THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Institute of Chemistry, Russell Square, W.C.1, at 5 p.m., on Friday, March 3rd, the President, Professor W. H. Roberts, in the chair.

Certificates were read in favour of the following candidates for Membership:—H. A. Frediani, Ph.D., B.A., M.S., and B. S. Platt, Ph.D., M.B., Ch.B.

The following were elected members of the Society:—F. C. Collins; R. Crosbie-Oates, B.Sc., F.I.C.; Professor H. E. Fierz-David; J. G. Fife, M.Sc., F.I.C.; W. C. Hughes; N. E. G. N. Iyengar; W. E. Kemp; H. C. Lockwood, B.Sc., F.I.C.; W. Marsden; F. Michel; A. H. Rheinlander, M.Sc., F.I.C.; L. W. Ruddle; J. Straub; R. G. Thin, B.Sc., F.I.C.; H. Wilkinson, B.Sc., Ph.D.; E. G. Williams, M.A., A.I.C.; F. R. Williams, Ph.D., B.Sc., A.I.C.

The Annual General Meeting of the Society then followed. The Honorary Treasurer, Dr. E. B. Hughes, presented the accounts for the year, and the Honorary Secretary, Mr. L. Eynon, presented the Report of the Council.

The following were elected as Officers and Council for the year 1939–40:

President.—Professor W. H. Roberts, M.Sc., F.I.C.

Past Presidents serving on the Council.—F. W. F. Arnaud, Bernard Dyer, John Evans, Edward Hinks, G. Roche Lynch, G. Rudd Thompson.

Vice-Presidents.—E. B. Anderson, J. R. Nicholls, W. H. Simmons, T. P. Hilditch (*Chairman, North of England Section*), T. Cockburn (*Chairman, Scottish Section*).

Hon. Treasurer.—E. B. Hughes.

Hon. Secretary.—Lewis Eynon.

Other Members of Council.—E. A. M. Bradford, R. C. Chirnside, D. C. Garratt, G. Van B. Gilmour, L. H. Lampitt, G. W. Monier-Williams, H. E. Monk, A. Scholes, W. M. Seaber, F. G. H. Tate, G. Taylor, E. Voelcker, J. B. McKean (*Hon. Secretary, Scottish Section; ex officio*), J. R. Stubbs (*Hon. Secretary, North of England Section; ex officio*).

Following the Annual General Meeting a lecture was delivered by Sir Henry Dale, C.B.E., M.D., F.R.S., on "Biological Standardisation."

The lecture will be published in THE ANALYST.

Obituary

ARTHUR SMITHELLS

ARTHUR SMITHELLS was born at Bury, Lancashire, on May 24th, 1860. The son of James Smithells, a railway manager, he was educated at the University of Glasgow; next, under Roscoe and Schorlemmer, at Owens College, Manchester, where he held a Dalton Scholarship; then, after graduating B.Sc. in the University of London, he took supplemental courses at Munich and, with Bunsen, at Heidelberg. In 1883 he was appointed assistant lecturer at Owens College, and two years later succeeded Professor T. E. (later Sir Edward) Thorpe as Professor of Chemistry in Yorkshire College, Leeds, which, in 1887, became a constituent college of the Federal Victoria University, Manchester, and in 1904 was incorporated as the University of Leeds. Having co-operated actively in all the affairs of the University, and for many years held the position of Pro-Vice-Chancellor, he retired from the Chair with the title of Emeritus Professor in 1923. Throughout his academic career he was a notable protagonist for the applications of science in the very widest sense to be given a prominent share in the science teaching in the universities. He insisted upon the part that the universities should play in the life of the community; the several departments of applied chemistry inaugurated in Leeds during the tenure of his Chair there, and the success which those departments achieved, were in no small measure due to his forceful advocacy of their incorporation in the organisation of his university. He received the degree of D.Sc. *honoris causa* from both Leeds and Manchester, and, in 1926, a Research Scholarship in his honour was founded in the former University.

He was a successful and popular teacher, having a clear and incisive delivery and remarkable experimental skill. No one realised more clearly than he did the increasing burden laid upon the students consequent upon the progress of the science. He steadily developed his department throughout his tenure of the Chair, and many of his students distinguished themselves in their subsequent careers.

From 1896 to 1899 he was Chairman of Convocation of Victoria University; in 1907, at Leicester, he was President of Section B at the seventy-seventh meeting of the British Association for the Advancement of Science, when he gave a masterly address on the subject of flame, ignition temperatures and the mechanism of luminosity, followed by a brief review of the state of chemical science at that time.

In the same year he became Honorary Educational Adviser on Home Science and Household Economics to King's College, London. In 1911 he was President of the Society of British Gas Industries, in which capacity he emphasised the importance of scientific research and exerted his influence with the industry to establish the Livesey Professorship in Coal, Gas, and Fuel Industries, in the University of Leeds. In 1912 he became a member of the Teachers' Registration Council; in 1913 and 1914 he was special lecturer in the University of the Punjab; in 1915 he was visiting lecturer in anti-gas training in the Northern Command, and from 1916 to 1919 held the rank of Lieutenant-Colonel—Chief Chemical Adviser (Anti-gas Training), G.H.Q., Home Forces—receiving, in 1918, the honour of C.M.G. in recognition of his services.

From 1923 to 1937 he was Director of the Salters' Institute of Industrial Chemistry, in which office he was mainly responsible for the selection of graduates who were provided with grants to continue their preparation for chemical industry —a post in which he was thoroughly happy.

His contributions to science related mainly to flame and spectrum analysis. He was also the author of papers, reports and addresses on educational subjects. A selection of his addresses was published in a book entitled *From a Modern University*, published by the Oxford University Press.

He was elected a Fellow of the Royal Society in 1901, and served on the Council from 1912 to 1913 and 1915 to 1917—the latter period including one year as Vice-President. He served on the Council of the Chemical Society from 1896 to 1900, was a Vice-President for three periods, 1905–1908, 1917–1920, and 1927–1930, and in 1935 was Harrison Lecturer. He was elected a Fellow of the Institute of Chemistry in 1887; he served as a Member of the Council for the periods 1890–1893, 1896–1899, and 1905–1908; as Vice-President from 1915–1917 and 1923–1926; as President, from 1927—the year in which the Institute celebrated the Jubilee of its foundation—to 1930; again as a Vice-President from 1930–1933, and as a Censor from 1927–1935.

He was elected an Honorary Member of this Society in 1927.

My first recollection of Professor Smithells goes back to May, 1892. A figure of distinguished bearing, he at once commanded my interest. He was speaking at a conference which had been called to consider the Regulations for the admission of Fellows and Associates to the Institute of Chemistry, and referred particularly to the difficulty of deciding which technical colleges and institutions should be recognised for the training of candidates for the Associateship. A previous speaker had stressed the importance of the academic attainments of the teachers, and it was perhaps characteristic of Professor Smithells that he remarked that, for his own part, he would as soon see the merits of the institutions adjudicated upon by the physical weight of the teachers as by their academic degrees!

Possessing great charm of manner and a happy fluency, his speeches at public functions were usually buoyant, encouraging and not without humour. At Council and Committee meetings he had generally something to say on any matter of interest outside the ordinary routine business, although, out of consideration for the feelings of others, he was at times perhaps too diffident in criticism. A kindly good man all through, and devoted to doing good, he was beloved by many friends, and honoured by his colleagues in the profession.

He died at Highgate on February 8th, 1939, in his 79th year.

RICHARD B. PILCHER

ARTHUR WILLIAM KNAPP

ARTHUR WILLIAM KNAPP died at the General Hospital, Birmingham, on Friday, January 6th, 1939, after an operation which followed a short illness. Born in Handsworth, Birmingham, in July, 1880, he was educated at King Edward's Grammar School, Aston, and at Mason's College, later the University of Birmingham. He graduated B.Sc. (London and Birmingham) in 1901, and M.Sc. (Birmingham) in 1928. He passed the Examination for the Associateship of the Institute of Chemistry in 1903, proceeding to the Fellowship in 1906. After a year spent as chief assistant to Mr. J. Kear Colwell, Public Analyst for Holborn, and three years in Belfast as chief assistant to Mr. R. Barklie, the Public Analyst of that city, he returned to Birmingham, where in the laboratory of the City Analyst, Mr. J. F. Liverseege, he was a colleague of Mr. H. S. Shrewsbury and, for a short time, of Dr. G. D. Elsdon. Then for a few months he was a research chemist in the laboratory of Lever Bros. at Port Sunlight, and in the autumn of 1911 he came back to Birmingham as the first research chemist to Cadbury Bros., Ltd., Bournville. At the end of 1923 he was appointed chief chemist.

Elected a Member of this Society in 1911, he was a Member of the Council in 1916. He had served, too, on the Councils of the Institute of Chemistry, of the Society of Chemical Industry, and of the British Association of Chemists, and had also been Chairman of the Birmingham Sections of these three bodies and of the Midland Chemists' Committee. His death removes a figure of international reputation from the cocoa and chocolate industry. Whilst he had carried out much research work of importance to the food industry as a whole, his knowledge of the problems of the cultivation and fermentation of cacao had made him an authority whose views on these subjects were sought by growers and manufacturers throughout the world, and gained for him, in 1935, the *Médaille de Mérite de l'Office International du Cacao et du Chocolat.* His book, entitled *Cacao Fermentation*, published in 1937, is the standard work on the subject. He was for many years a contributor to the scientific and technical press, and many papers of which he was either sole or part author have been published in the pages of THE ANALYST.

The growing knowledge of the importance of vitamins led Knapp to enquire into the vitamin D potency of chocolate products, and in 1928 he and Coward announced the fact that cacao nib had a vitamin D content of 1 International Unit per gram. This was followed in 1934 by the publication of research showing that cacao shell had a vitamin D potency of at least one-quarter that of cod-liver oil, and this led to further research into the fuller utilisation of this product in the feeding of cattle, with a view to the vitamin D enrichment of the milk and butter yielded.

He was a brilliant chemist and an inspiring chief of the chemical staff at Bournville. He was devoted to his profession and spared nothing in its service, being particularly active in support of all movements towards unification of the profession and the security of its less fortunate members.

Knapp was also a man of wide general interests. He was a member of the Fabian Society, and in his early days in Belfast had preached socialism to the dock labourers there—often at considerable personal risk. He was widely read, was

an able writer on many different subjects, a dramatist, an excellent amateur actor and dramatic producer, a clever artist and caricaturist. Of all men he was the most reserved as regards the mainspring of his own inner life and thought. He hated the sham and the false, which often aroused in him a caustic irony, but his gentle tolerance where he differed from the sincerely held views of others was a matter of envy to those of a hotter temperament.

His family life seemed to be ideal; there as elsewhere he was wise, courteous and loyal. The loss to his wife and family must be deep indeed, and we can but offer to them our sincere and respectful sympathy. J. R. JOHNSON

HARRY SILVESTER

HARRY SILVESTER died at Malvern on December 11th, 1938, in his 74th year.

He was a student for three years at Mason's College, Birmingham, under the late Professor (afterwards Sir William) Tilden. Later, at the University of Birmingham, he continued his studies under Professor Percy Frankland, and graduated B.Sc.

Meanwhile he obtained the Associateship of the Institute of Chemistry in 1887, and proceeded to the Fellowship in 1891; he served on the Council for two periods, 1917 to 1920 and 1923 to 1926. He joined our Society in 1892, and was a Member of Council in 1913 to 1914.

On leaving Mason's College, Silvester became an assistant in the laboratory of the Brymbo Iron & Steel Co., and a few years later was appointed chemist to Messrs. J. & S. Roberts, West Bromwich. About the year 1896 he established a consulting practice in Birmingham; he was mainly engaged there in metallurgical work, chiefly relating to the chemistry of iron and steel; he retired shortly before his death.

In 1894 he was appointed Public Analyst for the County Borough of West Bromwich and in 1902 Public Analyst for the County Borough of Dudley, and in 1904 he became consulting chemist to the then Oldbury District Council. He was also Gas Examiner for West Bromwich. He was a very active member of the Society of Chemical Industry, particularly of the Birmingham Section, which had his constant support. In 1899–1900 he was President of the Staffordshire Iron & Steel Institute. His reputation in the Black Country stood high.

And what of the man? Tall, well-built and of athletic tastes, he distinguished himself in games and sports; cricket, football, hockey and golf he played for many years, and played them all with more than average skill.

He was widely read, especially in scientific literature, and kept himself well up to date in all that related to analytical chemistry and in particular the chemistry of iron and steel.

Silvester and the writer were old schoolfellows, and the friendship begun in those days became closer with the passage of years and continued in intimacy to the end. He was a very genial, humorous and attractive companion and will be much missed by all who knew him.

JOHN WHITE

Annual Report of Council

MARCH, 1939

THE Roll of the Society numbers 857, an increase of 26 over the membership of last year.

The Council regrets to have to record the death of the following members:

E. R. Bolton
J. T. Dunn
H. D. Elkington
G. N. Huntly
P. H. Kirkaldy
A. W. Knapp
C. H. LaWall
H. Silvester
A. Smithells
F. W. Toms
A. Whitby

Bolton, who died at the age of 60, had been a member of the Society since 1905. He served the Society as Honorary Secretary for ten years and was subsequently elected President (1926–27), an office which he filled with high distinction. He continued to serve on the Council as a Past President until his death, and his loss both to the Council and to the Society will be deeply mourned.

Dunn, who died in his 81st year, had been a member of the Society for 33 years, and took a very active and distinguished part in its work. He was successively an Ordinary Member of the Council, Vice-President, and in 1930–31 President. As Past President he continued his service to the Council and the Society until his death. His loss is mourned by many members of the Society who knew him, and especially by members of the North of England Section (Obituary, ANALYST, 1939, **64**, 155).

Elkington, who died at the early age of 48, had been a member of the Society for 27 years. After a short experience of academic work he joined a firm of patent agents, and subsequently started practice as a chartered patent agent which he continued until his death (Obituary, ANALYST, 1938, **63**, 865).

Huntly, who died at the age of 72, had been a member of the Society since 1909. He was in practice as a consulting chemist and analyst and held appointments as Gas Examiner under a number of authorities. He served as Member of Council for two periods and was Vice-President in 1919–20 (Obituary, ANALYST, 1938, **63**, 775).

Kirkaldy, who died in his 68th year, had been a member of the Society for over 30 years and served as a Member of Council in 1917–18. He began his professional career as demonstrator at King's College, and was subsequently appointed Assistant Professor. He gave long and ungrudging services to the Institute of Chemistry as Member of Council and Hon. Treasurer (Obituary, ANALYST, 1938, **63**, 863).

Knapp, who died at the age of 58, joined the Society in 1911 and served on the Council in 1916. For many years he was Chief Chemist to Messrs. Cadbury Bros., and was an authority on cocoa and cocoa products (Obituary, ANALYST, 1939, **64**, 246).

LaWall, who died at the age of 67, was elected a member of the Society in 1911. He was engaged in practice as consulting chemist and analyst and had

been for 37 years on the staff and ultimately Dean of Pharmacy in the Philadelphia College of Pharmacy and Science. He made many contributions to pharmaceutical chemistry and for many years served on the Revision Committee of the U.S. Pharmacopoeia.

Silvester, who died at the age of 73, had been a member of the Society for 46 years. He was engaged in practice as a consulting and analytical chemist and was Public Analyst for Dudley, and he was well known as an authority on water analysis. He served on the Council of the Society in 1913–14 (Obituary, ANALYST, 1939, **64**, 247).

Smithells, an Honorary Member of the Society, died at the age of 78. He had had a very distinguished academic career and was for many years Professor of Chemistry at Leeds University. He was President of the Institute of Chemistry from 1927–30 (Obituary, ANALYST, 1939, **64**, 244).

Toms, who died at the age of 82, had been a member of the Society for 54 years. He was for 47 years Official Analyst to the States of Jersey and made many investigations on soils and fertilisers with special reference to conditions in Jersey (Obituary, ANALYST, 1938, **63**, 695).

Whitby, who died at the age of 71, was elected a member of the Society in 1910. He was engaged in practice as consulting and analytical chemist and metallurgist in Johannesburg.

During the year seven Ordinary Meetings of the Society have been held and the following papers have been communicated:

"Hair Dyes. I. The Chemistry and Analysis of Henna." By H. E. Cox, D.Sc., Ph.D., F.I.C.

"Microchemical Investigations on Siliceous Dusts." By Janet W. Matthews, Ph.D., F.I.C.

"The Gravimetric Estimation of Germanium." By G. R. Davies, B.Sc., Ph.D., and Sir Gilbert Morgan, D.Sc., LL.D., F.R.S.

"Analysis of Vinegar. Part I. Spirit, Artificial, Malt, and Distilled Malt Vinegars and their Differentiation." By F. W. Edwards, F.I.C., and H. R. Nanji, B.Sc., Ph.D., D.I.C., F.I.C.

"The Detection and Determination of Ouabain and Strophanthin." By W. D. Raymond, B.Sc., A.I.C.

"A New Colour Reagent for Lead and its Uses as an Indicator in the Titration of Various Cations and Anions." By B. S. Evans, M.C., D.Sc., F.I.C.

"A New Iodine Method for the Determination of Starch. Part V." By J. J. Chinoy, M.Sc., Ph.D., F.I.C.

"The Determination of Cobalt in Animal Tissues." By K. J. NcNaught.

"The Determination of Nitrogen in Mixed Fertilisers containing Nitrates and Chlorides." By Bernard Dyer, D.Sc., F.I.C., and J. Hubert Hamence, Ph.D., M.Sc., F.I.C.

"The Determination of Acid in Wool." By J. Barritt, B.Sc., A.I.C., H. H. Bowen, F. L. Goodall and A. Whitehead.

"The Vitamin-A and -D Contents of Butter. II. Seasonal Variation." By H. Wilkinson, B.Sc., Ph.D.

"Cacao Shell in Cocoa and Cacao Products." By H. C. Lockwood, B.Sc., F.I.C.

"The Selective Oxidation of Animal and Vegetable Fats: A new Constant." By W. A. Alexander, B.Sc., A.I.C.

"The Estimation of the Essential Oils of White and Brown Mustards." By R. C. Terry, M.Sc., A.I.C., and J. W. Corran, Ph.D., F.I.C.

"The Electrolytic Determination of Bismuth." By F. G. Kny-Jones, M.Sc.

The February meeting was a joint meeting with the Food Group of the Society of Chemical Industry, at which the following contributions were given on the

subject of The Analysis and Differentiation of the Composition of Iron, Phosphorus and Calcium Compounds in respect of Nutritional Requirements.

General Introduction by Professor J. C. Drummond, M.C., D.Sc., F.I.C.
Iron Compounds by R. A. McCance, M.A., Ph.D., M.D., M.R.C.P., M.R.C.S.
Phosphorus Compounds by Professor H. D. Kay, O.B.E., D.Sc.
Calcium Compounds by Professor E. C. Dodds, M.V.O., D.Sc., M.D., F.R.C.P., and J. D. Robertson, M.D., Ch.B., D.P.H.

THE ANALYST.—During the year THE ANALYST continued its forward progress; it contained 919 pages as compared with 914 in 1937. Forty-six papers were published, and these can be classified into 14 on food and drugs, 11 relating to organic chemistry, 15 on inorganic and metallurgical subjects, 2 on water analysis, and 5 on subjects relating to toxicology, including the masterly survey of certain narcotic drugs given by the outgoing President (Dr. Roche Lynch) in his Address. These figures show that the journal is being increasingly used as the scientific medium for papers on inorganic analysis. An outstanding instance was the publication, for the Department of Scientific and Industrial Research, of the paper by Sir Gilbert Morgan and Dr. G. R. Davies on the gravimetric determination of germanium.

Twenty-five notes on analytical and kindred subjects were published, and here again the range was wide, for the notes can be classified into 9 on food and drugs, 8 organic, 6 inorganic, and 2 on physical subjects.

As in former years, the Dominion Analysts have sent their reports and useful material has been abstracted from these. Reports have also been received from State Departments and Experimental Stations in the United States, and the Editor has received letters from the chemists of these Departments thanking the Society for the notice given to them.

HON. TREASURER'S REPORT.—The Hon. Treasurer reports that the financial position of the Society continues to be satisfactory, income more than balancing expenditure.

VISIT TO SOUTH EASTERN AGRICULTURAL COLLEGE, WYE, KENT.—On Friday, June 10th, members of the Society visited the South Eastern Agricultural College, by kind invitation of the Principal. A tour of the College premises and grounds was made, the objects of interest including the Dairy Herd, the Veterinary Research Laboratory, Commercial Poultry Plant, Pig Husbandry Research Station, Commercial Horticultural Section and the College buildings.

FOOD AND DRUGS BILL (now the Food and Drugs Act, 1938).—The President, Mr. F. W. F. Arnaud and Dr. H. E. Cox represented the Society at the meetings of the Joint Select Committee of the Houses of Parliament. Some important alterations were made in the Bill at the request of the representatives of the Society and are now embodied in the new Act.

AIR RAID PRECAUTIONS.—At the request of the Air Raid Precautions Department of the Home Office, a provisional Memorandum on Gas Detection and Identification Service was submitted to careful consideration by the Council, and a Report on the utilisation of the services of chemists in this connection was sent to the Home Office.

CONGRATULATIONS.—The Council has congratulated Dr. C. A. Seyler on the conferment of the D.Sc. degree (*honoris causa*) by the University of Wales.

ANALYTICAL METHODS COMMITTEE.—Although no reports have been published by the Committee during the year, substantial progress has been made in the work of some of its Sub-Committees, enabling reports to be drafted, the early publication of which may be expected.

A new Sub-Committee has been appointed, under the chairmanship of Professor T. P. Hilditch, to consider the standardisation of a Method for the Determination of Unpolymerisable Matter in Oils with especial reference to Tung Oil.

The Committee has to deplore the loss by death of Mr. G. Nevill Huntly. As his successor on the Committee, the Council has appointed Dr. A. D. Mitchell.

ANALYTICAL INVESTIGATION SCHEME.—One paper, "The Analysis of Vinegar, Part I," by F. W. Edwards and H. R. Nanji, has been published in THE ANALYST, 1938, **63**, 410, and there are three subjects now under investigation.

NORTH OF ENGLAND SECTION.—Five meetings have been held during the year. Eight papers have been read and one discussion held.

"The Chemical Analysis and Physical Testing of Refractories." By W. J. Rees, M.Sc., F.I.C.

"A Note on Nigerian Ginger." By P. H. Jones, F.I.C.

"The Determination of Mercury with Special Reference to some Pharmaceutical Preparations." By H. Brindle, B.Sc., F.I.C., and C. E. Waterhouse, A.I.C.

"The Estimation of Vitamins and Hormones." By R. A. Morton, Ph.D., D.Sc., F.I.C.

"A Note on the Behaviour of Rice Bran." By C. Loudon, B.Sc., F.I.C., and F. L. Kinsella.

"A Convenient Method of Estimating the Hydrocyanic Acid Generated by Linseed Cake." By C. Loudon, B.Sc., F.I.C., and H. Antrobus.

"On the Composition and Analysis of Hair Dyes." By H. E. Cox, D.Sc., Ph.D., F.I.C.

Discussion introduced by the President (Prof. W. H. Roberts, M.Sc., F.I.C.) on "The Food and Drugs Act, 1938."

The Annual Address by the Chairman (Professor T. P. Hilditch, D.Sc., F.I.C.) on "Speed Limits in Analytical Matters."

Attendances at meetings have been maintained up to the standard of previous years. The President has attended several meetings.

The ninth Summer Meeting, held at Scarborough in June, was very successful. Dr. G. Roche Lynch gave the paper. There was a very good attendance and the meeting afforded many opportunities for members to fraternise.

Nine candidates have applied for membership of the Parent Society through the Section.

One hundred and five subscriptions have been paid for the year, an increase of seven on the highest previous year.

The Honorary Secretary acknowledges with thanks the support of the Chairman, Officers and Members of the Committee in the working of the Section throughout another year.

SCOTTISH SECTION.—Three meetings were held in the year, at which the following papers by members of the Section were read and discussed:

"The Bakery Chemist's Point of View." By H. C. Moir, B.Sc., A.I.C.

"The Manufacture of Condensed Milk." By G. R. Howat, B.Sc., Ph.D.

"The Proportion of Copper present in Tomato Purée." By T. Cockburn, F.I.C., and M. Herd, B.Sc., F.I.C.

"The Estimation of the Organic Acids and Protein Decomposition Products in Silage." By A. M. Smith, Ph.D., D.Sc.

"The Estimation of Small Quantities of Gold in Urine." By A. R. Jamieson, B.Sc., F.I.C., and R. S. Watson, A.I.C.

"The Determination of Alumina in Water." By R. T. Thomson, F.I.C.

Thirty-nine subscriptions were received, an increase of five over the previous year. Eight new members joined the Parent Society through the Section and two members resigned on taking up residence outside the Scottish area.

With the passing of the Food and Drugs Act, 1938, which applies mainly to England, the Chairman and Hon. Secretary, on behalf of the Section, and with the consent of the Council of the Parent Society, addressed a letter to the Department of Health for Scotland, requesting that a similar Food and Drugs Bill be drafted for Scotland.

CONGRESSES, ETC.

Tenth International Congress of Chemistry, Rome, 1938.—The Society was represented by the President with Mr. A. H. Bennett, Dr. J. J. Fox, Dr. L. H. Lampitt, and Sir R. Robertson.

Royal Sanitary Institute Congress, Portsmouth, 1938.—The Society was represented by Mr. F. W. F. Arnaud and Mr. R. P. Page.

Rubber Technology Conference, London, 1938.—The Society was represented by Dr. P. Schidrowitz.

The Council desires to record its thanks to the members of the Society who have served on the Committees and Sub-Committees and to those who have represented the Society on other bodies.

W. H. ROBERTS, *President*
LEWIS EYNON, *Hon. Secretary*

The Practical Treatment of Dairy Effluents

BY C. A. SCARLETT, B.Sc., A.K.C., F.I.C.

(*Read at the Meeting of the North of England Section, December* 11, 1937)

THE question of the treatment of dairy effluents is one that has come very much to the fore in recent years, and a survey of the literature on the subject indicates that many attempts have been made to find a solution to this problem. Barritt[1] refers to an excellent summary of these methods by McDowall. They include among others:—(1) Land seepage. (2) Sedimentation. (3) Chemical precipitation. (4) Filtration through sand. (5) Biological treatment in septic tanks. (6) Biological treatment in contact beds. (7) Biological treatment on percolating filters. (8) Biological oxidation by the activated sludge process. (9) Various combinations of these processes.

The most common methods employed at milk factories in this country appear to involve preliminary treatment in tanks under aerobic or anaerobic conditions, followed by some kind of filtration through sand or coke or over biological filters.

Methods involving anaerobic conditions usually result in complaints due to the highly objectionable odours arising from the scum of decomposing fat and protein matter that forms on the surface of the holding tanks and filters. To overcome this trouble chlorine is sometimes added, but this usually results in the plant becoming practically sterile and useless as a purifying agent, the waste liquor passing through it with very little change except for mere mechanical filtration and subsequently creating a nuisance by polluting the brook or stream into which it flows.

In an attempt to remedy this difficulty of the formation of a scum on tanks

and filters, the holding period is sometimes reduced to a minimum, the tank merely acting as a balancing tank to give a constant supply of liquid to the filters. Two filters are then used in series and connected so that either can be a primary or secondary. When clogging and ponding occur on the primary filter, owing to deposition of protein and fat, the order of filtration is reversed, the primary filter becoming the secondary and receiving partially purified liquor which oxidises the scum on its surface. This method depends for its success on the provision of a plant of adequate capacity to deal with the volume of waste produced, so that the oxidation of the scum can be completed before fresh deposits are built up on the primary bed. A further objection to this method of alternating filtration may be that a primary bed which has developed its own organisms to deal with a liquid of a certain strength is suddenly called upon to purify a much weaker or stronger liquid, as the case may be, a procedure which might disturb the bacterial and other life in the bed and so upset its purifying capacity until the organisms have adapted themselves to the new conditions.

When sand filtration or land seepage is employed, clogging eventually occurs, owing to deposition of protein and fat, and fresh areas have to be provided until the original areas recover. In those plants working under aerobic conditions, it is essential that the sludge be removed daily in order to prevent its anaerobic decomposition during periods of settling, otherwise the odour may become a nuisance.

When the waste liquors are treated by the activated sludge process there are at least two methods of achieving aeration. In the Kessener method described by Rudolf,[2] lime is added to neutralise any acidity present and aeration is obtained by means of revolving brushes. Effluents of good quality are reported to have been produced by this process.

In the activated sludge plant at Ellesmere[3] aeration is obtained by blowing air through porous plates and the crude liquors are diluted with purified effluent before treatment. Strict control of working conditions is essential if satisfactory results are to be obtained by this method.

In this paper a method of treatment is described, based on storage of the waste liquors under controlled conditions during which fermentation occurs, with separation of fat and casein, sedimentation of the separated material and biochemical treatment of the clear supernatant liquor on percolating filters.

The waste liquors from a milk depot engaged in brine cooling, pasteurising and sterilising milk, butter-making, cream-bottling and condensing, will consist of a dilute solution of milk slightly alkaline in character by reason of the detergents used in washing down and cleaning of the plant, and containing more or less sucrose according to the amount of sweetened milk produced. The amount of milk in these wastes varies, but it usually lies between 0·5 and 2 per cent., being on the average under 1 per cent. If such a liquid is stored its pH will change, owing to fermentation of the lactose, the rate of change depending on the temperature of the liquid, and the amount of change on the quantity of alkali present.

Our own experiments on the fermentation of 1 per cent. milk solutions of varying pH under different conditions of temperature and aeration, together with the published results of other workers making similar experiments, lead to the following conclusions:

At about 4° C. the liquid is quite stable and no fermentation occurs for days.[4] At about 10° C. fermentation soon sets in and reaches a maximum between 25° and 35° C., ceasing again between 45° and 50° C.

The lactic acid bacilli chiefly responsible for this fermentation are facultative, *i.e.* they will grow under either aerobic or anaerobic conditions. Under anaerobic conditions other changes occur including proteolysis, and the decomposition products include substances of highly disagreeable odour, such as nitrogen bases of the indole or skatole types, which are objectionable in the vicinity of a dairy.

If the *p*H falls to 4·5 practically all the casein separates out, taking the fat with it,[5] and the fermented liquor can be kept for a further period under anaerobic conditions without appreciable change. If the *p*H is about 5·5 most of the fat but less protein separates, and if the liquid is stored for a further period the *p*H may increase and some of the precipitated protein may redissolve.

The Biological Oxygen Demand (B.O.D.), or dissolved oxygen absorbed in 5 days at 65° F., of the clear fermented liquor is lower than that of the original liquid, but if the *p*H increases and protein redissolves the B.O.D. will increase. There is thus no advantage in holding the liquid for too long a period if it is to undergo biological treatment later. Also, from the practical point of view, the shorter the period during which the liquid is held, the less chance there will be of protein decomposition, with the formation of nauseating odours. Continuous aeration of the liquid will prevent this protein decomposition to a certain extent, as it is essentially an anaerobic process. Intermittent aeration, however, will permit the formation of protein decomposition products when the aeration is stopped, and, on re-starting, the objectionable gases produced will be discharged.

Under proper conditions of aeration and temperature control, it was found that fermentation of a 1 per cent. milk solution was complete in less than 24 hours, and the separated solids showed no tendency to form a scum but rapidly fell to the bottom of the tank when aeration was stopped, the supernatant liquid being practically clear and containing only traces of suspended matter. This clear supernatant liquor can be run over percolating filters at a rate not exceeding 100 gallons per cubic yard per day,[5] with the production of an effluent that will have a B.O.D. less than 2. The filter is not likely to become clogged as there is nothing in the liquor to separate, the casein having already been removed.

The temperature at which the required changes were brought about in the shortest time was found to be about 30° C. and the best condition was that of continuous aeration or agitation to prevent the formation of a surface scum.

The plant required to treat a dairy waste on these lines consists essentially of a tank large enough to hold a day's output of effluent and supplied with the necessary equipment to hold the contents at the required temperature and to keep them in a state of constant agitation, together with percolating filter beds of sufficient capacity to deal with the volume of effluent produced.

Fig. 1 represents a diagrammatic flow sheet of the plant of which the following is a description:—A is a common collecting tank to which all drains are led. It is well sloped at the bottom, being 12 ft. deep at the centre and 10 ft. at the sides. It can hold about 2000 galls. and is provided with two automatic non-clog type pumps which pump the effluent into the holding or balance tank.

The effluent before entering this collecting tank passes through a strainer, B, of the basket type, which removes paper, matches and other larger sized material of similar nature. This strainer can be hauled up by means of lifting tackle for cleaning purposes.

The holding or fermentation tanks, C, are funnel-shaped and two in number. Each holds over 30,000 galls. or one day's supply of effluent. The top portion is approximately 20 ft. square and 10 ft. deep, and the funnel portion 10 ft. deep at the centre. These tanks are fitted with pipes, H, for blowing in air, and a steam-coil, J, about half-way down the funnel. There is an outlet, K, at the bottom of each tank for running off the sludge and a pipe through which any remaining liquor is returned to the collecting tank, A. Three outlets are provided for tapping off the liquid, one 7 ft. from the bottom of the funnel, another 5 ft. above this, and the third 5 ft. above the second. These allow the liquid to be run off as soon as possible, so that there is no necessity to wait until the suspended matter has settled to the bottom of the tank.

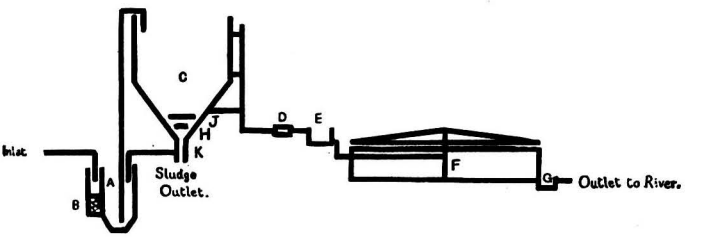

Fig. 1

From the fermentation tank the effluent passes through one of a pair of strainers, D. These consist of perforated cylinders of metal enclosed in cylindrical mats of coconut fibre, like large extraction thimbles. Any light suspended matter remaining in the liquid is removed during passage through these strainers.

From the strainer the liquid enters the syphon, which provides an intermittent flow over the beds, and consists of a small iron tank which has a capacity of about 225 galls., the inlet pipe being fitted with a valve controlled by a ball-cock.

The two filter beds, F, are 36 ft. in diameter and 6 ft. deep, and they work in parallel. The total volume of filtering medium is 452 cubic yards, which at a rate of 4 galls. per cubic yard per hour gives a filtering time of 16 hours for 30,000 galls. In actual practice the rate has always been higher than this, the day's supply of effluent usually being filtered in about 11 hours. The final effluent from the filters passes into a small sump, G, used as a sampling chamber and then through a 9-inch pipe to the stream, which it enters at the overflow of a dam about 100 yards lower down, so that excellent mixing with the river water is obtained. Room has been left for the installation of grit and detritus tanks if they are required.

The working of the plant is as follows:—The mixed effluent, after rough screening by passing through the basket filter, enters the collecting tank and is pumped into one of the fermentation tanks. Each of these holds a day's supply of effluent, so that, under working conditions, one tank is being filled while the

other is emptying. The pumps are automatic and the timing is so arranged that the collecting tank is kept as empty as possible to prevent the occurrence of decomposition and fermentation in it. In the fermentation tank aeration is continuous by means of a compressor blowing air through the perforated pipes and the steam-coil is automatically controlled to maintain the temperature at 30° C. On the following morning the steam and air are cut off, and the separated material quickly settles to the bottom of the tank. The practically clear supernatant liquor is then allowed to flow to the syphon, which has a working cycle of 10 minutes, being filled in four minutes and emptied in six. In this time approximately 400 galls. of effluent are passed over the beds, although the capacity of the syphon is only 225 galls. This is due to the fact that as the level of the liquid drops, the ball-cock falls and opens the valve on the inlet pipe, thus allowing more effluent to enter. As the outlet from the syphon is, however, larger than the inlet, the level of the liquid continues to fall until a certain point is reached when the outlet automatically closes and the syphon refills.

When the level of the liquid in the fermentation tank has dropped to that of the bottom tapping, about 3000 galls. are left. This contains the sludge which at the present time is run off into churns and spread on the land. Owing to the settling that has occurred, the whole of the sludge is removed in 3 to 4 churns, each of 17 galls. capacity. The remaining liquid is run off into the collecting tank and pumped up into the other fermentation tank, thereby "seeding" it to a certain extent.

The empty fermentation tank, the collecting tank and all pipe lines are washed down daily, and the whole plant is kept in as clean a state as possible. As a result of this there has been no nuisance from the odour of decomposing protein. The volume of effluent passing over the filters is about 30,000 galls. per day. At this rate a liquid with an average B.O.D. of 40 gives an effluent with a B.O.D. less than 1.

In the experiments carried out at Ellesmere by the Water Pollution Research Board during the period of August, 1935, to March, 1936,[3] the milk wastes leaving the primary sedimentation tank had an average B.O.D. of 70, and were diluted with about 4 times their volume of purified effluent to reduce the B.O.D. to about 20 before filtering at a rate of 80 galls. per cubic yard per day. The average B.O.D. of the final effluent was 0·7. This method of diluting the tank liquor to reduce its B.O.D. would be extremely uneconomical in practice, as it involves filtering 5 times as much liquid as the dairy produces daily in effluent. In later experiments the rate of flow was increased to 120 galls. per cubic yard of filtering medium per day without any deterioration in the quality of the effluent being observed.[3] Even when the rate was increased to 160 galls. per cubic yard per day there appeared to be little change in the quality of the final effluent.

However, even this high rate of flow only represents the equivalent of 32 galls. per cubic yard per day, based on the original effluent, owing to the dilution that has taken place, compared with the 130 galls. per cubic yard per day used in the plant here described.

Typical results obtained on our tank liquors, before and after aeration, and on the final effluent are shown in Table I. (The methods of analysis used are those recommended by the Ministry of Health in their 1929 issue of *Methods of Chemical*

Analysis as Applied to Sewage and Sewage Effluents, except for nitrates, for which the method employed was a modification of that suggested by Vey,[6] depending on the formation of 5-nitro-2.4-xylen-1-ol, which is volatile in steam and gives a highly coloured solution in dilute sodium hydroxide). The degree of purification obtained is shown as a percentage based on the B.O.D. The figures in brackets are calculated on the original crude liquor and indicate a purification of at least 99 per cent. The figures given for the "strength" of the various liquors are calculated from McGowan's formula: (Ammon. + organic N) × 4·5 + (Oxygen absorbed in 4 hours × 10·4). They are, of course, only approximate, but are introduced to illustrate how purification proceeds.

TABLE I

TYPICAL ANALYSES OF TANK LIQUORS AND EFFLUENT

No.:	Crude tank liquor M5012	Aerated tank liquor M5013	Final effluent M5014	Crude tank liquor M4350	Aerated tank liquor M4351	Final effluent M4352	Crude tank liquor M5714	Aerated tank liquor M5766	Final effluent M5767
Suspended solids ..	39	7·5	2·5	46	4	3	23	4	2·5
Organic suspended solids	33	6·5	1·5	43	3·5	3	19·5	3·5	2·5
Total solids	148	92	64	158	92	64	104	64	52
Loss on ignition of total solids	90	40	10	100	40	10	60	20	8
Mineral ash	58	52	54	58	52	54	44	44	44
Dissolved solids ..	109	84·5	61·5	112	88	61	81	60	49·5
B.O.D. dissolved oxygen absorbed in 5 days ..	77	41	0·92	80	37	0·68	41	13	0·24
Saline ammonia ..	0·03	1·08	0·002	0·06	0·43	0·003	0·028	0·42	0·006
Albuminoid ammonia	1·8	0·72	0·11	1·9	0·8	0·16	1·04	0·42	0·12
Nitrous nitrogen ..	nil	nil	nil	nil	nil	nil	nil	nil	nil
Nitric nitrogen ..	nil	nil	0·44	nil	nil	0·38	nil	nil	0·63
Combined chlorine ..	3·7	3·7	4·6	7·0	7·0	6·1	3·3	3·3	3·0
Oxygen absorbed from $N/80$ $KMnO_4$,									
in 3 minutes ..	1·8	1·18	0·12	—	—	—	1·22	0·64	0·10
in 4 hours ..	6·9	2·65	0·34	6·4	2·25	0·41	4·25	1·55	0·31
*p*H	6·4	6·6	8·3	6·0	6·6	8·3	6·3	6·8	8·1
Total nitrogen ..	4·37	2·6	0·59	3·89	1·75	0·63	—	—	—
Organic nitrogen ..	4·35	1·71	0·15	3·84	1·4	0·25	—	—	—
Strength	91	39	4	84	31	5	—	—	—
Percentage purification based on B.O.D. of:									
(1) Aerated tank liquor	—	—	98	—	—	98	—	—	98
(2) Crude tank liquor	—	(46)	(99)	—	(53)	(99)	—	(68)	(99)

Results expressed in parts per 100,000 except where otherwise stated.

As the tank liquor after aeration has had most of its suspended solids removed by sedimentation in the fermentation tank, it was thought that it might be interesting to observe the effect produced by filtering the crude tank liquor through paper and comparing the analysis of the filtrate with that of the aerated liquor.

Table II shows some of the results obtained. From these it would appear that in this particular instance, simple removal of the suspended solids of the crude tank liquor produced 30 per cent. purification based on the B.O.D., whereas aeration and sedimentation produced 37 per cent. purification on the same basis. The removal of the 3 parts of suspended solids remaining in the aerated liquor by filtration through paper resulted in a liquid showing 53 per cent. purification based on the B.O.D. of the original crude tank liquor.

TABLE II

TABLE SHOWING THE PURIFICATION EFFECTED BY FILTERING THE TANK LIQUORS

No.:	Tank liquor M5504	Tank liquor after filtering in Lab. M5504	Tank liquor after aeration M5518	Aerated tank liquor after filtering in Lab. M5518	Final effluent M5519
Suspended solids	17	nil	3	nil	2
Organic suspended solids	14·5	—	2·5	—	—
Total solids	128	—	82	—	54
Loss on ignition of total solids	82	—	38	—	10
Mineral ash	46	—	44	—	44
Dissolved solids	111	—	79	—	42
Dissolved oxygen absorbed in 5 days, B.O.D.	56	39	35	26	0·78
Saline ammonia	0·050	0·046	0·45	0·42	0·002
Albuminoid ammonia	1·44	0·88	0·64	0·48	0·13
Nitrous nitrogen	present	present	absent	absent	absent
Nitric nitrogen	absent	absent	absent	absent	0·6
Combined chlorine	4·2	4·2	4·1	4·1	3·8
Oxygen taken up from $N/80$ $KMnO_4$ in:					
(1) 3 minutes	1·32	0·98	0·96	0·74	0·12
(2) 4 hours	3·9	2·9	3·75	2·93	0·35
Total nitrogen	3·35	2·56	1·85	1·32	0·76
Organic nitrogen	3·31	2·48	1·48	0·97	0·16
Strength	56	42	47	36	4
*p*H	6·9	—	6·3	—	—
Percentage purification based on B.O.D. of:					
(1) Aerated tank liquor	—	—	—	25	98
(2) Crude tank liquor	—	(30)	(37)	(53)	(99)

Results expressed in parts per 100,000 except where otherwise stated.

Aeration and effective removal of suspended solids appear to account for half the purification effected on the basis of the B.O.D., but only about 25 per cent. on the permanganate figures.

The effect of the aeration is shown more clearly by comparing the two paper-filtered samples. There is a drop in the total nitrogen, albuminoid ammonia and B.O.D. figures and an increase in the saline ammonia, indicating that the process does bring about some improvement in the quality of the liquid.

TABLE III

FINAL EFFLUENT BEFORE AND AFTER FILTERING IN LABORATORY

No.:	Before M3449	After M3449	Before M3765	After M3765
Suspended solids	5	nil	3	nil
Total solids	74	68	70	66
Loss on ignition of total solids	14	8	12	10
Dissolved oxygen absorbed in 5 days, B.O.D.	0·51	0·22	0·90	0·63
Saline ammonia	0·010	0·011	0·013	0·013
Albuminoid ammonia	0·21	0·056	0·16	0·068
Oxygen taken up from $N/80$ $KMnO_4$ in 4 hours	0·45	0·24	0·36	0·23
Percentage purification based on B.O.D. of crude tank liquor	98	99·2	96	97·5

Results expressed in parts per 100,000 except where otherwise stated.

On several occasions the final effluent was found to contain more than 3 parts of suspended solids per 100,000. This was obviously due to the absence of a humus tank large enough to give efficient settling.

Table III shows the effect of removing these suspended solids in the final effluent by filtration through paper. The albuminoid ammonia is reduced by about 60 per cent. and the B.O.D. and oxygen absorbed from permanganate by about 30 per cent. The provision of a humus tank of at least 4 hours' holding capacity would, therefore, bring about considerable further improvement in the quality of the effluent.

After the plant had been working for about eight months the rate of flow was increased and Table IV shows the effect of this on the beds and on the quality of the final effluent.

TABLE IV

VARIATIONS IN FINAL EFFLUENT DUE TO INCREASING THE RATE OF FLOW OVER THE FILTER BEDS

No.:	M7317	M8478	M8523	M8828	M9147	M9497	M9498	N211 (80)	N308 (128)	N664 (24)	N1917 (36)	N4917 (37)
Suspended solids ..	3·6	3	2·5	2·5	3·5	11	7	10·5	14·5	5	2·5	4
Dissolved oxygen absorbed in 5 days,								(165)	(170)	(105)	(90)	(80)
B.O.D.	0·5	0·5	0·35	1·3	1·4	4·3	2·2	5·3	3·1	1·5	0·52	0·9
Saline ammonia ..	0·001	0·013	0·018	0·32	0·035	0·2	0·011	0·11	0·066	0·048	0·016	0·007
Albuminoid ammonia	0·112	0·088	0·096	0·18	0·19	0·45	0·35	0·50	0·52	0·19	0·096	0·018
Nitrous nitrogen ..	abs.	abs.	abs.	pres.	pres.	abs.	abs.	abs.	pres.	pres.	pres.	abs.
Nitric nitrogen ..	0·65	0·27	0·18	0·57	0·25	abs.	abs.	abs.	0·63	1·7	1·4	0·63
Oxygen taken up from $N/80$ $KMnO_4$ in: (1) 3 mins. ..	0·11	0·088	—	—	—	—	—	—	—	—	—	—
(2) 4 hrs. ..	0·13	0·26	—	—	—	—	—	—	—	—	—	—
Percentage purification based on B.O.D. of crude tank liquor	99	—	—	—	—	—	—	96	98	98·7	99	99
*p*H	8·0	8·1	8·0	7·4	7·6	7·6	7·6	7·7	7·9	7·8	8·0	8·1

Figures in brackets refer to corresponding crude tank liquor.
Results expressed in parts per 100,000 except where otherwise stated.

The main points noticeable are:

(1) A considerable increase in the amount of suspended solids. (When the rate was about double that normally used, much of this appeared to be inorganic, indicating the possibility of erosion of the filtering medium.) (2) An increase in the albuminoid ammonia and B.O.D. (3) A decrease in the amount of nitrates produced. These eventually disappeared when the rate was double that normally used. (4) A drop in the *p*H.

All these results indicate a considerable falling off in the ability of the beds to purify the volume of effluent passing through them. The maximum rate reached was about 250 galls. per cubic yard per day, compared with a normal rate of 130 galls. per cubic yard per day. On reducing the rate to its normal figure the beds rapidly recovered, and the analysis of the final effluent went back to normal.

Table V shows some analyses of the river water before and after the erection of the effluent plant. The first two columns show the condition of the river before

and after receiving the crude waste without treatment. Note the increased values for B.O.D., albuminoid ammonia and oxygen absorbed from $N/80$ $KMnO_4$, all of which indicate the adverse effect produced on the stream.

TABLE V

No.:	River water above dairy J3479	River water below dairy J3480	River water above dairy M462	River water below dairy M4103	River water below dairy M4644	River water below dairy N5456
Suspended solids	0·4	2·0	1·0	1·0	0·5	0·5
Total solids	41	44	34	33	—	—
Dissolved oxygen absorbed in 5 days, B.O.D.	0·17	0·51	0·24	0·32	0·16	0·2
Saline ammonia	0·046	0·022	0·068	0·066	0·014	0·015
Albuminoid ammonia	0·02	0·036	0·029	0·026	0·021	0·019
Nitrous nitrogen	trace	trace	absent	absent	present	absent
Nitric nitrogen	0·3	0·3	0·28	0·28	0·35	0·38
Oxygen taken up from $N/80$ $KMnO_4$ in 4 hours	0·086	0·12	0·20	0·21	0·16	0·11
*p*H	7·3	7·4	7·3	7·2	7·8	7·8

Results expressed in parts per 100,000 except where otherwise stated.
First two samples taken before installation of effluent plant.
Last four samples taken after installation of effluent plant.

The last four columns show the condition of the river before and after receiving the effluent from the plant. There is little significant difference between them.

SUMMARY.—A method of treating milk wastes has been described in which the crude liquors are held under prescribed conditions of temperature and aeration, allowed to settle, and then run over biological filters at a rate of 130 galls. per cb. yard per day.

Only primary filtration is used and over a period of 14 months the beds have remained perfectly clean, no clogging or ponding having occurred.

The final effluent produced is clear and bright, free from odour and stable on incubation.

It has an average B.O.D. of about 1, and the purification effected, based on the B.O.D. of the original crude waste, is 99 per cent.

I am indebted to my colleagues, Messrs. H. G. Coles and N. Hurt, for carrying out most of the analytical work involved, and to Mr. A. Glover and the Directors of the C.W.S. for permission to publish these results.

ADDENDUM.—Further experience obtained since this paper was read has been so satisfactory that a plant to deal with over 250,000 gallons a day has been erected and is giving excellent results.

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RESEARCH DEPARTMENT
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A Rapid Method for the Determination of Parachlorometaxylenol

By D. McNICOLL, M.A., B.Sc., Ph.D., R. P. MERRITT, Ph.C., and T. F. WEST, M.Sc., F.I.C.

The method proposed by Merritt and West[1] for determining parachlorometaxylenol is satisfactory as regards accuracy but involves a good deal of manipulation. The more rapid methods which we have now developed depend on the fact that, whilst most phenols (especially those of a feebly acidic nature) do not esterify readily, fatty acids readily form methyl esters when naphthalene-β-sulphonic acid is used as catalyst.[2]

After it had been established that this applied to *p*-chloro-*m*-xylenol a number of experiments with the pure phenol were based on this fact, and finally the alternative Methods I and II were adopted. The second method has been shown to yield satisfactory results for each of the solutions previously examined by Merritt and West (*loc. cit.*) which contained a variety of soaps and essential oils. As in the method of these authors, the present processes would not be successful if essential oils containing phenols were included in antiseptic solutions, although this appears unlikely in view of the oils available.

However, by the methods described below the feebly acidic constituents of such solutions are obtained in a practically pure state and the m.p. of the *p*-chloro-*m*-xylenol at this stage was in some instances 112–113° C.

The identity of the phenol in question may be confirmed by recrystallisation from benzene to m.p. 115° C. and by determining the mixed melting-point.

Method I.—Twenty ml. of the antiseptic solution were pipetted into a separator and acidified with 6*N* sulphuric acid. The oily layer was extracted three times with ether (25 ml.), the combined ethereal extracts were washed three times with 10 ml. of water, and the water was washed with ether (15 ml.). The ethereal solutions were united and dried over sodium sulphate and, after removal of the solvent, the residue was boiled for 45 minutes on a hot plate under reflux with 20 ml. of a 4 per cent. solution of naphthalene-β-sulphonic acid in methyl alcohol. The solution was then transferred to a separator with water (2 volumes) and extracted three times with 25 ml. of ether. The ethereal solution was extracted eight times with 25 ml. of *N* sodium hydroxide solution, the alkaline solution was washed with 20 ml. of petroleum spirit, and the petroleum spirit with 10 ml. of *N* sodium hydroxide solution. The combined alkaline extracts were acidified with 6 *N* sulphuric acid, and the liberated phenol was extracted three times with 25 ml. of ether. The ethereal extract was washed with water in the usual way, the solution was dried over sodium sulphate, and, after removal of the solvent, the residue was dried in a vacuum desiccator. The results obtained for solutions I to VI (see Merritt and West, *loc. cit.*) are shown in Table I.

Method II.—After extraction of the fatty acids, phenol and essential oils and esterification as in Method I, the methyl alcohol solution was transferred to a separator with twice its volume of *N* sodium hydroxide solution and 20 ml. of petroleum spirit, and the mixture was vigorously shaken. The petroleum spirit

was extracted three times with 10 ml. of *N* sodium hydroxide solution, a little alcohol being used if necessary to break the emulsions formed. The combined alkaline extracts were acidified with 6 *N* sulphuric acid and extracted three times with 25 ml. of ether, the ethereal extract was washed with water in the usual way and dried over sodium sulphate, the solvent was removed, and the residue was

TABLE I

ANALYSIS OF SOLUTIONS BY METHOD I

Solution No.	*p*-Chloro-*m*-xylenol: Added in 100 ml. g.	*p*-Chloro-*m*-xylenol: Determined in 100 ml. g.	m.p. °C.
I	2·491	2·547	112–113
II	3·500	3·465	108–109
III	3·318	3·290	112–113
*IV	3·078	3·290	108–111
V	3·507	3·543	109–111
*VI	3·339	3·509	106–109

* With solutions IV and VI it was necessary to purify the crude phenol by washing with petroleum spirit. For this reason Method II was developed and found generally applicable.

dried in a vacuum desiccator and weighed. In some instances the result at this stage was high and accordingly, as a general method, it is preferable to purify the crude phenol by dissolving in the smallest quantity of sodium hydroxide solution, diluting with water to 60 ml., and precipitating with carbon dioxide. The suspended phenol is then extracted with ether, separated, dried in the usual manner and weighed. The results shown in Table II for Solutions I to VI were obtained by including the purification with carbon dioxide in the method.

TABLE II

ANALYSIS OF SOLUTIONS BY METHOD II

Solution No.	*p*-Chloro-*m*-xylenol: Added in 100 ml. g.	*p*-Chloro-*m*-xylenol: Determined in 100 ml. g.	m.p. °C.
I	2·491	2·484	110–111
II	3·500	3·497	112–114
III	3·318	3·307	110–111
IV	3·078	3·098	109–110
V	3·507	3·522	113–114
VI	3·339	3·392	107–109

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The Micro-Electrolytic Deposition and Determination of Arsenic

By SYDNEY TORRANCE, A.R.C.S., B.Sc., D.I.C.

No gravimetric electrolytic method for the determination of arsenic on a micro-chemical scale has yet been published. The following is an adaptation of the author's method previously described[1] for ordinary scale electrolytic determinations of arsenic; it is based on the Reinsch test and consists in depositing arsenic as an alloy with copper from a solution containing about 15 per cent. of conc. hydrochloric acid, the cathode potential being controlled by means of a saturated-calomel auxiliary electrode. Further work has shown that the method is readily adaptable to micro-quantities of arsenic, the Lindsey–Sand micro-electrolytic apparatus and technique[2] being employed. Lindsey[3] has found that copper may be completely deposited from an acid chloride solution with an anode-to-cathode potential of 0·7 volt, when the electrolysis is carried out at a temperature of 65° to 70° C., hydrazine being present as a depolariser. This was confirmed for solutions of copper alone, even with the high acid-strength utilised, but with the addition of arsenic, it was found necessary to raise the anode-to-cathode potential to 0·9 volt, in order completely to deposit the copper.

Standard solutions of copper and tervalent arsenic were prepared by dissolving AnalaR copper sulphate in water, and pure arsenious oxide in sodium hydroxide solution and acidifying with hydrochloric acid. The standard solutions contained about 1 mg. of copper and 0·1 mg. of arsenic per ml. respectively. The copper solution was standardised by electrolysis, whilst the amount of arsenic in the arsenic solution was calculated from the weight of arsenious oxide taken. Five ml. of each solution were introduced into an electrolysis vessel, and 1·5 ml. of hydrochloric acid (sp.gr. 1·16) and 6 drops of 50 per cent. hydrazine hydrate were added. The mixture was electrolysed at a temperature of 65° to 70° C., with an anode-to-cathode potential of 0·9 volt. The initial current of about 100 milliamps fell to about 10 milliamps within 4 minutes. The electrolysis was continued for a further 5 to 10 minutes, and the copper and arsenic deposit was washed, dried and weighed. It was found that the arsenic was completely deposited with the copper. Results of several similar depositions obtained with a constant ratio of copper to arsenic of 10 : 1 are given in Table I.

TABLE I

Arsenic taken mg.	Copper added mg.	Copper and arsenic deposited mg.	Arsenic found mg.
0·53	4·95	5·49	0·54
0·53	4·95	5·48	0·53
0·53	4·95	5·48	0·53
0·21	1·98	2·20	0·22
0·21	1·98	2·20	0·22
0·11	0·99	1·10	0·11
0·11	0·99	1·10	0·11

Depositions were next made with decreasing ratios of copper to arsenic in order to ascertain the smallest ratio necessary to deposit all the arsenic simultaneously with the copper. From the results given in Table II, it would appear that the minimum ratio is 4 : 1.

TABLE II

Arsenic taken mg.	Copper added mg.	Copper/ arsenic ratio	Copper and arsenic deposited mg.	Arsenic found mg.
1·06	4·95	5	6·02	1·07
0·53	1·98	4	2·51	0·53
0·53	0·99	2	1·46	0·47
1·06	1·98	2	2·89	0·91
1·06	2·97	3	3·93	0·96
1·06	2·97	3	3·92	0·95

A standard solution of quinquevalent arsenic was prepared containing 0·25 mg. of arsenic per ml., by evaporating to fuming a mixture of 0·330 g. of arsenious oxide with 10 ml. of nitric acid (sp.gr. 1·42) and 5 ml. of sulphuric acid (sp.gr. 1·82) in a Kjeldahl flask. When the solution was cool, 0·2 g. of hydrazine sulphate was added, the mixture was evaporated again to fuming, and the solution was diluted to 1 litre. Two ml. of this solution were electrolysed with 5 ml. of the standard copper solution, in the presence of hydrochloric acid and hydrazine, as described above. As had been previously discovered with larger amounts (*loc. cit.*[1]), all the copper, but no arsenic, was deposited. A further portion of the arsenic was reduced in an electrolysis tube by adding to it 1 ml. of a saturated solution of sulphur dioxide. The tube was corked and placed in a boiling water-bath for 5 minutes. The reduced arsenic solution was then electrolysed in the usual manner with copper, hydrochloric acid and hydrazine. All the arsenic was found to have been deposited with the copper. Results of several determinations are given in Table III.

TABLE III

Arsenic taken mg.	Copper added mg.	Copper and arsenic deposited mg.	Arsenic found mg.
0·50	4·95	5·46	0·51
0·50	4·95	5·45	0·50
0·50	4·95	5·45	0·50
1·25	4·95	6·18	1·23
1·25	4·95	6·19	1·24
1·25	4·95	6·19	1·24
0·25	1·98	2·23	0·25
0·25	1·98	2·23	0·25

I wish to thank Dr. Lindsey for his interest in this work, and Imperial Chemical Industries, Ltd., for a grant which has been used to purchase part of the apparatus employed in this investigation.

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The Analysis of Linseed Oils of Various Origins

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Prior to the introduction by Kaufmann,[1] in 1925, of the thiocyanogen method for the estimation of linolenic, linolic and oleic acids in the presence of each other, only a very few reasonably complete analyses of linseed oil or linseed oil fatty acids had been published.

These published analyses are summarised in Table I.

Table I

	Fatty acids, per cent.				Glyceryl radicle Per Cent.	Unsap. matter Per Cent.
	Saturated	Oleic	Linolic	Linolenic		
Hazura and Grüssner[2] ..	10	5	15	15–α 55–β	—	—
Fahrion[3]	9·3	17·5	30·0	38·0	4·6	0·6
Friend[4]	10·0	5·0	59–48	21–32	4·6	—
Coffey[5]	8·1	5·0	48·5	34·1	4·3	—
Eibner and Schmidinger[6]	8·2	4·5	17·0–α 41·8–β	20·1–α 2·7–β	4·1	1·0

The findings of Hazura and Grüssner are obviously incorrect, as a mixture of the type they suggested would have an iodine value in excess of any found experimentally, whilst Fahrion made the assumption—now known to be untenable—that oleic acid on oxidation could be converted into dihydroxystearic acid in 60 per cent. yield.

Friend's figures represent average values calculated in 1917, and were based on the then existing knowledge of the iodine value and yields of hexabromides obtained on bromination, whilst Coffey estimated the amount of linolenic acid present from the amount of carbon dioxide and volatile acids resulting from the oxidation of linseed oil fatty acids. The investigation of Eibner and Schmidinger gave trustworthy figures for α-linolic and α-linolenic acids, but the values for *iso*linolenic, β-linolic and oleic acids were only approximate, as the only method then available for the determination of these acids in a mixture of all three depended upon the separation of the hexabromostearic acid produced from linolenic acid on bromination of the mixture, and it is now known that this is not a full measure of the linolenic acid originally present.

The most reliable analyses of linseed oil mixed fatty acids published since 1925 are summarised in Table II.

Table II

	Fatty acids, per cent.			
	Saturated	Oleic	Linolic	Linolenic
Eibner and Brosel[7] (Calcutta oil)	8·9	18·8	23·2	49·1
Kaufmann and Keller[8] (Plate oil)	9·0	8·0	46·7	36·3
,, ,, (Calcutta oil) ..	11·3	12·5	54·1	42·1
Gay[9]	10·8	12·4	26·6	50·2
Griffiths and Hilditch[10]	9·7	9·6	42·6	38·1

Eibner and Brosel used Eibner's technique[11] for hexabromostearic acid determination, and checked their results by means of the thiocyanogen method. Kaufmann and Keller's results were calculated on the basis of a thiocyanometric examination, and were later criticised by Gay, who claimed that the thiocyanogen method was unreliable as a means of determining partial unsaturation quantitatively under the conditions stipulated by them; his own recorded values were obtained by the use of a modified technique.

Griffiths and Hilditch analysed linseed oil fatty acids of unspecified origin by three different methods, namely, bromination and separation of hexabromostearic acid, thiocyanogen titration, and the oleic-elaidic transformation method of Hilditch.[10,12] They found that linolenic acid is not completely separable as insoluble hexabromide, but results obtained by the oleic-elaidic transformation (saturated, 9·7; oleic, 9·7; linolic, 42·2; linolenic acid, 38·4 per cent.) fully confirmed the values obtained by the thiocyanometric method. Criticism was also made of Cocchinaras' attempt[13] to analyse linseed oil by a bromination method followed by analysis of the resultant bromo-acids, and the findings of the present investigation support the contention that his results are based on an untenable assumption.

Davidsohn[14] observed that oils obtained from linseed and sunflower seed that have ripened in cold climates have a higher iodine value—and presumably a higher linolenic and linolic acid content—than oils obtained from similar seed grown in hotter climates where conditions apparently favour the production of oleic acid. Apart from this statement, and that of Griffiths and Hilditch (*loc. cit.*) that it seems almost certain that Argentine (Plate) and also Calcutta linseed oils contain a mixture of fatty acids consisting within approximate limits of about 10 per cent. of saturated, about 10 per cent. of oleic, about 40 per cent. of linolic and about 40 per cent. of linolenic acid, no record appears to have been made of any effort to determine and compare the compositions of linseed oils of varying origin.

With the aim of correcting this omission, typical samples of Baltic, Indigene, Calcutta and Plate linseed oils have now been analysed by methods of analysis proved to be capable of giving accurate and repeatable results.

The samples of raw linseed oil chosen for examination were known from previous experience to be truly representative of their type; the actual samples were withdrawn from new bulk supplies, and in each instance analysis was completed within two months of the date of crushing.

Particulars of the samples investigated are as follows:—Indigene oil (I), received February, 1935; Baltic oil (B), received March, 1934; Plate oil (P), received May, 1934; Calcutta oil (C), received July, 1934.

The seed from which the oil was expressed by the crushers was from the previous year's crop in each instance.

In addition to the above-mentioned samples of new oil, a sample of raw Baltic oil (BB) received and originally analysed in February, 1909, and subsequently stored in a sealed bottle full to the neck and kept in the dark, has been examined. This oil is very viscous and red in colour; it has a distinctive and fatty odour but is perfectly clear and free from "break." The oil when originally examined in 1909[15] had the following characteristics: Sp.gr. at 15·5° C, 0·9357; n_D^{20} 1·4840;

iodine value (Wijs method; 2 hours' contact), 198·5; saponification value, 185; free fatty acid content, 1·25 per cent.

EXPERIMENTAL.—The methods employed during the investigation were those generally accepted and are outlined below.

The refractive index was determined by means of an Abbé refractometer, the free fatty acid content was expressed in terms of oleic acid, the saponification value was determined by heating for 45 minutes under reflux with alcoholic potash, and the Wijs method was used for determining the iodine value, a two hours' contact period being allowed.

The thiocyanogen value was determined by the modification of Kaufmann's original method outlined by Griffiths and Hilditch (*loc. cit.*), and the results obtained both on the oil and on the constituent fatty acids fully confirm the statement of Griffiths and Hilditch that, provided great care is taken to keep all reagents absolutely dry, results agreeing well with each other may be obtained at any time.

TABLE III

	Indigene oil (I.)	Baltic oil (B.)	Calcutta oil (C.)	Plate oil (P.)	Baltic oil (BB.)
Raw oil					
Sp.gr. at 15·5° C.	0·9344	0·9347	0·9321	0·9323	0·9890
n_D^{20}	1·4800	1·4825	1·4808	1·4757	1·4875
Free fatty acid, per cent.	3·05	1·25	0·80	0·80	20·1
Sapon. value	190·0	189·0	190·3	190·2	206·4
Iodine value	189·1; 189·8	195·3	182·4	180·7	148·1; 147·2; 146·3
Thiocyanogen value	118·9; 119·2; 119·0	115·0; 113·4; 115·9	112·3; 111·4; 115·1	114·3; 115·0; 115·7	89·4
Unsaponifiable matter, per cent.	1·24	1·26	0·73	0·78	0·72
Fatty acids, per cent.	94·6	94·6	94·9	94·8	92·8
Fatty acids					
Equiv. weight	294·0	290·8	288·0	284·1	297·8
Iodine value	197·9; 198·2	203·4	191·6; 190·9	187·1; 186·4; 188·9	161·6; 162·2; 161·9
Thiocyanogen value	121·9; 122·1	126·5; 125·8; 126·8; 126·3	121·2; 120·1	119·8; 118·9	98·7
Constituents, per cent.:					
Saturated (*a*) (found)		5·3 } 6.6	7·8 } 9·3	8·2 } 9·7	26·4; 20·2; 18·2
(*b*) (found)	11·6; 11·1	7·9 }	10·8 }	11·3 }	10·7; 10·8
Oleic (calc.)	6·1	9·3	13·7	17·4	—
Linolic (calc.)	37·4	39·5	36·7	33·4	—
Linolenic (calc.)	45·2	44·1	40·3	39·5	

(*a*) Estimated by the lead salt and ether method.
(*b*) Estimated by Bertram's oxidation method.

The linseed oil mixed fatty acids were obtained by saponifying the oil (5 g.) by heating under reflux with aqueous potassium hydroxide (4 g. in the minimum amount of water) and rectified spirits (30 ml.) for 20 minutes, removing the solvent by distillation *in vacuo* over a boiling water-bath, dissolving the soap thus obtained in warm water (200 ml.), liberating the acids by addition of a few ml. of conc.

sulphuric acid, taking them up in ether, and washing the ethereal solution with water. After immediate evaporation of the solvent, the residual fatty acids were kept at 100° C. for one hour under reduced pressure, a capillary leak fed by coal gas being used throughout. The iodine and thiocyanogen values were then determined immediately, the bulk of the fatty acids being weighed prior to their addition dropwise to the reagent, and the amount added being found by difference. This was found to be a necessary precaution, as otherwise rapid oxidation was liable to occur, resulting in values appreciably lower than those obtained when this precaution was observed.

The estimation of the saturated acid content of the mixed fatty acids was made both by the lead salt and ether method[16] and by Bertram's oxidation method,[17] the precautions indicated by Hilditch and Priestman[18] and by Gay (*loc. cit.*) being observed in making the latter estimation. For the purposes of the later calculations the mean of the results obtained by the two methods has been taken as the saturated acid content.

The experimental results are recorded in Table III (p. 267).

From the results in that table, the constitution of the new oils has been calculated, use being made of the fact observed by Kaufmann (*loc. cit.*) that only two of the double bonds in linolenic acid and one double bond in linolic acid are reactive towards free thiocyanogen. This reasoning is applicable only when the mixed fatty acids are composed of individuals capable of reacting with thiocyanogen in a known manner, and in consequence cannot be applied to sample (BB), which has obviously undergone both oxidation and polymerisation during its twenty-six years of storage, with consequent formation of a complex the reaction of which with free thiocyanogen is uncertain.

The calculated composition of the four new oils is recorded in Table IV.

TABLE IV

	Fatty acids, per cent.				Glyceryl radicle Per Cent.	Unsapon. matter Per Cent.
	Saturated	Oleic	Linolic	Linolenic		
Indigene oil (I) ..	10·7	5·8	35·4	42·7	4·2	1·2
Baltic oil (B) ..	6·2	8·8	37·4	41·8	4·1	1·3
Calcutta oil (C) ..	8·8	13·0	34·9	38·3	4·4	0·7
Plate oil (P)	9·2	16·5	31·7	37·4	4·4	0·8

DISCUSSION OF RESULTS.—An examination of the results recorded in Tables II and IV shows that the composition of the mixed fatty acids obtained from Calcutta and Plate linseed oils from widely differing sources is fairly constant. The compositions of six out of the seven samples in question are comparable and fall within the following narrow limits: saturated acids, 8·5 to 11·3; oleic acid, 8·0 to 17·4; linolic acid, 33·4 to 42·6; linolenic acid, 36·3 to 42·1 per cent. The recorded composition of the seventh—that of Eibner and Brosel—can hardly be correct, as the iodine value of a mixture of the type indicated would be 193—a value far in excess of that normally obtained for an average oil of this type.

Comparison of the composition of the mixed acids obtained from sample (B), with the average composition of Calcutta and Plate oil acids, shows definitely that the markedly superior drying and heat-polymerising properties of the Baltic

type of oil are due to its containing a high percentage of the most highly unsaturated acids.

The results obtained from the examination of the sample (BB) of old Baltic oil, are of little immediate value; it had been hoped to examine this oil in more detail, but as the investigation had to be discontinued at this stage it was thought advisable to publish the results already obtained.

Sufficient has been done, however, to show that, on standing, a linseed oil of this type develops an appreciable free acidity—which accounts for the observed increase in the saponification value—and that considerable saturation of the double bonds takes place. It is also safe to assume from the experimental findings and from the excessive increase in viscosity observed, that polymerisation, rather than oxidation, is the principal cause of the apparent saturation. The saturated acid content of this old oil is very little, if any, greater than normal when determined by Bertram's oxidation method, from which it is apparent that the partially saturated oil on saponification affords acid products which are capable of fission by alkaline permanganate in a normal manner. The uncertainty of the lead salt method shows that, in addition to lead palmitate and lead stearate, acids are produced which give lead salts that are insoluble in ether. The equivalent weight of these acids is slightly higher than usual, but the observed values may be low, as it is possible that a certain amount of depolymerisation occurs during alcoholic saponification.

My thanks are due to the Directors of Messrs. Jas. Williamson & Son, Ltd., Lancaster, for permission to publish this paper, to Mr. Rowland Williams for his continued interest in the investigation, and to Mr. T. Newton for his assistance in carrying out some of the analytical work.

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RESEARCH DEPARTMENT
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December 24th, 1938

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.

SPIRIT VINEGAR CONTAINING MALT VINEGAR

THE analysis of a recent sample of "English Spirit Vinegar" may be of interest, since it is the only time to my knowledge that the presence of malt vinegar in spirit vinegar has been recorded.

The oxidation, iodine and ester values were determined by the methods proposed by Edwards and Nanji (ANALYST, 1938, **63**, 410) and were proved to be of considerable value in ascertaining the nature of the mixture.

For purposes of comparison the average percentage figures obtained with malt vinegars (61 samples) and spirit vinegars (*loc. cit.*) are given below with the range of oxidation values, etc., and also the results obtained with the sample.

	Malt vinegar	Spirit vinegar	Mixture 40 : 60	Sample	Caramel solution of equal colour
Total soluble solids, per cent.	2·16	0·23	1·00	1·23	0·30
Ash, per cent.	0·25	0·06	0·136	0·123	0·023
Nitrogen, per cent.	0·075	0·035	0·051	0·045	0·0054
Phosphoric anhydride, per cent.	0·070	0·025	0·043	0·044	0·000
Oxidation value	552–1320	88–225	274–663	625	1·4
Iodine value	688–1976	8–27	280–806	347	1·5
Ester value	29–66	6–14	15–35	67	1·2
Acetic acid	—	—	—	4·6	—

It was reported that the analysis indicated the presence of 40 per cent. of malt vinegar, with an observation that such admixture might render the article unsuitable for some of the purposes for which spirit vinegar is used.

The manufacturers of the vinegar were asked for an explanation; in reply, they denied that any malt vinegar was added to their spirit vinegar, and suggested that the soluble matter found on analysis might be derived from the caramel that is added to colour the spirit vinegar (to meet the public demand).

In the analysis, however, due consideration had already been given to the effect of the added caramel; an aqueous solution made from a sample of commercial caramel, as sold for colouring purposes, and diluted so as to contain the same percentage of total soluble solids as the vinegar, *i.e.* 1·23 per cent., was found to be four times as dark as the vinegar. This solution was diluted until its colour was equal to that of the vinegar and then analysed: the figures obtained are given in the fifth column above, and it may be seen from these results that the addition of such caramel could have had no appreciable effect on the phosphorus, oxidation, iodine and ester figures.

At a subsequent interview a director of the company manufacturing the vinegar stated that they had themselves since had bottles of the vinegar returned by a customer who had noticed a difference in the quality, and that on further investigation they had found that the samples did contain at least 40 per cent. of malt vinegar. The trouble arose in the pasteurising plant through a shop steward misunderstanding his instructions. He had always emptied the pasteuriser when switching over from spirit to malt vinegar but not when changing from malt to spirit, under the impression that it could not matter if a customer got some of the better article. This meant in practice that when the switch-over occurred some

dozens of bottles were filled with a mixture of malt and spirit vinegar, in gradually decreasing quantities of malt.

Malt vinegar is dearer than spirit vinegar, and the director expressed his regrets for the admixture and his gratitude for having had his attention drawn to a matter which meant a loss to his firm as well as possible loss of the custom of those manufacturers and retailers who might find the mixture unsuited to their particular needs.

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THE DETECTION OF ZINC IN PRESENCE OF IRON

IT is well known that zinc in a solution containing hydrochloric acid gives with an alkali ferrocyanide a white precipitate of potassium zinc ferrocyanide of uncertain composition. The reaction is probably $2Fe(CN)_6'''' + 2K^{\cdot} + 3Zn^{\cdot\cdot} = Zn_3K_2[Fe(CN)_6]_2$ (*cf. Treadwell's Analytische Chemie*, Vol. I, p. 184, 1935 edition, Zurich).

This test, first applied by Galetti, cannot be used when iron is present, because then Prussian blue masks the precipitate of the zinc complex. To prevent this, the test may be modified by adding an alkali fluoride, which eliminates the iron ions in the form of a complex: $Fe''' + 6F' = FeF_6'''$. This iron fluorine complex is soluble and in such a solution there are too few iron ions to form Prussian blue. There is no interference, however, with the zinc ions, so that the reaction may be used in qualitative analysis.

The procedure is as follows:—The solution under examination is treated with 0·5 to 1 ml. of 2 *N* hydrochloric acid and with sufficient alkali fluoride to cause decolorisation; according to the equation above the quantity of fluoride required depends on the quantity of iron ions present. To ascertain if enough fluoride has been added, a drop of the solution is applied to ferrocyanide paper; if the paper turns blue, there is insufficient fluoride. The mixture is filtered into another test-tube, the first tube and the funnel are washed with 1 to 2 ml. of water, and the washings are added to the filtrate. As thus obtained the solution is perfectly clear and gives with 1 to 3 ml. of potassium ferrocyanide solution a white amorphous precipitate. With a low concentration of zinc ions the precipitate is obtained 2 or 3 minutes later. The test must be made at the ordinary temperature; the solution must not be warmed because the acid then decomposes the ferrocyanide. The test is capable of detecting 0·1γ of zinc; the limit of dilution is 1 : 500,000. If the precipitate shows any trace of colour, too little fluoride has been used, and the test must be repeated after addition of more.

Numerous experiments have proved that potassium ferricyanide gives still better results than ferrocyanide. The precipitate is then of slightly brown tint. Although the degree of sensitivity is essentially the same as with ferrocyanide, the precipitate appears sooner and it is more easily seen. The composition of the precipitate is uncertain.

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TURMERIC TEST-PAPERS CONTAINING BORON

IN view of the extensive use of turmeric papers in qualitative tests for boric acid and borax, it was thought that a recent experience of mine would be of interest. It was found that books of turmeric papers supplied by a well-known firm gave a strongly positive reaction even when the solution under test was known to be free from boron compounds. So pronounced was the reaction that it was concluded that the papers themselves contained boron in some form, and this fact was

established by ashing several papers and obtaining methyl borate from the ash. On taking up the matter with the suppliers, their chemist was able to confirm the presence of boron in the papers. An apology was sent but no explanation of how the boron came to be present was forthcoming. It should be mentioned that these faulty test-papers were quite normal in appearance, and as such an occurrence does not appear to have been noticed before, it was considered desirable to place it on record.

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Notes from the Reports of Public Analysts

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

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FOURTH QUARTER, 1938

OF the 1402 samples submitted under the Food and Drugs Act, 26 were bought formally.

CARBOLIC ACID OINTMENT.—According to the B.P. this ointment is made by dissolving 30 g. of phenol in a mixture of 75 g. of beeswax, 50 g. of lard, and 845 g. of hard and soft paraffins, so that theoretically the finished article should contain 3·0 per cent. of phenol. It was mentioned in a paper read before the Pharmaceutical Conference in September, 1938, that if the temperature of the melted base is 60° C. amounts of phenol, ranging in test experiments from 3·7 to 5·2 per cent., are lost during the manufacture, *i.e.* the ointment should contain about 2·9 per cent. of phenol. Of 10 samples analysed, only 2 were in reasonable agreement with this figure, containing 2·9 and 2·7 per cent. respectively. Three others contained 2·1, 2·3 and 2·3 per cent. and, having regard to the difficulties in the process of manufacture, were passed as genuine. It was also stated in the above-mentioned paper that if the ointment is stored in pots with loosely fitting earthenware covers, phenol is rapidly lost; in one instance the loss amounted to 11·2 per cent. in 10 months and to 28·2 per cent. in 25 months. Under warmer conditions the loss reached 35 per cent. in 25 months. A sample kept at room temperature in a 2-oz. pot covered with grease-proof paper lost 28 per cent. from the top layer in 5 months as compared with 7·1 per cent. from the whole (mixed) sample. Samples of ointment bought from retail pharmacists contained from 0·5 to 2·7 per cent. of phenol. One of the samples examined in the Birmingham laboratory was in a cardboard container in the pattern of a chip-box; it contained only 1·8 per cent. of phenol. The stock was withdrawn from sale. A sample taken from a 1-oz. tin at the same shop contained 2·55 per cent. of phenol. Another of the 10 samples contained 1·9 per cent. of phenol and was sold from a 1-lb. jar purchased at the end of 1937. Two further samples from different retailers, but both bought from the same wholesale firm, contained only 1·3 and 1·2 per cent. of phenol respectively. The former had been supplied in March, 1936, and the latter in March, 1935. Both retailers were advised to purchase the ointment in the smallest possible quantities, or at least in small containers so as to reduce to a minimum the tendency to loss of phenol.

H. H. BAGNALL

COUNTY OF KENT

REPORT OF THE COUNTY ANALYST FOR THE FOURTH QUARTER, 1938

OF the 770 samples taken under the Food and Drugs Act, 47 were purchased informally.

Under the Fertilisers and Feeding Stuffs Act, 1926, the inspectors took 38 samples on the premises of sellers, and the official samplers took 89 samples formally at farms on behalf of farmers. Also, at the request of farmers 114 samples were taken informally, and purchasers sent 63 samples direct to the laboratory.

WHITE FISH MEAL.—A sample warranted to contain 5 per cent. of oil was found to contain 6 per cent. As the Fertilisers and Feeding Stuffs Act permits this product to contain 6 per cent. of oil but no more, the sample in question could be deemed to consist of "white fish meal," although its oil-content exceeded the warranty. A low oil warranty helps to sell a fish meal, and it is therefore important to see that the warranties given are complied with; there is a tendency for feeding fish meals to contain more than the permissible amount of oil.

WET SHODDY.—Of 68 samples of shoddy sold with a warranty, 35 were deficient in nitrogen. The largest deficiences were found in the following samples:

Water Per Cent.	Mineral matter Per Cent.	Nitrogen guaranteed Per Cent.	Nitrogen found Per Cent.	Nitrogen deficiency Per Cent.
39·0	11·6	5·76	3·06	2·70
45·0	12·2	5·76	2·89	2·87
37·0	11·8	5·76	3·38	2·38
38·0	15·6	5·76	3·49	2·27
39·0	9·4	5·76	3·67	2·09

These results show that the deficiencies occurred in one class of shoddy and that these shoddies contained excessive amounts of water. The mineral matter, too, was somewhat high. Nitrogen deficiencies exceeded 1 per cent. in 20 of the shoddies. For some years past few wet shoddies have been encountered, and it was assumed that greater care was being taken by shoddy merchants to protect shoddy from the weather. From the condition of some of the samples examined during the last few months it can be definitely stated that there are some merchants who have taken no trouble to prevent undue exposure. In any event, it is difficult to understand the conditions under which shoddy containing 45 per cent. of water could have been stored, for it would mean that on every ton of shoddy nearly one ton of rain fell and was absorbed. Before the days of the sale of shoddy at "unit value" it is alleged that it was a common practice to play a hose-pipe upon a bulk of shoddy before consigning it to a farmer. As a large proportion of the shoddy bought in the county is not examined, it would probably still pay an unprincipled merchant to take no precautions to prevent shoddy from becoming wet.

BAT GUANO.—A considerable quantity of this material, deposited by bats in caves years ago, was offered for sale. It was a dark brown powder containing 12 per cent. of nitrogen, 8 per cent. of phosphoric acid and 4 per cent. of potash.

F. W. F. ARNAUD

Legal Notes

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

DERMATITIS FROM WEARING APPAREL

GRIFFITHS *v.* PETER CONWAY, LTD.

ON February 28th the Court of Appeal dismissed, with costs, an appeal by the plaintiff from the judgment of Mr. Justice Branson in a case heard at the Bristol Summer Assizes on July 6th and 7th, 1938, in the High Court of Justice, King's Bench Division.

In June, 1937, the plaintiff bought from the defendants, who are retail tailors, a Harris tweed coat, which was specially made for her. She contracted dermatitis shortly after beginning to wear it and brought an action to recover damages for breach of warranty. Mr. Justice Branson held that the real cause of the trouble was that the plaintiff's skin was not normal, but had an idiosyncratic effect, so that what the plaintiff contracted was idiosyncratic dermatitis, a thing which no purveyor of cloth could really guard against to any further extent than purveyors of cloth have guarded against there being anything harmful in its texture.

The plaintiff relied upon the fact that she had made known to the defendants the particular purpose for which the goods were required, *i.e.* for her own use, and her counsel (Mr. Morris) contended that this brought the case within the exception to Sec. 14, Sub-sec. (1) of the Sale of Goods Act, 1893. This section negatives any implied warranty or condition as to the quality or fitness for any particular purpose of goods supplied under a contract of sale except "where a buyer expressly, or by implication, makes known to the seller the particular purpose for which the goods are required, so as to show that the buyer relies on the seller's skill or judgment, and the goods are of a description which it is of the seller's business to supply (whether he be the manufacturer or not), there is an implied condition that the goods shall be reasonably fit for such a purpose."

The Master of the Rolls, dealing with the argument that Mrs. Griffiths had expressly made known to the defendants the particular purpose for which the goods were required, said that there was one quite sufficient answer to the argument. Before the condition was implied as to reasonable fitness, it was necessary that the buyer should make known, expressly or by implication, first of all, the particular purpose for which the goods were required. The particular purpose for which the goods were required was for the purpose of being worn by a lady suffering from an abnormality. It seemed to him (the Master of the Rolls) that if a person suffering from such an abnormality desired an article of clothing for his or her use, and desired to obtain the benefit of the implied condition, he or she did not make known to the seller the particular purpose merely by saying "the article of clothing is for my own wear."

The essential matter for the seller to know in such cases with regard to the purpose for which the article was required consisted in the particular abnormality or idiosyncrasy from which the buyer suffered. It was only when he had that knowledge that he was in a position to exercise his skill or judgment. The fact that those essential characteristics were not made known, and indeed were not known, as in the present case they were not known, to the buyer, did not seem to affect the question. When he spoke of "essential characteristics" he was not, of course, referring to variations which took place and existed within the class of normal people. No two normal people were precisely alike, and in the matter of sensitiveness of people who would be described as normal, their sensitiveness must

vary in degree. But there was a line which it was no function of any Court, or indeed of any medical man, to draw with preciseness so as to cover all cases where normality ceased and abnormality began. It was a question that no judge and no jury would have any real difficulty in deciding on the evidence in any particular case. In this particular case the learned Judge had found the existence of abnormality, and that being so, it seemed impossible to say that the seller here had the particular purpose pointed out to him so as to show that the buyer relied on his skill and judgment.

Lord Justice Mackinnon and Lord Justice Goddard, who sat with the Master of the Rolls, concurred with the decision.

Department of Scientific and Industrial Research

REPORT FOR THE YEAR 1937–1938*

As Professor Fowler was unable, for reasons of health, to take office as Director of the National Physical Laboratory, the Committee of the Privy Council appointed Dr. C. G. Darwin, M.C., Sc.D., F.R.S., Master of Christ's College, Cambridge, to be Director. Until Dr. Darwin entered upon his duties on December 1st, 1938, Sir Frank Smith, the Secretary of the Department, was appointed to hold the office of Director.

The gross expenditure of the Department last financial year was £872,127, and the receipts from industry and other sources were nearly £235,000.

The Report makes the usual survey of the activities of the Department, and gives an account of some of the many problems the solution of which is being sought through the co-operation of science and industry.

FOOD INVESTIGATION.—Special attention is called to the results achieved under the Department's Food Investigation Board in the last few years, and particularly in the development of gas-storage. "Ten years ago there were no gas stores. To-day they provide three million feet of storage, and this is only a beginning."

Up to 1933 Australia and New Zealand could send us only frozen beef, but as a result of the Department's work it has been shown that chilled beef can be preserved for sufficiently long periods in special chambers containing carbon dioxide. This discovery has been rapidly developed commercially, and in 1937 Australia and New Zealand sent to this country about 750,000 cwt. of chilled beef carried in this way.

The Food Investigation Board is to be invited to review the whole field of research into the processing of foodstuffs and to submit proposals for embracing under their scientific supervision such work as they may consider to be desirable in the national interest.

GRAIN AND INSECTS.—Another new field of investigation to be undertaken by the Department is the study of the attack on grain by insects. It has been estimated that the destruction of grain by weevils and other pests in this country represents, on a conservative estimate, a loss of over £500,000 a year. The industrial interests concerned have, as a start, contributed £1200 to enable a complete survey of the problem to be made as a first stage in the initiation of research to solve it.

NUTRITIVE VALUE OF BREAD.—The results of investigations have emphasised the importance of bread and butter in the dietary. It has been shown that certain fats, such as lard or butter, reduce the effects of calcium deficiency in the diet, presumably by rendering the actual calcium-content of the food more completely

* H.M. Stationery Office, York House, London, W.C.2. Cmd. 5927. Price 3s. net.

assimilable. "At the same time it is well known," the report states, "that fat is not completely assimilated by the body except when eaten with a relatively large excess of carbohydrate such as bread or potatoes."

For Report of the Building Research Board see ANALYST, 1938, **63**, 499; Atmospheric Pollution Committee, *id.*, 1938, **63**, 340; Food Investigation Board, *id.*, 1938, **63**, 818; Forest Products Research Board, *id.*, 1938, **63**, 46, 430; Chemistry Research Board, *id.*, 1939, **64**, 35.

RESEARCH ASSOCIATIONS.—The development of co-operative research is strikingly illustrated by figures given in the Report. These show that over a period of ten years the annual amount subscribed by industry for such co-operative research has more than doubled, having increased from just over £120,000 in 1929 to about £265,000 in 1937. Work is now being carried out in more than twenty Research Associations with the assistance of grants from the Department. The two largest are the Cotton Research Association and the Electrical Research Association. The former has now an income of over £87,000 and the latter an income of over £85,000 a year.

During the year a new Research Association was formed. This is the British Coal Utilisation Research Association which has taken over the activities of the Research Department of the Combustion Appliance Makers' Association and is to develop research on the general problem of the utilisation of coal. As a result of the offers of grant assistance made by the Department, the Association will have a minimum income of £18,000 a year with a prospect of an annual income of £30,000 if full advantage is taken of the offer made.

Among the points of interest in the work of the Research Associations the Report directs special attention to the following:

POWDERED RUBBER.—A simple process has been devised by the Rubber Research Association for preparing powdered rubber from the ordinary dry rubber of commerce.

MEASUREMENT OF THE TEMPERATURE OF LIQUID STEEL.—The National Physical Laboratory is co-operating with the Iron and Steel Industrial Research Council and the Iron and Steel Institute in investigating methods for measuring the temperature of liquid steel in open hearth furnaces. The aim is to attempt to adapt the platinum thermo-couple and the optical pyrometer to the conditions of the open hearth furnaces. Refractory materials have been found which will afford adequate protection to the measuring instruments when immersed for short periods in molten steel without slag, and in the next stage of the investigation an attempt is being made to obtain such slag-free conditions in an actual furnace as will enable the "quick-immersion" method to be brought into use.

DETERIORATION OF BRICKS IN BLAST FURNACES.—Under the Refractories Research Association, investigations have been made on bricks taken from the linings of blast furnaces. The deterioration occurring at different zones of a furnace due to the action of carbon monoxide, alkali salts, zinc and lead compounds, etc., has been examined. The results have indicated methods for producing fire bricks which are resistant to the action of carbon monoxide. Suggestions have also been made regarding the composition of cements for joints between bricks in the various zones.

CAST IRON WITH INCREASED TENSILE STRENGTH.—The Cast Iron Research Association has now produced cast iron having a tensile strength of 60 tons per sq. in. A few years ago it was not possible to obtain a strength of more than about 12 tons per sq. in. Tests have been carried out at the National Physical Laboratory on crank-shafts cast from materials supplied by the Research Association. Aluminium cast iron shows particular promise as a heat-resisting material.

NON-SHRINKABLE WOOL.—Commercial working has begun on the Wool Industries Research Association's chlorination process for the production of wool resistant to shrinkage, and the trade mark "Woolindras" has been registered to

protect the new standard of unshrinkability attainable in woollen goods placed on the market.

An entirely new method of producing non-shrinkable wool is under investigation. In this process use is made of certain proteolytic enzymes. One type suitable for the process is papain. The activity of the enzymes can be controlled chemically, and they appear to have a specific action on certain regions of the wool fibre. It is too early to speak of the special advantages of this new type of treatment.

RUBBERISED WOOL.—The development of the process for the rubberisation of wool has been continued, and quantities of various types of wool yarn have been treated for members of the Association in order to test the properties of fabrics made from wool. The treatment has proved advantageous for various types of woven and knitted fabrics in which resistance to wear or avoidance of the objectionable "balling-up" which may result on wearing surfaces of garments made from loosely-twisted yarns are matters of importance. The resistance of carpets to wear also appears to be greatly improved.

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY

III. SULPHUR DIOXIDE*

THE third of the leaflets describing standard methods for the detection of toxic gases in industry (*cf.* ANALYST, 1937, **62**, 607; 1938, **63**, 658) deals with sulphur dioxide. It is pointed out that the situations where this gas may be encountered in possibly dangerous concentrations include bone and glue works, cold storage and refrigeration plant, dye-making, dyeing and bleaching works, glass and pottery works, ore roasting (metallurgical) works, petroleum refining works, rubber works, sulphuric acid works and tanneries. It is also encountered in fumigation and disinfection.

POISONOUS EFFECTS.—Sulphur dioxide in high concentrations is irrespirable and causes asphyxiation. In lower concentrations it is irritating to the eyes, nose, throat and lungs. It may also cause inflammation of the nose and throat and set up bronchitis from prolonged exposure to relatively low concentrations which, since they cause no immediate or marked discomfort, can be tolerated for a considerable time. The following figures (Henderson and Haggard, *Noxious Gases*, 1937) show the approximate concentrations that are permissible:

Parts per vol. (approx.)	Mg. per litre (approx.)	Effects
1 in 100,000	0·03	Maximum concentration allowable for several hours' exposure.
1 in 2000	1·4	Concentration dangerous even for short exposures.

METHODS of DETECTION.—The potassium chromate test is considerably less sensitive than the potassium ferricyanide and ferric chloride test or than the starch iodate test, and is not capable of detecting sulphur dioxide in concentrations such as are met with in the atmosphere of works. Potassium ferricyanide and ferric chloride test-paper is sufficiently sensitive, but readily becomes coloured when kept, and the test is therefore unsuitable for standardisation on a quantitative basis. For these reasons a test based on the use of starch—potassium iodate—potassium iodide—glycerol test-paper has been adopted as the standard method. By drawing the air *through* the test-paper (*cf.* Leaflet No. 1; ANALYST, **1937, 62**, 607) concentrations down to 1 part in 250,000 (0·0114 mg. per litre) can be estimated by making not more than ten strokes with a hand-pump. As the test is

* Leaflet No. 3. H.M. Stationery Office, York House, Kingsway, London, W.C.2. March 7, 1939. Price 2s. 6d. net.

not specific for sulphur dioxide, it is necessary, when the presence of other gases which would affect the test is suspected, to identify these gases and interpose a suitable trap for them.

DETAILS OF THE TEST.—Samples shall be taken at a point closely adjacent to the workers. In testing the atmosphere of a tank, prior to the entry of a workman, it may be necessary to take samples at intervals throughout the period of work.

Apparatus.—The hand-pump and the technique of sampling the atmosphere are as described in Leaflets Nos. 1 and 2 (ANALYST, *loc. cit.*).

Test-papers.—Twelve ml. of approx. $N/10$ barium hydroxide solution are added to 60 ml. of water. One g. of Lintner's soluble starch (of reagent quality) is made into a thin cream with about 10 ml. of the water so treated, and the remainer is boiled. To the boiling liquid are added 1 g. of potassium iodate and 2 g. of potassium iodide (both of reagent quality); when these are completely dissolved the starch cream is added and boiling is continued for a few minutes, after which the solution is cooled, 30 ml. of pure glycerol are added, and the mixture is thoroughly shaken and made up to 100 ml. with water. As thus prepared the reagent should have a *p*H of approximately 9·5.

The test-papers are prepared from Postlip No. 633 extra-thick white filter-paper (18 × 24; 60 lb.) cut into strips 2 in. wide. The strips are immersed for 30 seconds in the reagent, the excess of liquid is drained off, and the strips are pressed two or three times between dry filter-paper, and suspended for 10 minutes at 50° C. in a well-ventilated oven free from acid fumes. One inch at the top and bottom of each strip is cut off and discarded, and the remainder is cut into 3-in. lengths for use. The test-papers should preferably be used within a few hours after preparation; they may, however, be stored in a well-stoppered bottle in the dark, and used after 1 or 2 days if discoloration is not serious. The reagent may be used up to 7 days after preparation.

Method.—The test-paper is inserted in a special holder and the test is applied by a technique similar to that already described in Leaflets Nos. 1 and 2 (*loc. cit.*). Any stain obtained is compared immediately with the standard chart provided with the Leaflet; or, alternatively, other methods of comparing the colours may be used, such as a comparator using coloured glasses as a standard, a photo-electric colorimeter or an optical density meter, provided that the standards have been properly calibrated and are used according to standard instructions.

Methods of applying the test to air from a space which is not readily accessible are described.

FIRST AID.—Full details of the treatment of cases of gassing are given in Factory Form No. 395 (H.M. Stationery Office, price 1d. net).

IV. BENZENE VAPOUR*

BENZENE vapour is produced during the manufacture of coal gas and the distillation of coal tar. It may be encountered in dangerous concentrations in many industrial situations including aeroplane works, cellulose paint, lacquer and leather cloth works, dyestuffs and intermediate works, explosives works, fat and glue works, gas works and coke ovens, linoleum works, motor fuel blending works, paint and varnish works, pharmaceutical and perfumery works, rubber works, spray-painting works, and tar-distilling works.

POISONOUS EFFECTS.—In high concentrations benzene vapour acts as a narcotic (acute poisoning). In low concentrations over a prolonged period it affects the blood and the blood-forming organs of the body (chronic poisoning). Individual susceptibility is well recognised, women and young persons being particularly liable to suffer from chronic poisoning.

* Leaflet No. 4. H.M. Stationery Office. March 7th, 1939. Price 3d. net.

The following figures, based on Henderson and Haggard (*Noxious Gases*, 1927), show the effects of exposure to various concentrations:

Parts per vol. (approx.)	Mg. per litre (approx.)	Effects
1 in 700 to 1 in 300	5 to 11	Slight symptoms after several hours' exposure.
1 in 300 to 1 in 200	11 to 17	Max. concentration that can be inhaled for 1 hour without serious disturbance.
1 in 140	26	Serious illness after 30 to 60 minutes' exposure.
1 in 50	70	Rapidly fatal.

Analyses of air in factories where poisoning has occurred gave values ranging from 1 in 200 to 1 in 500 parts.

Owing to its low solubility in the blood, most of the benzene absorbed is eliminated through the lungs; from 15 to 30 per cent., however, is oxidised in the system and eliminated through the kidneys—a slow elimination which favours cumulative effect on repeated exposures.

In acute poisoning the symptoms in slight cases are giddiness and a state of excitement. If the vapour is inhaled in quantity, coma quickly follows. The skin becomes somewhat livid and convulsions or twitchings of the muscles are noticeable.

In chronic cases there is aplastic anaemia. The number of red corpuscles is reduced and there is first an increase and then a reduction in the number of white cells. Bleeding from the mucous membrane of the mouth is one of the earliest manifestations. Later, haemorrhages occur under the skin, and severe bleeding from the mucous haemorrhages is frequently the cause of death. This form of anaemia is usually fatal, and even when recovery takes place, convalescence is very slow.

METHODS OF DETECTION.—More than 1 mg. per litre of air (about 1 in 3500) must be present before the odour of benzene can be distinctly perceived. Most of the chemical methods of detection involve nitration to nitrobenzene with subsequent conversion into compounds that can be estimated colorimetrically. These are too long and complicated to be suitable as standard tests in industry. A more simple test has, however, been developed, involving the absorption of the vapour in conc. sulphuric acid containing a trace of formaldehyde; an orange-brown colour is produced even by traces of benzene (down to 1 part in 10,000).

The test is carried out by drawing a sample of the atmosphere under test through a tube containing the reagent by means of a hand-pump of definite capacity, and determining the number of strokes required to produce a certain standard depth of colour. From the number of strokes of the pump required to produce the standard colour, the concentration of benzene vapour present is obtained by reference to the table given in the detailed instructions in the Leaflet.

The test is slightly more sensitive to toluene than to benzene, but, since both vapours have roughly the same toxicity, no distinction between them will normally be necessary.

With solvent naphthas (xylenes and their higher homologues) little more than a qualitative indication would be given by the test. Naphthalene vapour interferes by producing a black film on the reagent. Vapours of crude benzoles may contain compounds, such as thiophen, which interfere with the test by imparting a yellow or red colour to the sulphuric acid. Their presence may be detected by pumping the air sample through a bubbler of conc. sulphuric acid alone, when the respective colour only will be produced. Usually, however, the quantities of such substance in commercial grades of benzole are insufficient to affect the test.

DETAILS OF THE TEST.—The method of sampling the atmosphere by means of a hand-pump is the same as previously described (Leaflets Nos. 1 and 2, *loc. cit.*). The sample is drawn through the reagent contained in a bubbler consisting of a

side-arm test-tube of approx. 0·75 in. internal diameter and about 6 in. long, fitted with a rubber bung through which passes a delivery tube (approx. 0·125 in. bore) reaching nearly to the bottom of the test-tube and terminating in a fine jet. The bubbler is mounted on the barrel of the pump in such a way that the reagent can be easily seen and the tube readily removed for comparison with the standard and replacement by a fresh tube. A trap is inserted between the pump and the bubbler to prevent the reagent being drawn into the pump.

A convenient arrangement of the apparatus is described and illustrated in the Leaflet.

Preparation of Reagent.—The measured quantity (0·5 ml.) of 40 per cent. formaldehyde is introduced into the bubbler by means of a graduated pipette, the volume is made up to 10 ml. with conc. sulphuric acid, and the mixture is well stirred.

Preparation of Standard Colour.—One g. of sodium nitroprusside (of analytical reagent quality) is dissolved in 100 ml. of water. If kept in the dark in a well-stoppered flask, the solution should not deteriorate in 2 weeks. A slight alteration in shade, but not in depth of colour, may occur; if this becomes marked, a fresh solution must be made up.

Method.—The pumping with the hand-pump must be continued until the depth of colour developed is approximately that of the standard colour (the number of strokes made being counted). The bubbler is then removed and immediately compared, side by side, with the standard tube, in daylight reflected from a white surface held 2 to 3 in. behind them. If the colour of the test sample is less than that of the standard, the bubbler is replaced and further strokes of the pump are made until equivalence is reached; if the test colour is the deeper the test must be repeated with a fresh tube of reagent.

The following table gives the number of strokes necessary for various ranges of concentration in order to obtain the standard colour:

Concentration	Number of strokes
Up to 1 in 700	Less than 1
1 in 700 to 1 in 1200	1 to 2
1 in 1200 to 1 in 1500	2
1 in 1500 to 1 in 2000	3
1 in 2000 to 1 in 2500	4
1 in 2500 to 1 in 3000	5
1 in 3000 to 1 in 3600	6
1 in 3600 to 1 in 4200	7
1 in 4200 to 1 in 4700	8
1 in 4700 to 1 in 5300	9
1 in 5300 to 1 in 6000	10
1 in 7000	12
1 in 8000	15
1 in 10,000	18

Note.—(1) The number of strokes required to give the standard colour at concentrations lower than those given in the table is roughly inversely proportional to the concentration present; an approximate estimate may be made by extrapolation from the above figures.

(2) The standard colour is that given by pure benzene. It may be found that crude benzoles give a slightly different shade of colour, but this should not interfere with the comparison of the depth of colour of the reagent and standard.

Directions are given for a procedure for sampling the atmosphere from a space that is not readily accessible, or where there is a possibility of highly toxic concentrations of benzene vapour being present.

Food Investigation Board

THE COLD STORAGE AND GAS-STORAGE OF EGGS*

THE purpose of this Leaflet is to describe briefly the principles and relative merits of the cold storage and gas-storage of eggs.

PRECAUTIONS IN SELECTING AND HANDLING EGGS FOR STORAGE.—Preferably only infertile eggs should be stored and they should be cooled and stored as soon as possible. On no account should eggs be washed. *Any* method of washing increases the number of rots, especially green rots. Stored eggs should be de-chilled artificially (in rapidly moving air at 50° F.) and consumed within a short period after removal from storage.

DETERIORATION DURING STORAGE.—The changes that may occur are:—(*a*) Growth of moulds on the shell; (*b*) penetration of shell by moulds and bacteria whose growth produces rots; (*c*) uptake of odours; (*d*) enlargement of air-cell and toughening of the shell membranes; (*e*) shrinkage and liquefaction of the thick white; (*f*) yellowing of the white; (*g*) weakening of yolk-membrane, (*h*) weakening of the yolk; (*i*) development of "storage taste." Some of these changes can be prevented, others only retarded. Control of atmospheric composition (including humidity) can prevent some and retard others.

COMPARISON OF METHODS OF STORAGE.—The following methods have been critically compared at the Low Temperature Research Station, Cambridge:—(i) Cold storage with control of humidity only; (ii) partial gas-storage (cold storage with control of humidity and addition of 2 to 2·5 per cent. of carbon dioxide); (iii) full gas-storage (cold storage with addition of 60 to 100 per cent. of carbon dioxide but no control of humidity).

The results refer only to selected, first-quality, unwashed eggs, held for 4 days at about 52° F. before storage. The characteristics of eggs stored by the three methods for periods between 6 and 9 months were as follows:

Cold storage	Partial gas-storage	Full gas-storage
Shell, smooth	Shell, slightly rough	Shell, slightly rough
Air-cell, large	Air-cell, large	Air-cell, small
White, distinctly yellow	White, faintly yellow	White, faintly yellow
Thin white, viscous	Thin white, viscous	Thin white, watery
Thick white,[1] weak (vol. 60–70 per cent. of new laid)	Thick white,[1] firm (vol. 60–70 per cent. of new laid)	Thick white,[1] firm but considerably shrunken[3] (vol. 40–50 per cent. of new laid)
Yolk, flabby	Yolk, firm	Yolk, firm
Storage taste[2]	No storage taste	No storage taste

[1] The amount of thick white depends not only on the method of storage but also upon the amount initially present; if it is large, the amount after storage will be correspondingly high.

[2] Shows up particularly in boiled eggs.

[3] Shows up particularly in water-poached or fried eggs, but not in steam-poached eggs.

Cold storage gives satisfactory results for periods up to about five months. Partial gas-storage has advantages over cold storage, notably prevention of development of "storage taste." In full gas-storage the white becomes very watery, but, on the other hand, this method is the most effective of the three in preventing rots; it cannot, however, prevent rots developing during marketing, since it does not always destroy the micro-organisms causing green whites, though it stops them growing during storage.

The Leaflet concludes with an outline of the main features of the three methods and a list of references to scientific literature.

* Leaflet No. 8. By T. Moran, D.Sc., Ph.D. 1939. Department of Industrial and Scientific Research, 16, Old Queen Street, Westminster, S.W.1.

Queensland

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDED JUNE, 1938

In his Annual Report Mr. F. Connah, F.I.C., states that 14,447 samples were examined as compared with 15,421 in the previous year. The Government Laboratory undertakes work for all the Departments of Public Service except the Department of Agriculture and Stock, which has its own laboratory and staff. The points of interest to which attention is directed include the following:

Milk Control.—The methods now in use comprise the freezing-point determination, the methylene blue test, the use of the "Minit" apparatus to measure visible dirt, and, since 1935, the phosphatase test, to distinguish milk pasteurised at 142° F.—the minimum temperature prescribed under the Queensland Food and Drug Regulations.

The fine laid down in the Health Act for the watering of milk is £1 for each per cent. of added water.

Coal-tar Dyes in Beverages.—It cannot be accepted that any coal-tar dye in the quantity found in some beverages is entirely harmless to the human organism. The use of even the permitted dyes should be limited as far as possible. The minimum quantity required to enhance sufficiently the appearance of various cordials and beverages for trade purposes may be determined, and it is suggested that no more than that amount should be permitted. Fruit beverages of the same type contained coal-tar dye in quantities ranging from ½ to 4 grains per pint. If the former amount was sufficient, the latter must surely be regarded as excessive.

Metallic Contamination of Soda Water.—Fifteen samples of soda water from soda fountains were examined, with the following results:—Lead was present in 9 samples in amounts ranging from 1/77th to 1/5th grain per gall., and in 4 in amounts from 1/1000th to 1/100th grain per gall. Copper (in addition to lead) was present in the 13 samples in amounts of 1/100th to 1/5th grain per gall. One sample, reported to have caused sickness and vomiting in children and adults, contained zinc in the proportion of 4 grains per gall.

Apparent Loss of Phytin in Breadmaking.—In using the phytin-content as a factor in calculating the proportion of whole meal in bread, it was found that there was an apparent loss of phytin during baking. Controlled baking tests gave the following results:

	Whole meal			Whole meal + 25 per cent. of bran			
	Flour	Dough	Bread	Flour	Dough	Bread	Bran
Total phosphorus, per cent.	0·35	0·35	0·36	0·60	0·60	0·63	1·34
Phytin phosphorus, per cent.	0·33	0·30	0·26	0·62	0·54	0·42	1·50
Phytin, per cent. ..	1·17	1·07	0·92	2·2	1·92	1·50	5·3

As there was no loss in the total phosphorus, it would appear that, under the influence of fermentation and baking, some of the phytin is so changed that it no longer registers as phytin.

Sweet Potatoes.—The yellow variety of sweet potatoes is not generally popular, although it has a good flavour and has been found to contain up to 16,000 International Units of vitamin A per lb., whereas the popular white variety is deficient in vitamin A. The percentage composition of samples of sweet potatoes and "English" potatoes from the local market was as follows:

	Sweet potatoes		"English" potatoes (Carmen)	
	Yellow variety	White variety	Stanthorpe	Forest Hill
Water	68·0	77·0	78·6	77·0
Protein	1·3	1·3	1·8	1·7
Ethereal extract (fat) ..	0·3	0·2	0·2	0·2
Sucrose	2·8	1·2	0·3	0·3
Invert sugar	0·5	2·8	nil	0·4
Crude fibre	0·9	0·7	0·5	0·6
Starch	25·1	16·0	17·6	18·8
Ash	1·1	0·8	1·0	1·0
	100·0	100·0	100·0	100·0
Phytin	0·13	0·13	0·1	0·18
Calcium (Ca)	0·026	0·013	0·0043	0·01
Phosphorus (P)	0·04	0·04	0·04	0·057
"Digestible calories," per lb.	550	390	366	360

Further work is necessary before the higher water-content of the white variety can be accepted as usual for sweet potatoes.

ACETANILIDE IN HEADACHE POWDER.—Acetanilide is a poison under the Queensland Poisons Regulations. Any package containing it must bear a label with the word "Poison" and "Unfit for children under 16 years." *The British Pharmaceutical Codex* states that some persons are extremely susceptible to acetanilide, and that even small doses will lead in these cases to cyanosis and collapse. It has been excluded from the British Pharmacopoeia.

VITAMINS IN COSMETICS.—In a world made vitamin conscious it was to be expected that vitamins would ultimately be incorporated in cosmetics. The use of vitamins A and D in cosmetic cream probably finds its origin in the beneficial effect of cod-liver oil on burns and other skin lesions. Samples of such creams said to contain 20,000 units of vitamin A per lb. were examined.

SOLUBLE LEAD IN PAINT.—Under the Health Act, 1937, it is not permissible to use any paint containing more than 5 per cent. of soluble lead upon verandah walls, gates, steps, etc., of any house or building, or upon any fence whatsoever, or upon any other exterior portion of any building to which children under the age of 14 years have easy access.

Paint containing any lead may not be used on the roof of any house or building.

Of the 102 samples of paint examined, 75 contained over 5 per cent. of soluble lead, 9 contained less than 5 per cent., and 18 were free from lead.

British Standards Institution

THE following Standard Specifications have been issued:*

NO. 823—1938. BRITISH STANDARD DENSITY—COMPOSITION TABLES FOR AQUEOUS SOLUTIONS OF SODIUM CHLORIDE AND OF CALCIUM CHLORIDE FOR USE IN CONJUNCTION WITH BRITISH STANDARD DENSITY HYDROMETERS.

The hydrometers and tables together provide a simple means of determining the strength of any given aqueous solution of sodium chloride or of calcium chloride or of making up a solution of known strength.

The appendixes to the tables give details of the British Standard density hydrometers available for such solutions, a note on the reading of standard density hydrometers in the solutions, examples of the use of the tables, and details of corrections to readings. It is often adequately accurate to take the reading at any temperature $t°$ C. as giving directly the density of the solution in g. per ml. at $t°$ C.

* Obtainable from the Publication Department, British Standards Institution, 28, Victoria Street, London, S.W.1. Price 3s. 6d. net, post free 3s. 8d., each.

No. 824—1938. BRITISH STANDARD DENSITY-COMPOSITION TABLES FOR AQUEOUS SOLUTIONS OF CAUSTIC SODA FOR USE IN CONJUNCTION WITH BRITISH STANDARD DENSITY HYDROMETERS.

From the density determined at any particular temperature the tables enable the density and composition of the caustic soda solution to be determined at any temperature within the range of the tables.

Appendixes give details of the British Standard density hydrometers available for aqueous solutions of caustic soda, a note on the reading of the hydrometers in these solutions, examples of the use of the tables, and details of corrections to the readings.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Starch-Iodine Coloration as an Index of Differential Degradation by the Amylases. C. S. Haines and M. Cattle. (*Proc. Roy. Soc.*, [B], 1938, **125**, 387–414; *J. Inst. Brewing*, 1939, **45**, 70–71.)—Iodine coloration was followed with a view to correlating it with enzymic breakdown by different amylases—α malt, *Aspergillus*, salivary, pancreatic, and β amylase. Absorption spectra were determined at intervals during the action of the amylases on starch, and the liberation of reducing groups was followed by means of both alkaline copper and alkaline hypoiodite reagents. A soluble starch substrate, as prepared by Small (*J. Inst. Brewing*, 1919, 180), was used, and the method of preparing the amylases is described in an appendix. The concentration of starch was 0·2 per cent. and the temperature of conversion 25° C. The so-called saccharogenic and dextrinogenic types of amylase can be distinguished almost from the beginning of their action by the manner in which the absorption characteristics of the iodine compounds are altered, and during each degradation process the relation between the changes in the iodine-colouring property and the liberation of reducing groups can be delineated accurately. The observations can be explained by two hypotheses. According to the first, a single species of "colouring group" would be considered to occur at regular intervals along the chain structure, and the absorption characteristics of the compound formed by the attachment of iodine at this group would depend upon the mode or degree of association of the molecular chains of a particular product. According to the second hypothesis, two or more distinct species of "colouring group," yielding compounds of different hue, might be assumed to be distributed in parallel along the chains, but of these, one species at least would be assumed to exist exclusively in molecular associations. Both of these theories incorporate the conceptions that the "colouring groups" are distributed homogeneously along the molecular chain structure, so that different portions of the molecule are approximately equivalent in this respect, and that differences in the hue of iodine colours exhibited by different products are related mainly to the phenomenon of molecular association. On either theory, the alterations in iodine colour observed during the action of β-malt-amylase are conceived as resulting from a progressive reduction in the number of "colouring groups" during the cleavage of maltose fragments from the end of the chain. The fact

that the intimate molecular associations of the residual dextrins are not broken down during this process would account for the approximately constant absorption characteristics of the iodine compounds. Conversely, with the dextrinogenic amylases, the marked alteration in the hue of the iodine colour is attributed mainly to a preliminary disruption of molecular associations, this being followed by a progressive destruction of "colouring groups" as the chains are cleaved into achroic dextrins. E. M. P.

"Iles Mannan Flour." J. E. De Groot, C. J. Van Hulssen and D. R. Koolhaas. (*Chem. Weekblad*, 1939, **36**, 69–73.)—The product known as "iles mannan flour" in the Dutch Indies is prepared from the tubers of varieties of the *Amorphophallus* family (*i.e. A. campanulatus*, *A. oncophyllus*, *A. variabilis*, *A. spectabilis*, *A. decus silvae* and *A. muelleri*). The tubers should be gathered in their second year of growth, when the leaves have withered and the tubers have attained their maximum diameter (about 20 cm.). They are dried, cut into slices and ground finely, and they then undergo a combined stamping and winnowing process which eliminates the cell walls and raphides (needle-shaped crystals of calcium oxalate). The raphides are particularly abundant in the wild plants; they are objectionable when (as in Japan) the flour is used as a foodstuff. *A. rivieri* ("devil's tongue") is processed in this way in Japan, and the resulting flour (which is known as "konjaku flour") has a mannan content (determined viscosimetrically, see below) of 60 per cent. (calculated on the dry substance). The mannan contents of the Javan varieties listed above are approximately 5, 24·4 to 52·4 (mean, 35), 6·7 to 21·6 (mean, 14), 30, 9, and 14 per cent., respectively. Existing knowledge of the chemistry of mannan is reviewed (*cf.* Haworth, *J. Chem. Soc.*, 1937, 784); Ohtsuki and Nishida (*Acta Phytochim, Japan*, 1928, **4**, 1) have shown that the mol. of konjaku mannan is built up from 1 mol. of glucose and 2 of mannose, whilst *X*-ray evidence (*cf.* Sakurada and Hutino, *Z. physik. Chem.*, 1933, **21**, 18) suggests that it can exist in two forms having different chemical properties. The flour is usually evaluated in terms of its mannan-content, but determinations, by means of phenylhydrazine, of the mannose produced by hydrolysis has not been found to give a reliable indication of the quality of the flour. The present authors prefer to determine the relative viscosity, as follows:—The tuber is slit, dried in a current of air at 40° to 45° C., ground finely, and passed through a 0·8-mm. sieve. The powder (1 to 2 g.) is then stirred with 300 g. of water at 55° C. for 2 hours, the water lost by evaporation is made good, and the solution is cooled to 27·5° C. and its relative viscosity determined at 27·5° C. A calibration curve relating the (Engler) viscosity and concentration of mannan was compiled from experiments with known quantities of mannan (see below) and is reproduced, and this may be used for actual determinations. Curves relating the viscosity and time of stirring are also reproduced; they show that the same maximum and constant viscosity is obtained under the above conditions as by stirring for 1 hour at 50° C. The temperature should not exceed 50° C., as otherwise the paste gels. The moisture-content of the flour should also be determined, *e.g.* by Aufhäuser's method of distillation with xylene (*Chem.-Ztg.*, 1922, **46**, 1149) because, if drying is carried too far, the colloidal structure of the flour is changed and low viscosities result. A rise in *p*H results

in a fall in viscosity, and this also may be important when the flour is used as a creaming-agent in latex which may contain ammonia. Mannan contents (percentages as determined by a chemical method) and relative (Ostwald) viscosities, for 0·23 per cent. solutions of three such products respectively, are:—Mannan, 63·4 and 7·7; bittchu powder (a high grade of konjaku flour), 50·1 and 4·9; and ordinary konjaku flour, 54·7 and 2·7. Mannan may be purified (*cf.* Ohtsuki, *loc. cit.*) by stirring the flour with water at a temperature not exceeding 55° C., and adding alcohol to the viscous solution which is obtained on cooling. The resulting precipitate of gluco-mannan is separated, and redissolved and reprecipitated several times. It is finally suspended in a mixture of alcohol and ether and filtered. It is then obtained as a white or grey powder and free from reducing sugars. Hydrolysis with 5 per cent. hydrochloric acid produces reducing sugars, and the mannose may be determined by the phenylhydrazine method. The mannose-contents (percentages on the dry sample) and (Ostwald) viscosities of 0·23 per cent. solutions at 27·5° C. for the mannans obtained from 3 sources are, respectively:—From konjaku flour, 63·4, 7·7; from *A. oncophyllus*, 59·8, 7·8; from *A. variabilis*, 63·6, 3·3. Uses of iles flour are as a substitute for gelatin (in foodstuffs), for agar-agar (*e.g.* in culture media) and for starch (*e.g.* to confer water-resistance and impermeability on paper). It is also used in insecticides, in cosmetic preparations, as a creaming-agent for latex, and as a flocculating agent for coal slurrys; suspensions of clay are flocculated if sufficient quantities of a solution of the flour and of a sodium hydroxide solution are added to produce concentrations of 0·0025 per cent., and 0·002 *N*, respectively. J. G.

Colorimetric Method for the Determination of Sugars. E. A. Schmidt. (*Das Mühlenlabor.*, 1938, **8**, 122–131.)—This method was worked out for the purpose of estimating the small quantities of sugar (maltose) present in flours or formed in the course of bread-making. When maltose solution is heated with alkali caramelisation occurs, and when the experimental conditions are rigidly standardised the intensity of the brown colour is a measure of the sugar concentration of the solution. By comparison with standard solutions or by photometric methods the amount of the sugar present may thus be determined. The degree of caramelisation varies with the nature of the alkali used and follows the order potassium hydroxide, sodium hydroxide, sodium carbonate, ammonium hydroxide. A normal solution of sodium hydroxide was found to be most suitable for the determination. Experiments showed that within certain limits the concentration of alkali is of secondary importance but the effect of variations in sugar concentration is incomparably greater. The procedure is as follows:—To 15 ml. of the sugar solution, which should be diluted until the concentration of sugar lies between 0·06 and 0·8 per cent., 5 ml. of *N* sodium hydroxide solution are added and the mixture is heated in a boiling water-bath for exactly five minutes, in which time the brown colour reaches its maximum intensity. The colour is then compared with that produced by standard solutions of the pure sugar treated in the same way. For the determination of maltose the colorimeter of Schmidt and Kühn, in which the intensity of the brown colour is measured by means of standard coloured discs, is described. Under the standard conditions maltose, glucose, fructose, mannose,

and arabinose are caramelised to the same extent. Lactose and galactose give somewhat deeper, and glycerose somewhat lighter colours. Sucrose, raffinose, starch, dextrin and the alcohols mannitol, sorbitol, etc., are not caramelised. Since the curve formed by plotting the degree of caramelisation against the concentration of sugar is not linear, it is necessary to employ a complete series of standard sugar solutions which are treated in the same manner as the sample solution to obtain the absolute amount of sugar present. When the solutions are matched in a colorimeter it is possible to obtain very exact results by the method. The albuminous constituents of flours, *viz.* amino acids, peptones and proteins do not interfere with the development of the colour and may be considered inert under the standard conditions of the method. A. O. J.

Cobalt-content of some Food Materials from different parts of the United States. Bashir Ahmad and E. V. Mc.Collum. (*Amer. J. Hyg.*, 1939, **29**, [A], 25–26.)—In view of the evidence that has accumulated in the last two years that traces of cobalt are essential for the nutrition of sheep and cattle and that cobalt deficiency may give rise to the so-called "coast disease," "bush sickness" or enzootic marasmus, the authors undertook a study of the cobalt distribution in some common foods collected from various parts of the country. They employed a modification of the colorimetric method of Stace and Elvehjem depending upon the formation of a stable red compound with nitroso-R-salt (nitroso derivative of 3·6-β-naphthol disulphonate). They found that considerable variation exists in the cobalt-content of different materials. On the whole leguminous seeds are richer than the cereal grains, the value for the former ranging from 0·018 to 0·0475 mg. and for the latter from 0·014 to 0·042 mg. per 100 g. of dry material. No correlation could be found between the cobalt-content and the sources of the food stuffs according to States; thus kidney beans from Colorado gave the highest value, whilst peas from the same State gave a somewhat low value. D. R. W.

Characteristics of Tobaccos of the Acid and Alkaline Groups. A. Wenusch. (*Z. Unters. Lebensm.*, 1939, **77**, 170–172.)—Tobacco smoke contains a number of substances which, during the burning, have been volatilised without change of chemical constitution, and these, together with other associated substances, influence the odour and taste of the smoke. Since these bodies, which belong to very diverse classes (*e.g.* higher hydrocarbons, resins, resin acids, nicotine, etc.), have different solubilities in different solvents, their partial separation can be effected by treatment of the finely powdered tobacco with these solvents. The tobacco is exhaustively extracted for several days in a Soxhlet apparatus with each of the following solvents:—Petroleum spirit, ether, alcohol, and water. After each extraction the solvent is removed by evaporation and the soluble residue is dried at 80° C. and weighed. After the final (aqueous) extraction the exhausted tobacco is washed with alcohol and ether, dried first at 80° C., and finally over phosphoric anhydride and weighed, and its volume is measured in a graduated cylinder. The bodies appearing unchanged in the smoke are extracted mainly by the non-aqueous solvents. Nicotine appears to be the only constituent of the aqueous extract occurring unchanged in the smoke. For the experiments five samples were used, *viz.* a very good and a somewhat inferior tobacco of each of the

two groups and a dried but not fully ripened raw tobacco (Zihna) of the acid group. The petroleum spirit extracts of the tobaccos of the acid and alkaline groups showed little difference, but the ethereal and alcoholic extracts were lower for the alkaline group than for the acid group, whilst the aqueous extracts were higher for the alkaline group than for the acid group. The opinion previously expressed (*Z. Unters. Lebensm.*, 1938, **76**, 433), *viz.* that tobacco leaves intended for the preparation of commercial raw tobacco of the alkaline group must be collected at a less advanced stage of development than those of the acid group is now supported by the observation that commercial tobacco of the alkaline group yields more water-soluble extract than tobacco of the acid group in spite of differences in the process of manufacture, which tend to reduce water-soluble matter in the tobaccos of the alkaline group and to conserve it in those of the acid group. The volume of dried exhausted residue per 100 g. is much lower with tobaccos of the acid group than with those of the alkaline group. This also shows that tobacco leaves for preparation of the acid group are collected at a later stage of development. The percentage amounts of extract found with Nigritta, Class I and Nigritta Refuse (the figures for the latter being in brackets), both of the acid group, were:—(*a*) Petroleum spirit, 5·18 (6·77); (*b*) ether, 6·59 (5·37); (*c*) alcohol, 31·91 (24·52); (*d*) water, 16·22 (21·36); (*e*) insoluble residue, 39·96 (41·96); (*f*) volume of exhausted residue from 100 g., 116 (168) ml. For Havana of very good quality (and Havana of lower quality), both of the alkaline group, the corresponding figures were:—(*a*) 6·09 (5·08); (*b*) 1·67 (1·42); (*c*) 8·96 (11·30); (*d*) 33·15 (34·80); (*e*) 50·01 (46·89); (*f*) 286 (336) ml.; for the high-quality Zihna tobacco of the acid group the figures were:—(*a*) 6·60; (*b*) 5·63; (*c*) 35·31; (*d*) 19·05; (*e*) 32·63; (*f*) 108 ml.

A. O. J.

pH Value of Fermented Tobacco Leaves and Cigarettes. C. Pyriki. (*Z. Unters. Lebensm.*, 1939, **77**, 157–170.)—Since the pH of tobacco varies only within narrow limits, its determination must be made with an accuracy of 0·01 to 0·02, and for this purpose the Ionometer of Lautenschläger (Kordatzki, *Taschenbuch der praktischen pH-Messung*, Munich, Verlag Müller und Steinicke, 1934, p. 68) is recommended for its simplicity and rapidity of application. Brückner (*Der Biochemie des Tabaks*, Berlin, Verlag Parey, 1936, p. 170) uses the combined calomel-quinhydrone electrode of Tödt with an extract prepared from 5 g. of powdered or shredded tobacco and 100 ml. of conductivity water under definite conditions, but the method takes much time. The method to be described is simpler and is applicable to a suspension of tobacco in distilled water. The powdered or shredded tobacco (0·5 g.) is thoroughly stirred with 10 ml. of distilled water for one minute and, after the addition of saturated quinhydrone solution, the stirring is repeated for ½ to 1 minute and the determination of pH value is made with observation of the temperature, the value being reduced to 18° C. by means of a curve. The results obtained agree well with those obtained by the method of Brückner. Although shredded tobacco may be used, powdered tobacco is preferable, the sample being dried at 30° C. for 3 hours before powdering. Experiments with a number of different tobaccos showed that those of pH 5·5 can be dried for 3 hours at 50° C. with little change of pH, and that those of lower pH

are not affected by drying at 95° C., but a Java cigarette tobacco of *p*H 6·5 was affected to a greater extent even when dried at ordinary temperature over calcium chloride. It has already been shown (Pyriki and Dittmar, *Z. Unters. Lebensm.*, 1931, **61**, 216; Abst., ANALYST, 1931, **56**, 407) that oriental tobacco does not lose any basic constituents when dried at 50° C. It is known that the quality of fermented tobacco improves from the lower to the higher leaves of the plant, and since the hydrogen ion concentration of the cell sap increases with higher position of the leaf, it follows that the *p*H of good-quality tobacco is lower than that of poorer qualities. As a rule young fermented leaves have a higher *p*H than older leaves. Experiments with Macedonian tobacco leaves showed that as the leaf turns brown the *p*H falls. Attempts to correlate *p*H and size of leaf gave irregular results and probably could be successful only with leaves taken from the same plant. By a classification of leaves according to their probable position on the stem it was possible, in spite of certain irregularities, to say that towards the apex of the plant the acidity of the leaf increases. It has been shown (Pyriki and Dittmar, *loc. cit.*) that portions of the leaf near the tip are richer in nicotine and poorer in sugar than portions near the stalk, and Andreadis and Toole (*Z. Unters. Lebensm.*, 1934, **68**, 431; Abst., ANALYST, 1935, **60**, 110) found that the nicotine-content increases from stalk to tip and from midrib to margin. Experiments showed that the *p*H diminishes from tip to stalk and from margin to midrib independently of the position of the leaf on the stem. The results obtained show that according to age, ripeness and position of the leaf on the stem the range of variation of *p*H is 4·7 to 5·8, although in individual instances values of 4·5 and 6·0 were obtained. As a rule the *p*H of tobacco of high quality is lower than that of inferior grades, the high acidity producing mildness in the smoke by fixing the nicotine and other basic substances (Pyriki, *Z. Unters. Lebensm.*, 1932, **64**, 273; Abst., ANALYST, 1932, **57**, 727). Investigation of certain brands of cigarettes (478 samples of 27 brands) gave a *p*H range of 4·95 to 5·29. Cigarettes of higher quality had lower *p*H values than those of lower quality, and this was found to be true also of raw tobacco intended for the manufacture of cigarettes. As a rule, storage of cigarettes promotes an increase of acidity, and no essential difference was found with cigarettes packed in cartons and in metal containers. With lower-priced cigarettes the acidity increased more rapidly than with higher-priced brands. With cigarettes stored loose on a shelf a somewhat greater lowering of *p*H occurred. It appeared also that the higher the initial *p*H of the cigarette the more rapidly it diminished. The cigarettes stored in metal containers for 12 months were infected with moulds and had a musty odour; those stored in cartons had a musty odour but were free from mould. Both mould formation and mustiness were less evident in the higher-priced brands. A. O. J.

Biochemical

Determination of Creatinine and Creatine. 1. Determination in Urine. E. C. Noyons. (*Chem. Weekblad*, 1939, **36**, 63–68.)—Improvements in Jaffé's picric acid method (*cf.* Chapman, ANALYST, 1909, **34**, 475; Greenwald and Gross, *id.*, 1928, **53**, 400; 1929, **54**, 60) are discussed. The colour produced with this reagent may be evaluated satisfactorily in the Pulfrich step-photometer if the

reagent and the creatinine to be used as a standard are prepared as follows:— To a boiling solution of 25 g. of anhydrous sodium carbonate in 600 ml. of water are added, in small quantities, 50 g. of technical picric acid. The mixture is boiled, filtered and cooled rapidly, and the resulting crystals are separated by filtration and washed well on the filter with 220 ml. of 12 per cent. sodium hydroxide solution. They are then shaken with 300 ml. of 10 per cent. hydrochloric acid, again filtered off, washed with water, dried at 100° C. and recrystallised at least twice from hot pure acetic acid. A solution in 10 per cent. sodium hydroxide solution should show no absorption in the step-photometer, using the S53 filter. The creatinine is purified by adding 15 ml. of a filtered, saturated solution of rufianic acid to a solution of 500 mg. of creatinine in a mixture of 10 ml. of water and 1 ml. of 5 per cent. sulphuric acid. After 3 days in the ice-chest the creatinine monorufianate is separated on a glass filter (G3) and recrystallised twice from water. The rufianic acid is then precipitated from a solution of the crystals in dilute ammonia by addition of finely-powdered baryta, followed by filtration, and removal of the excess of barium hydroxide by precipitation with a current of carbon dioxide and re-filtration. The pure creatinine is then obtained by evaporating the filtrate, a micro-determination of nitrogen being used to control its purity (*cf.* Zimmermann, *Z. physiol. Chem.*, 1930, **188**, 180; **189**, 155). A solution of 20 mg. of the pure creatinine in 100 ml. of water is then prepared, and 10-ml. portions (or 1 ml. diluted to 10 ml. where necessary) of this are taken. To 4 ml. of each solution are added 12 ml. of a saturated solution of picric acid, and to 10 ml. of this mixture are added 0·5 ml. of 10 per cent. sodium hydroxide solution (free from carbonate). The extinction of the solution is then evaluated in the step-photometer after 30 minutes, with the use of the S53 filter and at a depth of liquid of 30 mm. The relationship between the concentration of creatinine (0·2 to 3·2 mg. per 100 ml.) and the extinction is linear, and a graph (which is reproduced) is used for the evaluation of samples of unknown concentrations. Since the Jaffé reagent is not specific for creatinine, the following methods for the isolation of the creatinine are described, together with the experiments that justify their adoption:— (1) *Extraction.*—The sample is extracted with 10 ml. of warm *iso*butanol or *iso*pentanol, and to the extract are added 10 ml. of a mixture of 15 ml. of the picric acid reagent, 5 ml. of water, and 10 ml. of 10 per cent. sodium hydroxide solution; the resulting colour is matched as usual. Under certain conditions, however, extraction of the creatinine may not be complete, and the solvent may not be entirely selective for creatinine. (2) *Adsorption.*—A mixture of 1 ml. of the filtered urine and 9 ml. of water containing 0·5 g. of acid clay is shaken for 2 minutes and centrifuged, the liquid is poured off, and the operation is repeated, first with 3 ml. of water and then with 10 ml. of 1 per cent. sodium hydroxide solution. The last operation elutes the creatinine, and the liquid which separates should be neutralised with 25 per cent. hydrochloric acid and diluted to 100 ml. in a graduated flask. The colour is then allowed to develop in a mixture of 2·5 ml. of this solution with 7·5 ml. of the reagent and 0·5 ml. of the alkali; larger quantities of alkali than this give high results. To test the suitability of the acid clay 0·5 g. should first be shaken with 10 ml. of a solution of 20 mg. of creatinine in 100 ml. of 0·25 per cent. hydrochloric acid, the separated liquid being rejected and the clay washed

twice by shaking and centrifuging with two 3- and one 1-ml. portion of water. The last wash is tested colorimetrically for creatinine, which should be absent, and the clay is then eluted as described above; if a determination shows that all the creatinine has been recovered, the clay is satisfactory. This method has been tested exhaustively, and full data regarding the adsorbing properties and selectivity of common adsorbing agents are provided; acid clay is shown to be the only one that fulfils the requirements of the method. Creatine and creatinine in urine are determined by evaporating 1 ml. on the water-bath with 0·1 ml. of 25 per cent. hydrochloric acid, and treating a solution of the residue in 10 ml. of water with acid clay, etc., as described above. This process converts the creatine into creatinine, so that the difference between the creatinine-contents before and after applying it gives the creatinine derived from creatine; the factor 1·16 then gives the latter. Comparison with the Lieb and Zacherl method (*id.*, 1934, **223**, 169; 1935, **232**, 41) for urines containing known quantities of creatine and creatinine showed that the latter method gives very high results, the errors with the new method being only +0·7 to −0·8 mg. for 5 to 15 mg. of creatinine. (3) *Precipitation.*—One ml. of 25 per cent. hydrochloric acid is diluted to 100 ml. with the urine in a dry measuring flask, and after filtration 10 ml. are mixed with 5 ml. of a 5 per cent. solution of phosphotungstic acid; after the mixture has stood for 3 hours, it is filtered. A portion (*e.g.* 1·5 ml.) of the filtrate, and also of a mixture of 10 ml. of the unprecipitated solution and 5 ml. of water, is diluted to 100 ml., and 2·5 ml. of each of these new solutions are mixed with 7·5 ml. of a saturated solution of picric acid and 0·5 ml. of 10 per cent. sodium hydroxide solution. The colours are matched in the usual way, and the difference between the two values found from the curves gives the true creatinine-content. For the determination of creatine, 10 ml. of urine are evaporated with 1 ml. of the acid, a solution of the residue in exactly 10 ml. of 1 per cent. hydrochloric acid being treated as described above; the resulting creatinine value includes that derived from the creatine. The use of 3·5-dinitrobenzoic acid (*cf.* Langley and Evans, *J. Biol. Chem.*, 1936, **115**, 333) was also examined, but was found too dependent on working conditions to provide a reliable and yet rapid method. J. G.

Occurrence of Zinc in Human Blood. F. H. Vogelenzang. (*Pharm. Weekblad*, 1939, **76**, 89–99.)—The importance of zinc in the vegetable kingdom and its function in the human organism are discussed (*cf.* Zbinden, *Compt. rend.*, 1929, **188**, 1628) and analytical methods applicable to such investigations are outlined. There is a full bibliography. In the method of determination now recommended (*cf.* Hibbard, *Ind. Eng. Chem., Anal. Ed.*, 1937, **10**, 127) the sample (*e.g.* blood) is evaporated on the water-bath, dried at 120° C., and ignited at 490° C.; so long as the temperature of ignition is below 500° C. there is no risk of losses by volatilisation. The dithizone reagent used (*cf.* H. Fischer, ANALYST, 1937, **62**, 150) is prepared by shaking a solution of 15 mg. in 100 ml. of carbon tetrachloride with 0·02 *N* ammonia, the aqueous layer being subsequently acidified, and re-extracted with sufficient carbon tetrachloride to bring the concentration of dithizone to 6 mg. per 100 ml.; dilution of the strong stock solution in this way should be carried out every day. To a solution of the ash in 5 ml. of 2 *N* hydrochloric acid

are added 2 ml. of a solution of citric acid, from which any lead, copper or zinc has been removed by making a 10 per cent. solution weakly alkaline to litmus with 25 per cent. ammonia and extracting with successive portions of the dilute dithizone reagent until the carbon tetrachloride layer is coloured green. Pyrex glass vessels are recommended for all these operations, as some glasses (*e.g.* normal Jena glass) contain zinc. The solution is then made weakly alkaline to litmus with 2 *N* ammonia and extracted with small separate portions of the dilute dithizone reagent, until the carbon tetrachloride layer is green. The combined extracts are then shaken with two 5-ml. portions of 2 *N* hydrochloric acid, which causes the zinc to pass into the acid layer, leaving the copper in the carbon tetrachloride; the effects of lead in blood may be ignored, as the amounts concerned are normally too small to affect the results. The acid solution is made weakly alkaline with 2 *N* ammonia and again shaken with the dilute dithizone reagent, and the carbon tetrachloride layer then contains the red zinc-dithizone complex, with an excess of reagent which may be removed by shaking with 0·02 *N* ammonia. The carbon tetrachloride layer is then washed with water and filtered through a dry paper, any residue being washed with the solvent. The united filtrate and washings are diluted to a known volume with the solvent, and the colour is matched in a Pulfrich photometer against a standard prepared in a similar way from pure zinc sulphate. It was found that the coloured solution obeys the Lambert–Beer law, and that its absorption spectrum indicates a maximum absorption at 525$m\mu$; the colour filters S53 (green) and S47 (blue) may therefore be used, and the necessary extinction-coefficients are given. Direct extraction of the sample after treatment with trichloroacetic acid and filtration gives results similar to those obtained by ignition. It is necessary, however, to allow for a blank determination on the reagent, and trouble from the formation of an emulsion may also result. The amounts of zinc in the venous bloods from 30 patients are recorded, the values obtained being 0·34 to 0·90 (average, 0·612) mg. per 100 ml. for patients having diabetes mellitus, and 0·23 to 1·03 (average, 0·604) mg. per 100 ml. for others. The highest value recorded was obtained in a case of polycythemia, and the lowest in a severe case of hyperchromic anaemia. Tests on 10 samples showed that as a rule 88·6 to 92·2 per cent. of the zinc is contained in the blood cells, the remainder being in the plasma, but with 3 diabetics 100, 93·2 and 95·4 per cent., respectively, was found in the blood cells. In 2 cases of myeloid and lymphatic leucaemia, the amounts of zinc in the white cells were 0·193 and 0·091 and in the red cells, 0·39 and 0·43 mg. per 100 ml., respectively. The distribution of the zinc-contents of 27 samples showed averages of 0·52, 0·605 and 0·70 mg. per 100 ml., for those with less than $4{\cdot}3 \times 10^6$, $4{\cdot}3 \times 10^6$ to $4{\cdot}8 \times 10^6$, and more than $4{\cdot}8 \times 10^6$ erythrocytes, respectively, and it is concluded that the amount of zinc in blood is probably related to the number of cells present. J. G.

Influence of Zinc on the Reaction between Iodine and Insulin. E. H. Vogelenzang. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 201–206.)—The iodine-consuming power of insulin was measured at *p*H 7·2 in the presence of calcium, cadmium, aluminium, zinc and lead; cobalt, nickel, copper and iron were excluded to avoid complications of the reaction. Two methods were used: (1) To a solution

of the proteins was added a solution of the cation, and the *p*H was brought to 7·2 with a sodium phosphate buffer. An excess of iodine was added, and the unused iodine was titrated after a convenient time. (2) An insufficient quantity of iodine containing starch was added to the buffered solution, and the time required for decolorisation was measured. Ovalbumin (dried egg albumin), human serum, pancreatin (U.S.P.), pepsin (Witte), peptone (free from fibrin), and four insulin preparations (A, amorphous insulin—1 unit in 0·079 mg., about 75γ of zinc per mg.; B, crude insulin—1 unit in about 0·75 mg.; C, crude insulin—1 unit in about 1·7 mg.; D, crystalline insulin—1 unit in 0·042 mg., about 35γ of zinc per mg.) were used. Solutions were prepared containing 0·1 per cent. of dry substance in 0·005 *N* hydrochloric acid. Calcium chloride, cadmium chloride, zinc sulphate, zinc acetate and lead acetate were used in 0·004 molar concentrations, and aluminium sulphate in 0·0027 molar concentration. These solutions were calculated to contain the equivalent of 65γ of zinc in 0·25 ml. This quantity is sufficient to account for about 45 units of insulin. The buffer solutions used were 0·2 molar disodium hydrogen phosphate and disodium hydrogen phosphate-sodium dihydrogen phosphate mixtures of the same concentration. The iodine solutions were prepared by diluting 0·1*N* solution with water. The mixtures were acidified with phosphoric acid and titrated at 15° to 20° C. with 0·005 *N* sodium thiosulphate solution; the uncertainty of the titrations did not exceed 0·04 ml. The influence of *p*H was found to be negligible for small variations from 7·2.

Influence of zinc on the iodine-consuming power.—To 2·5 ml. of solution were added 0·25 ml. of zinc solution and 0·35 ml. of phosphate solution; in a second series the zinc solution was replaced by 0·25 ml. of water. To the mixtures was added 0·5 to 1·0 ml. of 0·01 *N* iodine solution. After 15 minutes the solutions were acidified and titrated, starch being used as internal indicator. The following results show that the difference found for insulin must be ascribed to the influence of the added zinc.

Substance	Iodine, ml. 0·01 *N*			Difference
	Added	Combined after 15 mins.		
		Zn present	Zn absent	
Ovalbumin ..	0·50	0·36	0·35	0·01
Serum proteins ..	1·00	0·53	0·53	0
Pepsin	0·50	0·10	0·08	0·02
Peptone	0·50	0·35	0·35	0
Pancreatin	0·50	0·12	0·13	−0·01
Insulin A	1·00	0·51	0·59	−0·08

In further experiments it was found that the velocity of the reaction is influenced by the time at which the starch is added and by the ratio between starch and iodine. To obtain reproducible and constant results it is necessary to ensure a constant iodine-starch ratio by adding starch to the iodine solution. The addition of starch evidently lowers by adsorption the available iodine concentration. The quantity of iodine combined increases with time, and from 0·25 minute upwards (to 125 minutes) is a linear function of log. time. As the difference caused by the addition of zinc remains constant over a rather long period, the presence of zinc must be regarded as causing an inhibition of the action of iodine on a definite

part of the insulin molecule and not as a retardation of the iodine-binding power of the insulin molecule as a whole, for in that event the difference would be expected to diminish gradually. The quantity of iodine combined, and the zinc effect, increase with physiological activity. The data presented are mainly of a qualitative nature. It was observed that a preparation of crystalline (zinc) insulin did not show the zinc effect after addition of extra zinc. The following facts suggest the possibility of a chemical method for the assay of insulin:—(1) The iodine-binding power of zinc-free and of zinc-containing insulin at *p*H 7·2 is probably a linear function of the physiological activity, and (2) the magnitude of the zinc effect is a function of the physiological activity of the insulin preparation. The latter method appears to be specific but is applicable only to zinc-free insulin, whereas the former may be of special value in the control of the industrial purification of insulin. With regard to the question as to which part of the insulin molecule is shielded by zinc, several considerations lead to the assumption that the zinc is bound to the sulphur of the insulin. E. M. P.

Bacteriological

Observations on Bacterial Growth in presence of Silver Foil. C. Siebenmann. (*Amer. J. Hyg.*, 1939, **29**, [B], 36–44.)—In contrast with the bactericidal action exerted by large silver surfaces in water, silver foil when added to broth is shown experimentally to have no growth-inhibiting influence on 15 out of 16 pathogenic micro-organisms tested. Only on one organism, the gonococcus, which is particularly sensitive to silver ions, was a small growth-retarding effect observed. These results are in accordance with the fact that sterilisation of water by silver surfaces is unsatisfactory if the water contains much organic matter. The author found that in Long's synthetic medium the growth of *B. coli* was inhibited by silver foil. In the experiments recorded the author has found that the silver foil is a good indicator for the formation of hydrogen sulphide, sulphides and polysulphides, the silver foil becoming discoloured whilst the controls remain bright. The results of the silver-foil test in broth cultures of 18 pathogenic organisms are recorded. The liberation of sulphides apparently depends partly upon the medium used. Thus while they were liberated with Difco Proteose Peptone by the coryne bacteria, they were not liberated with Parke Davis's peptone; with the latter, *B. suipestifer*, *B. typhosum*, *B. paratyphosum* A and *B. schottmülleri* (B) showed sulphide formation, and *S. haemolyticus*, *C. diphtheriae*, *C. xerosis*, *C. hoffmann staphylococcus aureus* and *pneumococci* showed none. D. R. W.

Longevity of Yeast. L. Fletcher and T. Mason. (*J. Inst. Brewing*, 1939, **34**, 96.)—Reference in the literature to cases of longevity of yeasts are not very frequent, but Chaston Chapman records the recovery of living yeast-cells from old beer deposits after 51 years and Hopkins and Hunter record recovery from bottled beer 49 years old. The classical method of preservation of pure cultures is in 10 per cent. sucrose solution, but in 1922 Ling recorded the recovery of living yeast from pure cultures kept on cotton-wool in Freudenreich flasks, eight in all, which were sealed up by Hansen in 1887—34 years previously. The authors have recently recovered living yeast-cells from a pure culture of

S. cerevisiae, Burton type, prepared by Ford in 1894, and after a little time-lag obtained vigorous growth. The properties of this culture at the time of isolation were carefully described by Ford and included the times taken for the appearance of ascospores under standard conditions at different temperatures. The authors have repeated the work on the revived 44-years-old culture and have found that the times of sporulation agree very well with those previously given. Moreover another pure culture of Burton yeast, which was originally isolated in 1894 and has been subcultured regularly up to the present time, has been examined by the authors and found to be very similar in appearance and in sporulation to the parent and sister cultures. It is of more than passing interest that an organism such as yeast should be capable of retaining its vitality and characteristics over a period of 44 years. D. R. W.

Microscopical Differentiation of Yeast Cells and Starch Grains by Differential Staining. E. Schmidt. (*Das Mühlenlabor.*, 1938, **8**, 140–142.)—In the examination of cattle fodder and poultry foods it is frequently necessary to decide whether the product contains starchy material derived from bread, pastry and similar substances. Since these products almost invariably contain starch from other sources and since the starch derived from baked products is frequently gelatinised, the detection of yeast cells is almost impossible unless they are made prominent by staining. Although treatment of the preparation with iodine in potassium iodide solution colours the starch grains blue, the faint yellow colour imparted to the yeast cells does not give them sufficient prominence. If, however, the preparation is counterstained with carbolfuchsin the yeast cells are stained red and are easily found among the violet-blue starch grains. The procedure is as follows:—A small crumb of the material is moistened with water on the microscope slide and rubbed vigorously in order to disengage the starch grains and yeast cells from the gluten and other coarse materials, which may be gathered together and removed from the liquid. If the presence of fresh yeast is suspected the preparation is warmed slightly to kill the cells, which then absorb the stain more readily. Undue gelatinisation of the starch grains may be prevented by the addition of a little alcohol. If time permits, the preparation is allowed to dry. Iodine in potassium iodide solution is added until the starch is uniformly stained, excess being avoided since iodine decolorises fuchsin. A few drops of carbolfuchsin are added and the preparation is thoroughly stirred. If the liquid portion of the preparation is stained too deeply the yeast cells are less prominent and the colour should be reduced by the cautious addition of dilute iodine solution. With skill and practice the staining can be so regulated that the cherry-red yeast cells stand out clearly in contrast with the violet-blue starch grains. A. O. J.

Agricultural

New Constituents of Derris Root. I. Th. M. Meyer and D. R. Koolhaas. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 207–217.)—The isolation and properties of a substance first discovered by Buckley (*J. Soc. Chem. Ind.*, 1936, **55**, 285T), and of a new optically active substance, termed derride, isomeric with Buckley's compound, and also of a second new substance and of *l*-toxicarol and sumatrol from

samples of derris root are described. The so-called derris resin, the ethereal extract of derris root of the type of *Derris elliptica*, freed from rotenone as far as possible by the ordinary method of analysis, was dissolved in ether and extracted 6 times with 0·5 per cent. sodium hydroxide solution. The ethereal layer was washed with water, shaken with dilute hydrochloric acid, washed twice with water, and evaporated, the last traces being removed *in vacuo*. The residue was dissolved in ethyl acetate, petroleum spirit was added, and carbon dioxide was passed through the solution, which was stored, tightly stoppered, in the refrigerator. After a week there was collected a material which after repeated recrystallisation from alcohol and ethyl acetate melted at 183° to 185° C. (at 183° C. it sintered) and had $[\alpha]_D$—2·7° (in benzene). A mixed melting-point determination with a sample of Buckley's substance gave no depression. The authors and also Harper (*J. Soc. Chem. Ind.*, 1938, **57**, 1059) suggest that this compound has the structure of *iso*rotenone, from which the *iso*propyl group is absent.

Isolation of Derride from Derris Root.—A weight of 1·620 kg. of derris root was exhaustively extracted with ether and there was collected 24·8 g. of a solid material which separated during the extraction. After concentration of the extract there was obtained a very sticky residue which after treatment with methyl alcohol and ethyl acetate gave 25·6 g. of a white solid, which was recrystallised from methyl alcohol, giving a substance crystallising in needles and having m.p. 162° to 163° C., and $[\alpha]_D$—19° in benzene, +13·7° in acetone. Analysis of the material dried at 100° C. in a high vacuum gave: C, 68·60, 68·61; H, 4·74, 4·61; methoxyl (determined according to Vieböck and Brecher, *Ber.*, 1930, **63**, 3207), 17·94, 17·84 per cent.; $C_{20}H_{16}O_6$ requires C, 68·18, H, 4·56, methoxyl, 17·61 per cent. The new compound is readily soluble in benzene, ethyl acetate and carbon tetrachloride, and sparingly soluble in methyl alcohol or ether.

Isolation of l-*Toxicarol and Sumatrol from Derris Root.*—The powdered root (750 g.) was extracted with ether, and a solid (about 16 g.) which separated during the extraction, and on keeping the concentrated ethereal extract in a refrigerator for a few days, was collected. When recrystallised from cyclohexane and acetone it gave a yellow-green precipitate which was recrystallised from methyl alcohol. On treatment with benzene part of the substance dissolved; the residue was recrystallised from methyl alcohol and then from benzene, and gave crystals melting at 244° C. and with $[\alpha]_D$+107°. Analysis of the material dried at 100° C. in a high vacuum gave: C, 65·33, 65·24; H, 4·50, 4·49 per cent.; $C_{20}H_{16}O_7$ requires C, 65·22; H, 4·43 per cent. From the mother liquor of this substance sumatrol was separated and purified by repeated recrystallisation from methyl alcohol; for the final purification use was made of the fact that sumatrol is moderately soluble in benzene, whilst the yellow material with which it is contaminated is very sparingly soluble. It had m.p. 195° to 196° C. and $[\alpha]_D$—184° in benzene. Analysis gave: C, 67·30, 67·49; H, 5·49, 5·58 per cent.; $C_{23}H_{22}O_7$ requires C, 67·31; H, 5·37 per cent. On treating with methyl alcohol and ethyl acetate the very viscous concentrated ethereal extract from which the first solid had been removed, about 30 g. of a yellowish-green substance separated on standing in the refrigerator. This was washed with a small quantity of methyl alcohol and ethyl acetate and recrystallised from ether; it had m.p. 98° C. and $[\alpha]_D$—70°. With ferric chloride it gave a dark

green colour. It was probably *l*-toxicarol (Martin and Tattersfield, *J. Soc. Chem. Ind.*, 1936, **56**, 77). From the mother liquor from this substance there was deposited impure sumatrol which, after recrystallisation from methyl alcohol, had m.p. 183° C. and $[\alpha]_D$ −176·5°, and gave a deep brown colour with ferric chloride. E. M. P.

Organic

Sodium Saccharin as a Reagent for Identification of Alkyl Halides. L. L. Merritt, Jr., S. Levey and H. B. Cutter. (*J. Amer. Chem. Soc.*, 1939, **61**, 15–16.)—Sodium saccharin reacts with alkyl halides to give *N*-alkyl saccharins, and when the reaction is carried out in butyl carbitol water well-crystallised derivatives are formed. No reaction occurs with tertiary compounds or branched chain chlorides. A mixture of 6 g. of sodium saccharin, 1 ml. of the alkyl halide, 25 ml. of butyl carbitol and 4 ml. of water are heated under reflux for 30 minutes, with the addition, with chlorides or methyl bromide, of 3·5 g. of potassium iodide. The mixture is then poured into 300 ml. of water and the suspension is cooled in an ice-bath. The *N*-alkyl saccharin usually crystallises, but if an oil forms it is separated, warmed until no odour of alkyl halide can be detected, and dissolved in hot alcohol, and water is added until a slight cloudiness results. On cooling, crystals are formed. The derivatives are recrystallised from aqueous alcohol. The yield varies from 0·5 to 0·8 g. except with *iso*butyl, when only about 0·25 g. is obtained and crystallisation is difficult. *n*-Propyl and *iso*butyl saccharin, and also allyl saccharin and bromoethyl saccharin have m.p. differing only by 1° C., but a mixture of the two shows in each instance a depression of 8° to 10° C. Ethylene dibromide requires to be heated under reflux for an hour. No derivatives could be obtained with methyl, ethyl, *iso*propyl, or secondary butyl chlorides, or with ethylene dichloride. The m.p. and elementary composition of a number of alkyl-group saccharins are given.

Alkyl group	Melting-points: Iodide °C.	Bromide °C.	Chloride °C.
CH_3	132	132	—
CH_3CH_2	94	94	—
n-C_3H_7	74	74	74
isoC_3H_7	134	134	—
n-C_4H_9	38–39·5	38	38
isoC_4H_9	75	75	—
s-C_4H_9	81	81	—
n-C_5H_{11}	58	58	58
$CH_2{=}CHCH_2$ ..	—	98	98
$BrCH_2CH_2$ ..	—	99	—
$C_6H_5CH_2$	—	—	110–111
p-$O_2NC_6H_4CH_2$ ..	—	175·5	—

D. G. H.

Determination of Fumaric and Maleic Acids. S. C. Ganguly. (*J. Indian Chem. Soc.*, 1938, **15**, 611–614.)—By adapting the methods used by Szegedy (*Z. anal. Chem.*, 1937, **109**, 316), Frieman, Kennedy and Lucas (*J. Amer.*

Chem. Soc., 1937, **59**, 722), and Lucas and Pressman (*Ind. Eng. Chem., Anal. Ed.*, 1935, **10**, 149) fumaric and maleic acids may be determined in acid solution in the presence of succinic acid and phosphates, mercuric sulphate being used as catalyst. A flask containing a known excess of bromide-bromate mixture (10 to 15 per cent.) is evacuated, and 5 ml. of 6 *N* sulphuric acid are introduced and left for 2–3 minutes while the bromine is liberated, after which the flask is wrapped in a black cloth and the required quantities of 0·2 *N* mercuric sulphate and the solution to be analysed are run in, the wash-liquid not being allowed to exceed 10 per cent. of the total volume. The flask is well shaken and left in the dark for 30 to 35 minutes, after which 15 ml. of 2 *N* sodium chloride solution are added to liberate the bromine, followed by 5 to 10 ml. of 20 per cent. potassium iodide solution. The flask is then shaken for ¼ minute, the vacuum is broken, and the liberated iodine is titrated with 0·02 *N* sodium thiosulphate solution. In comparing the mercuric sulphate method with Szegedy's method, it was observed that whereas high values were obtained with the latter in the direct halogenometric titration at a *p*H 8·4, low values were obtained when fumaric acid was titrated alone in acid solution in presence of phosphates, probably owing to HPO_4'' and H_2PO_4' being capable of catalysing the bromination of fumaric acid, whilst undissociated H_3PO_4 retards it.

D. G. H.

Glycerides of Japan Wax. M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1939, **42**, 22–23B; *cf.* also *Bull. Chem. Soc. Japan*, 1931, **6**, 325, 337; 1935, **10**, 213; Abst., ANALYST, **1932**, **57**, 266; 1935, **60**, 632.)—Dibasic acids (japonic acid) have already been shown to be present in Japan wax to the extent of 5·2 to 6·3 or even 7·1 per cent. of the mixed acids, and their main component to have the formula $C_{23}H_{44}O_4$. With a view to the isolation of these acids, glycerides with a concentration of the dibasic acids nearly four times that of the original wax have now been obtained. A petroleum spirit solution of the wax was chromatographically filtered through Japanese acid clay, with the result that the dibasic acid glycerides were more readily adsorbed than other glycerides, and thus accumulated in the upper layer of the clay. A further treatment of the clay after separation into the adsorbed and filtrate fractions was made and repeated four times, but the increase in dibasic acids was not marked after the second treatment, and the proportion of dibasic acids could not be made to exceed 24 per cent. It is suggested that the dibasic acids occur in Japan wax probably as mixed glycerides and in association with oleic acid.

D. G. H.

Brassicasterol. Empirical Formula and Hydrogenation. E. Fernholz and H. E. Stavely. (*J. Amer. Chem. Soc.*, 1937, **61**, 142–143.)—Brassicasterol, a phytosterol isolated from an unrefined rape-seed oil of Japanese origin, has been found to be very similar to, but not identical with, stigmasterol. Analyses based on combustion of the bromides, on which the formula $C_{28}H_{46}O$ has previously been assigned, were not sufficiently accurate to distinguish between homologues, but the results obtained with the dinitrobenzoates were more reliable, even though the differences between the homologues were smaller. These results indicated that brassicasterol has the same empirical formula as stigmasterol, $C_{29}H_{48}O$, and not $C_{28}H_{46}O$ as given in the literature. Catalytic hydrogenation of brassicasterol yielded

a saturated sterol not identical with that given by stigmasterol, so that the difference between these two compounds appears to lie in the carbon skeleton and not in the position of a double bond. D. G. H.

Pine-needle Extract and its Use. Anon. (*Chem.-Ztg.*, 1939, **63**, 99–100.) —Pine-needle extract contains the water-insoluble oil and the water-soluble extractives, including tannins, proteins, carbohydrates, resins, salts, bitter principles, plant acids and aromatic substances (*e.g.* aldehydes and ketones), as well as other substances of unknown nature present in pine-needles. It is prepared by digesting the ground twigs with hot water, removing the oil by steam-distillation, and evaporating the extract in a vacuum to a syrupy consistence. The oil is then stirred into the extract, the constituents of which serve to emulsify it. The conifers used are red fir (*Picea excelsa*), white fir (*Abies pectinata*), Scotch pine (*Pinus sylvestris*) and knee pine (*Pinus pumilio*). The corresponding oils differ in composition and in the character and intensity of their aroma, but the extractives are all similar, and their characteristics depend rather on the place of origin of the tree. The oil or extract is also marketed in the form of effervescing tablets, the other constituents of which are a bicarbonate and tartaric acid; or as a "milk," which is a colloidal solution or an emulsion of the oil (20 to 40 per cent.) in water, and which enables high concentrations of oil to be attained. These preparations, which have a soporific and sedative effect, are used principally in baths, and are beneficial for convalescents and in cases of rheumatism. Such baths should be taken at 34° to 38° C., and they should last 20 to 30 minutes and be followed by a rest-period of 90 minutes. It is believed that they increase the permeability of the skin towards inorganic salts and the oil; thus magnesium chloride added to the bath water could be detected subsequently in the urine of the subject. Good pine-needle extracts should contain 15 to 20 per cent. of tannin (see below), and they were used during the war as substitutes or diluents of tanning agents such as pine-bark or oak-bark extracts. The economics of this substitution are discussed (*cf.* Hübscher, *Pharm. Zentr.*, 1938, 665). The extract is marketed as a thick liquid (sp.gr. 1·25 to 1·3) which, when spread out on a glass plate and dried, should form a smooth, glazed, dark red-brown layer without cracking. The dry solids should not be less than 55 per cent., and the mineral substances approximately 5 per cent. The oil-content, as determined by steam-distillation, should be at least 1·5 per cent., and the ester-content of the oil, 5 to 25 per cent. (as bornyl acetate); the bornyl acetate content of the German oils is 4 to 10 per cent. although that of Siberian oils may rise to 40 per cent. When the equivalent of 10 g. of dry solids is diluted to 100 g. with water, it should give a strong foam on shaking, and a turbidity and a grey-brown precipitate should form. If a strip of filter-paper, 2 cm. wide, is immersed to a depth of 0·5 cm. in 5 ml. of the above-mentioned dilute solution, the maximum capillary rise of the liquid should be 4 to 8 cm., and the strip should appear light brown and have dark brown zones. Sulphite waste liquor, which is used as a diluent and adulterant, rises to above 8 cm. The water-insoluble matter of a genuine extract amounts to 2 to 3 per cent., and if the dry solids are determined on a 2 per cent. solution of the extract before and after filtration through a layer of weakly-chromed hide powder, the difference between

the results gives the tannin-content (see above). Sulphur dioxide (from sulphite waste liquor) is detected by suspending a potassium iodate and starch paper in a loosely-stoppered flask containing 10 g. of sample and 20 ml. of water, and heating in a water-bath. If the blue colour is developed after addition of phosphoric acid, sulphur dioxide in combination is indicated. The blue colour is fugitive, but a positive reaction may be taken as indicating the presence of sulphite liquor, because sulphur dioxide is seldom used as a preservative for pine-needle extracts. If 5 ml. of a filtered 2 per cent. solution of the extract is treated with 0·5 ml. and then 2 ml. of conc. hydrochloric acid, the solution remains clear for at least 10 to 15 minutes if less than 5 per cent. of sulphite liquor is present; in the presence of more than 10 per cent. a turbidity and precipitate are formed (Hirst–Procter reaction). In filtered ultra-violet light the pure extract and sulphite liquor fluoresce with a dark olive-green and grey colour, respectively, mixtures giving intermediate shades.

J. G.

Inorganic

Gravimetric Determination of Copper. P. Spacu. (*Z. anal. Chem.*, 1939, **115**, 423–425.)—The method enables a quantitative separation of copper from manganese to be made. The neutral or feebly acid solution (strongly acid solutions should be nearly neutralised with ammonia), measuring 100 to 150 ml., is treated with 0·5 g. of ammonium nitrate and an excess of pyridine, heated to 30° to 40° C., and treated with excess of a cold conc. solution of ammonium or potassium dichromate. On cooling, the liquid deposits dark green crystals of the composition $[Cu(C_5H_5N)_4]Cr_2O_7$. The precipitate is collected in a porous porcelain crucible with the aid of a solution containing 0·3 g. of ammonium dichromate and 0·3 ml. of pyridine in 100 ml., and washed three times with the same mixture, then 2 to 3 times with 1-ml. portions of acetone containing 1 ml. of pyridine per 100 ml., and finally a few times with 2-ml. portions of ether. It is dried *in vacuo* over sodium hydroxide and weighed. Copper factor: 0·10673. W. R. S.

Volumetric Determination of Traces of Arsenic. J. Bodnár, E. Szép and W. Cieleszky. (*Z. anal. Chem.*, 1939, **115**, 412–420.)—The iodimetric micro-titration of Gangl and Sánchez (ANALYST, 1934, **59**, 716) gives a negative error of less than 5 per cent. with quantities of 5 to 100γ. The authors recommend reduction with tin and hydrochloric acid (12 per cent. by weight) instead of zinc and sulphuric acid, the procedure requiring only 30 minutes instead of 2 hours with Gangl and Sánchez's evolution apparatus. The tin sponge is prepared from chemically pure stannous chloride dissolved in hydrochloric acid (1 : 1) and purest rod zinc placed in the solution. The sponge is washed with distilled water, and dried. The use of tin instead of zinc has the great advantage that antimony is not volatilised (ANALYST, 1935, **60**, 496); hence arsenic can be determined in presence of relatively large amounts of antimony by the modified procedure, the error not exceeding 5 per cent. W. R. S.

New Method of Separating Tin and Antimony and its Application to the Analysis of White Metals. U. Pelagatti. (*Chim. e Ind.*, 1938, **20**, 724–726.)—The method is based on the fact that in a medium acidified with dilute sulphuric

acid and containing tartaric acid, the ferrocyanide of quadrivalent tin is insoluble whilst the ferrocyanide of tervalent antimony is soluble. The tin ferrocyanide is easily filtered off and contains no trace of the soluble antimony salt. The following procedure is recommended:—A quantity of the sample containing not more than 0·20 to 0·25 g. of tin and copper together (that is, 1 g. of white metals containing lead, or 0·3 to 0·4 g. of white metals with a tin base) is treated with 5 to 10 ml. of conc. sulphuric acid (according to the quantity of alloy taken) in a tall 200-ml. beaker of resistance glass covered with a watch-glass and heated on a sand-bath. After 10 to 15 minutes the liquid is cooled and diluted with 50 ml. of water containing 5 g. of tartaric acid. If lead is present, the liquid is allowed to stand until the lead sulphate has separated completely. The precipitate is collected in a weighed Gooch crucible, washed several times with a 5 per cent. solution of tartaric acid containing a few drops of conc. sulphuric acid and finally with alcohol, calcined in a double crucible, and weighed. The filtrate, or, in the absence of lead, the original liquid diluted finally to 100 ml. with water, is warmed to 60° C. and treated with an excess of potassium ferrocyanide (10 to 15 ml. of 10 per cent. solution), which precipitates the tin and copper as the ferrocyanides. If the temperature is higher than 60° C., the potassium ferrocyanide decomposes and a small quantity of antimony is precipitated with the tin ferrocyanide; precipitation in the cold is slow and the precipitate is difficult to filter off. The liquid is cooled to room temperature and the precipitate is filtered off rapidly and washed 5 times with a cold solution of 10 g. of tartaric acid and 5 ml. of 10 per cent. potassium ferrocyanide solution in 200 ml. of water.

Determination of Antimony.—The filtrate is diluted to 400 ml. and treated with hydrogen sulphide first in the cold (for about 20 minutes) and then after slight warming (the temperature must not exceed 60° C.). The precipitate of antimony trisulphide is filtered off, washed with cold water containing sulphuric acid and saturated with hydrogen sulphide, and rinsed with the smallest possible quantity of water into a tall 400-ml. beaker. The contents of the beaker are evaporated to dryness on a water-bath, the residue is treated with 10 ml. of conc. sulphuric acid, and the beaker is heated on a sand-bath until solution is complete and no more fumes of sulphur dioxide are evolved (30 to 40 minutes). After cooling, the liquid is diluted with 50 ml. of water, treated with 10 ml. of conc. hydrochloric acid, and finally diluted to 200 ml. with cold water. The antimony is titrated at 15° C. with $N/10$ potassium permanganate solution until a pink colour persists for a few seconds, the method of titration being that of Wassilieff and Stutzer (*Z. anal. Chem.*, **78**, 97). One ml. of $N/10$ potassium permanganate solution is equivalent to 0·00601 g. of antimony.

Determination of Tin and Copper.—The ferrocyanide precipitate is transferred to a tall 200-ml. beaker with a jet of water, and the liquid is evaporated to dryness on a water-bath. If copper is not present, about 0·1 g. of copper sulphate is added to facilitate the decomposition of the organic matter. Ten ml. of conc. sulphuric acid are added, and the beaker, covered with a watch glass, is heated on the sand-bath, gently at first and then more strongly, until a brownish-yellow residue remains. After cooling, 50 ml. of water are added, the beaker is warmed until solution is complete, and the small quantity of carbonaceous matter is filtered off

and washed with 10 per cent. sulphuric acid. The filtrate is treated with 10 ml. of conc. nitric acid, diluted to about 300 to 350 ml. with water, and boiled for 15 minutes. Metastannic acid is precipitated (in the presence of less acid the precipitate contains large quantities of iron formed by the decomposition of the ferrocyanide). The beaker is allowed to stand on the water-bath until the precipitate has completely subsided, after which it is separated from the hot liquid on a slow filter, washed with water containing nitric acid, dried, calcined and weighed as tin dioxide. The metastannic acid may be yellowish owing to the presence of small quantities of organic matter, but this is destroyed during the calcination. Copper is determined electrolytically in the filtrate by evaporating to 100 ml., neutralising exactly with ammonia, adding 5 ml. of nitric acid and electrolysing. The following are typical results obtained by this method:

		1	2	3
Antimony	added	0·0995	0·1110	0·0372
	found	0·0990	0·1104	0·0370
Tin	added	0·1200	0·0258	0·0850
	found	0·1208	0·0263	0·0856
Lead	added	0·2000	0·6370	—
	found	0·2015	0·6383	—
Copper	added	0·0500	—	—
	found	0·0500	—	—

E. M. P.

Determination of Platinocyanide. H. Etienne and A. de Rassenfosse. (*Bull. Soc. Chim. Belg.*, 1938, **47**, 818–822.)—The only procedure giving satisfactory results is a volumetric process based on precipitation of silver platinocyanide, $Ag_2Pt(CN)_4$. Ten g. of magnesium nitrate are dissolved in a little water in a graduated 500-ml. flask, and 50 ml. of 0·1 *N* silver nitrate solution are added. The solution of the platinocyanide is run in during agitation and the volume is adjusted. The precipitate is allowed to settle, and part of the liquid is filtered. One hundred ml. of filtrate are treated with 5 ml. of 6 *N* sulphuric acid (with barium platinocyanide, barium sulphate will be precipitated) and 10 ml. of 10 per cent. ferric alum solution, and the excess of silver is determined by titration with 0·1 *N* thiocyanate solution standardised against the silver solution under the same conditions. The addition of magnesium salt minimises adsorption of silver nitrate by the silver platinocyanide precipitate. W. R. S.

Determination of Sodium. N. Schoorl. (*Chem. Weekblad*, 1939, **36**, 122–123.)—Some errors and points of interest connected with the use of the magnesium (or zinc) uranyl acetate method are indicated. The sodium triple salt has a solubility of approximately 5 per cent. in water, so that the reagent should be as concentrated as possible to minimise dilution from this source. The method should be regarded as one of quantitative crystallisation, rather than of quantitative precipitation, a minimum period of 1 hour (but preferably 24 hours) at a specified temperature (*e.g.* 20° C.) being necessary. An advantage is that the weight of the reaction-product is 65 or 67 times that of the sodium present (according as the magnesium or zinc salt is used, respectively). There is some doubt concerning

the quantity of water of crystallisation associated with the final precipitate, because this cannot be removed completely at 110° C. Determinations made after heating for 24 hours at 80° C. in a vacuum, in a Pregl desiccator, enabled a constant weight to be obtained corresponding with between 6 and 7 H_2O. On exposure to air the precipitate assumed a moisture-content which depended on the humidity of the atmosphere. Thus, figures of 6·14 and 6·17 H_2O were obtained at zero humidity, and 6·78 and 6·80 at 98 per cent. relative humidity by Blanchetière and Kolthoff, respectively. In Kahane's method, the precipitation is carried out in 45 per cent. (vol.) alcohol, since it is claimed that this lowers the solubility and increases the rate of crystallisation of the precipitate. Under these conditions the Pregl desiccator method gives a value corresponding with 8·6 H_2O, although part of this may be due to alcohol of crystallisation. The method tends to give low results, but the error is small (not exceeding 3 mg. on a theoretical weight of precipitate of 264 mg.), when 10 ml. of reagent are added to a solution of not more than 10 mg. of sodium chloride in 1 ml. of water. If a solution of the sodium chloride in 10 ml. of 45 per cent. alcohol is treated with 10 ml. of reagent, the minimum and maximum errors are 0·5 and 10 mg. for the precipitates from 2 and 10 mg. of sodium chloride, respectively. These data may be used as correction factors, and the author has also obtained similar correction data (not reproduced in the paper) for the effects of solubility, adsorption and occlusion. J. G.

Detection of Nitric Acid. R. Lantz. (*Bull. Soc. Chim.*, 1939, **6**, 279–280.)—The solution of asymmetric phenyl- or β-naphthyl-imino-8-dinaphthoxazine in strong sulphuric acid is violet, and the colour changes to green upon addition of a minute quantity of nitric acid. A drop of the sulphuric acid solution to be tested is placed on a porcelain plate near a drop of reagent (0·2 g. of the dye in 1000 g. of 93 per cent. sulphuric acid) and the two drops are cautiously mixed, the unknown being added to the reagent. As little as 0·005 per cent. by weight of nitric acid in sulphuric acid gives a decided reaction. If the reagent is diluted with sulphuric acid to one-tenth of the above concentration, a tenfold sensitiveness may be obtained. Nitric acid can thus be detected in aqueous solutions if these are gradually added to a large excess of reagent. W. R. S.

Determination of Nitrous Acid (as N_2O_3) in Sulphuric Acid. V. N. Zimarez. (*Zav. Lab.*, 1938, **7**, 555–557.)—The permanganate method is unsatisfactory for Glover acid (*cf.* Pieters and Manners, *Z. anal. Chem.*, 1930, **82**, 218–224; Abst., ANALYST, 1931, **56**, 65), and the standard Russian method for this acid is also not satisfactory. The following modification of the latter is proposed:—*Reagents.*—*Standard sodium nitrite solution*, equivalent to 0·01 mg. of N_2O_3 per ml. An aqueous solution of 0·1816 g. of pure sodium nitrite is made up to 1 litre and 10 ml. are diluted to 100 ml. to form the standard solution. *Griess reagent.*—(A) A solution of 0·1 g. of α-naphthylamine in 6 ml. of 80 per cent. acetic acid is made up to 100 ml. with water; it is kept in the dark. (B) Ten mg. of sulphanilic acid are dissolved in 100 ml. of water. For the analysis, equal volumes of (A) and (B) are mixed. The mixed solution must be kept in the dark and for not more than 24 hours. *Sodium acetate solution.*—25 g. of crystalline sodium acetate per 100 ml. of water. *Acetic acid*, 60 to 80 per cent. *Method.*—Ten ml. of the

acid to be tested are added to water in a graduated flask, care being taken to avoid loss of N_2O_3 through heating of the liquid, and made up to 100 ml. Two to three ml. of sodium acetate, 2 ml. of acetic acid, 5 ml. of the Griess reagent, and 1 ml. of the standard solution of N_2O_3, are introduced into a Nessler cylinder, with a side-tubulure, containing 20 ml. of water, and into a second cylinder are introduced 20 ml. of water, 5 ml. of sodium acetate solution, 5 ml. of the Griess reagent, 1 ml. of the diluted acid under examination, and 10 ml. of acetic acid. The solutions are stirred with glass rods, allowed to stand for 15 to 20 minutes, diluted with water to 80 ml. and again stirred. The colours are compared by looking vertically downwards, and the liquid with the deeper colour is diluted to 100 ml., stirred again and some (not more than 70 ml.) is run off. Acetic acid (up to 2 ml.) is added, and the solution is again diluted to 100 ml. If the colour is still too deep this process is repeated, less of the solution being run off each time, until the intensities of colour in both cylinders are approximately equal. The shades are then matched by the addition of either acetic acid (which makes the tint bluer) or sodium acetate (yellower tint) to the 80 ml. in the second cylinder, the contents of which are then made up to 100 ml. The deeper solution is diluted as before, until both colours are of equal depth. Then, if a and b are the number of ml. respectively of the standard and of the tested solutions, and d is the density (at room temperature) of the acid analysed, the percentage of nitrous acid (calculated as the anhydride) is $\frac{a}{b \times d \times 100}$ A blue tint is preferable to a yellow for colour matching. The advantages of this method over the previous titration method of determination of the dye formed are described. Results with synthetic mixtures agreed well with those obtained by the permanganate method. With Glover acid they differed from the results of the titration method and of the permanganate method, and the authors recommend the use of this new method for such acid. E. B. D.

Potentiometric Determination of small Amounts of Bromide. S. K. Afanasev, M. A. Portnov and Yu N. Chepelkin. (*Zav. Lab.*, 1938, **7**, 547–550.) —In the manufacture of bromine by extraction from sea-water (*cf.* Stewart, *Ind. Eng. Chem.*, 1934, **26**, 361) rapid control tests are required for (*a*) determination of bromide in the original material, (*b*) determination of bromine in the air-halogen mixture after chlorination and blowing. (*a*)—Chirkov's method (*Zav. Lab.*, 1935, **4**, 402), which consists in the potentiometric titration of a small amount of sodium or potassium chloride (kept saturated by contact with the solid chloride throughout the titration), is considered best for industrial control. For the brine of the Karabougaz–Goll bay, which was examined by the authors, a correction for organic matter was required. To 100 ml. of the brine were added 5 ml. of 20 per cent. sulphuric acid and 50 g. of sodium chloride (chemically pure), and the mixture was titrated potentiometrically with a 0·03 N solution of hypochlorite, a platinum wire and a saturated calomel electrode being used. Tests with synthetic mixtures showed that results were not affected by the presence of magnesium sulphate nor by changes in concentration of sulphuric acid and the substitution of hydrochloric acid for it. (Time of experiment, 15 to 20 minutes.) For the correction, the theoretical volume of the hypochlorite solution and 5 ml. of 20 per cent. sulphuric

acid were added to 100 ml. of brine; after 4 to 5 minutes potassium iodide was added, and the liberated iodine was titrated back with standard sodium thiosulphate solution; from the results the hypochlorite consumed by the organic matter was calculated. A blank titration was made to determine the bromide present (0·001 to 0·0015 per cent.) in the "chemically pure" sodium chloride used. Results obtained by the rapid method agreed well with those by other methods and were sufficiently accurate for a control test. The bromide ion could be determined at a concentration of 0·15 g. per litre.

(*b*)—The determination of bromine in the air-halogen mixture was effected potentiometrically after absorption. To simplify the analysis and increase its speed, absorption and reduction of the bromine were obtained simultaneously by replacing the sodium carbonate solution by a 1 per cent. solution of sodium bisulphite. The solution was titrated potentiometrically with $N/10$ silver nitrate solution. The indicator electrodes was a silver spiral (diameter 1 mm.) in a saturated solution of calomel. Satisfactory results were obtained with test solutions. The sudden increase of potential was well-defined only when the ratio Br′/Cl′ was greater than 1, but by a method of parallel lines (described by Chirkov) titration curves which were sufficiently accurate could be obtained with other ratios. The chlorine could also be determined simultaneously by this method, from a second sudden rise of potential. Excessive dilution of the solution titrated must be avoided. (Time of titration, approximately 20 minutes. Relative error, 1·3 per cent.) E. B. D.

Determination of the Salts in Cyanide Flux. A. A. Korinski. (*Zav. Lab.*, 1938, **7**, 550–554.)—The equation for the formation of cyanide flux or crude cyanide is:—$Ca(CN)_2 + 2NaCl \rightleftharpoons 2NaCN + CaCl_2$. For the control determination of the four compounds a method has been worked out based on the solubility of the two sodium salts and the insolubility of the calcium salts in liquid ammonia. The total sodium is determined in an aqueous solution of the flux by the zinc uranium acetate method; the total chloride and cyanide are also determined. Approximately 2 to 3 g. (unweighed) of the flux are then powdered coarsely and shaken with about 200 ml. of liquid ammonia (previously dehydrated by passing the vapour over solid caustic potash), in a conical flask in the stopper of which a calcium chloride tube containing solid caustic potash is fitted. After standing for 15 to 20 minutes, with shaking at intervals, the solution is filtered into a conical flask with side-tube (a vacuum flask is too thick to stand the cold ammonia). The side-tube is connected with a Drechsel flask in which are 25 to 30 ml. of $N/10$ silver nitrate solution. The filter is covered with a glass plate in which a hole, 2 mm. in diameter, permits ammonia fumes to escape. When 30 to 40 ml. have been filtered the funnel is replaced by a tight-fitting stopper. After the ammonia fumes have evaporated into the silver nitrate solution (in 1 to 1½ hours), the residue is dissolved in 100 to 120 ml. of water, the solution is shaken, and the cyanide is determined in 20 ml. by the Liebig method and the chloride by the Volhard method. From the ratio CN′/Cl′ and the amount of total sodium the percentages of sodium cyanide and chloride can be found. From these results and from the known total cyanide and chloride the calcium cyanide and chloride

can also be found. Preliminary experiments with synthetic mixtures had shown that in direct determination of the chloride and cyanide combined with sodium, some double decomposition occurred, probably through absorption of moisture from air during filtration and washing of the residue with ammonia. The shortening of the method by the determination of a ratio only, and the improvement in the apparatus, are therefore important. Test analyses with synthetic mixtures yielded results sufficiently accurate for a commercial control test. Thus, for one sample, results were:—NaCN, theory 41·52 per cent., found 41·66 per cent.; NaCl, theory nil, found 0·55 per cent.; $Ca(CN)_2$, theory and found, nil; $CaCl_2$, theory 56·13 per cent., found 56·20 per cent. In the commercial fluxes analysed only very small amounts (approximately 1 per cent.) of sodium chloride occurred, practically all the chloride being present as calcium chloride; both cyanides were present. Further experiments with many different samples of fluxes are required before a general statement can be made as to their composition. E. B. D.

Microchemical

Simplified Combustion Tube-Filling for Micro Carbon and Hydrogen Determinations. J. B. Niederl and V. Niederl. (*Mikrochem.*, 1939, **26**, 28.)—Lead chromate may be omitted from the combustion tube filling without any decrease in the accuracy of results in the determination of compounds containing sulphur. The metallic silver in the filling, at a temperature of 400° C. and above appears to be able to absorb quantitatively the oxides of sulphur. J. W. M.

Modifications of Pregl's Micro Carbon and Hydrogen Determination in Humid Tropical Atmospheres. M. C. Nath. (*Mikrochem.*, 1939, **26**, 165–169.)—Too low percentages of carbon were always obtained by the Pregl micro-combustion method during the summer in India. By using the following precautions accurate results may be obtained: the combustion time is increased from 10 to 15 minutes; the air and oxygen are drawn through at a rate of 4 to 5 ml. per minute; the rubber connection between the combustion tube and the calcium chloride tube is changed after each combustion. The other rubber connections between the absorption tubes are changed after three combustions. Immediately after being disconnected the absorption train is capped and transferred to the balance room where the humidity is kept constant. Two blank experiments are carried out, one just preceding and the other following the analysis of the substance, and the mean is taken, to avoid errors due to change in atmospheric conditions. J. W. M.

Detection and Estimation of Silver on Impregnated Filter-paper. N. D. Costeanu. (*Mikrochem.*, 1939, **26**, 170–174.)—Reagent papers are prepared by impregnation with a saturated solution of a suitable substance, and allowed to dry in the air. The following substances give a black or coloured stain in the pores of the paper with silver nitrate solutions: ferric ammonium citrate, hydroquinone, pyrogallol and tannin in aqueous solutions, phenylhydrazine and gallic acid in alcoholic solutions, formaldehyde, gum arabic, starch and protein in alkaline solutions, chloral in ammoniacal solution, boric acid in acetic acid solution, sodium bisulphite and potassium dichromate. Of these, the following are most

suitable: ferric ammonium citrate, phenylhydrazine, hydroquinone and formaldehyde. Standard papers are prepared by dropping equal-sized drops (0·25 c.mm.) of a series of standard silver nitrate solutions on to the papers impregnated with the reagent and dried. The standard solutions contain 1 mg., 0·5 mg., 0·1 mg., 0·05 mg., and 0·01 mg. of silver per ml., respectively. The weakest solution that will just give a stain on the papers contains 0·01 mg. of silver per ml., which, in a drop of 0·25 c.mm., implies a *limit of identification* of 0·0025γ of silver. For the estimation the silver is separated from other elements and converted into nitrate, and the solution is diluted to a known volume. A drop is transferred to the reagent paper, and the size and intensity of the fleck are compared with those on the comparison paper impregnated with the same reducing substance. The amount of silver present may then be calculated. The method is very useful for determining the silver-content of jewellery, medals and objects of art, as a sample may be taken without damaging the object. Photographs are given of 10 comparison papers. J. W. M.

Spot Test for Iron and Uranium. E. A. Kocsis. (*Mikrochem.*, 1938, **25**, 13–15.)—Quercetin and quercitrin (Schuchardt, Gönlitz) are used as reagents for iron and uranium. A drop of the test solution is placed on filter-paper (Schleicher–Schüll, No. 589), and before it is dry a drop of a 0·2 per cent. alcoholic solution of the reagent is added. After a few seconds an olive-green colour appears in presence of iron or a rust-brown colour in presence of uranium. Strong acids and coloured cations interfere with the test. Quercetin and quercitrin also react with arsenates, arsenites, cupric and zinc compounds and ammonia, giving bright yellow colours. The limit of identification for iron in the test is 0·3γ and for uranium 3γ. Ferrous and ferric ions react similarly. The reaction may be applied conversely to detect quercetin or quercitrin, uranyl nitrate being used as reagent; the limit of identification is 3γ. J. W. M.

Microscopical Detection of Rubidium in Presence of Caesium. H. A. Frediani and L. Gamble. (*Mikrochem.*, 1939, **26**, 25–27.)—Naphthol-yellow-S (potassium salt of 2·4-dinitro-α-naphthol-7-sulphonic acid), as 0·5 per cent. aqueous solution, is used as reagent. It gives a yellow precipitate with solutions of potassium or rubidium salts, but not with those of other alkali metals. Its effect on other metals was tested by mixing a drop (0·04 ml.) of the reagent with a drop of solutions containing the following ions at a concentration of 40 mg. per ml.:—sodium, lithium, ammonium, caesium, magnesium, thallous, silver, lead, bismuth, cupric, mercuric, stannic, zirconium, ferric, and cobalt. Of these, only the following gave precipitates:—silver, lead, cupric, mercuric, thallous, and stannic; these would ordinarily be removed before testing for the alkali metals. Potassium alone among the alkali metals reacts similarly to rubidium. Small amounts of free, strong acids prevent the formation of the rubidium salt; strong acids are therefore neutralised with sodium hydroxide (free from potassium and rubidium) before the test. Acetic and formic acids do not interfere. The concentration limit of the test for rubidium is 3·0 mg. per ml.; at this concentration yellow needles are formed immediately on mixing a drop of the solution with a drop of the reagent. The extinction angle is 76·4° in polarised light. The limit of identification, determined by the method of Benedetti-Pichler, is 6·8γ. J. W. M.

Reviews

LABORATORY MANUAL OF ORGANIC CHEMISTRY. By HARRY L. FISHER, Ph.D. Fourth Edition. Pp. xxiii + 412. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1938. Price 13s. 6d. net.

Those familiar with the famous practical text-books of Cohen, Sudborough and James, and Gattermann will be amazed on opening Fisher's Laboratory Manual to find an almost complete absence of formulae, equations and explanations, and so, perhaps, become possessed with a fear, fortunately not justified, that the volume under consideration is a mere "cookery" book. Further investigation, however, reveals many merits.

In Part I seventy-seven "laboratory experiments" are described. The first thirty-eight pages are devoted to boiling-point and melting-point determinations, together with a very full discussion of matters relevant to these topics. In particular the author recommends the recording of corrected values, and to this end urges standardisation of thermometers, or, better still, the use of short-range thermometers of his own design (which are similar to the well-known Anschütz type). The determination of molecular weights by Rast's Camphor Method is described in detail, and several substances suitable for the replacement of camphor are given. Mention is also made of the dual value of "K" according as the method is used on the macro- or micro-scale, but the fact that it varies for each observer seems to be overlooked.

The actual preparations are very varied, but seem to have no obviously logical sequence; thus a preparation involving a Grignard reagent precedes the preparation of ether (Expts. 13 and 14). Among the more unusual preparations may be mentioned Monastral Blue, Tyrian Purple, a synthesis of camphor, an example of the Diels–Alder reaction and the reagents dimethyl-glyoxime, dithizone and tetramethyl-base.

The arrangement of each preparation is reminiscent of "Organic Syntheses." Thus precise directions are followed, where necessary, by a set of notes and references. In place of the usual equations and explanations are numerous questions, which require considerable reading on the part of the student before satisfactory answers can be compiled. In many instances the student is helped by a list of references to such standard works as Cohen's *Organic Chemistry for Advanced Students*, Stewart's *Recent Advances* and Gilman's *Organic Chemistry*. Various journals are also referred to.

Part II is devoted to organic combustions and opens with an historical survey of considerable interest; a valuable discussion of weighing is also included. The methods recommended involve several modifications, of the author's own invention. As far as can be judged, without actual test, these modifications are quite sound and make for accuracy. Magnesium perchlorate is used as an absorbent for water, and the use of palladous chloride solution (a detector of carbon monoxide) is suggested as a check against incomplete combustion. The author, on the grounds of "no first-hand experience," omits all reference to micro- and semimicro-methods. The determination of nitrogen is treated in great detail and a method using a

manometer is minutely described. The determination of halogens, sulphur and phosphorus is, by contrast, very brief and somewhat disappointing.

Throughout the book there is evidence of practical experience, care and accuracy. Only one trifling error has been noticed: the melting-point of 2:4-dinitrophenol is not 12·8° C. (p. 160). Any student who works through this book, faithfully doing the *implied* reading and then answering the questions, will certainly have laid the foundation of a claim to the title of organic chemist. Dr. Fisher's book, though a departure from the orthodox, rightly used, is excellent.

HAROLD TOMS

TASCHENBUCH FÜR DIE LEBENSMITTELCHEMIE. By A. THIEL, R. STROHECKER and H. PATZSCH. Pp. xi + 173. Berlin: Walter de Gruyter & Co. Price RM.8.60.

This book contains a collection of tables for the use of those engaged in the chemistry of food products.

The tables, 66 in number, are in 7 sections dealing respectively with Milk, Water, Alcohol, Sugars, Wine, Fats and General Analysis. Several of the tables, especially those in the last-named section, are available in most handbooks of this type, and include hydrometer tables, tables giving densities of aqueous solutions of common acids and alkalis, densities of sugar solutions, physical and chemical constants of fats and oils, densities of alcohol-water mixtures, and so forth. Many of the tables, however, have been taken from comparatively recently published German journals and are for use in connection with special methods of analysis: for example, with Grossfeld's method for determination of the amounts of butter-fat and coconut oil in fat mixtures from the "A" and "B" values; Fincke's method for the polarimetric determination of sugars in chocolate; Tilmans and Luckenbach's method for determining the extent of neutralisation of milk.

The source of each table is given and in a few instances a summary of the method of determination and use of the table is included, but usually it would be necessary to refer to the original paper for details.

The book is well printed and the tables are clearly set out, determined values being printed in red, the values sought in black. A bibliography of relevant literature is given.

For anyone regularly using these German methods of analysis this book would be very useful. The general information provided is, however, very limited compared with that given in the well-known handbooks.

M. SHAW

NEWER METHODS OF VOLUMETRIC CHEMICAL ANALYSIS. Editor: WILHELM BÖTTGER. Pp. 268. London: Chapman & Hall, Ltd. 1938. Price 18s. 6d.

Text-books covering a wide field frequently tell us all too little about points of special interest. The present book is different, for it deals only with a limited number of processes and goes into them very fully. The work, which is an American translation by R. E. Oesper from the German, is a collection of seven monographs by authors the names of some of whom are well known in this country

in connection with the subjects on which they write. The contributions are: (I) The Elimination of the Titration Error in Acidimetric and Alkalimetric Titrations, by E. Brennecke (Fresenius Chemical Laboratory, Wiesbaden, Germany), 20 pp.; (II) Ceric Sulphate as Volumetric Oxidising Agent, by N. H. Furman (Princetown University, U.S.A.), 21 pp.; (III) Alkaline Permanganate as Volumetric Oxidising Agent, by H. Stamm (University of Halle, Germany), 9 pp.; (IV) Iodate and Bromate Methods, by R. Lang (Technical High School, Brünn, Czechoslovakia), 52 pp.; (V) Chromous Solutions as Volumetric Reducing Agents, by E. Brennecke, 19 pp.; (VI) Oxidation-reduction Indicators, by E. Brennecke, 37 pp.; (VII) Adsorption Indicators for Precipitation Titrations, by K. Fajans (University of Michigan, U.S.A.), 48 pp.

The object of the editor was to obtain from the various writers as uniform as possible a mode of presentation which would bring out (*a*) the fundamental basis of the processes, and (*b*) practical directions for carrying them out. The proportions of (*a*) and (*b*) vary appreciably in the different contributions, but the approach has been mainly from the practical angle, and the theoretical treatment is non-mathematical.

In the first contribution the effect, on the change-point of indicators, of temperature, concentration of salts, presence of carbon dioxide, and so on, is clearly discussed and methods for eliminating or correcting for these factors in accurate work are described. In one example given, methyl yellow is advocated for the titration of sodium carbonate with hydrochloric acid; the titration should be carried out to a standard shade by matching with a solution containing suitable coloured inorganic salts; the indicator correction is obtained by titration of a solution containing the same amount of sodium chloride as that formed in the first titration; carbon dioxide must be removed by boiling (the solution being afterwards cooled) as the acid character of carbon dioxide is considerably increased in the presence of salts. The chapter on ceric sulphate gives an excellent practical account of the uses of this volumetric oxidising agent in the determination of various metals and organic substances.

The section on alkaline permanganate is in the nature of an original contribution on a method developed by the writer himself, and applicable mainly to the determination of organic compounds. The principle is that the oxidation of the material being determined involves the rapid partial reduction of the permanganate to manganate, the slower further reduction of manganate to hydrated manganese dioxide not being allowed to occur; the excess permanganate is subsequently titrated back with a suitable reducing agent. The action of the permanganate under the conditions laid down is said to be specific, oxidation occurring when the compound contains an aliphatic carbon double bond, an alcoholic or phenolic hydroxy group or amino or carbonyl group, but not when it has only carboxylic, sulphonic, nitro, alkyl, halogen or ethereal oxygen groupings. Among the substances readily determined by this method are: hypophosphite, phosphite, iodide, iodate, cyanide, methanol, formaldehyde, glycol, glycerol, pentoses, hexoses, salicyclic acid and phenols; chloride, bromide and benzoic and toluic acids consume no oxygen and do not interfere.

Iodate and bromate methods reviewed in the fourth section have been found

applicable to the determination of a large number of metals and organic compounds. The familiar iodate method of Andrews is exhaustively discussed together with the newer iodine cyanide and iodo-acetone methods. The description of the György method and its modifications for the bromate titration of antimony in hydrochloric acid solution with methyl orange as indicator recalled to the reviewer that he had some time ago found that it was necessary to keep the hydrochloric acid concentration down to about 10 to 15 per cent. strength in order to secure sharp end-points and accurate results. It is interesting to note from this book that German work, carried out much earlier and apparently generally overlooked in this country, pointed to a similar conclusion.

The treatment of oxidation-reduction indicators is one of the best from the practical point of view that has yet appeared. Professor Fajan's contribution on adsorption indicators deals principally with the fundamental aspects and gives less analytical detail than most of the other authors' sections. The value of the book is enhanced by the comprehensive bibliographies which supplement the sections, and by an index.

From the standpoint of analytical practice, a method of determination is often only the last stage of a process, and it will be understood that for preliminary separations, where necessary, reference would generally have to be made elsewhere. Whilst the book can thus be looked on as an adjunct to existing text-books on quantitative analysis, it is one for which a need has existed, and the collection of the available information in the present convenient form will be widely appreciated.

S. G. CLARKE

WEEDS, WEEDS, WEEDS. By SIR CHARLES V. BOYS, LL.D., F.R.S. Pp. 113. 2nd Ed. London: Whitman & Co., Ltd. 1938. Price 2s.

It must not be surmised that the appearance of the second edition of this work so soon after that of the first indicates that remedies suggested for weed eradication have not been as effective as the author avowed; it means that a still wider public requires the work. On the seventieth and final page of the first edition Sir Charles said "adieu" to all his "gentle readers," but on the last and one hundred-and-tenth page of the present volume there is no such farewell. It may be fair, therefore, to presume that soon we may expect a large and authoritative work on weed eradication by the author, embodying the results obtained by the application of his scientific knowledge to the problem. There is a suggestion that this last volume results from talks with readers gathered under an apple tree on the author's lawn. The talks were only imaginative. Anyone standing on that lawn would surely place Professor Boys under suspicion until a survey of the lawn (and of the surrounding garden) had been made. What a sense of guilt would be experienced if a daisy were descried, even if the explanation were given that it was of the kind that had the habit of popping up in a single night! Can it be that the author has lost a little confidence, because he now states that certain remedies may have a successful action only if they are applied to weeds on particular soils? Be that as it may, the book now deals with theory and explains the action of both wetting agents and plant poisons, and it gives further information relative to the application of the well-known weedicides. There is one method of weed eradication

that perhaps it is not the purpose of the book to stress, and that is by digging. It may be that this is not done in the best weed-killing circles. Undoubtedly, a scientific superiority is experienced when a friend is informed that a nettle that once grew under a favourite apple tree was completely annihilated by cutting its stem and placing a drop of a concentrated solution of sodium chlorate on the bleeding stump. But a large amount of jubilation could have been experienced had the said nettle been lifted with a fork and then carried with suitable incantations to the kitchen stove. Under such conditions there is truly no resurrection.

Much information is contained in the recently published edition, and the expenditure of 2s. would always be justified if only to get the atmosphere, once more, of Sir Charles's individuality. F. W. F. ARNAUD

BACTERIAL METABOLISM. By MARJORIE STEPHENSON, Sc.D. Pp. xi + 391. London: Longmans, Green & Co. 1939. Price 21s. net.

This advanced text-book is the outcome of a monograph by the same author in the "Series of Monographs on Biochemistry" published in 1930. The book has, however, been entirely re-written and the new work of the past nine years has been incorporated, the subject having far outgrown the scope of a monograph. The aim of the work is to choose from the mass of data on the chemical reactions brought about by bacteria those facts that throw light on the essential chemical processes accompanying bacterial life. The author aptly compares the study of bacterial metabolism with an endeavour to gain an idea of the life of a household by observing the kind of articles daily imported by the various tradespeople and by a scrutiny of their ash bins. The headings of the chapters are as follows:— Introduction; Respiration; Polysaccharides; The Fermentation of Hexoses; The Decomposition of Proteins; The Metabolism of Nucleic Acid; Nutrition and Growth; Nitrogen Fixation; Autotrophic Bacteria; Bacterial Photosynthesis; Enzyme Variation and Adaptation. These are followed by an appendix, a bibliography and author and subject indexes. It is only possible in review to give a brief outline of the scope of some of these chapters. The introduction outlines the historical development of knowledge of bacterial metabolism up to the discovery of the enzyme zymase by Buchner, and proceeds to the consideration of energy relations of organisms to their substrates. It is shown on experimental evidence that with mould growth the formation of mould from substrate involves an expenditure of energy apart altogether from energy lost in respiration, and the requirement of energy for "maintenance" is discussed.

The subject of "Respiration"—used to denote any chemical process, aerobic or anaerobic, by which energy is liberated by the cell—is fully dealt with. The use of the methylene blue technique in the study of the catalytic transfer of hydrogen is described and the use of other oxidation-reduction indicators. Here we learn about the dehydrogenase enzymes, and the necessity of a "carrier" for the transfer by these enzymes of organic hydrogen to atmospheric oxygen; about cytochrome, its spectrum, which represents three haemochromogen-like substances, and its function as an oxygen "carrier"; about flavoprotein and co-enzymes I and II, peroxidase and catalase, glutathione and its function in the oxidation of protein; about anaerobic respiration, oxidation and reduction potential, redox indicators

and their capacity to function as reversible hydrogen and oxygen "carriers"; about anaerobic mechanisms for obtaining energy, in which by their enzymes organisms growing anaerobically use organic compounds as hydrogen donators and acceptors; and about "dismutations" in which similar molecules play the parts both of donator and acceptor.

The chapter on the polysaccharides deals with the breakdown of cellulose, starch, hemicelluloses, pectins, and so forth, and with the nature of gums and slimes. It is interesting to note that an organism has been isolated from the gum acacia tree which can produce a gum identical in character with true gum acacia, when grown on potato juice with 5 per cent. of cane sugar and 0·5 per cent. of tannic acid. The immunological importance of the polysaccharides of the capsules of pneumococci and *V. cholerae* is dealt with here.

The chapter on the fermentation of the hexoses opens with an account of recent knowledge concerning the transformations of the hexose molecule into carbon dioxide and alcohol by means of brewer's yeast. This molecule is shown to be transformed into no less than 14 intermediate compounds by means of a very complicated system of enzymes and carriers in which glycerophosphates and phosphoglyceric acids play a prominent part. Lactose fermentation by different bacteria follows, and glucose fermentation, an account being given of the formation of acetyl-methyl-carbinol, succinic, lactic, propionic, acetic and formic acids, and acetone. This chapter includes accounts of the fermentation of 3-carbon and 4-carbon compounds.

The chapter on the decomposition of the proteins deals first with the bacterial proteases which split the protein molecule to the amino acid stage, then with the mechanism of the breakdown of the amino acids which seems to be more intimately bound up with the cell structure. Nine types of such breakdown are discussed, such as "decarboxylation with formation of the amine" and "anaerobic breakdown with production of hydrogen," and there follows a table setting out the various amino acids, the class of breakdown, and the organisms which have been observed to effect it. The breakdown of tryptophane is given special treatment, as is also the production of indole and skatole. The chapter on nutrition and growth is of special interest; it includes some of the researches of Fildes, Knight, Koser and Rettger, and deals with the requirements of bacteria ranging from those that can synthesise all their amino acids from glycerol and ammonium phosphate to those requiring a formidable list of amino acids and vitamins. In the chapter on the autotrophic bacteria one finds a good account of these very remarkable micro-organisms and of the way in which they obtain the energy necessary for the metabolism by inorganic oxidations of ammonia, nitrites, sulphur and sulphur compounds, atmospheric hydrogen, and carbon monoxide and by oxidations of the very simple organic compounds, formic acid, formaldehyde and methane, of the way in which some can tolerate such an extremely acid pH as 0·6, and of the inhibitory effect, upon the growth of the nitrobacter, of the addition of organic compounds. The chapter on bacterial photosynthesis describes the work of Van Niel on the purple and green sulphur bacteria and that of Muller and Graffon on the purple bacteria and shows how these curious micro-organisms depend on carbon dioxide for their supply of carbon and upon solar radiation for their energy,

and that the pigments they contain are closely related to, but not identical with, chlorophyll.

The book is very well written, for the author has a complete mastery of this extremely difficult and comprehensive subject together with a free and unhampered style. If there is anything to be desired it is perhaps some sort of summary—chapter by chapter, or a summary of contents at the heading of each chapter, to assist the infirmities of the reader.

The book has a good index and a very good bibliography; it is well compiled and the subject-matter well arranged. The paper and type are excellent, and as an advanced text-book on the subject the work can be strongly recommended.

D. R. Wood