water, which immediately becomes brownish-yellow with malt-coffee, but remains colourless with barley-coffee. If 96 per cent. alcohol is used instead of water, exactly the reverse takes place. In either case, the maximum development of colour is reached after 10 to 15 minutes. By this means the presence of 10 per cent. of either coffee in the other may be detected. T. H. P.

Some Indian Seed Fats. Mowha (*Bassia latifolia*) and Tamal (*Garcinia morella*) Fats. D. R. Dhingra, G. L. Seth and P. C. Speers. (*J. Soc. Chem. Ind.*, 1933, **52**, 116–118T.)—*Bassia latifolia.*—Mowha seeds from United Provinces, India, yielded, on extraction with ether, 47 per cent. of a pale yellow butter-like fat with setting point 42·6° C.; $n_D^{40°}$, 1·4581; saponification equivalent, 293·6; iodine value, 55·8; unsaponifiable matter, 1·0 per cent.; and acid value, 29·7. The saponified fat was treated by the lead salt and alcohol method, and the liberated acids were converted into methyl esters and fractionated under a

high vacuum; the component fatty acids were found to consist of myristic, 1·0; palmitic, 16·0; stearic, 25·1; arachidic, 3·3; oleic, 45·2; and linolic acid, 9·4 per cent.

Garcinia morella fat.—The kernels of the fruit of the gamboge tree (tamal or gurgi) yielded 22 per cent. of a brownish-yellow fat of pleasant odour with the following characteristics: Setting point, 56·7° C.; $n_D^{40°}$, 1·4612; saponification equivalent, 294·0; iodine value, 48·3; unsaponifiable matter, 0·1 per cent.; acid value, 5·4. The component fatty acids of the fat were found to be: Myristic, 0·3; palmitic, 7·2; stearic, 42·5; arachidic, 0·3; oleic, 43·6; and linolic acid, 6·1 per cent. The acids of the 2·7 per cent. of fully saturated glycerides consisted of 61·0 per cent. of stearic and 39·0 per cent. of palmitic acid. About 45 per cent. of the main portion of glycerides consisted of oleo-disaturated glycerides, and about 50 per cent. of dioleo-monosaturated glycerides. The component fatty acids of both fats conformed to Hilditch's generalisation for the seed fats of their particular botanical families. Both fats yield good soap, but vegetable stearine can be more profitably extracted from the mixed fatty acids from *Garcinia morella* than from those of *Bassia latifolia*.

D. G. H.

New Unsaturated Acid in the Kernel Oil of "Akarittom" (*Parinarium laurinum*). M. Tsujimoto and H. Koyanegi. (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 110–113B.)—The fruits of *Parinarium laurinum*, from Palao in the Western Caroline Islands, weighed 121–137 grms. each, and contained a yellowish-white kernel surrounded and penetrated by a dark violet-red thin rind. The kernel weighed 57 to 68 grms. and contained 45·4 per cent. of moisture and 15·0 per cent. of fat. The orange-yellow fat had the following characteristics: M.pt., 49–50 C.; sp.gr. at 50° C., 0·9379; $n_D^{50°}$, 1·5610; saponification value, 186·8; iodine value, (Wijs), 214·1; unsaponifiable matter, 1·15 per cent.; acid value, 1·31. Spread as a thin layer and kept at 100° C., the oil dried in 40 minutes, and polymerised to a brittle solid occurred at 280° C. The solution of the mixed fatty acids in 95 per cent. alcohol deposited large lustrous crystals, which, on recrystallisation, showed no appreciable change in m.pt. (83°–84° C.), and had an iodine (Wijs) value of 229·6 in 2 hours and 274·1 in 24 hours, and an iodine (Rosenmund–Kuhnhenn) value of 241·0. The neutralisation value was 200·5. The acid was soluble in alcohol and in ether; sparingly soluble in petroleum spirit; no precipitate was found on bromination, and oxidation occurred readily in air. On hydrogenation stearic acid resulted. An isomer of m.pt. 95–96° C., iodine value 237·4, and neutralisation value 202·9, was formed by treating a petroleum spirit solution with iodine and exposing it to light. The formula of the acid was calculated to be $C_{18}H_{30}O_2$, and it is regarded as an α-isomer of elaeostearic acid, the acid of higher m.pt. being the β-modification. It is improbable that the acid is identical with "couepic acid," m.pt., 74°–75° C., isolated by van Loon and Steger from the seed oil of *Couepia grandiflora* (*Rec. Trav. Chim. Pays-Bas*, 1931, **50**, 936), but further work is being carried out. D. G. H.

Fatty Acid and Glyceride Structure of the Seed Fat of *Myristica malabarica*. G. Collin. (*J. Soc. Chem. Ind.*, 1933, **52**, 100T.)—A re-examination of the structure of the seed fat of *Myristica malabarica* confirms its exceptional nature, in that the molecular ratio of saturated and unsaturated acids in the

non-fully-saturated glycerides corresponds with 1 : 1 instead of with 1·3–1·4 : 1. The fat is not such an extreme case of preferential formation of tri-saturated glyceride as is laurel fat, but is a definite exception to the majority of seed fats hitherto examined. The proportion of fully saturated glyceride in the true fat was 14·9 per cent., and the derived mixture of fatty acids consisted of myristic acid, 63·8; palmitic, 28·5; stearic acid, 6·7; and unsaponifiable matter, 1·0 per cent.

D. G. H.

Sodium Morrhuate. Variation in Commercial Samples. R. T. M. Haines. (*Lancet*, 1933, **224**, 748–749.)—An examination of 5 commercial samples of "sodium morrhuate 10 per cent." showed that the term is very differently interpreted, and that a standard is needed. It will be seen from the iodine values that only in sample C has an attempt been made (almost completely successful in this case) to free the drug from sodium oleate; B and D are partly purified, and A and E contain all the original oleic acid from the cod-liver oil. The determination of the iodine value of the fatty acids is important, since sodium oleate is very possibly both more toxic and less active as a sterilising agent than are the sodium salts of the more highly unsaturated fatty acids. In the subjoined table the colour values are those obtained with Lovibond's tintometer (1 cm. cell).

Sample.	A	B	C	D	E
Appearance	Semi-solid, curdy yellow	Liquid, clear yellow	Liquid, clear orange	Liquid, turbid yellow	Gelled, turbid orange
Colour, yellow units ..	11·8	18·0	16·0	9·2	59·6
„ red units	2·2	2·2	2·4	0·4	15·6
„ general absorption..	5·4	0	0·6	4·8	13·2
Total	19·4	20·2	19·0	14·4	88·4
Fatty acid content, per cent.	9·45	9·03	9·74	7·0	8·15
Iodine value, found ..	178·5	183·9	241·2	193·5	169·5
Preservative in fatty acid after isolation	Phenol per cent. 3·4	Phenol per cent. 3·5	Tricresol per cent. 2·6	Phenol per cent. 4·9	Phenol per cent. 3·8
Iodine value, corrected ..	159·3	164·1	226·5	165·8	148·0

D. G. H.

Anaesthesine. *p*-Amino-benzoic Acid Ethyl Ester. M. Wagenaar. (*Pharm. Weekblad*, 1933, **70**, 322–326.)—Anaesthesine is a white powder (m.pt. 90 to 91° C.) which is slightly soluble in cold water, very soluble in hot water, and readily soluble in alcohol, ether, chloroform and fatty oils. It may be sublimed, and the sublimate recrystallises in characteristic bundles of large crystals from a drop of alcohol or acetone. In the following tests the hydrochloride should first be produced by evaporation of a crystal with dilute hydrochloric acid. Dilution with an alkali (preferably ammonia) produces a white turbidity, the sensitiveness of the reaction being 0·04 mgrm. in a dilution of 1 : 500. A crystal of potassium chromate is gradually converted into colourless flat needles when placed in a drop of a solution of the hydrochloride (0·05 mgrm., 1 : 200); small crystals of potassium dichromate are produced simultaneously at the edges. Picric acid and chloroplatinic acid each deposit well-formed star-shaped groups of needles (0·1 mgrm., 1 : 100; *d*-rotatory in the former case), and a crystal of potassium ferrocyanide

produces a precipitate of small *d*-rotatory crystals (0·1 mgrm., 1 : 100). If a crystal of anaesthesine is added to a 15 per cent. solution of furfuraldehyde in oleic acid a violet streak is produced where it dissolves, and the method may be used to detect 1 per cent. in novocaine (*cf.* ANALYST, 1933, **58**, 179). A solution of iodine in potassium iodide solution produces an amorphous precipitate which changes to a dichroic (black to brown) crystalline periodate (0·1 mgrm., 1 : 100).

J. G.

Evaluation of Rubber Hosing, containing Antimony Pentasulphide, for use in the Food Industries. II. B. Bleyer and E. Spiegelberg. (*Z. Unters. Lebensm.*, 1933, **65**, 328–338.)—It is shown that the presence of sulphuric or nitric acid (or both) affects the sharpness of the end-point and the result in the titration of antimony by the titanium chloride and sodium bromate method, and that removal of the latter acid by volatilisation at a low temperature gives low results owing to loss of antimony. Satisfactory results are obtained by boiling 40 c.c. of the sample (*e.g.* beer, vinegar, cider) in a 500-c.c. flask containing 2 small glass balls, so as to remove the bulk of the alcohol; 5 c.c. of strong nitric acid are then added, and after concentration to about 20 c.c., 5 c.c. of strong sulphuric acid and 30 c.c. of water. The oxidation is then continued, and the mixture is heated for 10 minutes after the beginning of the evolution of fumes of sulphuric acid. It is then cooled and warmed with a mixture of 30 c.c. of water and 10 c.c. of a 5 per cent. solution of sodium oxalate, which serves to remove last traces of the nitric acid, the excess of oxalate being destroyed by the sulphuric acid on further concentration. The completely-oxidised solution is then reduced with titanium chloride in the presence of a further 65 c.c. of water and 30 c.c. of 19 per cent. hydrochloric acid, and is titrated with *N*/750 sodium bromate solution (cf. *id.*, 1932, **64**, 209). Samples of rubber hose weighing about 20 grms. were placed in 400 c.c. of beer, lemonade, syrup or wine, which was then stored in a flask containing carbon dioxide under a pressure of from 0·5 to 6·5 atm. for 11 to 60 days. New rubber of the best quality yielded from 4 to 28 mgrms. of antimony to 100 grms. of solvent, the figures for a poorer quality being 1·51 to 9·58, and for hosing 20 years old 29·9 to 326·5. The highest values were given by lemonade containing 20 per cent. of citric acid, and storage at room-temperatures resulted in a greater loss of antimony than at cellar-temperature. New hosing was little affected by pre-treatment with hot or cold 2 per cent. solutions of disinfectant, but the amount of antimony removable from old hosing was increased thereby.

J. G.

Biochemical

Determination of Glycogen. C. A. Good, H. Kramer and M. Somogyi. (*J. Biol. Chem.*, 1933, **100**, 485–491.)—Various workers with Pflüger's method have tried to devise procedures for the elimination of the precipitation and purification of glycogen. The acid hydrolysis of tissues is discussed, but the conclusion is reached that the method of Pflüger is still the only adequate method for the determination of glycogen. However, abbreviations of the Pflüger method are described, which make it possible to make an accurate determination of

glycogen in a few hours. Lower alcohol concentrations than generally employed and application of heat for the precipitation of glycogen are shown to accelerate the procedure. The modified analytical technique is as follows:—A 15-c.c. Pyrex test-tube is charged with 30 per cent. potassium hydroxide solution, approximately 2 c.c. per grm. of tissue, stoppered and weighed; the material to be analysed is added, and the tube is again stoppered and weighed. The stopper is removed, the tube is immersed in a boiling water-bath, and, when the tissue is in solution, 1·1 to 1·2 volumes of 95 per cent. alcohol are added to cause precipitation. The mixture is heated again until it begins to boil, then cooled to room temperature and centrifuged, the mother liquid is decanted off, and the material is allowed to drain. The alcohol still present is rapidly expelled if the tube is heated for a few minutes in a water-bath. It is then heated for 2 to 2·5 hours with 0·6 *N* hydrochloric acid or *N* sulphuric acid in order to hydrolyse the glycogen, acid in amounts commensurate with the quantity of glycogen being used; this should also govern the volume of the final solution in which the sugar is to be determined. For sugar determination, copper reagents are preferable, since ferricyanide oxidises to an appreciable extent some non-fermentable substances present, which with copper solutions show but negligible, if any, reduction. In exceptional cases, when the total amount of glycogen is expected to be less than 1 mgrm., and the material under analysis is known to yield no appreciable amount of non-sugar-reducing substances, the entire procedure is carried out in a single 25×200 mm. Pyrex test-tube. The smallest amount of glycogen is found adhering to the bottom of the tube after centrifuging; 2 c.c. of 0·6 *N* hydrochloric acid are added to hydrolyse the glycogen, the test-tube being provided with an air reflux condenser during the hydrolysis. The contents are neutralised with sodium hydroxide (a drop of phenol red is used as indicator), the volume is made to 5 c.c., 5 c.c. of Shaffer–Hartmann reagent (composition not stated) are added, and a sugar determination is made in the usual way, with a correction for the effect of salt upon reduction. When dealing with a large bulk of tissue in a glycogen determination the simplest procedure is to dilute the alkaline hydrolysate to a definite volume and to use aliquot parts for the rest of the analysis. P. H. P.

Application of the Iodimetric Method to the Determination of Sugar in Blood. H. Bierry, B. Gouzon and (Mlle) C. Magnan. (*Compt. rend.*, **1933, 196**, 862–864.)—The blood must first be freed from non-saccharine substances, especially proteins, capable of reacting with iodine. The blood, treated with 2 per cent. of fluoride, is centrifuged. By means of a pipette, marked to give the true volume by blowing, 5 c.c. of the plasma obtained are introduced into a 30-c.c. measuring flask, together with three 5-c.c. quantities of water used to rinse the pipette. The liquid is treated, drop by drop, and with agitation, with 5 c.c. of mercuric nitrate solution (see below) and then, similarly, with 2 *N* sodium hydroxide solution until a drop of the solution, withdrawn on a platinum wire, colours bromocresol purple paper (see below) violet; the solution should still redden sensitive neutral litmus paper. The p_H value is then 6·5. The volume is made up to 30 c.c., and the liquid filtered by suction. The mercury is eliminated by treatment with powdered reduced copper (zinc must not be used) and, after this

is filtered off, absence of mercury is confirmed by testing with bright copper turnings. The solution thus prepared should be colourless or, at most, pale blue, without showing the biuret reaction.

Twenty c.c. of the liquid are treated, in a Pyrex Erlenmeyer flask, with sufficient of a 15 per cent. solution of crystallised sodium carbonate to make it give a persistent blue reaction with neutral litmus paper (5 to 6 drops usually suffice), 1 c.c. extra of the same solution, and 20 c.c. of 0·01 *N* iodine solution. After standing for 30 minutes at 18° to 20° C., the solution is acidified with 2 c.c. of 2 *N* hydrochloric acid, and the excess of iodine is determined by titration with 0·01 *N* thiosulphate solution, finally in presence of soluble starch; 1 c.c. of the thiosulphate ≡ 0·9 mgrm. of glucose. Tests made on the blood plasmas of several horses by the above method, by Bertrand's method, and by a micro Bertrand method gave results in satisfactory agreement.

The mercuric nitrate solution used is prepared by dissolving 400 grms. of the crystalline salt in 700 c.c. of water at about 45° C., adding the exact quantity of nitric acid required, and agitating until solution is complete. The cooled liquid is treated with concentrated sodium hydroxide solution until a permanent yellow precipitate is formed, and is then made up to 1000 c.c. and filtered. The bromo-cresol purple paper is made by immersing the strips in a 4 per cent. solution of dibromo-*o*-cresolsulphone phthalein in 60 per cent. alcohol; it should have a yellow colour. T. H. P.

Gliadins of Rye and Wheat. H. Kühl. (*Chem.-Ztg.*, 1933, **57**, 333–334.)—The work of Osborne and his collaborators has shown that the seeds of plants of one and the same species are virtually constant in composition and contain identical proteins, and that the proteins of different species always show slight differences in properties. The differences between wheat- and rye-gliadins are shown, in the present work, by extracting the meals with 60 per cent. alcohol and precipitating the extracts thus obtained with acetone in various proportions. The gliadin obtained from wheat by treatment with 60 per cent. alcohol is found to be, not a chemically pure protein, but a mixture of various components.

T. H. P.

Isolation of Catechol from Pigmented Onion Scales and its Significance in Relation to Disease Resistance in Onions. K. P. Link and J. C. Walker. (*J. Biol. Chem.*, 1933, **100**, 379–383.)—Recently Link, Angell and Walker (*J. Biol. Chem.*, 1929, **81**, 369; ANALYST, 1929, **54**, 240; *Proc. Nat. Acad. Sci.*, 1929, **15**, 845), Link, Dickson and Walker (*J. Biol. Chem.*, 1929, **84**, 719; ANALYST, 1930, **55**, 60) and Angell, Walker and Link (*Phytopathology*, 1930, **20**, 431) reported the isolation of protocatechuic acid (3, 4-dihydroxybenzoic acid) from the outer scales of pigmented onions (*Allium cepa*), and pointed out the significance of its occurrence in relation to disease resistance in the onion. The authors have now isolated catechol (3, 4-dihydroxybenzene), another toxic phenolic entity, from the outer scales of pigmented onions (the resistant varieties). It is not present in the scales of the white onions (the non-resistant varieties). By the method which is outlined 0·2 to 0·1 grm. of crude catechol can be readily isolated from 100 grms. of dry scales, but this does not represent all of the catechol present initially. Phenol

determinations on solids obtained in the various steps indicated that not more than 50 per cent. of the catechol was obtained in a crystalline condition. Catechol, together with protocatechuic acid, appears to be the chief toxic substance that enables the pigmented onion to resist the invasion of the fungus *Colletotrichum circinans*, the organism responsible for the onion disease known as *smudge*. It is shown that catechol is somewhat more toxic than protocatechuic acid to this organism. So far as the authors have been able to ascertain from the literature, the isolation of catechol and protocatechuic acid represents the first instances wherein resistance to, or immunity from, a disease in plants has been definitely shown to be due to specific chemical compounds produced by a resistant host (pigmented onions) and absent from a susceptible host (white onions). P. H. P.

Chemical and Biological Analyses of Tikitiki (Rice Bran) Extracts. A. J. Hermano and F. Anido. (*Philippine J. Sci.*, 1933, **50**, 189–195.)—The rice polishings (darak) used in the Philippine Islands for making these extracts consist mostly of the brown coating (pericarp), the germ, tiny particles of broken kernels, and a small quantity of husks. The crude material forms a good feed for hogs, horses, chickens, etc., and the very fine, non-rancid kinds, when mixed with wheat flour, make good bread and cakes. The extracts are used widely for the prevention and cure of infantile beri-beri, of adult malnutrition, and of poly-neuritis in pigeons, chickens, etc.

Crude rice polishings showed the following percentage composition: Moisture, 9·02; fat (ether extract), 16·96; protein (N × 6·25), 13·81; ash, 11·94; crude fibre, 9·91; carbohydrates (by difference), 38·36. Samples of seven brands of tikitiki extracts, prepared by different manufacturers, gave the following results: Sp.gr. at 27·5° C., 1·3189 to 1·5894; total solids, 45·92 to 71·03 per cent.; ash, 3·54 to 8·99 per cent.; alkalinity of the ash in grms. of KOH per 100 grms. of sample, 0·34 to 2·37; nitrogen 0·58 to 1·77, P_2O_5 1·49 to 2·70, sucrose 1·27 to 18·13, reducing sugars 19·16 to 28·35 per cent.; all were free from borates, salicylates, and alcohol. These results were obtained by means of the Official and Tentative Methods of the Association of Official Agricultural Chemists (1925).

Biological tests on rats showed that three of the seven extracts were very good, and three moderately good, sources of anti-neuritic vitamin, whilst one contained very little of the vitamin. T. H. P.

Properties of Halibut-Liver Oil. R. T. M. Haines and J. C. Drummond. (*British Med. J.*, 1933, 559–561.)—The vitamin *A* value of halibut-liver oils varies very markedly, but the analytical and other results tabulated show no obvious correlations which might be of significance from the medicinal value point of view; *e.g.* there is no general rise in the proportion of unsaponifiable matter with increased content of vitamin *A*. The oil containing the highest unsaponifiable fraction (12·7 per cent.) shows the smallest cholesterol content (43·4 per cent. of the unsaponifiable fraction). The graph correlating the extinction coefficients at 3280 Å.U. in a concentration of 1 per cent. (E1 cm./1 per cent.) with the "blue values" of the antimony trichloride test is a straight line. By extrapolation to the value E1 cm./1 per cent. 1600, the highest recorded figure for the purified vitamin *A*, the "blue value," referred to 10 per cent. dilution, would be

44,080 (Carr and Jewell, *Nature*, 1933, **131**, 92), and this result encourages belief in the trustworthiness of the antimony trichloride test for assaying vitamin *A* values in halibut-liver oils of high potency. The blue values on the original oils varied from 300 to 1720. D. G. H.

Bacteriological

Effect of Nitrates on the Formation of Fungoid Growth in Liquor Arsenicalis B.P. 1932. J. Rae. (*Pharm. J.*, 1933, **130**, 339.)—Several experimental batches of Liquor Arsenicalis B.P. 1932, made up by various workers, were stored in corked, and also stoppered bottles, in the dark and in the light, in full and partly-filled bottles, and after four months they were all quite sound, but it was found that with certain batches of Liquor Potassae mould developed, and this suggested that nitrates might be the contributing cause. Dilute nitric acid, B.P. 1914, was boiled under a reflux condenser for 4 hours to destroy any possible contamination from this source. A 1 per cent. solution of potassium nitrate was made with distilled water, and similarly boiled. A batch of 300 c.c. of Liquor Arsenicalis was made with distilled water and Acid. Hydrochlor. Dil, and Liquor Potassae (both tested and found free from nitrates), and divided into 3 batches of 100 c.c. each. To A was added 0·5 c.c. of the sterile dilute nitric acid, to B 1 c.c. (0·01 grm. of potassium nitrate) of the sterile potassium nitrate solution, and C was used as a control. All were exposed to light. In 2 days A developed a fungoid growth at the bottom of the bottle; in 4 days B had a growth suspended through the liquid; C remained clear. B had a garlic-like odour, but A remained odourless. Ten days after the appearance of the mould the following percentages of arsenic trioxide were found:—A, 0·977; B, 0·856; C, 0·980. In B the mould was different from that in A, and was attacking the arsenic. Free hydrochloric acid has a definite bactericidal value; the small quantity of free acid in normal gastric secretion can exert an antiseptic action. This property may be the reason why there has been no trouble with Liquor Arsenicalis Hydrochlor. B.P.1914, in the past. Some Liquor Arsenicalis prepared in October, 1932, which had remained clear, produced moulds when the sterile solutions of nitric acid and nitrate were added. It is therefore evident that care should be taken to see that both the dilute hydrochloric acid and the solution of potassium hydroxide are quite free from nitrates. P. H. P.

Bactericidal Properties of Silver Chloride. J. Dekker and C. H. Dekker-Koers. (*Pharm. Weekblad*, 1933, **70**, 23.)—To each of 2 plates of gelatin-broth medium was added 1 c.c. of a saturated solution of silver chloride (containing about 1·5γ of silver). One was placed in an incubator at 22° C. immediately, and the other was added after exposure for 1 hour to light and air. After 24 hours the former was sterile, the latter contained 2 colonies, and two control plates, in which the silver chloride solution was replaced by distilled water, contained 67 and 73 colonies (*cf.* H. Moser, *id.*, 1932, **69**, 1351; *Apoth. Zeit.*, 1932, 1341). J. G.

Toxicological and Forensic

Copper-Content of the Urine of Normal Individuals. I. M. Rabinowitch. (*J. Biol. Chem.*, 1933, **100**, 479–483.)—Chemical and spectroscopic analyses indicate that copper is a universal constituent of biological material, and that failure to detect it in the past was largely due to the limitation of methods then available for its detection when present in minute quantities. It appears, also, that it is an essential element rather than a contamination. With proper attention to details it is now possible to determine quantitatively as little as a few micrograms of copper with a fairly high degree of accuracy, and an investigation was therefore made to determine whether copper is invariably found in urine, and, if so, to what extent. The method adopted was as follows:—The urine (100 c.c.) was evaporated to a few c.c., the organic matter was oxidised by means of sulphuric, perchloric and nitric acids, the copper was precipitated as sulphide, and the copper sulphide was converted into nitrate, which was then dissolved in 10 c.c. of water. The aqueous solution was treated with 10 c.c. of 0·1 per cent. diethyl dithiocarbamate, and the resulting copper compound was extracted with amyl alcohol and determined colorimetrically by McFarlane's method (ANALYST, 1932, **57**, 802). The urines of 50 subjects were examined, all patients with no histories of any undue exposure to copper, and precautions were taken in the analyses to insure that reagents, glassware, and particularly water, were copper-free. The tabulated results show that copper appears to be a constant constituent of the urine of normal individuals. The amounts found ranged between minute traces and 0·4 mgrm. per litre, and between traces and 0·7 mgrm. per 24 hours. In two copper "balance" experiments, in which the subjects were given copper by mouth, the amounts were appreciably larger: 0·63 and 0·81 mgrm. per litre, and 0·84 and 1·01 mgrm. per 24 hours, respectively. In view of the widespread and increasing use of copper as a therapeutic agent and the possibility of copper poisoning, the above findings are of more than academic interest, in that, in the interpretation of urinary data, consideration must be given to the fact that the differences between health and disease are quantitative and not qualitative. P. H. P.

Colorimetric Determination of Thallium. P. A. Shaw. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 93–95.)—To determine thallium in toxicological material, poison bait, etc., the sample is treated with hydrochloric acid and potassium chlorate to destroy organic matter, and the thallic chloride is extracted with ether. The ethereal solution is evaporated, the residue is heated with the addition of sulphuric acid and nitric acid to destroy any remaining organic matter, cooled, treated with 30 c.c. of 15 per cent. ammonium chloride solution, and evaporated to dryness. This residue is dissolved in water, the solution is treated with bromine, boiled to remove excess of bromine, and treated with potassium iodide. Iodine is liberated according to the equation: $TlCl_3+2KI=TlCl+2KCl+I_2$. The liberated iodine is extracted with a definite volume of carbon disulphide, and the coloration compared with that produced by a known amount of thallium. Copper, lead, iron, arsenic, mercury, tungsten, and molybdenum do not interfere with the method, but unsatisfactory results are obtained if chromates are present.

W. P. S.

Alcohol in the Blood of Motor Drivers. K. Hansen. (*Tidsskrift for den Norske Laegeforening*, Jan. 15, 1933; *Lancet*, 1933, **224**, [Apr. 22nd], 892.)—The author, who is Professor of Pharmacology at the University of Oslo, summarises the results obtained during the preceding 18 months with 373 samples of blood which had been sent by 52 doctors from different parts of Norway to the Pharmacological Institute, having been taken from men suspected of being under the influence of alcohol while driving motor cars. In 318 cases the samples were accompanied by a report from the doctor giving his opinion whether the man was (1) sober, (2) under the influence of alcohol, or (3) drunk. The results are summarised in the following table:

Alcohol in the blood Parts per 1000	Cases	Clinical diagnosis			Percentage of positive diagnosis	
		Sober	Under the influence of alcohol	Drunk	In this series	In a Swedish series for comparison
0·01–0·20	15	13	2	0	13	0
0·21–0·40	3	1	2	0	66	0
0·41–0·60	3	2	1	0	33	0
0·61–0·80	9	4	5	0	55	0
0·81–1·00	11	6	5	0	45	20
1·01–1·20	20	7	13	0	65	37
1·21–1·40	30	8	21	1	73	42
1·41–1·60	36	7	27	2	80	69
1·61–1·80	36	7	28	1	80	80
1·81–2·00	50	4	37	9	92	88
2·01–2·20	33	0	26	7	100	91
2·21–2·40	33	0	27	6	100	94
2·41–2·60	21	2	11	8	91	94
2·61–2·80	9	0	6	3	100	100
2·81–3·00	4	0	0	4	100	100
3·01–3·20	2	0	0	1	100	100
3·21–3·40	1	0	0	1	100	100
3·41–3·60	—	—	—	—	—	—
3·61–3·80	1	0	0	1	100	—
4·81–5·00	1	0	0	1	100	—

It is suggested that, in practice, the clinical distinction into three groups is not satisfactory; it was largely responsible for the much higher proportion of positive clinical diagnosis in the Norwegian series than in 500 cases investigated by Wildmark in Sweden. In several of the present series of cases the clinical evidence was not in favour of the motor driver. In one instance the blood of a driver who had been found by the doctor to be "under the influence of alcohol," contained only 0·03 part per 1000 of alcohol, *i.e.* the normal alcohol-content. There were special reasons in his case for exceptional nervousness, and, but for the result of the blood test, the faulty diagnosis would have had serious legal consequences.

Water Analysis

Determination of Small Quantities of Aluminium in Waters. E. Naumann. (*Chem.-Ztg.*, 1933, **57**, 315–316.)—A description is given of Hatfield's colorimetric method (*Ind. Eng. Chem.*, 1924, **16**, 233), which depends on the formation of the coloured lake produced with soluble aluminium salts and haematoxylin in a solution buffered with ammonium carbonate. The method has been used with success in a Prussian agricultural institute, where it was found that other

metals which may occur in water, *e.g.* lead, zinc and copper, do not interfere with the test for aluminium; the interference of iron may be avoided by adding a similar quantity of it to the aluminium comparison solution. S. G. C.

Organic Analysis

Determination of Formaldehyde by means of Potassium Bromate. L. Spitzer. (*Chem.-Ztg.*, 1933, **57**, 224.)—Two grms. or 2 c.c. of the formaldehyde solution to be tested are diluted to 100 c.c. with water. To 5 c.c. of this solution, contained in a glass-stoppered flask, are added 20 c.c. of water and 25 c.c. of 0·1 *N* potassium bromate solution containing 15 grms. per litre of potassium bromide, and the mixture is acidified with hydrochloric acid. After the liberation of bromine, the solution is rendered alkaline with sodium hydroxide. The solution is kept for about 30 minutes at 20° C., to allow of the oxidation of the formaldehyde to formic acid, and it is then acidified with hydrochloric acid, when the formic acid becomes further oxidised to carbon dioxide and water. The solution is well shaken, and the excess of oxidising agent is determined by adding solid potassium iodide and titrating the liberated iodine with standard thiosulphate solution; 1 c.c. of 0·1 *N* potassium bromate is equivalent to 0·00075 grm. of formaldehyde. No test results are cited. S. G. C.

Distinction between Aldohexoses and Ketohexoses by the Resorcinol Reaction. C. Sampietro and K. Täufel. (*Z. anal. Chem.*, 1933, **92**, 241–245.)—Although subject to limitations, Seliwanow's method of detecting ketohexoses by means of resorcinol is capable of furnishing useful indications if carried out under proper conditions. It is not, however, applicable directly to material with a pronounced colour which cannot be removed beforehand. Such a case may be met by distilling the oxymethylfurfural (formed when the ketohexose is heated with acid) and condensing this with resorcinol to give the cherry-red product. Under these conditions, 1 grm. of glucose, galactose, lactose, maltose, or starch gives negative results, whereas 1·5 mgrm. of laevulose or 3·4 mgrms. of sucrose is detectable with certainty. When mixed with 100 times the weight of an aldose, 10 mgrms. of sucrose or 6 mgrms. of laevulose show a distinct coloration in this test. It is noteworthy that, when equimolecular quantities of sucrose and laevulose are tested separately, the red colour with resorcinol develops in 9 minutes with the sucrose, but only after 13 to 15 minutes with the laevulose. Thus, the laevulose obtained by hydrolysis reacts more readily than ordinary laevulose.

The procedure is as follows: A long test-tube, somewhat constricted at the lower end, is provided with a ground glass stopper, through which pass one tube almost reaching the bottom of the test-tube, and another passing just through the stopper. By means of the second tube, connection is made with an exactly similar test-tube with the same fittings and connected with a suction pump so that air may be drawn through the contents of the two test-tubes in turn. Both test-tubes are immersed in water-baths. The first is charged with the solid or liquid to be tested and with 3 c.c. of 5 per cent. hydrochloric acid solution, and the second with

2 c.c. of 1 per cent. aqueous resorcinol solution and 2 c.c. of concentrated hydrochloric acid. The first water-bath is heated to boiling-point and a rapid stream of air is passed through the apparatus. After the lapse of 5 minutes, the second water-bath is heated to 80–90° C. Within 15 minutes at most, the cherry-red coloration appears if a ketohexose is present. The test is discontinued after 20 minutes, as subsequent coloration may result from decomposition of aldoses. When a ketose is used, the residue in the first test-tube usually consists of a brown or black carbonaceous mass, whereas aldoses leave a brown or black syrup. After each test, the whole of the apparatus, especially the rubber-tube connection between the two test-tubes, must be thoroughly cleaned. T. H. P.

Volumetric Determination of Anthranilic Acid and its Salts. H. Funk and M. Ditt. (*Chem.-Ztg.*, 1933, **57**, 334.)—According to Day and Taggart (*Ind. Eng. Chem.*, 1928, **20**, 545), when anthranilic acid in hydrochloric acid solution is left in contact with excess of bromine for 30 minutes, each molecule of the acid takes up six atoms of bromine. The authors find it more convenient to titrate the acid directly with bromide-bromate solution. The anthranilic acid is dissolved in hydrochloric acid (about 4 *N*) and titrated with the standard bromide-bromate mixture in presence of an indicator prepared by dissolving 0·2 grm. of indigocarmine and 0·2 grm. of styphnic acid in 100 c.c. of water. As is usual with bromimetric determinations, it is advisable to add a further quantity of the indicator towards the end of the titration. The titration is continued, not merely to the complete precipitation of the bromo-derivative, but until the colour of the indicator changes from blue to yellow, this showing a slight excess of bromine. A few c.c. of approximately 0·2 *N* potassium iodide solution are at once added, and the liquid is then diluted and the separated iodine titrated with thiosulphate in presence of starch. With this procedure, one molecule of anthranilic acid takes up four molecules of bromine almost instantaneously, provided that the concentration of the hydrochloric acid does not exceed 1·5 *N*. One c.c. of 0·1 *N* bromate solution corresponds with 3·427 mgrms. of anthranilic acid. T. H. P.

Halogen Values of Aleurites Oils. P. Levy. (*Compt. rend.*, 1933, **196**, 549–552.)—The true iodine values of *Aleurites* oils cannot be found by the usual methods, but it has been proved that accurate results may be obtained by means of Toms's bromine-vapour method (ANALYST, 1928, **53**, 71). A sample of oil from *Aleurites fordii*, extracted in the laboratory, gave a bromine value of 145 ± 2, representing an iodine value of 231 ± 3. The result is independent of the weight of oil taken and the time of exposure. Different China wood oils gave iodine values between 228 and 234 with corresponding values for $n_D^{20°}$ ranging from 1·5132 to 1·5203. Any substitution of bromine in the molecule was ruled out by experimental evidence (absence of liberated hydrobromic acid). Oils heated at 295° C. had $n_D^{20°}$, 1·5103 and 1·5060, and iodine values (calculated from the bromine absorption) of 165 and 173, respectively, corresponding with the disappearance of one ethylene linkage in the elaeostearic group. A sample of tung oil, which had a very low refractive index ($n_D^{20°}$ 1·4956) and was suspected of being adulterated, gave a bromimetric iodine value of 181. D. G. H.

Oxycellulose and Hydrocellulose. H. A. Thomas. (*J. Soc. Chem. Ind.*, 1933, **52**, 79T.)—In the initial stages of the formation of "oxy-" and "hydro-" cellulose, the products obtained are similar in properties. The difference between the two types of degradation products is to be found in the end-groups of the chains. Typical "oxycelluloses" and "hydrocelluloses" were prepared, but the terms "carboxylic cotton-dextrin" and "aldehydic cotton-dextrin," respectively, are suggested. Both exhibit reducing properties, but the former, containing carboxyl and aldehyde groups, have a marked affinity for metals from solutions of their salts and for basic dyestuffs, with poor affinity for direct dyestuffs, whereas the latter, containing aldehyde groups only, have no affinity for metals or basic dyestuffs.

Carboxylic cotton-dextrin was prepared by immersing cotton piece for 15 minutes at 18° C. in sodium hypochlorite solution (sp.gr. 1·02) containing 0·5 per cent. of soda-ash calculated on the total weight of solution. The material was then squeezed, air-dried, washed in water, then in 0·5 per cent. sodium hypochlorite solution at 60° C., and finally in water. Aldehydic cotton-dextrin was prepared by steeping cotton piece in 5 per cent. hydrochloric or sulphuric acid for 15 minutes at 18° C. The material was squeezed, air-dried, washed in hot water, cold sodium carbonate solution (0·1 per cent.) and water. The dyeing properties of these two products were tested by immersing equal weights of each and of untreated cotton piece in the same dye-bath with representative dyestuffs of the direct, basic, sulphur, and vat classes. With direct dyes the aldehydic material had a slightly less, and the carboxylic material considerably less affinity for the dyestuffs than the cotton. With basic dyestuffs, mordanted with tannic acid and tartar-emetic, there was no difference shown by the three materials, but if dyed without mordanting the carboxylic material had much the greatest affinity for all the dyestuffs employed.

Carboxylic cotton-dextrin, in the presence of aldehyde cotton-dextrin, may be detected by reason of its affinity for metals from solutions of their salts, and this property might possibly be utilised for its determination by determining the metal absorbed. The materials are immersed in a cold 1 per cent. solution of lead acetate for 5 minutes, and then washed in several changes of warm water, followed by a 5 minutes' immersion in 1 per cent. sodium chromate solution. Cotton is tinted faintly yellow, the aldehydic material a cream, and the carboxylic a deep yellow colour. The most satisfactory test is the production of Turnbull's blue. Ten minutes' immersion in 1 per cent. ferrous sulphate solution is followed by several washings in warm water, with subsequent immersion in 1 per cent. potassium ferricyanide solution for 5 minutes. After a final washing cotton is faintly blue, and the aldehydic material still more faintly blue, whilst the carboxylic cotton dextrin is coloured a very deep blue.

If boiled in Fehling's solution for 5 minutes and then washed, cotton is tinted faintly blue, but the two cotton-dextrin materials are both stained reddish-brown. These two materials can therefore be detected in the presence of grey or raw cotton, since the latter, after being boiled for 10 minutes in a solution containing 3 grms. of Perminal KB and 5 grms. of sodium carbonate per litre, do not reduce Fehling's solution. Grey cotton has also only a slight affinity for metals.

Dyed material may be tested after stripping the dyestuff either with 0·5 per cent. sodium hydrosulphite and a little ammonia at 40° C. for 30 minutes, or with a 0·1 per cent. solution of titanous sulphate or chloride at 40° C. for 30 minutes, or with a solution of soap (1 per cent.) and sodium carbonate (0·5 per cent.) with decolorising charcoal (carboraffin) for 15 minutes at boiling point. R. F. I.

Potentiometric Titration of the Acetyl Group in Cellulose Acetates. M. Abribat. (*Ann. chim. anal.*, 1933, **15**, 145–157.)—Methods involving hydrolysis in sulphuric acid and removal of the acetic acid by steam-distillation (Ost, *Z. angew. Chem.*, 1906, **19**, 993) are unsuitable for routine work and often give erroneous results, whilst alkaline hydrolysis after Cross and Bevan, and also Eberstadt (*cf.* Battegay and Penche, *Bull. Soc. Chim.*, 1929, **45**, 132) is objectionable on account of the slow rate of reaction. Hydrolysis curves, obtained potentiometrically, for 0·5 *N* alkali and for concentrated hydrochloric acid at 20° C. show that 41 per cent. of CH_3CO is liberated after 5·75 hours in the latter case, and 39·5 per cent. after 60 hours in the former. For the determination, 2 grms. of a portion of sample which has previously been dried at 105° C. until constant in weight, are mixed well with 10 c.c. of hydrochloric acid (sp.gr. 1·19) in a flask cooled continuously in running water. The sample passes from a gel to a viscous liquid, and when its viscosity is no longer decreasing 40 c.c. of cold water are added. Hydrolysis is then allowed to continue for a period which varies from 2 to 10 hours according to the nature of the sample. The influence of the concentration of the acid is discussed, and it is concluded that the action is one of progressive depolymerisation, and occurs only when the concentration of acid exceeds a certain value. Quinhydrone is added to the mixture, which may then be linked up with a saturated calomel electrode, and titrated with sodium hydroxide solution in the usual way; an approximately 2 *N* solution may first be used to neutralise the hydrochloric acid, and a 0·5 *N* solution thereafter (*i.e.* from −390 millivolts). Neutralisation curves are given which show a distinct point of inflexion at p_H 8·5, corresponding with neutralisation of the acetic acid; in one case 37·75 per cent. of CH_3CO was found (Ost, 38·5; Eberstadt, 37·8). The method is unaffected by nitric acid (which is titrated as a strong acid), but nitrous acid is titrated with the acetic acid, and must therefore first be destroyed by means of hydrogen peroxide. Attempts to use the titration value of acetic acid plus nitrous acid as a measure of the latter were not successful. J. G.

Analysis of Cotton and Viscose Rayon Mixtures. B. P. Ridge and K. Turner. (*J. Soc. Chem. Ind.*, 1933, **52**, 86T.)—Since both cotton and viscose rayon consist of cellulose, analysis of mixtures requires special methods. The fluidity of a 0·5 per cent. solution of raw cotton in cuprammonium hydroxide has a value of 1–2, whereas a solution of viscose rayon of the same concentration has a fluidity value of 36–40 (*J. Text. Inst.*, 1928, **19**, 77). A linear relationship holds between the percentage of viscose fibre in a mixture and the logarithm of its fluidity. $P = a(\log_{10} F - b)$, where P is the percentage of viscose in the mixture, F the fluidity, and *a* and *b* are constants depending on the kind of cotton and viscose in the mixture. Points for Memphis–Vistra mixtures appear to lie on a significantly lower curve than those for Sakel, Uppers, Texas cottons, and A quality

and Vistra rayons. The method is more suitable for mixtures containing over 25 per cent. of viscose and for unbleached yarns.

An alternative method is the "hypobromite–copper number" method, which depends on the fact that viscose rayon, when oxidised by alkaline sodium hypobromite under specified conditions (*J. Text. Inst.*, 1930, **21**, 85), has a copper number more than double that for cotton similarly treated. After the standard treatment the copper number of scoured cotton is 1·5, that of trade mercerised cotton 2·2, and that of viscose rayon nearly 4. The percentage composition of a mixture of normal cotton and viscose is obtained from the equation $P=40C-60$, and for mercerised cotton and viscose $P=35C-120$, where P is the percentage of viscose, and C the observed copper number of the oxidised mixture. This method is more suitable than the above for mixtures containing small amounts of viscose and for bleached materials. Neither method is claimed to be precise, since the constants depend on the exact nature and condition of the components. The fluidity method can also be applied to mixtures of cotton and wool or silk.

R. F. I.

Influence of Ash Constituents on the Electrical Conduction of Cotton. A. C. Walker and M. H. Quell. (*J. Text. Inst.*, 1933, **24**, 123T.)—The improvements in electrical properties secured by the water-washing of cotton have led to its substitution for silk, to a large extent, in the telephone industry. Washing achieves a decrease in the inorganic ash-content of cotton from 1·0 to 0·3 per cent., and this is accompanied by a rise in the insulation resistance of 50- to 100-fold. This is termed the electrolytic improvement. A total improvement of 150- to 200-fold is secured if the washed cotton is dried under certain conditions. Washing the cotton with waters containing salts of the alkaline earths, but low in salts of the alkali metals, gives higher resistance to conduction than washing with waters containing appreciable amounts of sodium and potassium salts, or even with distilled water. If the washed cotton is oven-dried, its initially high insulation resistance is not retained if it is exposed to atmospheres of very high relative humidity.

R. F. I.

Determination of the Acetyl Content of Carbohydrate Acetates. H. L. Parsons. (*J. Text. Inst.*, 1933, **24**, 167T.)—The acetylated cellulose (0·5 grm.) of known moisture-content, is placed in a bottle provided with a stirring-rod stopper. Five c.c. of 19·5 *N* sulphuric acid (1 vol. of concentrated sulphuric acid with equal vol. of water) are added, the mixture is well stirred, and the bottle is placed in a thermostat at 30° C. for 5 hours, with occasional stirring. The mixture is transferred to a 100-c.c. round-bottomed flask, being washed in with 30 c.c. of water, and the flask is heated under a reflux condenser for 15 minutes, after which it is cooled and the contents diluted to 50 c.c. Ten c.c. of this solution are put into a 30-c.c. narrow-necked stoppered bottle, 20 c.c. of purified ether are added at 20° C., the bottle is shaken for 30 to 60 seconds, and then left in a thermostat at 20° C. for 1 hour. A 10-c.c. pipette, with a capillary tube and 3-way cock sealed to its upper end, is clamped on a stand with the bottle at such a level that the tip of the pipette is well below the surface of the ethereal layer. The ether is drawn up to the mark, the bottle is removed and replaced by a 100-c.c. conical

flask containing 20 c.c. of 75 per cent. alcohol, and the 10 c.c. of the ethereal solution are allowed to fall into it, the whole being then titrated with 0·01 *N* sodium hydroxide, with phenolphthalein as indicator. As sulphuric acid is insoluble in ether, this titration represents only acetic acid. The ether should be purified by shaking 2 litres of commercial quality with 100 c.c. of *N* sodium hydroxide solution and 80 c.c. of *N* silver nitrate solution at intervals for 24 hours, separating, and shaking with fresh solutions for 20 minutes. The separated ether is washed free from alkali, dried over potassium carbonate, and finally over powdered sodium, and fractionally distilled. It should boil between 34·5° and 35° C., and should give little or no colour with Schiff's reagent (for acetaldehyde), vanadic acid (for peroxides) or anhydrous copper sulphate (for water). Under standard conditions the acetic acid yield A is obtained from the equation $A = \frac{fV}{W}$, where f is a constant, V the volume of alkali required to neutralise the acid, and W the dry weight of acetylated cellulose taken. The mean value of f for acetic acid (yield 100 per cent.), acetylated cellulose (yield 53·4 per cent.), cellobiose octo-acetate (yield 70·81 per cent.), and glucose penta-acetate (yield 76·93 per cent.) has been found to be 1·285.

Dyed samples must be stripped by shaking with a mixture of 40 to 60 parts methylene chloride and 60 to 40 parts of benzene, usually in the cold. The solvent is allowed to evaporate spontaneously, and the residue is heated at 80° C. for 30 minutes to 1 hour. The method is very rapid and convenient. R. F. I.

Qualitative Detection of Casein in Woods. T. H. Whitehead. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 150.)—To detect the presence of casein in woods which have been treated with a soluble caseinate and formaldehyde solution, sections of the wood are soaked in water for fifteen minutes and then immersed in haematoxylin solution (haematoxylin 4 grms., 95 per cent. alcohol 25 c.c., saturated ammonium alum solution 400 c.c., glycerol 100 c.c., and methyl alcohol 100 c.c.). After two minutes the sections are removed, washed, and dried. A violet coloration is imparted to the parts of the wood where casein is present.

W. P. S.

Inorganic Analysis

Qualitative Analysis in Presence of Phosphate. T. B. Smith. (*J. Chem. Soc.*, 1933, 253–257.)—The acid solution of the mixture (1 grm.) is freed from heavy metals by hydrogen sulphide, and the iron is oxidised as usual. The solution is then treated with ammonium chloride, ammonium phosphate and ammonia to precipitate all the metals except alkalis. The precipitate is collected, and a small portion dissolved in nitric acid and tested for manganese with sodium bismuthate. The remainder is dissolved in dilute hydrochloric acid, the solution is neutralised with ammonia until a slight turbidity forms, and treated with formic acid, sodium formate, and ammonium sulphate. The precipitate formed may contain phosphates of aluminium, chromium, and iron, and sulphates of barium and strontium; it is suspended in cold water containing sodium sulphate, sodium peroxide is added, and the excess decomposed by boiling. Aluminium and

chromium go into solution; in the insoluble residue, iron is separated from the alkaline-earth sulphates by extraction with dilute sulphuric acid. The formate filtrate from the preceding sub-group is treated with hydrogen sulphide, zinc sulphide being precipitated. The filtrate is tested for calcium with ammonium oxalate. The lime-free solution may still contain (in addition to manganese) cobalt, nickel, and magnesium, which are tested for in separate portions: cobalt with nitroso-β-naphthol, nickel with dimethylglyoxime, and magnesium with titan-yellow. W. R. S.

Determination of Copper with Salicylaldoxime. S. Austin and H. L. Riley. (*J. Chem. Soc.*, 1933, 314–315.)—The high price of the reagent is a disadvantage of the method (*cf.* Ephraim, *Ber.*, 1930, **63**, 1928), but an approximately one per cent. solution can be made as follows: salicylaldehyde (2·22 grms.) is dissolved in 8 c.c. of alcohol, and the solution is added to 1·27 grm. of hydroxylamine hydrochloride dissolved in 2 c.c. of water. The liquid, after dilution with 15 c.c. of alcohol, is stirred slowly into 225 c.c. of water at 80° C.

W. R. S.

Quantitative Determination of Palladium by means of Ethylene. S. C. Ogburn, jr., and W. C. Brastow. (*J. Amer. Chem. Soc.*, 1933, **55**, 1307–1310.)—The slightly acid chloride solution is treated at 80° C. with a rapid stream of ethylene until reduction is complete and the precipitated metal coagulates. It is collected in a Gooch crucible, washed with warm water, and dried at 105° C. to constant weight. The other platinum metals are not precipitated. W. R. S.

Determination of Niobium with *o*-Hydroxyquinoline. P. Süe. (*Compt. rend.*, 1933, **196**, 1022–1024.)—An oxalate solution of niobium gives with hydroxyquinoline a lemon-yellow, microcrystalline precipitate, ignition of which yields the pentoxide. The solution of potassium niobate (0·04 grm. Nb_2O_5 in 120 to 150 c.c.) is treated with 0·5 grm. of oxalic acid and 5 c.c. of 10 per cent. ammonium acetate solution, neutralised with ammonia against phenolphthalein, and heated to 70° C. An excess of reagent (hydroxyquinoline 3 grms., alcohol 70 c.c., water 30 c.c.) is added, and the liquid is boiled for half an hour to complete the precipitation in a crystalline form. After 15 minutes' standing the precipitate is collected in a porous glass crucible, washed with 125 c.c. of warm water, and dried at 115° C. for two hours. The niobium may be determined volumetrically by Berg's method (solution in hydrochloric acid, addition of a measured excess of bromate, and back titration with thiosulphate after addition of iodide). The composition of the crystalline precipitate is given as $Nb_2O_5.5{\cdot}5(C_9H_7ON).4H_2O$, but does not appear to have been established with certainty. [No separations are described.] W. R. S.

Some Effects of the Addition of Tellurium to Lead. W. Singleton and Brimley Jones. (*Engineering*, 1933, **135**, 317–318.)—This article, which is an abridged version of a paper read before the Institute of Metals in March, 1933, gives an account of some properties of tellurium-lead, an alloy which is practically 99·9 per cent. lead with up to 0·1 per cent. of tellurium. The presence of this small proportion of tellurium affects the properties of lead in a unique manner which

would indicate important applications for this material. *Mechanical Properties.*—Tellurium-lead shows enhanced toughness as compared with ordinary lead. Thus in tensile tests carried out at very slow rates of straining (*e.g.* 0·018 inch per minute) tellurium-lead gave an ultimate stress 50 per cent. greater than ordinary lead, together with increased elongation (92·4 per cent. as compared with 51·3 per cent., on 8-inch gauge-length, for lead). The improvement is due to the fact that the work-hardening effect produced by, *e.g.* straining, is permanent at the ordinary temperature with tellurium-lead because the metal cannot self-anneal owing to the recrystallisation temperature being above the ordinary temperature, whereas the work-hardening effect in ordinary lead is very temporary as the metal is self-annealing at the ordinary temperature. In tensile tests carried out in the ordinary manner, *i.e.* with rapid straining, under which conditions the temporary strain-hardening of pure lead comes into effect, less difference between the two materials was shown, but even then the tellurium-lead had appreciably higher ultimate stress than ordinary lead (2,650 to 2,900 lbs. per sq. inch, as compared with 2,000 to 2,400 lb. per sq. inch. for lead), and a slightly greater elongation (55 to 67 per cent. as against 30 to 65 per cent., on 8-inch gauge length, for lead). When removed from the testing machine, the fractured lead test-pieces, although stiff at first, owing to the work-hardening, softened considerably within a short time, whereas those of tellurium-lead remained permanently stiff; ordinary lead lacks toughness owing to the recrystallisation which takes place at the ordinary temperature. The effects of cold-work on tellurium-lead result in toughening rather than in the brittleness usually associated with severely cold-worked metals. It would appear from the results obtained that the effect of tellurium is complete at 0·05 to 0·06 per cent. of tellurium. *Effect of Frost on Pipes.*—The ability of tellurium-lead to work-harden when strained is of considerable practical value, and indicates that pipes made from it would withstand a much greater expansion than lead pipes before commencing to weaken locally. Tests were carried out on samples of pipes of similar dimensions, made from both materials, filled with water and repeatedly frozen until bursting occurred. The ordinary-lead pipes showed marked local distension after the first freezing, and fractured during the next freezing with the formation of a large bulge. The tellurium-lead pipes were quite symmetrical after three freezings; failure occurred after five freezings, with a moderate local bulge. Hydraulic bursting tests, before and after freezing, further supported the superiority of tellurium-lead pipes. In the application of lead and lead alloys where severe deformation is to be expected, initial softness and pliability, combined with an ability to develop toughness, are desirable. *Fatigue Resistance.*—The fatigue resistance of extruded lead containing 0·05 per cent. of tellurium was determined in a Haigh fatigue-testing machine. On a basis of the range of stress which would not cause fracture after 10×10^6 reversals, the fatigue range was found to be $\pm 0{\cdot}50$ ton per sq. inch—nearly three times that of ordinary lead. *Corrosion Resistance.*—Tellurium-lead shows an increased resistance to corrosion by sulphuric acid as compared with ordinary lead. In the "flash test" of the British Standard Specification No. 334 (1928) for "chemical" lead ("flashing" signifies violent reaction with hot concentrated sulphuric acid), tellurium-lead does not "flash," and will withstand, for short periods, the action of

boiling concentrated sulphuric acid, a property not possessed by any other type of lead or lead alloy. This increased resistance to attack by sulphuric acid has been substantiated by actual exposure tests in a sulphuric acid plant, where the loss in weight of tellurium-lead was only one-seventh that of the most highly resistant "chemical" lead under the same conditions. The much-increased resistance to corrosion, combined with the mechanical strength shown by tellurium-lead, is of importance where "chemical" lead sheet, although mechanically weak, is used because of its resistance to corrosion. The manufacture of tellurium-lead is stated to present no difficulties, either in the preparation of the metal or in the processes of cold-rolling or extrusion. Tellurium is stated to confer improved properties on various alloys of lead with other metals. S. G. C.

Separation of Tantalum from Niobium by the Tannin Method. H. T. S. Britton and R. A. Robinson. (*J. Chem. Soc.*, 1933, 419–424.)—In the course of a physicochemical study of the complex acids of tantalum and niobium, electrometric investigations were applied to solutions of the oxalo-earth acids in presence of tannin under the conditions of Powell and Schoeller's separation method (ANALYST, 1932, **57**, 750). It is concluded that the control of the hydrogen ion concentration is of no service in effecting the separation (*cf.* ANALYST, 1932, **57**, 290). The need for fractional precipitation is recognised, as well as the method of controlling the operation, *i.e.* by means of the coloration of the tannin precipitates. W. R. S.

Picrolonic Acid as a Reagent for Alkali Metals. Y. Volmar and M. Leber. (*J. Pharm. Chim.*, 1933, **17**, 366–372.)—A survey has been made of the possibilities of picrolonic acid (dinitrophenylmethyl pyrazolone) as a qualitative precipitating agent for the alkali and alkaline earth metals. Solutions of the following, as chlorides, gave yellow precipitates on the addition of aqueous picrolonic acid: potassium, sodium, ammonium, barium, strontium, calcium; no precipitate was produced with lithium chloride. The limiting concentration of solution, taken as the concentration below which no precipitate was formed in half an hour after 10 drops of approximately 0·02 *N* picrolonic acid solution were added to 2 c.c. of the chloride solution, was *N*/12 for potassium chloride and *N*/9 for sodium chloride; the precipitation was found not to be favoured by the addition of alcohol or acetic acid. Comparative tests showed that picric acid is a less sensitive reagent for potassium than picrolonic acid. S. G. C.

Colorimetric Determination of Nitrates by means of Diphenylaminesulphonic Acid. I. M. Kolthoff and G. E. Noponen. (*J. Amer. Chem. Soc.*, 1933, **55**, 1448–1453.)—The cold solution (10 c.c.), which should contain 10 grms. of potassium chloride per litre, is treated with an equal volume of strong sulphuric acid from a pipette; the flask is cooled in running water, and 0·1 c.c. of a 0·006 molar solution of sodium diphenylaminesulphonate is added. A set of 10 c.c.-standards is prepared from 1 per cent. potassium chloride solution to which 0·1, 0·2, 0·3, 0·4, 0·5, 1·0, 2·0, 3·0, 4·0, 5·0 mgrm. of nitrate ion per litre as potassium nitrate has been added. The unknown solution is matched in a colorimeter against the two nearest standards, respectively stronger and weaker than the unknown.

The comparison with the two standards is repeated. The attainable accuracy is of the order of 5 per cent. Nitrites interfere, but can be eliminated by boiling with ammonium chloride; urea should not be used, as it interferes with the colour formation. W. R. S.

Volumetric Determination of Nitrates with Ferrous Sulphate as Reducing Agent. I. M. Kolthoff, E. B. Sandell, and B. Moskovitz. (*J. Amer. Chem. Soc.*, 1933, **55**, 1454–1457.)—The nitrate sample (0·1 to 0·2 grm.) is introduced into a 250-c.c. conical flask fitted with a two-holed rubber stopper, one hole carrying a medicine dropper containing 1 per cent. ammonium molybdate solution (catalyst), the other a tube for the escape of acid vapour. A 50 per cent. excess of ferrous ammonium sulphate solution and 70 c.c. of 12 *N* hydrochloric acid are introduced; sodium bicarbonate (3 to 5 grms.) is added gradually to displace the air, the stopper is inserted, and the solution boiled. After 2 to 3 minutes' boiling, the catalyst is added and boiling continued for 10 minutes. The flask is cooled in running water, unstoppered, and 35 c.c. of 6 *N* ammonium acetate and 3 to 5 c.c. of 85 per cent. phosphoric acid per 50 c.c. of solution (100 to 150 c.c.) are added. The solution is slowly titrated with 0·1 *N* dichromate, with 6 to 8 drops of diphenylamine sulphonate as indicator. The ferrous solution is standardised under the same conditions. The accuracy is given as 0·5 per cent. A few mgrms. of nitrate can be determined with an error of about 2 per cent. W. R. S.

Determination and Occurrence of Fluorides in Sea Water. T. G. Thompson and H. J. Taylor. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 87–89.)—The fluorine is determined colorimetrically by means of a reagent consisting of zirconium nitrate and sodium alizarin sulphonate. Chlorides and sulphates present in sea water interfere with the determination, but their influence is eliminated by using comparison fluoride standards containing equivalent quantities of chlorides and sulphates. The reaction between the fluoride and the reagent is accelerated by boiling, and, after cooling, the mixtures are kept for four hours before the colour comparisons are made. The fluorine content of sea water varies with the salinity, and ranges from 1·0 to 1·4 mgrm. per litre. W. P. S.

Microchemical

Isolation, Identification and Quantitative Determination of Ethyl Alcohol normally present in Human and Animal Tissues. A. O. Gettler, J. B. Niederl, and A. A. Benedetti-Pichler. (*Mikrochem.*, 1932, **11**, 167–199.)—Ethyl alcohol is isolated, identified and determined from the brain, liver and blood of abstinent humans, dogs and pigs. The average amount of ethyl alcohol present normally in the tissues analysed is as follows:—Human brain, 0·0004; human liver, 0·00256; human blood, 0·004; dog brain, 0·0003; dog liver, 0·0007; dog blood, 0·0013; and pig brain, 0·00007 per cent. The ethyl alcohol is separated by repeated fractional distillations, dried, and identified by: (1) boiling-point determinations; (2) carbon and hydrogen determination; (3) preparation of ethyl benzoate, identified by its b.pt., solubility and odour; (4) preparation of ethyl iodide, identified by its b.pt., freezing-point, solubility and analysis. *Methods.*—The

fresh tissue is frozen, ground up in 500-grm. portions and mixed with 300 c.c. of distilled water and steam-distilled, with the aid of an adapter and a receiver cooled in ice, until 500 c.c. of distillate have been collected. The distillates from three 500-grm. portions are combined, except when the total sample of tissue is too small. The alcohol is concentrated by repeated fractional distillation from distillation-flasks with condenser, flask and filling tube in one piece, the flasks have capacities 1000 c.c., 500 c.c., 100 c.c., and 60 c.c.; 40 per cent. of the volume is collected each time. It was found experimentally that when 1000 c.c. of dilute ethyl alcohol solution (0·06 per cent.) is fractionally distilled, the first 40 per cent. of the distillate being collected each time until the final volume is 5 c.c., the loss of ethyl alcohol involved is under 10 per cent. The more dilute the solution the greater is the percentage of alcohol present which comes over in the first fractions. The tissue distillate is distilled first from slightly acid solution (sulphuric acid), then from slightly alkaline solution (sodium carbonate), and, finally, from neutral solution until the volume of the distillate is 80 c.c., when it is allowed to stand a few days with freshly-prepared silver oxide to oxidise the aldehydes present, and, without filtering, is fractionally distilled again until a distillate measuring about 4 c.c. is obtained. The final distillate is then fractionally distilled in a rectification flask, shaped like a micro-Kjeldahl flask with the pear-shaped bulb of 12 c.c. volume and a narrow neck of 8 mm. diameter blown out to a bulb 2 cm. in diameter about 5 cm. above the pear-shaped bulb; above this the neck (which is 16 cm. long) is still further constricted to a diameter of 4 mm.; a further 6 cm. of the neck is bent round to a double knee-shaped bend. A small amount of zinc dust is added to prevent bumping, and the neck is carefully dried in the flame, after the addition of the liquid. The long part of the neck is then cooled with wet filter paper, and the liquid in the bulb is heated very gently. As soon as a ring of liquid passes the knee-bend the flame is removed, and the drop that collects in the second knee-bend is removed by means of a capillary tube drawn out to a fine tip. After cooling, another fraction of distillate is obtained, until in all there are 7 or 8 fractions of volumes varying from 16 to 44 c.mm. The b.pt. of the fractions, after sealing the fine tip, is taken in the capillary tubes by Emich's method (Emich–Schneider, *Microchemical Laboratory Manual*, London, 1932, p. 33). The b.pt. of the first two fractions, and also the odour, indicate that acetone is present. This is confirmed chemically. Approximately the 5th fraction from the various tissues boils at 78–79° C., showing that it is probably pure ethyl alcohol; a micro analysis of this fraction, by the Pregl method, gave 51·8 per cent. of carbon (theoretical value for ethyl alcohol 52·1 per cent.). Further ethyl alcohol from the fractions containing acetone can be prepared by fractionation in Emich's micro-fractionating tube (Emich–Schneider, *Microchemical Laboratory Manual*, London, 1932, p. 34, and Brown, in Mitchell's *Recent Advances in Analytical Chemistry*, Vol. II, p. 382). The higher boiling fractions (79°–83° C.) can be dried over calcium oxide (of slightly greater volume than the alcohol) in a bulb at the end of a narrow tube, which is sealed after the alcohol has been introduced. After 2 or 3 days the alcohol is driven from the bulb into the neck of the tube by heating to 95° C., the neck is cut off, and the alcohol is obtained pure. *Identification by Preparation of Ethyl Benzoate.* —About 10 mgrms. of fractions boiling between 77°–80° C. are placed in a glass tube

(10 cm. long and 3 mm. inner diameter) previously sealed at one end, and mixed with an equal volume of benzoyl chloride by means of a fine glass thread, and left stoppered overnight. Sodium bicarbonate (to neutralise any benzoic acid and hydrochloric acid) and a few drops of water are added, and the mixture is stirred at intervals for 6 hours, after which ether to a height of about 3 cm. is added, and, after shaking, the ethereal extract is siphoned through a capillary into another tube of the same type, and left overnight with freshly-dehydrated potassium carbonate.—The ethereal solution is then transferred to an Emich fractionating tube, drop by drop. After each addition the ether is removed by very gentle warming with an electric light bulb. Finally, the ether-free ester is fractionally distilled and redistilled, and the last three fractions are used for boiling-point determination (Emich method); the third fraction gave b.pt. 203°–212° C., whilst ethyl benzoate by the same method gave 205°–213° C. All the tissues tested gave benzoates with b.pts. within a few degrees of the value for ethyl benzoate prepared from pure ethyl alcohol. *Identification by Preparation of Ethyl Iodide.*—About 5 c.c. of the concentrated aqueous distillate from tissues, after treatment with moist silver oxide, is placed in a side-arm test-tube containing 5 grms. of anhydrous potassium carbonate. The side-arm of the test-tube is a long glass tube pulled out to a capillary tip and bent rount to fit into the side-arm of Pregl's ethoxyl apparatus. The ethoxyl apparatus is charged in the usual way with wash liquid and 1·5 c.c. of hydriodic acid; the receiver is a narrow tube immersed in a freezing mixture at −80° C. in a vacuum flask. A stream of carbon dioxide of 2 to 3 bubbles per second is passed through the apparatus, first through the side-arm test-tube, which is heated to boiling over a water-bath. The hydriodic acid is also boiled, for about 30 to 50 minutes. The distillate is purified by washing several times with water (with which it is not miscible), and each time the water is drawn off by means of a fine capillary. The b.pt. of the oil is then determined. From all tissues except the dog's brain the iodide derivative gave a b.pt. within a few degrees of that for pure ethyl iodide. The quantitative ethoxyl determinations were made by means of the usual Pregl method, except that the ethyl alcohol solution was placed, as already described, in the side-arm test-tube. J. W. B.

"Spot" Tests for some Organic Compounds. I. M. Korenman. (*J. Chem. Ind.* [*Russ.*], 1931, **8**, 508–510; *Mikrochem.*, 1932, **11**, 473–475.)—A number of macro-scale reactions of aromatic amines and aldehydes are adapted for use as "spot" tests. *Aniline* (i).—A drop of a solution of aniline salts on a filter paper moistened with saturated calcium chloride solution gives a blue-violet colour, turning red-brown, and finally disappearing. The smallest amount detectable is 1γ of aniline sulphate. If, after the blue colour has faded, the paper is held over ammonium sulphide a rose-red colour appears; 0·25γ of aniline sulphate can be detected. Benzidine, under the same conditions, gives a blue fleck; 0·02γ can be detected. Sulphanilic acid gives no colour until the paper is held over ammonium sulphide vapour, when a red coloration appears; 0·7γ can be detected. (ii) When a drop of an aniline salt solution, a drop of calcium chloride solution, and a drop of aqueous phenol are superimposed on a piece of filter paper, and the paper

is held over ammonia, the edge of the drop is flecked with blue. The reaction is sensitive to 0·75γ of aniline sulphate. Sulphanilic acid gives the same reaction, benzidine does not.

Sulphanilic Acid.—(i) A piece of filter paper is moistened with sulphanilic acid solution, with an α-naphthylamine solution in acetic acid, and then with sodium nitrite solution. A yellow-brown red-edged fleck is formed; the test is sensitive to 0·1γ and aniline does not interfere. (ii) A drop of sulphanilic acid is treated with nitrous oxide and then with α-naphtholate solution; a red fleck is formed, sensitive to 0·02γ. Aniline gives a red-brown colour.

Diphenylamine.—When a drop of an alcoholic solution of diphenylamine is treated on filter paper with a dilute sulphuric acid solution of potassium dichromate, a blue fleck is formed; the test is sensitive to 0·1γ. In the presence of aniline a dark blue or green colour appears after a few minutes. Benzidine does not interfere.

Benzidine.—(i) An acetic acid solution of benzidine is treated on filter paper with a drop of potassium dichromate; a dark blue colour is formed, sensitive to 0·05γ. Dilute mineral acids decolorise the fleck. (ii) A drop of dilute copper sulphate solution, benzidine in acetic acid, and potassium cyanide solution, give a dark blue fleck on filter paper, sensitive to 0·1γ; aniline does not interfere. (iii) Gold chloride solution gives with benzidine on filter paper a red-brown, blue-rimmed fleck; sensitive to 0·0075γ. Other amines give similar colours.

α-Naphthylamine.—A drop of the hydrochloride of α-naphthylamine in solution, mixed with solution of potassium dichromate, acidified with sulphuric acid, gives a red-violet or blue fleck; sensitive to 0·3γ of α-naphthylamine hydrochloride.. β-Naphthylamine does not interfere.

β-Naphthylamine.—Filter paper strips moistened with an alcoholic solution of β-naphthylamine hydrochloride and acetic acid, and placed in furfural vapour or in an acetic acid solution of furfural, give a violet coloration, developing slowly; sensitive to 0·3γ. α-Naphthylamine does not interfere, but aniline and benzidine give a blue colour.

Phenylhydrazine.—A drop of a saturated solution of ammonium molybdate, followed by a drop of phenylhydrazine hydrochloride on a filter paper, and held over ammonia, gives a green-blue colour; sensitive to 0·1γ.

Pyridine.—A drop of a pyridine solution, followed by a drop of aniline or aniline water, and a drop of brom-cyanide (concentrated potassium cyanide solution and bromine), when placed on filter paper, give a yellow-red colour, sensitive to 0·1γ.

Formaldehyde.—(i) Filter paper moistened with formaldehyde solution is treated with a fragment of phenylhydrazine hydrochloride and then with a drop of sodium nitroprusside solution. On adding concentrated sodium hydroxide solution a blue evanescent colour appears. In the absence of formaldehyde the reagents give a red-yellow colour; the test is sensitive to 0·1γ. Acetaldehyde does not interfere. (ii) A drop of formaldehyde solution on filter paper (free from iron and copper) is treated with powdered phenylhydrazine hydrochloride and a drop of 5 per cent. potassium ferricyanide solution and concentrated hydrochloric acid. A red-violet fleck is formed; sensitive to 0·04γ. Acetaldehyde does not interfere. (iii) A formaldehyde solution is placed on filter paper and treated with a drop of

phloroglucinol solution, and then with dilute sodium hydroxide solution. A red-brown fleck is formed; sensitive to 0·03γ.

Acetaldehyde.—When a drop of acetaldehyde solution, piperidine, and sodium nitroprusside solution are placed on filter paper, a rim of blue is formed, changing to red with alkali; sensitive to 0·4γ. Formaldehyde does not interfere. Acetone gives a light red colour.

Furfural.—When treated with a solution of aniline in 80 per cent. acetic acid (1 : 1) a blue colour is formed; sensitive to 0·05γ. The reactions with benzidine and α-naphthylamine are not so sensitive.

Vanillin.—A drop of alcoholic vanillin solution, when treated with a drop of phloroglucinol in concentrated hydrochloric acid, gives an orange fleck, turning red; sensitive to 1γ. J. W. B.

Sensitive Micro-Chemical Reaction of Picric Acid with Salts of Copper and some other Heavy Metals. I. M. Korenman. (*J. Chem. Ind.* [*Russ.*], 1931, **8**, 276; *Mikrochem.*, 1932, **11**, 473.)—Picric acid gives characteristic crystals with a number of heavy metals. The reagent is a mixture of 2 parts of a saturated aqueous solution of picric acid and 1 part of 10 per cent. ammonia. The smallest amount detectable of copper is 0·05γ, silver 20γ, nickel 0·1γ, cadmium 1γ, mercury 0·15γ, gold 0·2γ. J. W. B.

Physical Methods, Apparatus, etc.

Solar Ultra-violet Radiometry. I. Ultra-violet Limit of Sunlight. W. D. Fleming. (*Philippine J. Sci.*, 1933, **50**, 185–188.)—From solar spectrographs made at Manila in 1910, Freer and Gibbs (*ibid.*, 1910, **13**) concluded that the short wave-length limit of sunlight as it reached the earth there was 291mμ, which agreed closely with results obtained elsewhere. The following technique has now been used: The photographic emulsion is coated, before exposure, with a thin layer of mineral oil (liquid petrolatum, heavy, U.S.P.), which is washed off with carbon tetrachloride and alcohol after exposure. The plate is then rinsed in water and developed as usual. When ultra-violet light strikes the coating of oil, it causes this to fluoresce, and thus impresses the image on the emulsion.

Two exposures were made from an aeroplane at an altitude of 10,000 feet. Wave-lengths were located roughly by the wave-length scale of the instrument, photographed on the plate, and were checked by a line spectrum of mercury photographed on the plate close to the solar spectrum. The results yielded no evidence that the solar spectrum in Manila and Baguio extends further into the ultra-violet than the limit found by Freer and Gibbs. T. H. P.

Funnel-fitting for Rapid Filtration. H. Tramm. (*Chem.-Ztg.*, 1933, **57**, 225).—The fitting was designed for use with ordinary glass funnels and folded filter papers to permit of rapid filtration for quantitative purposes with the aid of suction. It is stated to offer considerable advantages in the filtration of large volumes of liquid in a short time and in filtering off gelatinous precipitates. It consists of a perforated porcelain cone with an unperforated border at the open end, there being an integral outer ring at the join of the border and the perforated

part, forming a seating for a rubber sealing ring; the cone is provided with projections near the apex to allow of it centring in a funnel. A folded filter paper is used in the cone as in a plain funnel. The funnel containing the cone is used in conjunction with an ordinary Buchner filtering flask. The funnel-fitting can be obtained in various sizes from Herren W. Feddeler, Wächtlerstr., 39, Essen-Ruhr, Germany.

S. G. C.

Reviews

CATALYSIS AND ITS INDUSTRIAL APPLICATIONS. By E. B. MAXTED, D.Sc. Pp. xii+519. London: J. & A. Churchill. 1933. Price 30s.

Whilst the complete explanation of the mechanism of heterogeneous catalytic action does not appear to be in sight, even in spite of the large volume of work carried out in the last decade, it is as well to have available from time to time an unbiased opinion on the present state of the subject. Many books on catalysis follow rather too closely the lines of Mrs. Beeton to be of any assistance to one interested in the why and how of these interesting reactions, whilst others are written from the *ex cathedra* altitudes of conviction in the correctness of some specific hypothesis. Dr. Maxted's book must be warmly welcomed as a most readable book, and, furthermore, one which will be of service to investigators, as it does contain a very fair and adequate account of the complexities and hypotheses advanced to account for surface action. It is now generally accepted that at suitably high temperatures the speed of various heterogeneous reactions of gaseous decomposition can be accounted for on the kinetic theory. At lower temperatures this is not the case, and we have to postulate some type of interaction of the gas with the solid. Examination of adsorption phenomena has revealed two quite distinctive types of adsorption; one where what are called Van der Waals forces are operative, and the other in which some electron interchange energy is involved, chemiadsorption. It appears that catalysis is associated with chemiadsorption, although certain types of electron-spin tautomeric changes, as in the ortho-para hydrogen conversion, are exceptions. It is still a moot point whether in a bimolecular surface action both reactants have to undergo the process of chemiadsorption, or if only one, *e.g.* in ethylene and hydrogen, which one is involved. Whether chemiadsorption takes place equally readily all over the surface or preferentially at certain particular spots on the surface is the next question to be asked. The evidence for the existence of particular active spots rests primarily on two experimental points—a higher heat of adsorption and a preferential adsorption of poisons. Dr. Maxted, himself, has been one of the chief experimentalists whose work goes far to show that both these experimental points are, in fact, incorrect; the heat of adsorption is constant, and the effect of poisoning is linear, at least over a wide range of the catalytic activity. How an irreversibly adsorbed poison finds the right place to condense on is again one of the world's minor problems awaiting solution. One notes a few portions in the theoretical section of the book which might well be amplified or altered in a subsequent edition: the principle that a gas striking a surface undergoes either condensation

or specular reflection without energy exchange is now no longer tenable, and one can be more dogmatic as to the different functions which promoters may play in augmenting the catalytic activity of a solid.

The volume is really an excellent one, both in substance and in style, well printed and bound—certainly a book to read.

ERIC K. RIDEAL

SÄURE-BASEN-INDICATOREN. (ACID-BASE INDICATORS.) By Dr. I. M. KOLTHOFF, with the co-operation of Dr. HARRY FISCHGOLD. 4th Ed. Pp. xi+416. Berlin: Julius Springer. Price RM. 19·80.

The present edition of Kolthoff's "Indicators" has been so completely revised that it may be regarded as an entirely new book: in fact, it now appears under a new title. Although a great deal of the previous editions (for review of English translation, see ANALYST, 1927, **52**, 254) has been incorporated, so much new material has been added that the works appear to be quite different. In one respect at least, and that is in their high standard of excellence and accuracy, however, they do resemble one another. The book is now divided into three sections: the first is called "The Dissociation of Strong and Weak Electrolytes," and includes chapters on "The reactions of acids, bases and salts," "Amphoteric substances," "The theory of the dissociation of strong electrolytes," and "The Brönsted definition of acids and bases." It is a matter for regret that the name of Lowry is not mentioned in this last chapter, the ideas discussed therein were put forward independently by him at the same time as Brönsted. The second section, on "The Properties of Acid-Base Indicators," deals with "The colour change of indicators," "The influence of the solvent on indicator properties," and "The theory of indicators." Section III of the book, which is the longest and the most important from the practical standpoint, deals with "The Colorimetric Determination of Hydrogen Ion Concentrations," and its chapter headings are "Buffer solutions," "The colorimetric determination of hydrogen ion concentrations," "Sources of error in the colorimetric method," and, finally, "Indicator papers." The book concludes with useful tables of data and complete subject- and author-indexes.

The praise which has been meted out to previous editions can, without hesitation, be extended to the new work. The subject matter is complete and up-to-date, and, for a German book, its style is exceptionally lucid. The Debye-Hückel theory of strong electrolytes and the activity concept are introduced at an early stage of the book, and ample use is made of them throughout, especially in connection with the effects of dilution on buffer solutions and the salt error of indicators. A small mistake has been noted on page 64; it is stated that A of the Debye-Hückel equation is "inversely proportional to the dielectric constant of the solvent," whereas it is, of course, inversely proportional to the 1·5th power of that constant.

Kolthoff has adopted the curious procedure of commencing Section II with the simple but inadequate theory of Ostwald for explaining the colour-change of indicators, and completes the same section with a discussion of the more modern theory based on the existence of indicators in tautomeric forms. Since both theories lead to the same final equation, although the constants have a different

significance, the treatment may be justified; in a complete book of this kind the more scientific method would be to give, at the commencement, the theory which is generally accepted at the present time, in spite of its apparent complexity.

It is hardly necessary to add that the book can be recommended without hesitation to all who are interested—and who is not?—in the use of acid-base indicators. As already implied, the German is quite readable, but for those chemists who prefer to read scientific books in their mother-tongue, it is hoped that an English translation of this new edition will not be long delayed.

S. GLASSTONE

ENTWICKELUNG UND LEISTUNGEN DER ORGANISCHEN STRUKTURLEHRE. By Dr. RUDOLF PUMMERER. Palm and Enke, Erlangen. 1931. Pp. 27. Price RM 1.

This pamphlet is an address on the "Development and Achievements of the Theory of Organic Structure," delivered by Dr. Rudolf Pummerer on the occasion of his taking over the rectorship of the University of Erlangen. He traces the development of organic chemistry from the days of Liebig and Wöhler to the present time. In doing so he quotes from Kekulé concerning the now famous ride from Islington to Clapham Common, during which Kekulé saw "spots" moving before his eyes. We are still left to surmise the cause of these spots, and are told only that their movements resulted in Kekulé's formulation of the modes of carbon linkage in organic compounds. In a very interesting way, too, the author reminds us that the "Benzene Theory" is the result of another of Kekulé's dreams.

The development of the theory of structure is traced through the work of Baeyer, Küster, Fischer and Willstätter, and finishes with an account of the evidence for the existence (momentarily at least) of the CH radical during the cracking of mineral oil. A warning is also given to Germany of the possible effects of "feverish" efforts on the part of foreign nations to become manufacturers of organic chemicals. The speech makes good reading, although little mention is made of the work of chemists who are not German.

HAROLD TOMS