



THE ANALYST

A Monthly Publication
dealing with all branches
of Analytical Chemistry:
the Journal of the Society
of Public Analysts and
Other Analytical Chemists

Editor: F. L. OKELL, F.R.I.C.

7-8, IDOL LANE, LONDON, E.C.3

Telephone: MANSion House 6608

Published for the Society by
W. HEFFER & SONS, LTD., CAMBRIDGE, ENGLAND

Volume 77

Price 6s. 6d.

Subscription Rate, inclusive of Abstracts C, 80/- per annum, Post Free

No. 919, Pages 497-552

October, 1952

WHATMAN FILTER PAPERS

FOR ALL TYPES OF WET CHEMICAL ANALYSIS

QUALITATIVE GRADES	Nos. 1, 2, 3, 3MM, 4, 5, 7, 11 and 20
HARDENED GRADES ..	Nos. 50, 52 and 54
SINGLE ACID WASHED GRADES	Nos. 30, 31 and 32
SINGLE ACID WASHED GRADES, HARDENED..	Nos. 530 and 531
DOUBLE ACID WASHED GRADES	Nos. 40, 41, 42, 43 and 44
DOUBLE ACID WASHED GRADES, HARDENED..	Nos. 540, 541, 542 and 544

There are in addition to these several other grades and specialities for specific purposes made by W. & R. BALSTON LTD., MAIDSTONE, KENT

For full details of these papers, write for a set of Whatman literature to the sole agents

H. REEVE ANGEL & CO. LTD.,
9, Bridewell Place, London, E.C.4

A list of the recognised suppliers of Whatman filter papers will also be sent on request



A group of Alumina 609 Mortars and Pestles

MORTARS and PESTLES

Analysts everywhere need these new Thermal Alumina 609 mortars and pestles. Suitable for grinding extremely hard materials, they have an octagonal shape, and four different sizes are available.

THE THERMAL SYNDICATE LTD

Head Office: Wallsend, Northumberland.

London Office: 12-14 Old Pye Street, S.W.1.

IMPORTANT NOTICE TO SUBSCRIBERS

(Other than Members of the Society)

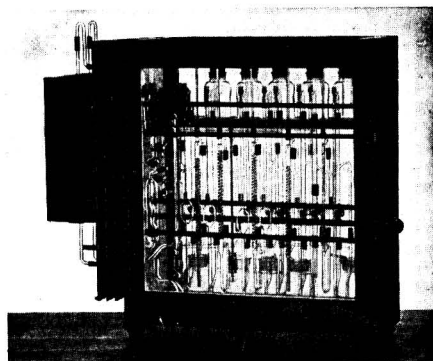
All Subscriptions and renewals to the Journal, including Abstracts C., should be sent through a Bookseller or direct to

W. HEFFER & SONS LTD., CAMBRIDGE, ENGLAND.

Price 6/6, postage 2d.; or to Subscribers in advance post free £4 per annum

N.B.—Members send their subscriptions to the Hon. Treasurer

SOAP FILM GAS ANALYSIS



A NEW RAPID ACCURATE SIMPLIFIED EQUIPMENT

This New Soap Film Apparatus achieves percentage analyses of almost any gaseous mixture with unique simplicity. The alternation of special soap film gas meters—all simultaneously controlled by one sliding bar—with reagent scrubbers, enables constituent gases to be determined by noting the change in position of soap films.

Especially designed for Town Gas, this apparatus constitutes a major advance in equipment. Gaseous mixtures may be passed through the system, under their own pressure or by means of the fitted pump, with no appreciable back pressure—and without temperature corrections having to be made.

Furnaces provided at the side of the apparatus, for use in oxidising some constituents, are thermally insulated from the system. All fittings and controls are designed to provide the maximum degree of simplicity.

Full details. Please write for a reprint of the paper by W. J. Gooderham which fully describes this apparatus.

GRIFFIN & TATLOCK LTD.
SCIENTIFIC INSTRUMENT MAKERS SINCE 1826



LONDON: Kemble Street, W.C.2.

MANCHESTER: 19, Cheetham Hill Rd., 4.

GLASGOW: 45, Renfrew Street, C.2.

EDINBURGH: 8, Johnston Terrace, 1.

BIRMINGHAM: Standley Belcher & Mason Ltd.,
Church St., 3.



OERTLING RESEARCH

PAYS YOU DIVIDENDS!

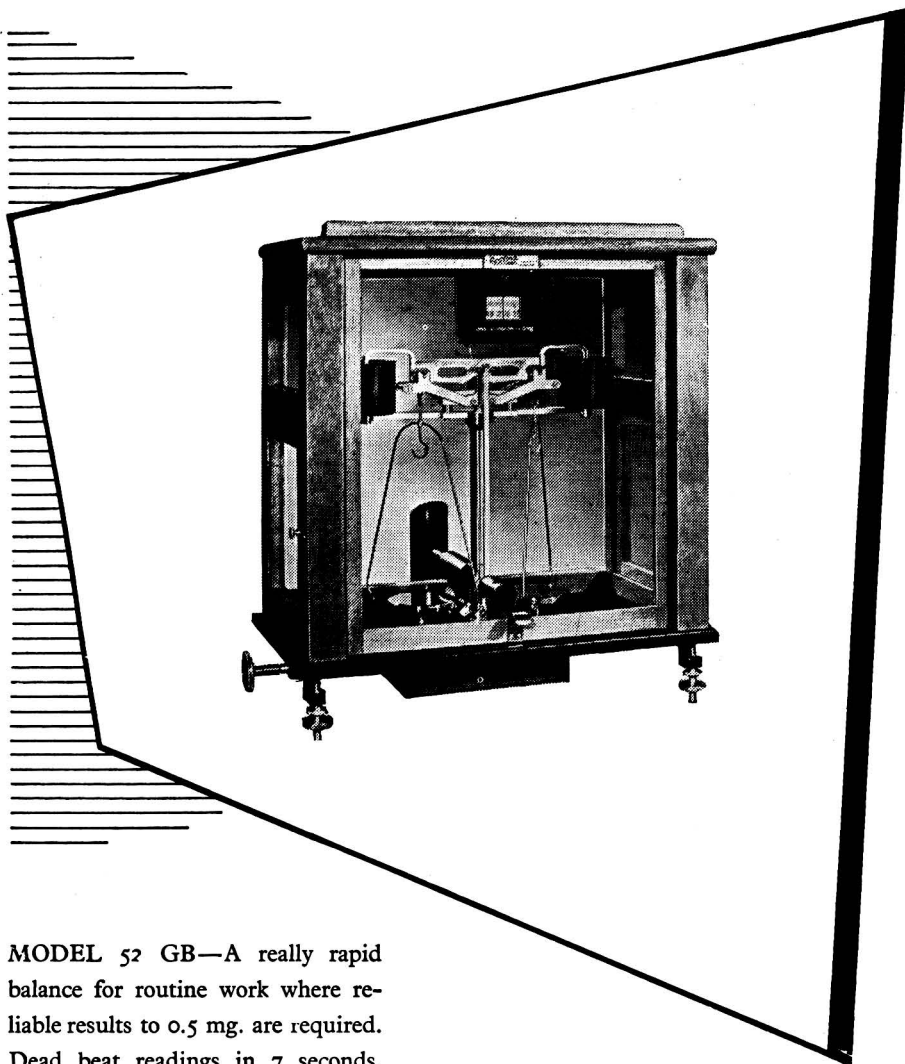
Proved design and speedy operation with less fatigue—these are a few of the scores on which Oertling balances economise in time and increase the output of skilled personnel.

The workmanship and dependability, which have led to the installation of Oertling balances in so many of the world's Standards Laboratories and Scientific Centres, pay dividends too when applied in the commercial laboratory.



Oertling

Let us send you latest specifications



MODEL 52 GB—A really rapid balance for routine work where reliable results to 0.5 mg. are required. Dead beat readings in 7 seconds. Capacity 200 gm. It is fitted, of course, with 'Corundum' planes.

MODEL 52 GB

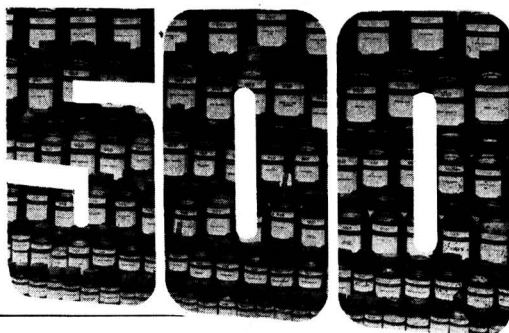
BUILT BY THE PEOPLE WHO KNOW BALANCES
**L. Oertling Ltd., Cray Valley Road, St. Mary Cray,
Orpington, Kent**

Telephone: Orpington 5771 (5 lines)

PIONEERS IN BALANCE DESIGN FOR OVER 100 YEARS

For your everyday
laboratory requirements

... insist
on **M&B**



Over 500 different organic and inorganic chemicals, all produced to published laboratory standards, are available to the user of the **M&B** range. Drawing from long experience in the manufacture and use of fine chemicals, we have made a selection of specifications to serve a wide variety of procedures in general laboratory practice. These specifications are clearly set out on the labels of the containers, giving immediate indication of the field of

usefulness of the contents, and are carefully maintained by modern methods of analytical control.

Pre-packed stocks of every item in popular-sized containers are held at Dagenham and by stockists throughout the country, so that orders can be promptly dealt with. Moreover, the specially designed bottles are convenient to handle, and ensure that the contents are adequately protected in storage and transit.

M&B LABORATORY CHEMICALS & REAGENTS

manufactured by **MAY & BAKER LTD · DAGENHAM · ENGLAND** 'phone *ILFord 3060*. Extension 40
LA28

STERLING BRAND Chemical Reagents



"Sterling" Brand Chemical Reagents are manufactured under close laboratory supervision and are guaranteed to conform with the specification stated on the label.

These specifications have been compiled with the object of providing material suitable for all general analytical and research purposes.

"Sterling" Brand Chemical Reagents comply with the specifications of the British Pharmacopoeia 1948, Appendix I, where such reagents are listed.

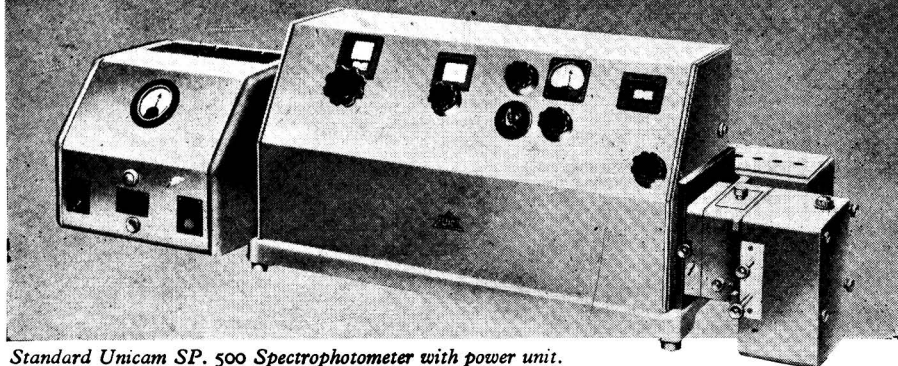
The range of "Sterling" Brand Chemical Reagents is constantly being increased. The present list is not a full and complete one, but represents a selection of those chemicals most generally used.

A list of prices and specifications is at your disposal

Thomas Tyrer & Co. Ltd.

STRATFORD, LONDON, E.15

ULTRAVIOLET AND VISIBLE ABSORPTION MEASUREMENTS



Standard Unicam SP. 500 Spectrophotometer with power unit.

The Unicam SP.500 Quartz Spectrophotometer is designed for the rapid and accurate identification, qualitative and quantitative analysis of chemical solutions by measurement of light absorption or transmission at wavelengths from $2,000\text{\AA}$ to $10,000\text{\AA}$. This instrument combines simplicity of operation with performance factors of a high order, including fine resolution, an excellent degree of reproducibility, and exceptionally stable dark current, which reduces the necessity for check readings. The adaptability of the spectrophotometer is increased by the addition of accessories. These include a reflectance attachment for the measurement of opaque surfaces, a fluorimetry or nephelometry attachment and a rocm cell housing to facilitate the examination of gases or vapours.

An illustrated leaflet describing the instrument in detail will gladly be sent on request.

UNICAM

UNICAM INSTRUMENTS (CAMBRIDGE) LTD. ARBURY WORKS. CAMBRIDGE. ENGLAND

UIIIT



pH INDICATORS . . .

Hopkin & Williams Ltd specialise in the production of pH Indicators for analytical purposes. With increased production and utilising modern techniques, Hopkin & Williams Ltd are in a position to offer bulk supplies of pH Indicators at competitive prices.

A complete range of Indicators, as listed in the H & W Chemical Catalogue, is available, and the following Indicators can be supplied on particularly favourable terms.

Code No.

2138	<i>Benzylaniline-azo-benzene-p-sulphonic acid</i>
2340	<i>Bromocresol green</i>
2342	<i>Bromocresol purple</i>
2368	<i>Bromophenol blue</i>
2376	<i>Bromothymol blue</i>
3096	<i>Chlorophenol red</i>
3524	<i>o-Cresol phthalein</i>
3526	<i>m-Cresol purple</i>
3528	<i>o-Cresol red</i>
5768	<i>Methyl orange, screened</i>
5792	<i>Methyl red, screened</i>
6614	<i>Phenol red</i>
6620	<i>Phenol thymol phthalein</i>
6622	<i>Phenol violet</i>
7304	<i>Quinaldine red</i>
8568	<i>Thymol blue</i>
8572	<i>Thymolphthalein</i>

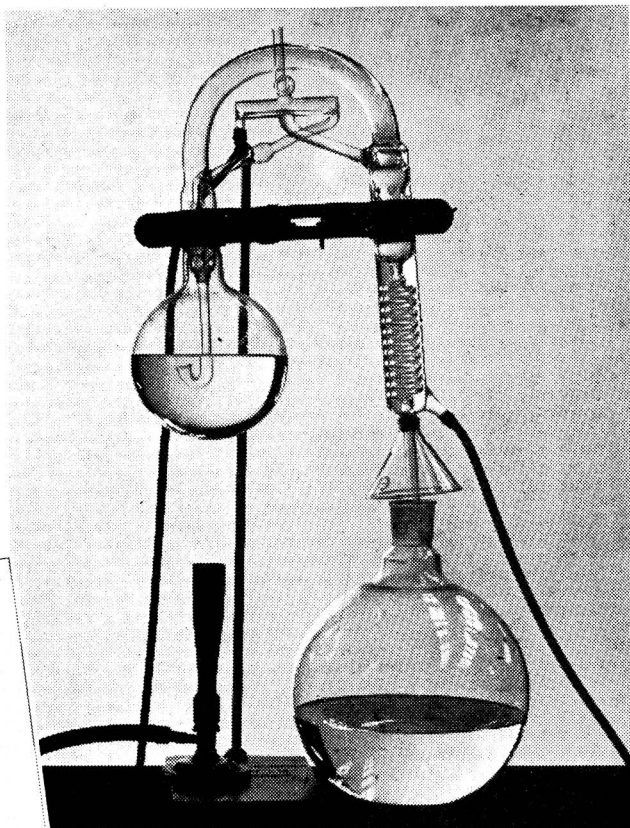
Quotations for bulk supplies will be provided on request.



HOPKIN & WILLIAMS LTD

Manufacturers of pure chemicals for research and analysis.

Freshwater Road, Chadwell Heath, Essex.



*This leaflet gives
fuller information*

“QUICKFIT” Stadler Still for the continuous distillation of water

The assembly of the Stadler Still is quite simple and consists of only three main components: a standard interchangeable 1,500 ml. flask, a specially designed condenser and a pivoting clamp. Water level is maintained by balancing the Still on a special pivot arrangement integral with the clamp, which can be mounted in an ordinary retort stand boss. An economical supply of highest quality distilled water is thus provided easily and automatically.

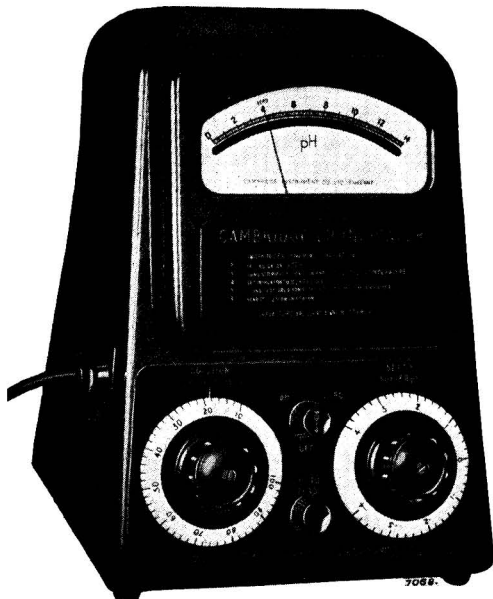
QUICKFIT & QUARTZ, LTD.

INTERCHANGEABLE LABORATORY GLASSWARE · INDUSTRIAL PLANT IN GLASS

Orders and Enquiries to Dept. O.B., “Quickfit” Works, Stone, Staffs

Phone: Stone 481

HEAD OFFICE: 1, Albemarle Street, London, W.1



CAMBRIDGE DIRECT READING pH INDICATOR

A new indicator characterized by portability, robustness and great stability, covering the full range of 0 to 14 pH. Directly readable to 0.1 pH, and by estimation easily to 0.05.

All mains operated.

Details are given in **SHEET 294-U**

CAMBRIDGE INSTRUMENT COMPANY LIMITED

13 GROSVENOR PLACE - LONDON - SW1

NIVOC APERIODIC BALANCES

for speed with accuracy

We would commend for the attention of all users of Aperiodic Balances the following range:

Nivoc Aperiodic Balance
200 gm x 0.1 mg A.6500

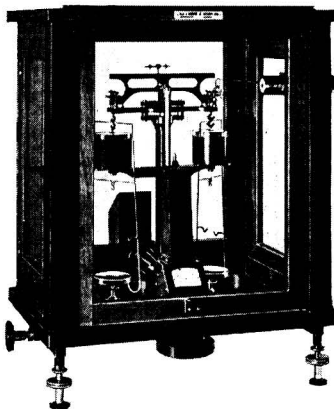
Nivoc Semi-Micro Aperiodic Balance
(illustrated) A.6510

Nivoc Automatic Aperiodic Balance
200 gm x 0.1 mg A.6520

Despite the heavy demand, planned production enables us to offer the above for

IMMEDIATE DELIVERY

Please write for further details



faster weighing saves time and money

W & J GEORGE & BECKER LTD

EALING ROAD, ALPERTON, WEMBLEY, MIDDX
157 GREAT CHARLES STREET, BIRMINGHAM, 3

NIVOC HOUSE

Telephone: PERivale 3344
Telephone: CENtral 7641

THE ANALYST

EDITORIAL

INTERNATIONAL CONGRESS, OXFORD, 1952

THE First International Congress on Analytical Chemistry to meet under the patronage of the International Union of Pure and Applied Chemistry was held at Oxford from September 4th to 9th, 1952. The President was Sir Robert Robinson, O.M., D.Sc., F.R.S., and the Vice-President was Sir Wallace Akers, C.B.E., F.R.I.C., F.R.S. The number of registered members of the Congress was 689, from 26 different countries.

The Congress owed its inception to the expression, at the gathering of Analytical Chemists at Utrecht in 1948, of the hope that the next such gathering should take place in England. This desire was brought to the notice of the Society of Public Analysts and Other Analytical Chemists; and shortly afterwards, Dr. G. Roche Lynch invited a number of distinguished chemists to a meeting, which was held in the rooms of the Royal Society under the Chairmanship of Sir Robert Robinson. Committees were appointed to take active steps to further the matter and the suggestion that had emanated from Utrecht was developed towards maturity. Mr. R. C. Chirnside, F.R.I.C., became the Honorary Secretary of the Congress, and Mr. George Taylor, O.B.E., F.R.I.C., was made Chairman of the Executive Committee. The Committee turned to our Society for some preliminary assistance, and the Society pledged the help of *The Analyst* in publishing the papers and discussions. A brief glance at the committees listed in the Congress Handbook shows the extent to which leading members of the Society have given freely of their time.

The Congress was recognised from its inception by the International Union of Pure and Applied Chemistry and was, in effect, the first Congress of the Analytical Section of the Union.

The Congress proved immensely successful and we hope it will form the pattern for future Congresses; one of its most notable features is the rapidity with which the proceedings are being published. This has involved two factors. The papers had to be prepared beforehand so that they could be set in type before the event, and publication had to be carried out by already-organised machinery. That this has been accomplished is in no small measure due to the diversion of the efforts of the Society's permanent staff and the facilities afforded by the printers of *The Analyst*. And although, by pre-printing the scientific papers, work on the publication was effectively started on May 8th, it is by no means finished as this issue appears, for the Congress Lectures could not be put into type before the meetings at Oxford, and the discussions, by their very nature, were available only after the meetings. The willing help of the contributors to the discussions and of the authors in preparing their replies has greatly assisted the task that we have faced.

The fruition of these plans will be apparent in the next two issues of *The Analyst*. The November issue will contain a report on the Congress, the three main Congress Lectures, and the first part of the Scientific Papers and the discussions on them; the December issue will contain the balance of the papers and discussions. All other matter has had to be excluded from these two issues.

It is hoped that the bound Proceedings of the Congress, which will include the papers appearing in the November and December issues together with their own index, will be available early in 1953.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

AN Ordinary Meeting of the Section was held at the Engineers' Club, Albert Square, Manchester, on Saturday, April 26th, 1952, at 2 p.m.

The Vice-Chairman, Mr. T. W. Lovett, F.R.I.C., presided over an attendance of 58. The following paper was presented and discussed: "Some New Methods in Analytical Chemistry," by R. Belcher, B.Sc., F.R.I.C., F.Inst.F.

THE Fifteenth Summer Meeting of the Section was held at the Imperial Hotel, Llandudno, from Friday, June 13th, to Monday, June 16th, 1952.

The Chairman, Mr. A. A. D. Comrie, B.Sc., F.R.I.C., presided over an attendance of 40. On the morning of Saturday, June 14th, a paper was read by Dr. J. Haslam, F.R.I.C., on "The Analyst in the Plastics Industry" and a number of plastic products now in common use were exhibited. A tour of the district was made by motor coach on Sunday afternoon.

BIOLOGICAL METHODS GROUP

THE Summer Meeting of the Group took the form of a visit to the premises of Boots Pure Drug Co. Ltd.

In the afternoon of June 12th, 1952, visits were made to the Pharmacology, Bacteriology and Bio-assay Divisions at West Bridgford. The following morning the party visited the Beeston factory, and after lunch, which was kindly provided by Messrs. Boots, was shown the Veterinary Science Division.

Finally, a scientific session was held, at which the following papers were presented: "The Assay of Adrenaline in Adrenaline Cream," by G. F. Somers; "The Assay of Pertussis Vaccines for Antigenicity and Toxicity," by P. W. Muggleton.

Shortage of time prevented a discussion of the second paper and a demonstration of the "Evaluation of Histamine-Release by Skin Tests in Volunteers, Introducing a Rapid Method for Measuring Small Irregular Areas," by H. O. J. Collier and Barbara Macauley.

The Chemical Composition of Milk Between 1900 and 1950

By J. G. DAVIS

(Presented at the meeting of the Society on Wednesday, November 7th, 1951)

It has been suggested, during the past few years, that the chemical quality of milk in this country has deteriorated over the last twenty or thirty years. The difficulties encountered in an attempt to answer this question are discussed in some detail. One of the most important requirements is the systematic testing of samples selected at random all over the country by the same analytical methods, over the period under consideration. There is insufficient information to allow any dogmatic assertion about the trends in milk quality. In the present paper, the results of over half-a-million samples tested in various parts of England during the period 1900 to 1950, have been tabulated and examined. It appears that there has been a slight rise in fat content, with a peak at 1926 to 1930, and subsequently a slight fall. The solids-not-fat values appear to have risen steadily from 1900 to 1921-1925 and since then to have fallen appreciably. Further evidence is produced to suggest that there has been a similar fall in the quality of milk in Wales, whereas the fat content of milk in Scotland has increased.

Methods for maintaining or improving the quality of milk are discussed, and it is suggested that the logical solution is a universal method of payment by quality. The total solids content is suggested as being the most suitable from chemical aspects and also from the points of view of justness, simplicity, and methods of utilisation. The evidence available from other countries suggests that where milk is bought on a quality basis, the fat and solids-not-fat contents are at least maintained, if not improved, and where payment is independent of quality, the chemical composition tends to deteriorate.

THE trends of composition of our national milk supply obviously depend on the methods used to obtain analytical data. No conclusion can be drawn from any figures unless the methods of sampling are above reproach and the analytical methods used have been consistent throughout the period under consideration. It is not necessary that methods be absolutely accurate in order to decide whether the composition has altered.

SAMPLING—

It might appear that if all herd milks in the country had been tested regularly over a period, it would be possible to answer this question. A little thought will show, however, that a number of factors can affect the result even if the sampling is, from the scientific point of view, constant. For example, let us suppose that at the beginning of the period all herds in the country were of equal size, one half giving richer milk having average values for fat and solids-not-fat of 4.0 per cent. and 9.0 per cent., and the other half giving a poorer milk with averages of 3.5 per cent. and 8.5 per cent. of fat and solids-not-fat. If the herds giving the poorer milk doubled in size, the final averages of the country's milk would then be not 3.75 per cent. and 8.75 per cent. but 3.67 per cent. and 8.67 per cent., *i.e.*, a difference in both figures of nearly 0.1 per cent. This example will show that any method used for assessing the chemical composition can be criticised from some point of view. Averages taken from values for herd supplies will not necessarily be the same as those found by random sampling of tanker or consumer milk.

From the point of view of analytical control, milk can be sampled in three ways: (1) as produced by the cow, (2) as sold from the farm and (3) as sold to the public.

Obviously, to assess trends in composition accurately, milk should be tested as produced by the cows, but analytical figures for this type of milk are quite inadequate for the present purpose. Studies made by dairy scientists on trends in the composition of milk are usually based upon milk as sold from the farms or as bought by collecting depots, while statements

made by Medical Officers of Health and Public Analysts are usually based upon the testing of consumer samples.

We have no precise knowledge about the relationship between these three types of milk, but we know that any differences, if they occur, will always be in the direction of poorer milk as we pass from (1) to (2) and from (2) to (3).

HUMAN FACTORS AFFECTING COMPOSITIONAL DATA--

The handling of milk is always accompanied by the possibility of weakening of composition, and this can occur in two ways: by the addition of water and by the abstraction of fat. It might generally be thought that adulteration is, in practice, the major factor, but some consideration of the matter will show that abstraction of fat may be more important from the point of view of general composition. For example, all dairy farmers use some of their milk to supply their households and staff, and if milk for this purpose is taken from the top of an unplunged churn of evening milk, the milk removed will be much higher in fat than the remainder. A simple calculation will show that, for an average farmer producing daily 20 gallons of milk containing 3.75 per cent. of fat, if four pints of milk richer in fat are removed every day, the fat content of the remainder will be reduced to 3.5 per cent. if the milk removed contains 10 per cent. of fat, and to 3.25 per cent. of fat if the milk removed contains 20 per cent. of fat.

It is emphasised that we have no precise knowledge of the magnitude of this operation on the fat content of the country's milk supply, but estimates that I have received from dairy farmers indicate that the extent of this practice is about 90 per cent. It is a very old-established practice and this figure is probably about right.

Precise information is only available in isolated instances, but some interesting data illustrating this point are shown in Table I. This table gives average values for large numbers

TABLE I
EFFECT OF PLACE OF SAMPLING ON FAT CONTENT

Year	A		B		C		D	
	Sampled at farm		Sampled in shops or at creameries		Sampled at schools		Retail samples	
	Fat	S.N.F.	Fat	S.N.F.	Fat	S.N.F.	Fat	S.N.F.
1948	4.07	8.83	3.65	8.80	3.74	8.86	3.68	8.78
1949	4.06	8.83	3.73	8.75	3.67	8.89	3.65	8.84
1950	4.16	8.89	3.77	8.89	3.77	8.92	3.72	8.82

of samples taken by one authority under different conditions, group A samples being taken at the farm and groups B, C and D being taken at the point of distribution or consumption. It will be observed that, whilst the solids-not-fat values are remarkably even, the fat values for the samples taken at the farm are much higher than those taken during distribution. It would not be justifiable, of course, to suggest that these figures are true for the whole country, but they illustrate the point that the place of taking the sample may have an appreciable effect on the fat but not on the solids-not-fat values. Further, farms are not the only places at which abstraction of fat may take place. Public Analysts who worked in the earlier days of the dairy industry will recall how remarkably consistent some retailers were in selling milk containing just over 3 per cent. of fat. Although not manufacturers and not equipped with a laboratory, such dairymen frequently possessed a Gerber outfit.

Abstraction of fat by removing a portion of the milk that is richer in cream will have only a negligible effect on the solids-not-fat value, while adulteration of milk by water, which is not always intentional, will affect fat and solids-not-fat equally, considered as a percentage of the material present, but in terms of percentage of the milk will have rather different effects. For example, the addition of 1 per cent. of water to a milk will lower 3.75 per cent. of fat to 3.71 per cent. and 8.75 per cent. of solids-not-fat to 8.66 per cent., while a 5 per cent. adulteration will lower these values to 3.56 and 8.31 per cent. From the point of view of the *absolute* change in percentage of the constituents, therefore, the addition of water will affect solids-not-fat values more than fat values.

FACTORS AFFECTING THE COMPOSITION OF MILK

It is well known that a number of factors can affect the composition of milk from day to day and season to season. These, however, level out when average values for years, or groups of years, are considered, so that such factors need not be discussed in the present paper. Further, it is known that the milk from one cow, or even from one herd, can vary in composition from day to day, especially in respect of fat content, but these individual variations, and variations for which no precise cause can be ascribed, do not come into the consideration of yearly values. There are, however, some very important factors, not only physiological but economic and industrial, that play their part in affecting the composition of milk over a period of years, and these will now be considered.

CHANGES IN THE RELATIVE NUMBERS OF DIFFERENT BREEDS—

It is well known that breed is a most important factor, and typical figures are shown in Tables II and III. No accurate figures are available for the total numbers of cows of each breed in Great Britain, but Table IV, which gives the numbers of licensed bulls of each breed, allows us to make an estimate of the relative numbers of cows of each breed.

TABLE II
REPORTED AVERAGE FAT AND S.N.F. VALUES FOR BREEDS

Date	1880	1885	1899		1899					
Source	Penn. State Fair*	Barham	Richmond	Richmond	Lewin (Bell)					
Ayrshire	3.89			3.68 9.02	4.24	9.22				
Devon	5.57									
Friesian	3.58	2.97 8.83		3.51 8.61	3.75	8.65				
Guernsey	5.50	4.8 9.29		5.02 9.46	5.16	9.3				
Jersey	3.91	4.26 9.34	5.66 9.23	4.78 9.56	5.43	9.22				
Shorthorn		3.79 8.91	4.03 8.85	3.65 8.80	3.93	8.85				
South Devon										
Date	1899		1914	1909-21		1920-22				
Source	Collier*		Lythgoe*	B.D.F.A.† Milking Trials		Essex County Milk Records				
Ayrshire	3.57 9.45	3.68 9.02	4.01 8.63	9.05						
Devon	4.15 9.59			9.13						
Friesian	3.46 8.96	3.51 8.61	3.41 8.28	8.74		3.36				
Guernsey	5.12 9.47	5.02	5.23 9.37	9.26						
Jersey	5.61 9.80	4.78 9.56	5.65 9.10	9.20						
Shorthorn		3.65 8.80		9.08		3.70				
South Devon				9.16						
Date	1925	1926	1927		1929		1936			
Source	Tocher	Bibby	Drakeley		Overman <i>et al.</i> , Illinois*		Davies			
Ayrshire	4.09	3.9	3.97 9.09		4.14 8.94		3.85 9.05			
Devon		4.5								
Friesian	3.63	3.45	3.67 8.78		3.55 8.97		3.45 8.48			
Guernsey	5.16	5.31	4.88 9.29		5.19 9.68		4.98 9.57			
Jersey	5.43	5.56	5.18 9.30		5.18 9.51		5.14 9.59			
Shorthorn	3.91	4.14	3.78 9.00				3.63 8.94			
South Devon			4.02 9.09							
Date	1948-49		1948-49		1948-49		1949		1950	
Source	West Region		South-Eastern Region		National Milk Records		N.I.R.D.‡		Bartlett	
Ayrshire	3.88		3.76		3.81		3.72 8.78		3.60 9.05	
Devon					4.18				3.88 9.13	
Friesian	3.51		3.41		3.45		3.49 8.59		3.47 8.74	
Guernsey	4.65		4.52		4.56		4.55 9.01		4.53 9.26	
Jersey	5.11		5.00		5.05				4.86 9.20	
Shorthorn	3.65		3.52				3.56 8.71		3.63 9.08	
South Devon					4.26				3.81 9.16	

* American figures. † British Dairy Farmers' Association.

‡ National Institute for Research in Dairying.

It may be remarked in passing that the figures taken for the over-all breed average composition are the figures for registered or otherwise selected herds. Nevertheless it is reasonable to assume that these figures, although selected, apply generally to all the cows of each breed in the country. Jersey and Guernsey are, beyond question, the richest milks, and Devon, South Devon and Ayrshire are usually richer than the average. Shorthorn milk approximates closely to the average milk supply of the country, whilst Friesiae milk is generally poorer in composition. Other things being equal, therefore, any trends in the relative numbers of cows of different breeds might be expected to affect the average

TABLE III

YIELD AND FAT PERCENTAGE OF MILKS OF VARIOUS BREEDS (EDWARDS¹)

Breed or breed type	Number of cows considered		Yield of milk, lb.	
	1934-35	1948-49	1934-35	1948-49
Ayrshire	3278	43,112	7514	8088
Friesian	13,438	70,657	9291	9141
Guernsey	6224	13,183	6891	7473
Jersey	3797	8458	6635	7051
Red Poll	3742	6147	7589	7476
Shorthorn	41,726	72,456	7318	7365

Breed or breed type	Number of cows and heifers (tested)		Fat, %	
	1934-35	1948-49	1934-35	1948-49
Ayrshire	906	50,673	3.71	3.81
Friesian	2908	71,779	3.26	3.45
Guernsey	2639	18,456	4.63	4.56
Jersey	1296	13,324	4.86	5.05
Red Poll	650	6333	3.65	3.60
Shorthorn	2822	36,260	3.56	3.58

TABLE IV

TOTAL BULLS LICENSED IN ENGLAND AND WALES (1934 TO 1951)*

Breed	1934	1941	1945	1950
Ayrshire	192	750	2684	3115
Friesian	1210	6125	8220	9308
Guernsey	969	1037	1219	1582
Jersey	328	369	548	944
Red Poll	417	377	467	425
Shorthorn	13,908	21,023	14,593	7902
Aberdeen Angus	635	512	458	439
Hereford	1806	2191	1740	1784
Others	3142	4172	3260	2043
Total	22,607	36,556	33,189	27,542

* Figures from the Ministry of Agriculture and Fisheries.

composition of the country's milk. It is known that the Shorthorn has been the predominant breed in this country from the time when analytical data for milks first became available until fairly recently; the numbers of cows of other breeds have been relatively small. However, during the last 15 or so years there has been a significant change in the numbers of Shorthorn and Friesian cows and bulls in this country. Whereas 15 years ago the number of Friesians was relatively small, to-day there are roughly as many Friesian cows as there are Shorthorn. This fact does not, of course, *prove* that the quality of the country's milk has necessarily fallen, as it is conceivable that the average values for Shorthorn milk have fallen over this period and the average values for Friesian milk have risen. However, there is a strong presumption that the increase in the proportion of the cows giving milk of poorer quality will result in a lowering of the compositional analysis for the milk supply as a whole. Provan and Jenkins² point out that the fat values for breeds, other than Channel Island, have remained stationary, the Channel Island value having fallen by 0.5 per cent. The figures for solids-not-fat have fallen for all breeds except the Friesian, which has increased

slightly. It is claimed that the difference in solids-not-fat between the Friesian and Shorthorn is now only about 0.1 per cent., and that the increase in numbers of Friesian cows cannot explain the observed fall in solids-not-fat values.

THE EFFECT OF BREEDING OR SELECTION POLICY—

Two factors in recent years have had the effect of making the country more milk conscious—

- (1) The foundation of the Milk Marketing Board in 1933, which organised the marketing of the country's milk and has done much to publicise the value of milk.
- (2) Advances in our knowledge of nutrition, which have made the public and all those concerned with health and feeding more conscious of the need for an adequate supply of milk for each individual. This was rounded off during the war when milk was given a high priority and special arrangements were made for ensuring that those most urgently needing milk got an adequate supply without any financial burden. Thus slightly over half of the country's milk goes to the priority classes and the average consumption has risen from about 0.37 pints per day in 1938 to 0.75 pints per day in 1950.

The new marketing arrangements have been accompanied by an appreciable increase in the price of milk paid to the farmer, with the result that milk production has become a much more profitable and less hazardous business than it was before 1933, when surplus milk in the flush period might be sold for as little as 6d. or 4d. a gallon. The value of milk as a marketable product has naturally resulted in farmers paying more attention to it as a business proposition, and there has been generally a marked increase in the efforts of farmers to produce the largest possible quantity of milk from any one farm.

It will be obvious that the greater the quantity of milk produced from a single cow the more economic will be production of the milk, as most of the overheads remain roughly the same. Considerable attention has been paid by farmers to producing milk from high-yielding cows, and this principle applies not only to Friesian, but to all breeds. This has resulted in a greater interest in Friesians and high-yielding Shorthorns, and the increased attention that is paid to production figures for cows and herds has been concentrated on production as measured in gallons. The farmer is paid for his milk on a quantity basis, and provided that it contains at least 3.0 per cent. of fat and 8.5 per cent. of solids-not-fat and, of course, is of satisfactory bacteriological quality, the milk must be accepted without question by any buyer. In fact, a large amount of milk containing less than 8.5 per cent. of solids-not-fat is now accepted, especially in late winter and early spring. From the business point of view an intelligent farmer would merely take precautions to ensure that his milk complied with the presumptive legal requirements and from that point concentrate on the production of the greatest possible quantity. Farmers who adopt a scientific and systematic breeding policy would naturally base the policy on the production of milk in terms of gallons rather than in terms of milk quality.

It has been suggested by Kay³ that these two factors, the increase in the proportion of Friesian cattle and breeding for quantity without regard to quality, have been the two most important factors responsible for the alleged decline in the composition of milk in this country. Trends in yield by cows of different breeds are shown in Table III (p. 502).

MASTITIS—

There has been much conflict of opinion on the quantitative significance of mastitis in dairy herds as a cause of low compositional quality. About 1938, surveys indicated that roughly one-third of the dairy cows in milk suffered from mastitis in some form or other.^{4,5} Only about 5 per cent. of infected cows showed clinical symptoms and so would be recognised as infected by the farmers and milkers. Nevertheless, it was shown that sub-clinical infections could result in a lowering of the compositional quality of the milk, especially the solids-not-fat.^{6,7}

Considerable advances have been made recently in combating mastitis with penicillin and other antibiotics and drugs, and it is probable that to-day the average incidence of mastitis (of all types) is something between 15 and 10 per cent. It is reasonable to assume, therefore, that the mastitis effect, whatever its magnitude, is to-day only one-third to one-half of what it was about 1938.

MACHINE MILKING—

The fat content of milk is considerably affected by the efficiency of "stripping," or removing the last amounts of milk from the udder, as this fraction is the richest in fat. Such "strippings" may contain 13 per cent. of fat and amount to one-fifth of the volume of an efficient milking. Machine milking may result in a less efficient removal of the last milk, especially if hand-stripping is not done properly or is omitted. Only fat values will be affected.

DECREASE IN THE NUMBER OF PRODUCER - RETAILERS AND INCREASE IN WHOLESALERS—

The last 50 years have seen a significant revolution in this country in the methods of selling milk. Whereas in early days milk was sold direct by the farmer to the public—the farmer was running his own retail round—to-day the bulk of the milk is collected from the farm by the buyer's lorry and taken to a collecting depot where all supplies are regularly tested. There was, therefore, in the early days of the dairy industry, little check on the quality of milk as sold to the public, apart from the occasional sampling by Food and Drugs authorities. Even then the "appeal to the cow" method still permitted a milk producer to sell milk below the legal presumptive standards if the authorities were satisfied that the milk was genuine. To-day, however, nearly all milk supplies going to a country creamery are tested regularly, usually once a month, in the buyer's laboratory, and any deficiencies or near-deficiencies in fat and solids-not-fat are, or should be, immediately brought to the farmer's notice. Quite apart from the reporting of low fat and solids-not-fat values, there is no doubt that the mere fact that a producer's milk is tested regularly will have some influence in making the farmer pay more attention to the quality of his milk. Hence, the present system by which milk is bought will act in one direction by making the farmer interested in obtaining high yields without much consideration of quality, but the collecting and testing system under which the milk is marketed will always pull him up if his milk falls below a certain level. Thus, although the general average may have fallen, there are probably far fewer herd supplies of grossly poor quality. Public Analysts have commented on the fact that the passing of milk sales to the big distributors has usually resulted in a decrease in the number of deficient and adulterated samples.

This point is illustrated by figures for a London borough (bulked milk) and a Home County (mostly producer - retailers) in 1948. Of 479 samples taken in London, not one was deficient in fat or contained added water (when tests were made). Of 326 samples taken in the county, 7 contained added water, 18 were deficient in fat and 4 were both adulterated and deficient in fat. Altogether, 3.4 per cent. were adulterated and 6.8 per cent. were deficient in fat.

THE EXTENT OF ADULTERATION OF MILK—

From the Public Analysts' point of view adulteration can take place at any time between the milk leaving the cow and the inspector taking the sample. For the creamery testing milk as sold from the farm, adulteration is limited to any that takes place on the farm and is therefore likely to be less, but in both instances the extent is unknown. The freezing-point test did not come into general use until 1925 to 1935, and even then only a minimum adulteration of 3 per cent. could be detected.

SEASON AND FEEDING—

The large mass of evidence on this topic is hopelessly confusing and contradictory. Reference is made on p. 505 and 520 to low values for solids-not-fat.

EARLY INFORMATION ON THE COMPOSITION OF MILK

Analyses of milk before 1900 must be treated with suspicion for more than one reason. Methods then in use are now known to be inaccurate, and the sampling and degree of adulteration were then probably greater sources of error than they are to-day. Wanklyn's fat method, which was semi-officially adopted by the Society of Public Analysts in the 1870's, gave very low fat values (as much as 0.5 per cent. too low) and therefore correspondingly high solids-not-fat values, although the total solids values were also possibly high at this time owing to failure to drive off all the moisture.

One of the earliest tables recording breed values is that given by Barham⁸ in 1885 for a 5-year average of British Dairy Farmers' Association figures, reproduced in Table V. The

low fat and high solids-not-fat values for the milks of Crossbred and Dutch cattle are remarkable, but it is likely that these fat values are all low and the solids-not-fat values all high.

The various editions of Richmond's "Dairy Chemistry"⁹ and Ingle¹⁰ give the average composition of milk as shown in Table VI.

TABLE V
BREED VALUES RECORDED BY BARHAM IN 1885

Breed	Fat	S.N.F.
Guernsey	4.8	9.29
Jersey	4.26	9.34
Shorthorn	3.79	8.91
Crossbred	3.15	9.16
Dutch (Friesian)	2.97	8.83

As the Vieth and Richmond results were taken from samples received at a creamery, and Macdougall's results were from commercial samples, the difference gives some indication of the extent of adulteration and abstraction of fat. On this straightforward assumption, the difference in fat figures indicates an over-all adulteration of about 2½ per cent. and the difference in solids-not-fat figures about 3½ per cent. This estimate should be regarded with caution, as the figures are not from the same herds or over the same years. It is significant, however, that the later the point of sampling, the lower are the average values.

TABLE VI
AVERAGE COMPOSITION OF MILK ACCORDING TO RICHMOND⁹ AND INGLE¹⁰

	Richmond*			Ingle (1900)
	(Before 1899)	(1897-1914)	(1900-1920)	
Fat	3.90	3.74	3.75	3.90
Solids-not-fat	9.00	8.91	8.91	9.00
Protein	3.40	3.40	3.40	3.40
Lactose	4.75	4.70	4.70	4.75
Ash	0.75	0.75	0.75	0.75

* Richmond's values are based on analyses of milk sent to the Aylesbury Dairy Co.

Other data published about this time and quoted by Ingle¹⁰ are as follows—

Authors	No. of samples	Fat	S.N.F.
Vieth and Richmond	200,000	3.9	9.0
Macdougall	12,000	3.82	8.68

From cow to depot there is evidence for a fall in fat and from depot to consumer there is evidence for a fall in both fat and solids-not-fat, which suggests that on the farm there was abstraction of fat and, by the dairyman at that time, there was an appreciable adulteration.

The average values quoted by Pearmain and Moor¹¹ are 3.6 per cent. of fat and 8.8 per cent. of solids-not-fat, so that an average milk would have to be adulterated by 4 per cent. before detection by determination of solids-not-fat and by 31 per cent. before detection by determination of fat (2.75 per cent. taken as standard). Bell, in 1892, found average values of 4 per cent. of fat and 8.9 per cent. of solids-not-fat, and Vieth, in 1892, found 4.1 per cent. of fat and 8.8 per cent. of solids-not-fat, according to Pearmain and Moor¹¹ (*loc. cit.*, p. 14).

THE INCIDENCE OF MILK CONTAINING LESS THAN 8.5 PER CENT. OF SOLIDS-NOT-FAT

During recent years, attention has been directed to the large proportion of herd supplies coming into creameries that are below the legal presumptive limit of 8.5 per cent. of solids-not-fat.

Cranfield¹² found that 16 per cent. of herd samples were below 8.5 per cent. of solids-not-fat in 1923 to 1925, and Burr¹³ found that 13 per cent. in 1934 and 9 per cent. in 1935 fell below this standard. During and since the war this has been most noticeable in late winter and early spring.

Rowland¹⁴ reported in 1944 that as many as 81 per cent. and 86 per cent. of samples at two creameries contained less than 8.5 per cent. of solids-not-fat at the times of lowest solids-not-fat. The solids-not-fat values rose abruptly in May.

Although it was formerly commonly stated that feeding had no effect on solids-not-fat values, the shortage of concentrates during the war resulted in renewed investigation of this problem and it is now accepted that low protein, and especially low calorie intake, can result in low solids-not-fat values.^{15,16,17} The effects of season and feeding cannot easily be separated, but recently Featherstone, Rickaby and Cavell¹⁸ have shown that it is possible for a herd that is efficiently managed and well-fed to give milk low in solids-not-fat in late winter and early spring.

Those outside the dairy industry may believe that this is a relatively recent observation, but this is far from the truth. It has been recognised for over 50 years that cows may secrete milk that has less than 8.5 per cent. of solids-not-fat, and evidence for this has been published by Richmond (quoted in the Wenlock Report¹⁹) and Tocher²⁰, and a most useful summary of this particular problem was given by Hanley.²¹

This problem was fully recognised by the Wenlock Committee, and the Sale of Milk Regulations of 1901 recognised the so-called "appeal to the cow" test, which was designed to prevent the unjust conviction of a dairy farmer whose cows happened to produce milk low in solids-not-fat. The "appeal to the cow" test was, in fact, suggested many years earlier by a magistrate and was immediately put into use by some Public Analysts.

With the state of scientific knowledge at the time, this was undoubtedly a most useful measure, because there was no test that could detect adulteration with any degree of accuracy. Probably, at that time, added water could only be detected when present to the extent of, say, 10 per cent. or more.

The reasons for cows secreting milk low in solids-not-fat were but little understood in 1901. Presumably there was no trouble due to shortage of concentrates and other artificial foods at that time, as cows would have been fed almost entirely on grass and hay supplemented by other home-grown crops. However, sub-clinical mastitis, which is now recognised to be a considerable predisposing factor to low solids-not-fat in certain herds, was not recognised at this time, and this factor was ignored in papers on the subject until the 1930's.

THE FIXING OF PRESUMPTIVE STANDARDS IN 1901

It is of interest to note that although there was considerable argument about the fat standard in the Wenlock Committee deliberations (11 witnesses recommended 2.75 to 2.8 per cent., 21 a value of 3.0 per cent. and 3 a limit of 3.25 per cent. of fat), the standard of 8.5 per cent. for solids-not-fat appears to have been unquestioned. This had been in use by the Society of Public Analysts for many years, although Richmond had recommended a limit of 8.25 per cent. for July to September. It is therefore clear that the present trouble with late winter and early spring low solids-not-fat was unknown at that time. The variety of recommendations about the fat standard may have been partly due to the errors of the methods previously used (*e.g.*, the Wanklyn method is now known to give results about 0.5 per cent. low compared with the Adams coil method, but this itself may give high results). It is also obvious that a method giving a low fat result would *ipso facto* give a high solids-not-fat result, because the latter value was at that time calculated by the difference between fat and gravimetric total solids tests.

Richmond made a statistical analysis of 76,058 fat tests taken over 6 years, but it is important to realise that this period of 6 years (1894 to 1899) is not necessarily an adequate sample in respect of yearly variations and, further, Richmond had no knowledge of the extent of adulteration of these samples. Richmond's values yielded an average of 3.84 per cent. and a mode of 3.75 per cent. and there were about 700 results of less than 3 per cent. Richmond's monthly figures show a minimum "standard" fat of about 2.8 per cent. in May and June, 1898, and a minimum "standard" solids-not-fat of 8.3 per cent. in August, 1897, but he had no real knowledge of the extent of either the abstraction of fat or addition of water. His standards were obtained by statistical treatment of his test results, equivalent to excluding the lowest 2½ per cent. of the values (Hanley²¹).

DIFFICULTIES IN COMPARING 1900 DATA WITH DATA TO-DAY

There are two major sources of error in comparing the average composition of milk in 1900 with that of to-day. At that time the adulteration of milk was notably more extensive than it is to-day because the inspection and testing of milk was less efficient, and the freezing-point test was then not in use. Further, there was about this time a change in analytical methods. Previously, milk was tested almost universally by the weighed total solids and

a direct fat method. It is obvious that, since the solids-not-fat was calculated by difference, the use of any method giving a low fat percentage would automatically give a high solids-not-fat percentage. The Wenlock Committee, which issued its report in 1901, appears to have assumed a value of 8.9 per cent. for the solids-not-fat content of milk at that time, and I understand that this was based mainly upon Richmond's evidence and Ingle's report.¹⁰ It is possible that this value was high because the generally accepted values for solids-not-fat at that time were high on account of low fat extraction.

THE IMPORTANCE OF ANALYTICAL METHODS

In general the milk supplies of our country are controlled by two very simple routine sorting tests—the Gerber test for fat and the lactometer or "Richmond" test for solids-not-fat. These have been in general use by milk buyers for nearly 50 years and are to-day commonly used by Public Analysts for the routine or first testing of milk samples, the more accurate methods being used only when these routine tests indicate a deficiency. The Gerber test for fat can be briefly dismissed by saying that, properly carried out in a calibrated apparatus, it is a very accurate method, the error being at the outside 0.1 per cent. of fat. Users of the test will probably consider that their results are accurate to 0.05 per cent., but there should be no opportunity for errors of any magnitude.

The test for solids-not-fat is a little more complicated and requires some discussion. The Richmond method derives the solids-not-fat value from the known fat content and the specific gravity of the milk. The Richmond formula—

$$\text{Total solids} = \frac{G}{4} + \frac{6F}{5} + 0.14$$

was derived by Richmond about 1895 from his analysis of about 240 samples of milk at different seasons of the year. His formula was derived by the method of best fit to accurate analytical data.

Unfortunately there are a number of sources of error associated with this method. In the first place, no two milks are identical in composition; it follows therefore that a specific gravity method can only be worked out to give an average value and the error, other things being equal, will be the greater the more abnormal the composition of the milk.⁹ Further, apart from milks of abnormal composition, there are other factors that can affect specific gravity, particularly the degree of aeration of the milk and the condition of the fat. Aeration such as might be caused by allowing milk to fall into a tanker can result in a decrease in specific gravity equivalent to as much as 0.15 per cent. of solids-not-fat.

If it is assumed that the aeration effect is nil and the milk is of average composition, there still remains the most important disturbing factor, that due to the slow solidification of the fat in milk when it is held for some hours at low temperatures. Although milk fat melts at about 32° C, solidification is still a slow process at temperatures much below 32° C. This effect, commonly called the Recknagel effect, can result in a difference in specific gravity equivalent to as much as 0.2 per cent. of solids-not-fat. It is a matter of considerable importance, therefore, to standardise the condition of the fat globules.

It is not clear whether the Richmond results were obtained on milks in which the Recknagel effect had not taken place or on milks in which it had been completed, and subsequent investigations of this problem still leave the matter in some confusion.

Some years ago Boden and Campbell,²² in Scotland, found that refrigerated milk samples gave correct results for solids-not-fat by the lactometer method and they therefore assumed that the Richmond formula was intended to be used with milks in which the Recknagel effect had been completed. At Reading, however, Rowland²³ found that the Richmond lactometer method used on refrigerated milks (*i.e.*, with the Recknagel effect completed) gives values about 0.15 per cent. higher than the gravimetric method, while the method carried out on milk samples that have been warmed and cooled (*i.e.*, with no Recknagel effect) gives values about 0.03 per cent. lower than the gravimetric value. The difference between the two hydrometer methods is thus about 0.2 per cent. of solids-not-fat. Slight differences can be found according to the method used for drying in the gravimetric determination of total solids, but the general picture is not affected, the differences being only of the order of about 0.02 per cent. of total solids. It appears, therefore, that the ordinary Richmond method, usually carried out at about 60° F, gives results that in cold winter weather may be as much as 0.2 per cent. higher than those by the same method in warm summer weather.

The British Standards Institution in 1938 published a method that attempted to standardise the technique in respect of the Recknagel effect and there has been much confusion over the two methods. The B.S.I. formula—

$$\text{Total solids} = \frac{D}{4} + 1.21F + 0.66$$

is really the same as the Richmond formula, the only adjustment made being that for the difference in the specific gravity, the B.S.I. method using density (grams per ml) at 20° C whilst the Richmond method uses specific gravity (60° F/60° F). Although the B.S.I. method involves warming to 40° C and cooling to 20° C in order to reverse any Recknagel effect that may have taken place, the method is not really concerned with the Recknagel effect as such. It follows, therefore, that both the B.S.I. and the Richmond methods will give virtually identical results if made on milks in which no solidification of fat has taken place, but that if the methods are used on a milk in which the Recknagel effect has been completed, Richmond's method will give a result that is about 0.2 per cent. higher than the B.S.I. method for solids-not-fat, not because of the difference in the formula for the B.S.I. method but because the warming and cooling, which is an essential part of the B.S.I. method, reverses the Recknagel effect and so lowers the specific gravity. If, therefore, a laboratory changes from the old Richmond method to the new B.S.I. method it may be expected that more accurate results will be obtained throughout the year, the general level being roughly 0.05 per cent. lower than the true gravimetric value. In cold winter weather, however, results obtained with the B.S.I. method can be as much as 0.2 per cent. lower than they would have been had the Richmond method continued in use.

Hence a laboratory that uses the ordinary Richmond method will record solids-not-fat values up to 0.2 per cent. higher in winter than in summer, and up to 0.15 per cent. higher than the true (gravimetric) result. Thus low solids-not-fat values reported by the Richmond lactometer in winter would be even lower if the B.S.I. or gravimetric method were used.

OTHER INVESTIGATIONS IN ENGLAND

Fat and solids-not-fat figures as determined by creameries in England have been examined and reported on by Provan and Jenkins.² Results for the period 1923 to 1946 indicate a fall of about 0.3 per cent. (8.9 to 8.6 per cent.) for solids-not-fat and a fall of about 0.05 per cent. (3.60 to 3.55 per cent.) in the Midlands area. Bartlett and Kay¹⁷ consider that since 1920 fat has fallen from 3.75 to 3.55 per cent. (a 6 per cent. decrease) and solids-not-fat from 8.90 to 8.65 per cent. or less (a 3 per cent. decrease). Hence, although Provan and Jenkins² suggest a serious fall in solids-not-fat and only a slight fall in fat, the fall in fat *as a percentage of the fat itself* is the more serious aspect of compositional deterioration if the figures of Bartlett and Kay are accepted.

CONSIDERATION OF DATA FROM PUBLIC ANALYSTS

Through the most helpful co-operation of Public Analysts, not only in England and Wales, but also in Scotland, I have been able to obtain data covering various parts of Great Britain over the period 1900 to 1950. It will, of course, be appreciated that these results are based on samples of milk taken as delivered to the public and that there may therefore be differences between these figures and those presented by workers, such as Provan^{2a} and Provan and Jenkins,² who have studied the results of milk samples as delivered to creameries.

In requesting these data from Public Analysts, I have been most careful to lay down certain requirements, and only data from those Public Analysts who have assured me that their figures meet these requirements have been used in this paper. These requirements were laid down as follows—

- (1) That the sampling has been random as far as possible. In practice, Food Inspectors usually have a system that ensures that each supplier is sampled at certain intervals, *e.g.*, monthly. It may appear that this system might attach more significance to big suppliers than to small ones. This is probably not as serious as might be thought at first, because a big dairy company selling milk in London, for example, might sell 100 or 1000 times as much milk as a small dairyman, but whereas the small dairyman would be sampled by only one authority, the big supplier would be sampled by a number of authorities. This system of sampling, therefore, probably gives a reasonable average of the milk supply as sold to the public.

- (2) That the number of follow-up and "appeal" samples form only a negligible proportion of the whole. Such samples naturally tend to be low and would have the effect of bringing down the average if they formed a large proportion. However, it can easily be calculated that a few per cent. of such samples will not have any significant effect on the average and, furthermore, the proportion appears to be approximately the same for all Public Analysts.
- (3) That the methods of analysis have been the same throughout the whole period under consideration or, if a change has been made, that the two or more methods that have been used have been shown to give virtually identical results.

The effect of selecting samples in various ways is well illustrated by some data which were sent to me by the Public Analyst for one authority. The annual average values were worked out in four groups as follows—

- (1) All samples.
- (2) Excluding appeal samples.
- (3) Genuine milks (including those deficient in solids-not-fat but with normal Hortvet freezing-points).
- (4) As (3), but with averages derived from quarterly averages in order to compensate for unevenness in sampling throughout the year.

From 1931 to 1950 there was a close agreement between the four sets of average values for both fat and solids-not-fat from the point of view of the trends in quality. It was also evident that the exclusion of appeal samples made no difference to the final average value, and differences were very much smaller than the error of the methods used. The exclusion of those deficient milks that were shown to be adulterated by the freezing-point test resulted in a value that was on the average about 0.05 per cent. higher. As might be expected, this difference was less noticeable with the fat values on account of the smaller absolute amount of fat in milk.

These figures show quite clearly that if there had been differences in the methods of selecting samples by the Public Analysts whose data have been presented in this paper, such differences would not affect the general results and conclusions.

There are obviously certain factors that can act as sources of error in any consideration of results of this nature. For example, morning samples are almost invariably appreciably lower in fat than the evening samples, but here again it is customary for Food Inspectors to equalise the two types of milk when the milkings are known to be sold separately. Most milk is now sold by big dairy companies and this is all mixed evening and morning milk.

A further important factor is the proportion of Channel Island milk. Since, however, this milk will find its way into the sampling system whether sold separately or incorporated in the bulk, it is unlikely that this will affect the over-all average. The effect of omitting Channel Island and known adulterated samples was shown by classified data to have very little effect on absolute values and none at all on the trend of composition.

TREATMENT OF DATA—

Altogether analytical figures for milks sampled under the Food and Drugs Act have been received from analysts for 32 authorities, extending over the period 1900 to 1950. Figures for the beginning of the century were relatively few, so that the data can be considered more reliable for the later years. For this reason not too much reliance should be placed upon trends indicated before 1920, but from 1930 onwards the number of data and the number of different parts of the country from which the data have been derived are sufficiently great to make the results reliable. The annual numbers of results considered for England have increased from about 360 in 1900 to over 29,000 in 1950. For Scotland the annual number of 1200 in 1907 has increased to about 5000 in 1949.

When annual averages were studied it was found that the yearly variations, well recognised to be due to climatic conditions, obscured any trends, and therefore averages of 5-year periods were calculated. These data are given in Tables VII to XIII. Only clearly-defined trends are commented on, and it is suggested that a rise or fall of 0.1 per cent. or greater is significant.

WEIGHTED AND UNWEIGHTED AVERAGES—

It is usual in summarising data such as these to use weighted averages. In the present problem the question is not a straightforward one. For example, if one analyst has obtained

TABLE VIII—continued

Authority No. Analytical methods Selection of samples	51		59		61		67		6 later 1		Unweighted average values		Weighted average values	
	(a)		(d)		(d)		(a)		(a)		Fat S.N.F.		Fat S.N.F.	
	No.	Fat	No.	Fat	No.	Fat	No.	Fat	No.	Fat	No.	Fat	No.	Fat
1906-10														
1911-15														
1916-20														
1921-25														
1926-30														
1931-35	446	3.67	812	3.63	87	3.80	8.86 (2)	1220	3.55	8.75 (1)	3.61	8.81	12,785	3.61
1936-40	1052	3.65	878	8.81				12,785	3.61	8.81	3.67	8.88	14,912	3.67
1941-45	1337	3.76	880	8.81				14,912	3.67	8.88	3.65	8.95	17,293	3.66
1946-50	1320	3.85	879	8.73				14,336	3.67	8.98	3.69	8.86	17,802	3.77
	2084	3.75	874	8.77				13,995	3.73	8.91	3.65	8.83	20,636	3.71
								15,046	3.71	8.81	3.69	8.81	20,118	3.70
								7164	3.71	8.60	3.70	8.75	45,256	3.63
								22,496	3.70	8.63	3.65	8.74	64,908	3.61

Rise in fat; rise and marked fall in S.N.F.

Rise and fall in S.N.F.

TABLE IX

NORTH-EASTERN REGION

Authority No. Analytical methods Selection of samples	2		42		60		Unweighted average values		Weighted average values	
	(a)		(b)		(d)		Fat S.N.F.		Fat S.N.F.	
	No.	Fat	No.	Fat	No.	Fat	No.	Fat	No.	Fat
1906-10										
1911-15										
1916-20										
1921-25										
1926-30										
1931-35										
1936-40										
1941-45										
1946-50										

Rise in fat; rise and marked fall in S.N.F.

Rise and fall in S.N.F.

1000 samples from a million gallons of milk and another 100 samples from 100,000 gallons of milk then a weighted average would obviously be the method to be employed. If, however, both the 1000 samples from one authority and the 100 samples from another authority are taken from one million gallons of milk, then obviously it would be more accurate to take an unweighted average. In the present investigation both methods have been used and weighted and unweighted averages have been calculated. The results have been grouped in regions and on a national basis. Weighted and unweighted averages give results that agree closely.

CODE USED IN TABLES VII TO XIII

Analytical methods—

- 1 = Richmond lactometer or other gravity method and Gerber.
- 2 = gravimetric total solids and Gerber.
- 3 = gravimetric total solids and Leffman - Beam.
- 4 = gravimetric total solids and specific gravity.
- 5 = gravimetric total solids and Werner - Schmidt.
- 6 = specific gravity and Leffman - Beam.

Selection of samples—

- (a) = all samples ("follow up" and "appeal" samples less than 5 per cent. of total).
- (b) = excluding adulterated (Hortvet) samples.
- (c) = excluding samples below presumptive limits.
- (d) = excluding "follow up" samples.

Division of columns—

- No. = number of samples.
- Fat = percentage of fat.
- S.N.F. = percentage of solids-not-fat.

The small figure in brackets after solids-not-fat values indicates the number of years considered when the figures for the complete 5-year period are not available. Only data for complete 5-year periods are included for calculation of average values.

DISCUSSION OF DATA AND CONCLUSIONS—

Table VII (London and Home Counties)—All authorities show a fall in fat. The combined averages fail to show this fall because of the inclusion of No. 49 with a high fat value for the last period.

Table VIII (North-Western area)—Of nine authorities, two show a fall in both fat and solids-not-fat and two a fall in solids-not-fat only. Combined averages show a fall in solids-not-fat.

Table IX (North-Eastern area)—The results for these three authorities are remarkably constant, apart from one high fat value for 1941 to 1945.

Table X (Midland area)—Of six authorities, one shows a rise and fall in fat and one a rise and fall in solids-not-fat. The averages show a slight rise and fall in solids-not-fat.

Table XI (Southern area)—Both authorities show a marked rise and fall in both fat and solids-not-fat.

Table XII (Western area)—The data for this region are insufficient to allow conclusions to be drawn.

Table XIII (Wales)—Figures for the single Welsh authority show a fall in both fat and solids-not-fat.

Table XIV (Scotland)—Of the two authorities concerned, one shows a fall and rise in fat and the other a rise in fat. The averages reveal a significant rise in fat.

The general conclusions are summarised below—

	Region	Trend
London	Slight fall in fat.
North-Western	Rise and fall in S.N.F.
North-Eastern	Constant.
Midland	Rise and slight fall in S.N.F.
Southern	Marked rise and fall in fat; less marked rise and fall in S.N.F.
Western	Insufficient evidence.
Wales	Fall in fat and (possibly) S.N.F.
Scotland	Marked rise in fat.

The combined averages for all English authorities are shown in Table XIV. These unadjusted figures indicate that the solids-not-fat values have increased from 1900 to 1921-25 and since fallen. There appears to have been an increase of about 0.25 per cent., and since 1921-25 a fall of about 0.1 per cent. The fat appears to have increased slowly up to 1941-45 and since then fallen. It should be remembered, however, that in these figures those areas showing a fall in composition in recent years (North-Western, Midland and Southern) have contributed a greater number of results (17 out of 28 authorities) than those regions that have shown no changes in composition.

TABLE X

MIDLAND REGION

Authority No.	3			4			13			26		
Analytical methods	2			3			4			2 later 1		
Selection of samples	(a)			(a)			(a)			(a)		
	No.	Fat	S.N.F.	No.	Fat	S.N.F.	No.	Fat	S.N.F.	No.	Fat	S.N.F.
1901-05	5167	3.61	8.61 (6)									
1906-10	4349	3.53	8.70									
1911-15	4355	3.59	8.70									
1916-20	4345	3.63	8.69				103	3.67	8.96 (1)			
1921-25	4365	3.64	8.73				672	3.70	8.97			
1926-30	4400	3.60	8.80	1575	3.74	8.85 (2)	751	3.61	8.88			
1931-35	4404	3.60	8.81	1629	3.67	8.88	1095	3.64	8.90	8333	3.63	8.76
1936-40	4376	3.65	8.75	3233	3.62	8.90	895	3.71	8.79	9847	3.65	8.75
1941-45	4358	3.62	8.72	2909	3.64	8.80	837	3.59	8.84	7933	3.63	8.69
1946-50	4358	3.59	8.72	5434	3.68	8.82				11,911	3.59	8.68

Rise and fall in S.N.F.

Authority No.	41			62			Unweighted average values		Weighted average values		
Analytical methods	1			2							
Selection of samples	(b)			(b)							
	No.	Fat	S.N.F.	No.	Fat	S.N.F.	Fat	S.N.F.	No.	Fat	S.N.F.
1901-05							3.61	8.61	5167	3.61	8.61
1906-10							3.53	8.70	4349	3.53	8.70
1911-15							3.59	8.70	4355	3.59	8.70
1916-20							3.63	8.69	4345	3.63	8.69
1921-25							3.67	8.80	5037	3.65	8.75
1926-30							3.61	8.84	5151	3.60	8.81
1931-35				1004	3.63	8.80 (1)	3.64	8.84	15,461	3.62	8.79
1936-40	50	3.77	8.91 (1)	4524	3.68	8.80	3.66	8.80	22,875	3.65	8.78
1941-45	303	3.72	8.84	4240	3.72	8.72	3.65	8.77	20,580	3.65	8.79
1946-50	263	3.66	8.83	4932	3.59	8.73	3.62	8.75	26,898	3.61	8.72

Rise and fall in fat

Rise and slight fall in S.N.F.

Rise and slight fall in S.N.F.

TABLE XI

SOUTHERN REGION

Authority No.	68			71			Unweighted average values		Weighted average values		
Analytical methods	2			1 later 2							
Selection of samples	(b)			(a)							
	No.	Fat	S.N.F.	No.	Fat	S.N.F.	Fat	S.N.F.	No.	Fat	S.N.F.
1921-25	540	3.68	8.92 (3)								
1926-30	976	3.60	8.98	2032	3.69	8.85	3.65	8.92	3008	3.66	8.89
1931-35	1424	3.76	8.90	2422	3.82	8.91	3.79	8.91	3846	3.80	8.91
1936-40	1244	3.98	9.03	1645	3.92	8.90 (3)	3.98	9.03	1244	3.98	9.03
1941-45	900	4.01	8.92	1226	3.88	8.78 (3)	4.01	8.92	900	4.01	8.92
1946-50	1059	3.81	8.89	1605	3.74	8.72	3.78	8.81	2664	3.78	8.78

Rise and fall in both fat and S.N.F.

Rise and fall in both fat and S.N.F.

Rise and fall in both fat and S.N.F.

Rise and fall in both fat and S.N.F.

TABLE XIV

ENGLAND

Period	No. of samples	Unweighted average values		Weighted average values		Adjustment factor	Adjusted weighted averages*	
		Fat	S.N.F.	Fat	S.N.F.		Fat	S.N.F.
1900-05	3415	3.61	8.61	3.61	8.61	1.05	3.78	9.05
1906-10	6511	3.51	8.72	3.53	8.70	1.05	3.70	9.13
1911-15	21,686	3.60	8.78	3.60	8.78	1.04	3.74	9.10
1916-20	27,860	3.65	8.79	3.66	8.83	1.04	3.80	9.20
1921-25	34,448	3.68	8.87	3.65	8.91	1.03	3.76	9.18
1926-30	43,695	3.65	8.83	3.70	8.83	1.03	3.81	9.09
1931-35	61,160	3.68	8.84	3.67	8.81	1.02	3.74	8.98
1936-40	93,376	3.69	8.82	3.65	8.79	1.02	3.72	8.96
1941-45	90,078	3.71	8.77	3.64	8.76	1.01	3.67	8.85
1946-50	139,661	3.64	8.75	3.62	8.74	nil	3.62	8.74

* See p. 517.

THE EFFECT OF ADULTERATION ON TRENDS IN QUALITY

The question as to whether a sample of milk is adulterated or not rests on the opinion of the Public Analyst. The freezing-point test, in general use since about 1930, permits the detection of over 2.6 per cent. of added water if a depression of 0.530° C is assumed to be the limit for genuine milks. It does not detect abstraction of fat. Between 1901 and about 1930 it was customary for Public Analysts to report as adulterated any sample of milk below 3.0 per cent. of fat and 8.5 per cent. of solids-not-fat, although prosecution normally took place only when the results were 5 per cent. or more below the legal presumptive limits, *e.g.*, 2.8 per cent. of fat or 8.0 per cent. of solids-not-fat. Before 1901 there were no legal presumptive limits and analysts had to make the best use of their analytical results and existing knowledge. Obviously until about 1930 only a proportion of adulterated milks were detected, since a milk containing 3.7 per cent. of fat could "absorb" about 19 per cent. and a milk containing 8.8 per cent. of solids-not-fat about 4 per cent. of water without adulteration being detected. Probably at least twice the numbers detected were in fact adulterated. The criteria for adulteration in these three periods (before 1901, 1901 to about 1930 and since about 1930) have thus been somewhat different, and even if data were available for the average percentage adulteration they might be misleading if used to compare the three periods.

Liverseege²⁵ discusses trends in adulteration and gives the figures recorded in Table XV.

TABLE XV

PERCENTAGE OF SAMPLES ADULTERATED

	England and Wales		London	Birmingham
1873	—	40.6
1879	13.8	20.6
1889	9.9	12.7
1899	8.6	7.9
1909	8.3	7.1
1919	6.3	4.6
1929	5.4	5.5
1930	4.8	3.7

Before 1901 standards of 2.75 per cent. of fat and 8.5 per cent. of solids-not-fat were in use by the Inland Revenue Department, although Public Analysts preferred a fat standard of 3 per cent. (Pearmain and Moor¹¹), and the figures shown in Table XVI were obtained for adulteration.

Data for the percentages of milk samples found adulterated are given in the extracts from the Annual Reports of the Local Government Board and (later) the Annual Reports of the Ministry of Health.

For historical aspects of the difficulties in the early work on the detection of adulteration and methods of analysis, see Dyer and Mitchell.²⁶

ADJUSTMENT OF NATIONAL CURVES-

We have no accurate information about the extent of adulteration of the milk of the country as a whole over the period 1900 to 1950 but we can be reasonably sure that it was appreciable in 1900 and is negligible to-day—almost certainly less than 1.0 per cent.* Although the term adulteration has always been prominent in connection with milk for the simple reason that milk is a food that is very easily adulterated by the addition of water, yet we

TABLE XVI
PERCENTAGE OF ADULTERATION BEFORE 1901

	Total number examined	Adulteration, %
1890	11,967	12.8
1891	12,151	13.4
1892	13,633	13.3
1893	15,543	14.9
1894	16,305	11.5
1895	18,307	11.1

can say to-day with certain knowledge that milk as sold by reputable dairies is not only one of our best foods, but also one of our purest. If we had any accurate knowledge of the extent of adulteration over this 50-year period it would be possible to adjust these figures to give values that would be a more correct representation of the quality of milk as produced by the cows of the country. As such accurate information is not available, the best we can do is to make some estimate—an estimate that, although based only on general impressions, is backed by experience and will probably give a picture that is truer than the figures without any adjustment at all. For the purpose of this argument, therefore, I have assumed a 5.0 per cent. adulteration over the period 1900 to 1910, 4.0 per cent. over the period 1910 to 1920, 3.0 per cent. over the period 1920 to 1930, 2.0 per cent. from 1930 to 1940 and 1.0 per cent. for the period 1940 to 1945. I have assumed that milk from 1945 to 1950 contains no added water.

Although this is admittedly only an estimate, it is supported broadly by figures for percentage of adulterated samples that have been given by Public Analysts. These figures show quite conclusively that adulteration has progressively decreased during the century and the very small proportion of milks that are genuinely deficient (*viz.*, non-adulterated samples below 3 per cent. in fat or 8.5 per cent. in solids-not-fat) will not affect this main conclusion.

More precise information can be drawn from freezing-point data for bulk milk. Such figures have been published by Macdonald²⁷ and in Table XVII it has been worked out, from Macdonald's figures over the period 1942 to 1947, what would be the expected amount of added water in bulk milk. These figures show a progressive decline in exactly the same way that the Public Analysts' percentage deficiency figures also decrease.

TABLE XVII
ADULTERATION OF BULK MILK

Year	Percentage of tanker bulks adulterated†	Average water content of adulterated milk	Average water content of all milk
1942	32.6	1.7	0.55
1943	8.9	1.3	0.12
1944	2.1	1.7	0.04
1945	2.3	1.7	0.04
1946	6.7	1.5	0.10
1947	3.8	1.4	0.05

† It is assumed that a bulk milk with a freezing-point depression of less than 0.540 is adulterated; it would contain at least 1 per cent. of added water.

These figures do not suggest an appreciable adulteration of milk since 1942, but the lower figures of about 0.1 per cent. were the result of "follow-up" work based on systematic testing.

* Calculated as average percentage of water in all milk sold.

It is reasonable to assume that in the absence of this checking the average adulteration of bulk raw milk in the period 1940 to 1950 was somewhat greater than 0.5 per cent.

Aschaffenburg²⁸ has also published information on the extent of adulteration of the milk supply as a whole. His figures from freezing-point data on bulk milk indicated an over-all adulteration of 0.6 per cent. for the period 1938 to 1942. It must be remembered, however, that Aschaffenburg took a depression of 0.530° C as a limit for pure milk. This limit can ignore 2.6 per cent. of added water, so that the *true* extent of adulteration was certainly greater than 0.6 per cent., probably about 3.2 per cent. These findings of Aschaffenburg are broadly in agreement with the adjustments made in this paper.

When we come to apply these assumed percentages of adulteration to the figures, we see that the apparent rise in the quality of milk no longer exists (see Table XIV, last column). The fat values remain fairly constant throughout the whole period, but there is a marked and steady fall in solids-not-fat from 1900 to 1950. The adjusted solids-not-fat values for the beginning of the century will appear to be high, possibly excessively high, but they are at least in line with the earlier figures reported by Barham,⁸ Ingle¹⁰ and Bell and Vieth. The differences *may* be due to the fact that Barham, Ingle, and Bell and Vieth quoted results from samples taken (at least mainly) at the farm.

TRENDS IN MILK COMPOSITION IN OTHER COUNTRIES

I have endeavoured to obtain the latest information about trends in milk composition in other countries and the present position is summarised in Table XVIII. It is a remarkable fact that few countries have any precise information about trends of the composition of their milk supplies.

TABLE XVIII
TRENDS IN MILK COMPOSITION IN OTHER COUNTRIES

Country	Changes
Eire	No change observed (Harnett ²⁹)
New Zealand	Fat risen from 4.3 per cent. in 1937 to 4.51 per cent. in 1950 owing to increase in proportion of Jerseys (Riddet ³⁰)
Sweden	No indication of change in fat; S.N.F. not normally tested (Thomé ³¹)
South Africa	Fall in fat and S.N.F. in some areas, the latter due to fall in protein. Change in breed proportions alleged responsible. Fall in fat and rise in S.N.F. in other areas (Bakalor ^{32,33,34})
Netherlands	Fat increased by 0.54 per cent. and S.N.F. increased by 0.38 per cent. (Janse ³⁵)
Norway	Fat increased from 3.53 (1925) to 3.83 (1950) (<i>Norw. Off. Statist.</i>). S.N.F. rising, but declined during war (Mork ³⁶)
Denmark	No data on fat and S.N.F. Lactose fallen from 4.7 to 4.5 (anhydride) in 10 years (Mogensen ³⁷)
U.S.A., Northern Ireland, Portugal, Canada, Australia, Germany, Switzerland, Spain	No data available

METHODS FOR IMPROVING THE CHEMICAL QUALITY OF MILK

The evidence presented in this paper supports that summarised by Provan and Jenkins,³ in that there has been, at least in some areas, a decline in the solids-not-fat value, and possibly also of the fat value, of milk in recent years. It is, therefore, highly desirable that some actively constructive measures should be put into practice to combat this decline. Whilst there must be the greatest support for education and advisory work amongst dairy farmers to put them in possession of the latest information about the causes of poor milk quality, those who have been actively engaged in the dairy industry will agree that there must be a definite incentive for a farmer to produce a higher-quality milk. The most effective measure is to put into operation as soon as possible a scheme of quality payment that will make it worth while for the farmer to take the necessary steps to produce milk of the highest grade, both chemically and bacteriologically. It is an interesting fact that, although we have in this country toyed with the idea of special payments for fancy grades of milk from 1923

onwards, we are about the only advanced dairying country in the world that has not yet put into operation a simple, straightforward and businesslike scheme of quality payment.

As far as the chemical aspect of milk is concerned, it should be noted that the farming world appears to be only interested in the fat content of milk and to consider that quality payment should be made in terms of fat, if at all. Scientists outside the dairy industry, in contrast, when discussing the subject, put forward complicated schemes based on calories or using formulae weighted to give prominence to protein, and so on. Whilst all these schemes are scientifically most interesting, and from the nutritional point of view have much to be said for them, it must be remembered that any quality payment scheme will involve more administrative machinery and inevitable cost³⁸ and it is therefore essential that the testing side of the scheme be made as simple as possible.

After consideration of this problem for many years, the author favours a scheme in which payment varies directly with total solids,^{39,40} for the reason that it is the solids that the cow has to put into the milk and for which the farmer has to pay, whether the feeding stuffs are home-grown or imported. Although payment should be based on the total solids content (*i.e.*, a farmer would be paid per pound of milk solids and not per gallon of milk), it is most important that the farmer should be given the fat and solids-not-fat figures separately in order that he can take the necessary steps to correct a low value in either. Certain factors, such as mastitis, may affect the solids-not-fat more than the fat, while other factors, *e.g.*, the heredity of the bull, may affect the fat more.

It has been argued that, as fat and solids-not-fat are correlated, it would be sufficient to pay on a fat test. While it is true that, broadly speaking, fat and solids-not-fat are well correlated, this is not so true for individual herds, and payment on fat only would not, therefore, be as just as a payment on total solids. It is important that any quality payment scheme should go out of its way to emphasise the solids-not-fat aspect for the following reasons—

- (1) The solids-not-fat aspect has been more neglected in the past than the fat aspect.
- (2) Genuine milks are more frequently below 8.5 per cent. of solids-not-fat than they are below 3.0 per cent. of fat.
- (3) About 70 per cent. of all the solids in milk are solids-not-fat, so that it is by far the more important part of the milk without any reference to nutritional value.
- (4) While one cannot compare the nutritional value of fat with that of the solids-not-fat fraction, most nutritionists would agree that, of the two fractions, the solids-not-fat is the more important, especially for children. For example, while babies and children could live quite well on skim milk (with certain necessary additions), cream would be of far less use to them.
- (5) Although fat has a much higher energy or calorie value than protein and sugar, being about $2\frac{1}{4}$ times more valuable, the solids-not-fat fraction of milk provides about 15 per cent. more calories than does the fat fraction.
- (6) Emphasis on low solids-not-fat figures would be of considerable value in making the dairy farmer more conscious of the dangers of sub-clinical mastitis.
- (7) Whilst we cannot definitely account for the greater fall in solids-not-fat, it is by no means impossible that this is due, at least in part, to the fact that in the past there have been local quality payment systems in use by buyers in which a bonus was paid only for high percentages of fat. Before the war it was a common practice for some manufacturers to pay 0.1 pence for every extra 0.1 per cent. of fat above 4.0 per cent. Thus there has been, over many years, an incentive to produce a milk high in fat, especially in the west and south, which are the main manufacturing areas.
- (8) Whilst the chemical quality of milk is not a matter of great importance to the local milk distributor, it is of great importance to the manufacturer. The importance of the constituents of milk, especially fat and casein, naturally varies with the product being made.⁴¹

It is a practice in some countries to pay according to the product-yielding value of the milk. In New Zealand, payment for milk for cheesemaking is made on a fat and casein basis. Obviously for butter and cream, only the fat content is of interest. Nevertheless, from the point of view of simplicity, and in fairness to the farmer from all points of view, payment on a total solids basis is the best all-round method.

It is naturally difficult to prove that in any set of conditions a quality payment scheme would result in an improvement in quality, and the views of those who have urged the adoption of quality payment may perhaps be biased. The following extract from a letter from Dr. F. J. T. Grigg, Director of the Dominion Laboratory, Wellington, Department of Scientific and Industrial Research, New Zealand, may be of interest—

“ . . . In the North Island there is no evidence of deterioration in fat or solids other than fat over the last 30 years. As previously stated, this Island is the main dairying area of New Zealand.*

“In the South Island, over the last 10 years or so, there has been a deterioration in fat and a very serious deterioration in solids other than fat, particularly at Christchurch. The demand for milk for human consumption has increased very considerably over that period owing to the introduction of a school milk scheme, and also the demands of military camps during the war period. There is no system of payment on quality and the tendency has been to increase volume by the extended use of lower testing cows. There is relatively little provision made by farmers in the South Island for supplementary feeding during winter months, resulting in a subnormal plane of nutrition; and in the absence of incentive payments there is no reason to expect that the position will improve.

“Summarising, the decline in the South Island is a result of economic consideration, the principal cause being the lack of incentive payments for quality. . . .”

Andrew⁴² records that for the Wellington district the fat rose steadily from 4.05 per cent. in 1917 to 4.27 per cent. in 1926, the solids-not-fat remaining steady at about 9.0 per cent. Grigg⁴³ reports that in the Christchurch district the fat rose from 4.08 per cent. in 1926 to 4.37 per cent. in 1936, and then fell to 4.09 per cent. in 1946. Over the same period the solids-not-fat fell from 8.97 to 8.72 per cent. For the whole of New Zealand, fat rose from 4.3 per cent. in 1933 to 1938 to 4.51 per cent. in 1950 to 1951, owing to the increase in the proportion of Jerseys (N.Z. Dairy Board Report, 1949-50). In the Auckland district, Riddet³⁰ reported that the fat fell from 4.6 to 4.48 per cent. and the solids-not-fat from 9.0 to 8.75 per cent. over the period 1936 to 1950.

For Australia there are no precise data available, but the best-informed opinion based on much analytical work is that, whilst there is no over-all deterioration, where milk is bought on a gallonage basis (in contrast to the butterfat basis used elsewhere), the composition soon deteriorates.⁴⁴

THE QUESTION OF STANDARDS AND THE “APPEAL TO THE COW” TEST

A study of the discussions of the Wenlock Committee will show quite clearly that the Committee was concerned not only with ensuring a supply of pure milk for the public, but also with the prevention of the unjust conviction of milk producers for adulteration. With the extent of knowledge at that time and the accuracy of analytical methods then available this was a difficult problem. Few will cavil at their decision to institute legal presumptive standards together with the right of the producer to have an “appeal to the cow” test made to prove the genuineness of milk below the presumptive standards (Sale of Milk Regulations, 1901).

However, the time has come when, with the more extensive knowledge and more accurate methods available to-day, we can reconsider the whole question of standards. The “appeal to the cow” test really satisfies nobody and is the cause of endless trouble and considerable expense. Basically it is unsatisfactory because the milk from any one herd can vary from day to day, especially in the fat content, and even, to some extent, in the solids-not-fat content. The Wenlock Committee was concerned primarily with establishing the genuineness or otherwise of a sample of milk, but this is not an adequate consideration. To give a simple analogy, a purchaser of fruit and vegetables would not be satisfied with what he had bought merely because he was satisfied that they were genuine articles. When one buys a pear one wants something more than a fruit that has genuinely been produced by a pear tree—one wants an attractive article of food with all the properties associated with those of a satisfactory pear. The same reasoning should be applied to milk, and it is wrong in principle to guarantee a market and exempt a producer from responsibility merely because a poor-quality milk has been shown indisputably to come from a cow.

* Quality payment is in force [J. G. D.].

It is suggested, therefore, that the government should give five years notice of its intention to abandon presumptive standards and institute absolute standards. This period of five years would give owners of herds producing poor-quality milk time to improve them. On the question of standards there is much to be said for retaining the 3.0 per cent. of fat and 8.5 per cent. of solids-not-fat as absolute standards, but the problem of low solids-not-fat is now much more acute than it was in 1901.^{15,16} This is well illustrated by the figures produced by Richmond at that time showing what he called values for "standard" milk at different times of the year over a period of six years.

These "standard" milks had a minimum fat content varying from about 2.85 per cent. to about 2.95 per cent. in May and June—the spring flush when the yield of milk rises considerably and the fat is at its minimum. This general picture presented by Richmond's data is virtually identical with the picture to-day. With solids-not-fat, however, the picture given in 1894 to 1899 is very different from that to-day. Richmond's "standard" milks invariably had their minimum values (from about 8.3 to about 8.45) in July and August, there being no other minimum in the curve. During the last ten years this seasonal variation of solids-not-fat for milks as a whole has changed considerably. The percentages of herd samples below 8.5 per cent. of solids-not-fat at the present time show two very clearly marked peaks, one in late winter and early spring and the other in late summer corresponding to the minimum in Richmond's curves.

There is little doubt, therefore, that whilst an absolute standard of 3.0 per cent. of fat would cause no undue hardship, an absolute standard of 8.5 per cent. of solids-not-fat would get many producers into trouble during March to May and July to September. To overcome this difficulty two alternatives may be considered; one would be to have a temporary absolute standard of 8.3 per cent. of solids-not-fat for a further period of five years, and the other would be to have absolute standards of 11.5 per cent. of total solids and 3 per cent. of fat. This would mean that if a farm milk fell below 8.5 per cent. of solids-not-fat, provided the fat was reasonably good, the milk would pass the test. For example, a milk of 8.2 per cent. of solids-not-fat (which is an extreme case of genuine low solids-not-fat not frequently met with) would pass an absolute standard of 11.5 per cent. of total solids provided the fat content was at least 3.3 per cent., which is not very high. It is of interest to note in respect of this latter suggestion that Lord Wenlock himself personally favoured a standard of 12.0 per cent. for total solids together with a standard of 3.0 per cent. for fat. One further suggestion is that all statutory tests should be made on mixed milks, *i.e.*, the whole of the evening milk combined with the whole of the morning milk. In practice buyers purchase both evening and morning milk together and it is unfair that any farmer should be penalised on account of the low quality of his morning milk without consideration of any compensation derived from the richer quality of his evening milk.

If absolute standards were adopted there would no longer be any argument about the genuineness of milk and much unsatisfactory legislation and many time-consuming investigations and prosecutions would be avoided. A satisfactory procedure in my opinion would be the imposition of a nominal fine for the sale of genuine milk below these standards and the imposition of a heavy fine when milk below the standards was shown to be adulterated, especially if the adulteration had been persistent. The present procedure has long been recognised as tending to bring the law into disrepute.

The "appeal to the cow" test would, of course, cease to exist as far as the standards themselves were concerned, but an "appeal to the cow" test should be allowed for freezing-point test purposes. It is now recognised that on rare occasions a herd supply can have a freezing-point depression smaller than that hitherto accepted.^{45,46}

Under this new system the only possible chance for a producer to be unfairly convicted would be if his herd happened, on one of these rare occasions, to give a genuine milk with an abnormally low freezing-point depression. In such rare cases an "appeal to the cow" test would readily settle the matter.

The opinion has been expressed that, whilst such a quality payment scheme is logical and just, the complicated administrative requirements and expense make it impracticable. An alternative would be to standardise a "National Milk" of, say, 8.7 per cent. of solids-not-fat and 3.7 per cent. of fat and ask farmers to breed to conform to this standard. Any farmer whose milks failed on average throughout the year to reach these figures would be subject to a graded penalty. Due allowance for seasonal variations could be made and such a scheme would be compatible with absolute standards.

It gives me great pleasure to express my thanks to the following Public Analysts and others who have collaborated so fully with me in the preparation of this paper. Not only have they sent me all the data that were available, but they have given me all the information for which I have asked in respect of these data.

Messrs. A. Alcock, D. J. T. Bagnall, H. H. Bagnall, F. C. Bullock, C. H. Chalmers, J. F. Clark, A. Dargie, A. P. Davson, S. Dixon, Dr. J. Hawthorne, Messrs. T. R. Hodgson, A. Houlbrooke, E. T. Illing, Dr. G. V. James, Messrs. A. R. Jamieson, R. Mallinder, C. W. McHugo, T. McLachlan, D. D. Moir, F. Morris, F. H. Myers, W. M. Paulley, Dr. A. Scott-Dodd, Messrs. C. J. H. Stock, R. W. Sutton, Dr. G. H. Walker, Messrs. R. W. Watridge, E. G. Whittle, A. L. Williams and A. Wilson.

I am also indebted to many others who have helped me to obtain information, especially Dr. Joseph Edwards, Professor W. Riddet, Mr. W. R. Muir, Monsieur G. Mocquot, Dr. S. J. Rowland and those to whom acknowledgment is made in the references for personal communications.

My thanks are specially due to Miss Catherine Gilgallon for her assistance in the treatment of the analytical figures.

REFERENCES

1. Edwards, J., *J. Fmrs.' Cl.*, 1950, No. 6, 80.
2. Provan, A. L., and Jenkins, D. I., *J. Soc. Dairy Tech.*, 1949, **2**, 88.
3. Kay, H. D., *J. Roy. San. Inst.*, 1947, **6**, 515.
4. Davis, J. G., McClelland J., and Rogers, H. J., *J. Dairy Res.*, 1939, **10**, 59.
5. Stableforth, A. W., *J. Minist. Agric.*, 1935, **61**, 945.
6. Foot, A. S., and Shattock, P. M. F., *J. Dairy Res.*, 1938, **9**, 166.
7. Rowland, S. J., and Zein-el-Dine, M., *Ibid.*, 1938, **9**, 182.
8. Barham, G., *J. Brit. Dairy Fmrs.' Ass.*, 1885, **2**, 48.
9. Richmond, H. D., "Dairy Chemistry," Charles Griffin & Co., Ltd., London, First to Fifth Editions, 1899, 1914, 1920, 1942, 1952.
10. Ingle, H., "Report on the Solids in Cows' Milk," Yorkshire College, Leeds, 1900.
11. Pearmain, T. H., and Moor, C. G., "The Analysis of Foods and Drugs," Baillière, Tindall and Cox, London, 1897.
12. Cranfield, H. T., *J. Agric. Sci.*, 1927, **17**, 62.
13. Burr, H., M.Sc. Thesis, Reading University, 1939.
14. Rowland, S. J., *J. Dairy Res.*, 1944, **13**, 261.
15. —, *Dairy Ind.*, 1946, **11**, 656.
16. —, *Chem. Ind.*, 1948, 106.
17. Bartlett, S., and Kay, H. D., *J. Roy. Agric. Soc.*, 1950, **111**, 87.
18. Featherstone, J., Rickaby, C. D., and Cavell, A. J., *J. Dairy Res.*, 1951, **18**, 155.
19. Board of Agriculture, Rep. Dept. Ctte. Regulations for Milk and Cream (Cd. 491) H.M. Stationery Office, London, 1901.
20. Tocher, J. F., "Variations in the composition of Milk," H.M. Stationery Office, London, 1925.
21. Hanley, J., "Progress in Milk Technology," J. Bibby & Sons, Ltd., Liverpool, 1936.
22. Boden, S. M., and Campbell, C. H., *J. Dairy Res.*, 1942, **13**, 45.
23. Rowland, S. J., Personal communication, 1951.
24. Provan, A. L., *Int. Dairy Congr.*, 1949, **2**, 217.
25. Liverseegee, J. F., "Adulteration and Analysis of Food and Drugs," J. & A. Churchill, Ltd., London, 1932.
26. Dyer, B., and Mitchell, C. A., "Fifty Years of the Society of Public Analysts," W. Heffer & Sons, Ltd., Cambridge, 1932.
27. Macdonald, F. J., *Analyst*, 1948, **73**, 423.
28. Aschaffenburg, R. A., *J. Dairy Res.*, 1944, **13**, 281.
29. Harnett, P., Personal communication, 1951.
30. Riddet, W., Personal communication, 1951.
31. Thomé, K. E., Personal communication, 1951.
32. Bakalor, S., Department of Agriculture, S. Africa, Bull. No. 287, 1947.
33. —, Department of Agriculture, S. Africa, Bulls. Nos. 285 and 301, 1948.
34. —, Personal communication, 1951.
35. Janse, L. C., *Neth. Milk Dairy J.*, 1950, **4**, 1.
36. Mork, R., Personal communication, 1951.
37. Mogensen, M. S., Personal communication, 1951.
38. Davis, J. G., *J. Soc. Dairy Tech.*, 1948, **1**, 81.
39. —, *Dairy Ind.*, 1945, **10**, 27.
40. —, *Dairy Farmer*, 1951, August, p. 19 and September, p. 15.
41. — "Dictionary of Dairying," Leonard Hill, Ltd., London, 1950.
42. Andrew, R. L., *N.Z. J. Sci. Tech.*, 1928, **10**, 229.
43. Grigg, F. J. T., *N.Z. J. Sci. Tech.*, 1947, **29**, 101.
44. Loftus-Hills, G., Personal communication, 1951.
45. Hillman, H. C., Provan, A. L., and Steane, E., *Chem. & Ind.*, 1950, 333.
46. Sykes, D. A., Macdonald, F. J., and Davis, J. G., Unpublished observations, 1946.

DISCUSSION

THE PRESIDENT said that this was a most important subject, and not many people were in a position to deal with it. The Society was, therefore, fortunate in having Dr. Davis present this paper for discussion. There were many factors that might bring about a change in quality of milk, such as the considerable increase in the numbers of Friesian cows. Farmers had always been concerned with fat content, and an increase in fat content was often accompanied by a slight increase in solids-not-fat. An important difference between present-day practice and that of the earlier quarter of this century was that almost all milk was now artificially cooled; the fact that coolers had a tendency to leak slightly on occasion might lead to a small reduction in the percentage of solids-not-fat.

DR. N. J. BERRIDGE pointed out the possibility of condensation of atmospheric moisture on excessively cooled milk.

DR. DAVIS said that the extent of adulteration from condensation of atmospheric moisture on excessively cooled milk was probably of the same order as that due to residual rinsing water in utensils, and would not be a highly significant factor.

DR. E. C. WOOD said that it must surely make a difference whether the Public Analyst received all the samples of milk taken by the sampling officers, or whether they "sorted" the samples and sent only the suspicious ones to the analyst. He wondered if Dr. Davis had taken this into account. He added that, in his experience, there were certainly more samples deficient in non-fatty solids than in fat, if all the samples were considered; but, if one removed the samples shown by the Hortvet test to be watered, there remained more fat deficiencies than non-fatty solids deficiencies. Finally, he asked if Dr. Davis had noticed an apparent negative correlation in some of his curves, between fat content and non-fatty solids content over a period of years.

DR. DAVIS said that care had been taken to make sure that only a very small proportion of "follow up" samples had been considered in computing the average values. This probably was always less than 5 per cent., and would not have any significant effect, and further, it appeared to be approximately the same for all authorities. Dr. Wood's point about differences in the nature of deficiencies in genuine and watered samples was reasonable, if one remembered that watering would reduce fat and solids-not-fat, whereas in genuine samples a common source of error was failure to keep fat properly distributed. Other things being equal there would be more chance of a milk being deficient in solids-not-fat than in fat because of the relation between average values and the legal presumptive limits. There is always some correlation between fat and solids-not-fat values because the greatest change in the monthly average values takes place when the cows go out to grass. There is always a marked increase in yield accompanied by a rise in solids-not-fat and a fall in fat.

MR. C. W. MCHUGO said that there was one point with which Dr. Davis had not dealt in his very comprehensive review. This was the well-known fact that morning milkings, especially at certain periods of the year, were liable to be low in fat, and it was by no means unusual to find that the fat content of such milks was appreciably below the Statutory minimum of 3.0 per cent. He was aware that the large dairy companies overcame this difficulty by bulking together the morning and evening milkings, but in certain areas where producers had not the necessary facilities for doing this, morning milkings were being sold direct to the public. He felt, therefore, that the authorities responsible for the distribution of milk should take what steps might be necessary to see that morning and evening milkings were properly blended, and so ensure that the public received milk of at least average good quality.

The Government had recently set up a Working Party on Quality Milk Production, and he trusted that this important aspect of the subject would receive their attention.

DR. DAVIS agreed with the importance of this point but in his opinion a milk producer should be judged on the mixed meals of the morning and evening milking, and not on the morning milk alone. Most milk was now bulked and the public nearly always got the mixed morning and evening milk.

MR. N. HERON said that he had experienced in the north of England a strong suggestion of widespread adulteration of a minor nature. Large batches of milk were encountered with a remarkably constant set of figures, *viz.*, 3.3 ± 0.2 per cent. of fat, 8.6 ± 0.05 per cent. of solids-not-fat and a freezing-point range of 0.528 to 0.535, which indicated about 2 per cent. of added water.

DR. DAVIS thought that the consistency of the analytical figures might be due to controlled adulteration, but it must be borne in mind that when milk is bulked the composition tends to be very consistent for any one area.

MISS B. M. FISCHER supported the author's contention that the quality of milk was declining. Her experience was that bottled milk had shown a steady, although slight, decline since 1937 in the solids-not-fat content, rather than in fat content. The averages for bottled milk were as follows—

				Fat, %	Solids-not-fat, %
November, 1937	3.86	8.72
November, 1950	3.9	8.69
April, 1938	3.46	8.70
April, 1951	3.62	8.48

When individual producers were considered, the fall was even greater, as shown by the following figures—

				Fat, %	Solids-not-fat, %
1944-1945	3.6	8.38
1950-1951	3.35	8.16

with fourteen out of fifteen samples below 8.5 per cent. of solids-not-fat and one below 3 per cent. of fat in 1950-1951.

That the fall in quality of bulk milk was not more serious was due to the fact that while many producers' supplies had deteriorated or remained consistently poor, others had maintained or even improved the composition of their milks. The proposal to pay for milk on quality was supported as the only effective measure to improve the situation as a whole. Some farmers were already taking steps to improve the quality of their milk in anticipation of quality payment.

DR. J. H. HAMENCE said that he was delighted to find, at last, a man after his own heart who supported his suggestion of an absolute standard for milk. He believed that this was the only method by which the quality of milk would ever be maintained and that, unless some rigid deterrent was provided, the standard of milk would gradually go down and down. He was disappointed that Dr. Davis had not given more information as to the proportion of abnormal milks, that is, the proportion of milks falling below the standards laid down in the Sale of Milk regulations. As a Public Analyst, Dr. Hamence was seriously concerned at the big increase in abnormal milks over the last 20 years, and this applied to all the different parts of England for which he acted. Whereas in 1930 it was rare to find appeal-to-cow samples that contained less than 8.5 per cent. of non-fatty solids and less than 3 per cent. of fat, a substantial proportion of appeal-to-cow samples examined to-day were below the standard, and some of them had dropped to very low levels indeed. He felt that, if milk were sold to the consumer at a price based on quality, there would be a general tendency to buy the lower-priced article, and this would, in turn, tend to encourage the production of poorer milk. Dr. Hamence realised that there would be many difficulties in the way of establishing an absolute standard, but he was of the opinion that it was the only way to stop the fall in quality.

DR. DAVIS pointed out that the question of the proportion of abnormal milks containing less than 3 per cent. of fat or 8.5 per cent. of solids-not-fat had been dealt with by Dr. S. J. Rowland and other workers in this field. It was true that at certain times of the year, especially in the late winter and early spring, the solids-not-fat content of a large proportion of farmers' milks could fall below 8.5 per cent. He had known of some creameries where this proportion was, on occasion, as high as 50 per cent. It was generally agreed by those who had studied the subject, that the most important factor was the difficulty of feeding-stuffs, although the increase in winter production, the increase in the proportion of Friesian cattle and the general breeding policy were also significant factors. It was comparatively rare for farmers' milks to have a fat content of less than 3 per cent.

MR. F. N. GINGELL agreed with the author's findings of a downward trend in quality, but thought that this was due to differences in breed. At one time a Friesian herd was unusual; now there were more Friesians than Ayrshires. The English breeds of big-framed cows gave milk with the higher solids-not-fat contents. He suggested that the fall in quality was not due to any emphasis on quantity; the increase in the quantity of milk produced had come from an increase in the number of dairy herds.

DR. G. H. WALKER asked why, if the decrease in solids-not-fat was caused by an increase in the number of Friesian herds, there was not a similar decrease of fat content. In Lancashire a marked drop in solids-not-fat had occurred since 1941 rather than a slow drop over the last 20 to 30 years, and he asked whether any other districts had shown a similar trend.

DR. DAVIS said that the fall in solids-not-fat being more noticeable than the fall in fat was in agreement with the theory that the major factor responsible for the decline in milk quality was feeding difficulties.

MR. J. R. ROWLING agreed with Dr. Davis about the downward trend in quality, but asked whether, in considering average figures taken from Public Analysts, allowance had been made for the segregation of Channel Island milks into the premium market. This could lead to the Public Analyst being called upon to analyse a smaller proportion of Jersey milk samples in comparison with samples of ordinary milks, and this could colour the figures quoted by Dr. Davis.

DR. DAVIS said that he had not overlooked this point; however, it could readily be calculated that irrespective of whether Channel Island milk was incorporated in the bulk or sold as such, the effect on the average of a large number of Public Analysts' samples would be the same. Nevertheless, the proportion of Channel Island milk was very small and would be unlikely to affect the over-all average.

MR. R. W. SUTTON did not agree with Dr. Hamence that unless something was done, quality would go down and down. A few years ago there was a drive towards increased milk production. Clearly this could only be attained either by an increased cow population or by an increased yield per cow, and in this country, with its diminishing area of agricultural land, the second factor had necessarily received greater attention. There had been a swing over to the breeds with higher yields and, in his opinion, this accounted for the changes in average composition that had been recorded. In all the breeding for production, there did not appear to be much evidence of any decline in the average figures for fat and non-fatty-solids within any particular breed.

The changes that had been recorded appeared to be variable. In the Derbyshire area they were not marked. The average fat content had fallen from 3.63 per cent. in 1935 to 3.59 per cent. in 1949, but during this interval had been as high as 3.77 per cent. and as low as 3.56 per cent. The average figure for non-fatty-solids had fallen from 8.80 in 1935 to 8.72 in 1949, and had ranged from 8.83 to 8.67 in the intervening years.

Payment on a quality basis was now advocated, but this raised the very great question as to how quality should be assessed. Determinations of percentages of fat and milk solids would naturally give a measure of manufacturing quality, but as a large proportion of the milk produced in this country was sold for liquid consumption, nutritional quality and hygienic quality ought surely to receive consideration. Dr. Davis had shown a table to indicate that milk could be a most important food in supplying our daily requirements of calcium, vitamin A and riboflavin and other members of the vitamin-B complex. Unless it could be shown that there was a good positive correlation between these factors on the one hand, and the percentages of fat or milk solids on the other, it was clear that no simple tests were available for the reliable assessment of nutritional quality. The assessment of hygienic quality required separate tests, and might be considered as outside the scope of the present paper; but it was reasonable to suppose that the average consumer of liquid milk would expect some attention to be paid to this factor in any attempt to measure quality.

There were, he understood, about 160,000 registered milk producers in the country. Since there were daily variations in the quality of milk from any herd and since there were variations in the composition of the herds throughout the year, many samples would need to be examined. Even if the examination were limited to the simple determinations of fat or milk solids, it was clear that the cost of the work would be great, and if to this is added the recognition that the tests might still not provide a true measure of quality, it seemed to him that the cost would be out of all proportion to the value of the work.

Finally, it seemed to him that a limited application of these proposals was available to the Dairy Companies at present. In a report on "The Cost of Milk Distribution" that had been published in 1940, there was evidence of very considerable variation, the cost of distributing a gallon of milk ranging from sixpence or less, at one extreme, to a shilling or more at the other. Even if this gap had been closed to some extent, it was likely that differences would still be found, and since the distributors' margin was a level one and since the larger Dairy Companies would be counted as the most efficient, it seemed to him that there might be ample margin at present for the large companies to pay a bonus for quality, and this could quite properly be based entirely on their own assessment of quality.

Dr. Davis thanked Mr. Sutton for raising some very important questions. He had given considerable thought to the question of criteria for quality payment, and he was strongly of the opinion that the criterion must be a very simple one and the same for all producers. From the chemical and nutritional aspects he considered that the total solids was the best. A dye reduction test would be adequate for bacteriological quality, bearing in mind that only the average of a number of results would be used as a basis. He did not agree that the cost of testing for a quality payment scheme would be out of all proportion to the value of the work. Buyers were already testing farmers' milk for chemical and bacteriological quality at least once a month. The present system of testing, which was practically the same throughout the country, could, with suitable modifications, become the basis of a quality payment scheme.

He did not feel that he could deal with Mr. Sutton's last point since the question of distributors' margins and increases in costs of handling milk was a very controversial one. He would merely say that before the War manufacturing firms frequently paid an extra premium for good chemical quality, and that some buyers of milk that was used for liquid consumption paid a premium for good bacteriological quality. The number that paid premiums in present circumstances was extremely small.

ERRATUM: August (1952) issue, p. 419. On the 16th line from the bottom, for "ferrous" read "cuprous."

A Nomogram for the Calculation of Urinary 17-Ketosteroids

BY E. R. COOK AND MARGARET E. ROOKS

If 24-hour urine specimens are diluted to multiples of a specified volume, the total urinary 17-ketosteroids can be calculated without loss of accuracy by the use of a nomogram, the construction of which is described. The graph can be used for several different methods by taking suitable volumes of urine and solvent.

The accuracy of the correction by equation and by nomogram has been tested, and the close agreement of corrected values obtained by the procedures of Callow, Callow and Emmens (1938),⁷ Hamburger (1948) and Cook (1952) is shown.

URINARY 17-ketosteroids are determined by hydrolysis of the specimen with hydrochloric or sulphuric acid and extraction with an organic solvent, followed by colorimetric or polarographic estimation of the washed and dried extract. The crude extracts generally contain non-specific chromogenic material that does not interfere with the polarographic procedure of Barnett *et al.*,^{1,2} but which intensifies the colour produced in the widely-used Zimmerman determination, sometimes increasing the results to twice their true value. This interference can be eliminated by the Girard-T chemical separation, as described by Girard and Sandulesco,³ Talbot, Butler and MacLachlan,⁴ Pincus and Pearlman⁵ and Cook,⁶ or by use of a correction factor.

This paper describes such a factor and its application in a graphical method for the calculation both of crude total 17-ketosteroids and of the corrected values in mg per 24 hours. The nomogram has been applied to three different methods for the estimation of urinary 17-ketosteroids, and the results compared.

CORRECTION FACTOR

The equation depends on the difference in the absorption maxima shown by the interfering chromogens and 17-ketosteroids in the anhydrous Zimmerman colour reaction, which makes use of alcoholic potassium hydroxide and *m*-dinitrobenzene, as described by Zimmerman⁷ and Callow, Callow and Emmens.⁸ The chromogens show a broad absorption maximum in the violet, and the 17-ketosteroids have a sharp maximum in the green. Detailed accounts have been published by Gibson and Evelyn,⁹ Fraser, Forbes, Albright, Sulkowitch and Reifenstein,¹⁰ Werner,¹¹ Talbot, Berman and MacLachlan,¹² Engstrom and Mason,¹³ Hamburger¹⁴ and Allen.¹⁵

The equation used in this procedure is—

$$\text{Corrected } E_g = \frac{(K_c \times E_g) - E_v}{K_c - K_p},$$

where E_g = extinction with Ilford No. 604 Spectrum green filters of the sample under test,
 E_v = extinction with Ilford No. 601 Spectrum violet filter of the sample under test,
 $K_c = E_v/E_g$ of the non-specific chromogenic material, and
 $K_p = E_v/E_g$ of pure 17-ketosteroids.

In order to determine K_c , a large-scale Girard-T separation was carried out on 600 mg of crude 17-ketosteroids, which were obtained by combining the benzene extracts from more than 300 24-hour specimens. The E_v/E_g of the non-ketonic fraction so prepared was 1.20, while the E_v/E_g of pure androsterone was 0.36. These values must be established by each individual laboratory.

The correction factor then reduces to—

$$\text{Corrected } E_g = \frac{1.20 E_g - E_v}{0.84}.$$

The use of this equation assumes that the value of E_v/E_g for the non-specific chromogenic material remains constant for all specimens received. This is not correct, as there is some

slight variation in this value between individuals, and even from day to day in the same individual, but for clinical purposes the effects on the calculated result is negligible.

CONSTRUCTION AND USE OF NOMOGRAM

By use of the correction factor described above, a nomogram, Fig. 1, was constructed, based on that of Hamburger,¹⁶ by which the corrected E_g (A) can be found for any sample for which values of E_v (B) and E_g (C) have been determined. By superimposing a standard

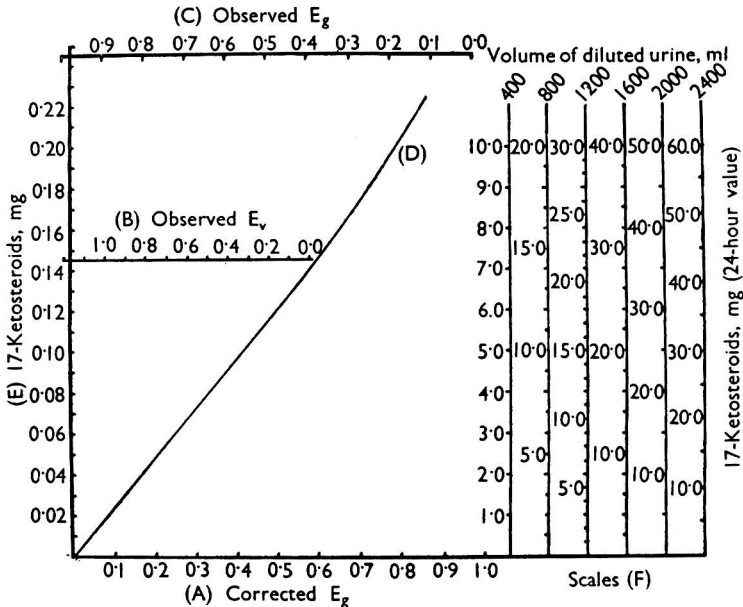


Fig. 1

A, B, C: nomogram relating observed E_g and E_v to the corrected E_g .
 A, D, E: standard graph of androsterone or dehydroisoandrosterone.
 Scales F: volume scales relating the corrected weight (in mg) of
 17-ketosteroid to the 24-hour value

curve (A, D, E), drawn for androsterone or dehydroisoandrosterone as reference substance, it is possible to read directly the weight in milligrams of 17-ketosteroid equivalent to the corrected E_g , and to calculate the result in mg per 24 hours by the scales (F). The principle of these scales is simple and of general application, and by appropriate choice of volumes of urine and solvent, calculations for several methods can be made on the same set of scales. In the present study three different procedures have been compared, and in each the 24-hour urine specimen was diluted to the nearest multiple of 400 ml with distilled water.

Method I (Callow, Callow and Emmens⁸)—A solution consisting of 240 ml of diluted urine and 37 ml of concentrated hydrochloric acid was heated under reflux for 1 hour with 45 ml of carbon tetrachloride; this procedure was repeated twice with two further 45-ml portions of carbon tetrachloride. The extract was washed with 2 N sodium hydroxide and then with water, and was diluted to 150 ml with carbon tetrachloride; 5-ml aliquots of this solution were evaporated to dryness for the colorimetric determination.

Method II (Hamburger¹⁶)—A solution consisting of 40 ml of diluted urine, 4 ml of 40 per cent. v/v sulphuric acid and 40 ml of benzene was heated under reflux for 35 minutes. The washed extract was diluted to 50 ml with benzene, and 10-ml aliquots were taken for the estimation.

Method III (Hamburger,¹⁶ modified by Cook⁶)—A solution consisting of 240 ml of diluted urine and 24 ml of 40 per cent. v/v sulphuric acid was heated under reflux for 35 minutes with 45 ml of benzene; this procedure was repeated twice with two further 45-ml portions of

benzene. The washed extract was diluted to 150 ml with benzene and 5-ml aliquots were taken for the estimation.

The calculation for Methods I and III then becomes—

$$\begin{aligned} \text{Ketosteroid, mg per 24 hours} &= \text{corrected weight of ketosteroid} \times \frac{150}{5} \times \frac{400 \times M}{240} \\ &= \text{corrected weight of ketosteroid} \times 50 M, \end{aligned}$$

and for Method II it becomes—

$$\begin{aligned} \text{Ketosteroid, mg per 24 hours} &= \text{corrected weight of ketosteroid} \times \frac{50}{10} \times \frac{400 \times M}{40} \\ &= \text{corrected weight of ketosteroid} \times 50 M, \end{aligned}$$

where M = 1, 2, 3, and so on, and all weights are in milligrams.

The scales (F) are calculated in milligrams of androsterone $\times 50 M$, and give the corrected 17-ketosteroids in mg per 24 hours corresponding to the total diluted volume of 24-hour urine and the determined E_g and E_v . An example will make this clear. A 24-hour urine specimen was diluted to 1600 ml and the determination carried out. The extinction readings were $E_g = 0.473$ and $E_v = 0.325$. The crude 17-ketosteroid present is found by drawing a vertical line from 0.473 on (A) to line (D) and then drawing a horizontal line from this point of intersection to the 1600-ml scale (F). The result is 22.6 mg per 24 hours. The corrected value is found by drawing a line from 0.473 on scale (C) through 0.325 on (B) to the point of intersection on (A), which gives the corrected E_g . A vertical line drawn from this point to the curve (D), then a horizontal line drawn from (D) to the 1600-ml scale gives 13.5 mg per 24 hours, which is the "true" value. The standard androsterone curve should be checked frequently, but since all other scales remain fixed, it is a simple matter to erase curve (D) and substitute the new standard.

RESULTS

To check the accuracy of the correction factor, 240-ml aliquots from the urines of 50 patients were hydrolysed and extracted by the modified Hamburger procedure (Method III). The Zimmerman reaction was carried out on the extract, and the extinctions with Ilford Spectrum green (No. 604) and Spectrum violet (No. 601) filters were used to calculate the corrected 17-ketosteroid values. The ketonic material in the crude extract was obtained by a micro-scale Girard-T separation.⁶ Table I shows the close agreement between results corrected by chemical separation and those corrected with the formula. These results

TABLE I
ACCURACY OF CORRECTION FORMULA
17-Ketosteroids, mg per 24 hours

Uncorrected	Corrected by chemical separation	Corrected by formula
41.0	36.5	30.5
22.2	16.8	16.1
21.0	17.4	16.4
20.6	13.1	12.5
18.4	14.6	14.7
16.8	11.7	11.4
15.8	12.9	12.3
14.5	8.3	7.8
13.6	10.0	9.5
10.3	8.6	7.5

are comparable with those of Morris¹⁷ and Butt, Morris, Robinson and Warren,¹⁸ who showed that results by polarographic methods, in which the non-specific chromogens are not estimated, are in good agreement with those by colour correction methods. The 17-ketosteroid values found by chemical separation are generally slightly higher than those obtained by calculation, probably because of the small amount of residual non-specific chromogenic material that the Girard-T separation fails to remove.

Table II was constructed with hypothetical values of E_g and E_v , and shows the close agreement between values found graphically and by calculation.

TABLE II
COMPARISON OF CORRECTIONS BY FORMULA AND BY GRAPH

Extinction values		Corrected E _g	
E _g	E _v	By formula	By graph
0.10	0.04	0.095	0.094
	0.06	0.071	0.068
	0.08	0.047	0.043
0.20	0.08	0.190	0.192
	0.12	0.143	0.142
	0.16	0.095	0.093
0.40	0.16	0.382	0.386
	0.24	0.286	0.286
	0.32	0.191	0.186
0.60	0.24	0.571	0.576
	0.36	0.429	0.430
	0.48	0.286	0.281
0.80	0.32	0.763	0.765
	0.48	0.572	0.570
	0.64	0.381	0.375

Table III shows the similarity between the results of the three extraction procedures described above. The temperature of the urine during the simultaneous hydrolysis and extraction with benzene is approximately 91° C, while with carbon tetrachloride it is only 68° C. This difference may account for the smaller amount of non-specific chromogenic material found in carbon tetrachloride extracts, which results in lower uncorrected values than those found in the benzene extraction.

TABLE III
COMPARISON OF EXTRACTION METHODS

Sample	17-Ketosteroids, mg per 24 hours					
	Method I		Method II		Method III	
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
1	51.4	45.0	50.0	45.0	—	—
2	32.7	29.0	35.0	28.2	43.0	36.1
3	28.1	24.5	33.8	25.1	33.0	28.3
4	25.5	21.2	29.0	22.9	29.5	24.0
5	17.0	13.0	19.7	13.2	21.4	14.3
6	13.4	10.7	15.5	10.7	18.4	13.0
7	11.1	9.5	15.1	10.7	—	—
8	11.5	8.6	14.8	8.8	14.7	8.7
9	10.3	7.5	13.1	7.2	—	—
10	11.8	7.9	11.0	8.4	13.4	9.8
11	9.2	7.9	10.2	7.7	10.7	9.2
12	6.0	4.8	8.5	5.7	8.5	5.7
13	6.9	3.7	5.7	1.0	8.0	3.7
14	4.1	2.3	5.4	2.5	5.8	2.7
15	3.6	2.3	3.5	1.8	—	—

The authors gratefully acknowledge the valuable technical assistance given by Miss Jean Rex and Mr. A. E. Hall.

REFERENCES

- Barnett, J., Henley, A. A., and Morris, C. J. O. R., *Biochem. J.*, 1946, **40**, 445.
- Barnett, J., Henley, A. A., Morris, C. J. O. R., and Warren, F. L., *Ibid.*, 1946, **40**, 778.
- Girard, A., and Sandulesco, G., *Helv. Chim. Acta*, 1936, **19**, 1095.
- Talbot, N. B., Butler, A. M., and MacLachlan, E. A., *J. Biol. Chem.*, 1940, **132**, 595.
- Pincus, G., and Pearlman, W. H., *Endocrinology*, 1941, **29**, 413.
- Cook, E. R., *Analyst*, 1952, **77**, 34.
- Zimmerman, W., *Hoppe-Seyl. Z.*, 1936, **245**, 47.
- Callow, N. H., Callow, R. K., and Emmens, C. W., *Biochem. J.*, 1938, **32**, 1312.

9. Gibson, J. G., and Evelyn, K. A., *J. Clin. Invest.*, 1938, **17**, 153.
10. Fraser, R. W., Forbes, A. P., Albright, F., Sulkowitch, H., and Reifenstein, E. C., *J. Clin. Endocrinol.*, 1941, **1**, 234.
11. Werner, S. C., *Ibid.*, 1941, **1**, 951.
12. Talbot, N. B., Berman, R. A., and MacLachlan, E. A., *J. Biol. Chem.*, 1942, **143**, 211.
13. Engstrom, W. W., and Mason, H. L., *Endocrinology*, 1943, **33**, 229.
14. Hamburger, C., *Acta Endocrinol.*, 1948, **1**, 19.
15. Allen, W. M., *J. Clin. Endocrinol.*, 1950, **10**, 71.
16. Hamburger, C., *Acta Endocrinol.*, 1948, **1**, 375.
17. Morris, C. J. O. R., *J. Endocrinol.*, 1948, **5**, lxxi.
18. Butt, W. R., Morris, C. J. O. R., Robinson, A. M., and Warren, F. L., *Ibid.*, 1951, **7**, xii.

BIOCHEMICAL AND ENDOCRINOLOGICAL RESEARCH DEPARTMENT
BRISTOL MENTAL HOSPITALS
BARROW GURNEY, BRISTOL

April, 1952

The Determination of Small Amounts of Calcium in Plant Material

By A. C. MASON

Small quantities of calcium (10 to 500 μg) can be estimated quickly and accurately by titration with an aqueous solution of sodium ethylenediamine tetra-acetate, with Murexide as indicator. Phosphates, which interfere, are removed by ion exchange on a resin column. The design of such a column and its reliability in effecting the complete and rapid removal of phosphate is discussed. The method, which is free from interference by magnesium, iron or manganese, in amounts usually encountered, gives results that are in good agreement with the oxalate method. The standard error for 16 determinations on a plant ash solution is 2.84 μg in 212 μg , which corresponds to a coefficient of variation of 1.35 per cent.

AN accurate method of estimating small quantities of calcium in biological material has long been required. The standard method, which depends on the precipitation of calcium oxalate, besides being somewhat laborious, ceases to be satisfactory for quantities much less than 1 mg of calcium, on account of solubility difficulties.

Sodium ethylenediamine tetra-acetate (subsequently referred to as EDTA) has been used by Willson¹ for the determination of calcium and magnesium in leaf tissue. He claimed satisfactory results for 4 to 8-mg quantities of calcium, but took no steps to avoid interference from phosphate ions, although he was aware of this source of error; consequently, his method is of limited application. Independently, Mason² briefly outlined in a preliminary note a method for estimating smaller quantities of calcium (100 to 200 μg) in plant material. Early results indicated that phosphate interference could be avoided, without a separation, by adding an excess of EDTA before making the solution alkaline (so preventing formation of calcium phosphate) and subsequently titrating back with standard calcium solution. However, extended experience showed the method to be unreliable for routine work and it became obvious that it is imperative to remove interfering phosphate ions.

Essentially the method to be described consists in percolating the sample, after suitable dilution, through a small resin column, whereby the calcium and other cations are held in the column while the phosphate ions pass through. The calcium is then eluted with hydrochloric acid and titrated with EDTA.

PRELIMINARY EXPERIMENTAL WORK

DESIGN OF THE RESIN COLUMN—

In order to achieve speed in operation, experiments were made to find the smallest dimensions of the resin bed consistent with complete retention of calcium. The particle size of the resin was standardised by sieving the ground resin between Nos. 60 and 120 B.S. sieves. This fairly fine fraction was chosen to give an adequate surface area of resin without

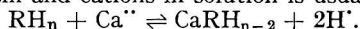
unduly impeding the percolation. The results of many trials indicated that retention of calcium was uncertain if the bed depth was much less than 25 mm, but the diameter of the bed could be varied considerably without effect. In all tests 500 μg of calcium, contained in 5 ml of water, were run through the freshly regenerated and washed resin column, and the effluent was titrated with EDTA.

From tests carried out on columns prepared as described under Method on p. 531, it was found that there is a risk of calcium ions leaking through the column if the percolation rate exceeds 0.6 ml per minute.

The resin selected for preliminary work was Zeo-Karb 215, a cation-exchange resin that contains sulphonic acid and hydroxyl groups. The high-capacity sulphonic-acid resin Zeo-Karb 225 was also tested to see whether the percolation rate could be increased or the bed depth decreased, but the results were unsuccessful.

ELUTION OF CALCIUM—

The reaction between resin and cations in solution is usually represented as—



When the concentration of hydrogen ions is sufficiently low the equilibrium is displaced to the right, and calcium ions are removed from solution and held by the resin (the effect of acid concentration in preventing ion exchange is shown in Table I). As the concentration of hydrogen ions is increased the reaction is displaced to the left, and calcium ions are liberated;

TABLE I

EFFECT OF ACID CONCENTRATION ON ION-EXCHANGE EFFICIENCY

505 μg of calcium were taken in each example and mixed with hydrochloric acid, and the calcium held by the column was estimated

Concentration of hydrochloric acid	Calcium recovered, μg			
1.0 N	110,	107,	90,	95
0.1 N	502,	504,	503,	504
0.01 N	502,	507,	507,	505

the latter process, referred to as elution, is efficient in the presence of 5 N hydrochloric acid. Concentrated hydrochloric acid attacks the resin and interferes with the final titration. Experiments were carried out to determine the minimum volume of acid for complete elution; for 1000 μg of calcium this was established as 6 ml. There is a tendency for the last few micrograms of calcium to be held rather more tenaciously by the resin, and this is illustrated by the figures given below, in which 4 or 6 ml of 5 N hydrochloric acid were used to elute 207 μg of calcium.

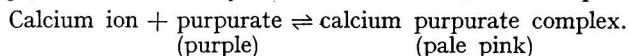
Calcium recovered when 4 ml were used, μg —201, 199, 194.

Calcium recovered when 6 ml were used, μg —206, 208, 207.

The volume required was not affected by raising the temperature of the acid to 60° C.

MUREXIDE INDICATOR—

The titration procedure, which is based on the work of Schwarzenbach, Biedermann and Bangerter,³ depends on the stoichiometrical combination of EDTA with calcium ions to form a complex compound, the equivalence point being indicated by the change in colour, from pale pink to purple, of a small quantity of added Murexide (ammonium purpurate). This colour change, which occurs only in alkaline solution, can be represented as—



When the concentration of calcium ions in the solution is high, the reaction proceeds to the right and the dominant colour is pink, but in the absence of free calcium ions the reaction proceeds to the left and purple is dominant.

As with acid - base titrations the amount of indicator used is a matter of personal choice. It should be sufficient to give a well-marked colour change, but not enough to upset the stoichiometry of the main reactants, particularly in dilute solutions.

EFFECT OF SOME IONS ON THE TITRATION—

Phosphate—This is the only ion in plant material that interferes seriously with the titration. Calcium phosphate is precipitated on adding the sodium hydroxide, and a direct titration with EDTA results in a premature and fugitive end-point. Estimations on a plant-ash solution that contained 212 μg of calcium were made without the preliminary separation of phosphate ions, and the calcium found was 205 μg (mean of three discordant results).

Magnesium—A precipitate with Murexide is produced both in the presence and in the absence of calcium, but the end-point is not affected. The volume of EDTA required to titrate a solution containing 20 μg of magnesium and 200 μg of calcium was the same as for 200 μg of calcium alone.

Iron and manganese—In the absence of calcium, these ions do not affect the purple colour of the Murexide and do not produce a precipitate. However, in the presence of calcium the characteristic colour of the calcium - Murexide complex is modified somewhat, and may make recognition of the end-point more difficult. The volume of EDTA required to titrate a solution containing 200 μg of calcium, 12 μg of iron and 12 μg of manganese was the same as for 200 μg of calcium alone.

EFFICIENCY OF PHOSPHATE SEPARATION—

Aliquot portions of a plant-ash solution of known phosphate content were percolated through resin columns and the amount of phosphate in each effluent determined.

Phosphate content of each aliquot, 15.6 μg of phosphorus.

Phosphate recovered (mean of 8), 15.5 μg of phosphorus.

METHOD

SPECIAL APPARATUS—

Micro-burette—Of 0.5-ml capacity.

Tubes—Select a piece of glass tubing, of 7-mm bore, and draw off one end to form a coarse jet; flair the other end, 70 mm from the constriction. Prepare eight or more tubes and mount them in a rack of any convenient design. A distance between holes of 2 inches allows 15-ml beakers to be placed below each column. A rubber ring round each tube prevents it from slipping too low in the rack.

Teat pipettes—Select a piece of glass tubing, of 7-mm bore, and draw off one end to form a coarse jet 2 inches long. Cut the tube 3 inches from the constriction and flair slightly. One inch from the open end constrict the tube to a capillary by thickening the glass, and fit a teat. Graduate by sucking 1 ml into the pipette and making a scratch at the meniscus level. Construct one teat pipette for each resin column.

REAGENTS—

All reagents should be of recognised analytical purity.

Di-sodium ethylenediamine tetra-acetate (EDTA)—Dissolve 0.86 g of sodium hydroxide in about 800 ml of water, add 4.0 g of the disodium salt of ethylenediamine tetra-acetic acid, and dilute to 1 litre. Standardise immediately before use.

Murexide indicator—Grind together thoroughly 0.1 g of Murexide (ammonium purpurate) and 50 g of sodium chloride. The indicator gradually deteriorates and should be discarded after about 2 months.

Standard calcium solution—Weigh accurately 100 mg of calcium carbonate, which has been previously dried for 3 hours at 105° C and cooled, and dissolve in about 2 ml of *N* hydrochloric acid. Transfer to a 100-ml graduated flask and dilute with water to the mark. 1 ml \equiv 400 μg of calcium.

Sodium hydroxide solution—Dissolve 4 g of sodium hydroxide in 100 ml of water.

Hydrochloric acid, 5 *N*—Mix 250 ml of concentrated hydrochloric acid (sp.gr. 1.18) with an equal volume of water.

Resin—Grind about 10 g of cation-exchange resin (Zeo-Karb 215) in a mortar, sieve and take the material that passes through the 60 B.S. and is retained by the 120 B.S. sieve, soak in 5 *N* hydrochloric acid overnight and wash several times with water by decantation.

PREPARATION OF THE RESIN COLUMN—

Pack a small tuft of cotton wool loosely into the lower constricted part of each of the special tubes to form a pad 1 to 2 mm thick, and then pour a slurry of prepared resin and

water into the tube until the bed is 25 mm deep. Lightly press another tuft of cotton wool on top of the resin bed and wash the column with distilled water until the pH of the effluent is not less than 4, as shown by a test paper. Regulate the speed of flow through the column by tamping with a glass rod until between 2.5 and 3 ml of water runs through in 5 minutes. When not in use store the columns with the tips standing in water to prevent them drying. Always wash with one bed-volume (2 ml) of water immediately before use.

STANDARDISATION OF EDTA—

Transfer exactly 0.5 ml of standard calcium solution (200 μg of calcium) into a small specimen tube, by means of a pipette, and add approximately 0.1 ml of sodium hydroxide

TABLE II

RECOVERY OF CALCIUM FROM STANDARD SOLUTIONS

Taken, μg	Found, μg			
	10.04,	10.04,	10.04,	10.04
10	10.04,	10.04,	10.04,	10.04
50	49.50,	49.50,	51.51,	50.17
500	495.0,	497.6,	501.1,	501.1
1000	998.0,	990.0,	989.3,	1000.7

by means of a small teat pipette, and then 10 to 15 mg of indicator, measured on the blade of a micro-spatula. Titrate with EDTA until the colour changes from pink to a definite bluish-purple. In the presence of some other cations, *e.g.*, magnesium, iron and manganese, the end-point is difficult to distinguish at first, but with practice it can be precisely noted. Repeat the standardisation until concordant results are obtained.

Let 1 ml of EDTA solution = y μg of calcium.

PROCEDURE—

Prepare a solution of plant ash in dilute hydrochloric or nitric acid⁴ and accurately transfer a convenient small aliquot (say 0.1 ml) into a 15-ml beaker and add 5 ml of water. Transfer the solution to the column by means of a teat pipette; use a separate pipette for each sample.

Wash the beaker and column with two separate 1-ml amounts of water and reject the effluent. Elute the calcium with 6 ml of 5 *N* hydrochloric acid, collect the eluate and

TABLE III

COMPARISON OF EDTA AND OXALATE METHODS

Sixteen samples of the same plant material were ashed and the calcium contents determined at different times by both methods

EDTA method—

Calcium content, μg —206, 206, 212, 206, 206, 206, 209, 210, 213, 211, 212, 212, 212,
213, 211, 212

Mean, μg —209.8

Standard error, μg —2.84

Coefficient of variation, %—1.35

Oxalate method—

Calcium content, μg —202, 208, 209, 207, 207, 205, 211, 208, 208, 208, 216, 210, 218,
212, 214, 219

Mean, μg —210.1

Standard error, μg —4.66

Coefficient of variation, %—2.22

evaporate to dryness on a water-bath. Dissolve the dry residue in about 1 ml of water and transfer to a specimen tube by means of a teat pipette. Proceed exactly as for the standardisation of EDTA solution.

Wash the resin column with water till free from acid; it is then ready for use again.

Run a blank through the whole procedure concurrently with each batch of samples.

If x ml of EDTA is the titre of the sample and b ml the titre of the blank, then the calcium content of the sample is $(x - b)y$ μg . The purity of the reagents should be such that b is small compared with x .

RESULTS

The sensitivity, accuracy and precision of the method can be assessed from the data given in Tables II and III.

Replicate determinations on a standard sample of plant material (apple leaves) are consistent, and there is satisfactory agreement with the values for calcium determined by the oxalate method.⁴

From Table II it is seen that 10 μg of calcium can be determined accurately and the sensitivity is considerably better than is attainable by the oxalate method.

The ease and speed of analysis is also improved, for one person can comfortably complete 32 determinations in a day.

The author wishes to express his thanks to Mrs. M. Souter who carried out the experimental work.

REFERENCES

1. Willson, A. E., *Anal. Chem.*, 1950, **22**, 1571.
2. Mason, A. C., *Ann. Rep. E. Malling Res. Sta. for 1950, 1951*, p. 122.
3. Schwarzenbach, G., Biedermann, W., and Bangerter, F., *Helv. Chim. Acta*, 1946, **29**, 811.
4. Mason, A. C., *Ann. Rep. E. Malling Res. Sta. for 1949, 1950*, p. 111.

EAST MALLING RESEARCH STATION
MAIDSTONE, KENT

May, 1952

The Polarographic Determination of Titanium in Aluminium Alloys

BY R. P. GRAHAM AND A. HITCHEN

A precise and accurate method for the polarographic determination of titanium in a variety of aluminium-base alloys is described. The supporting electrolyte is *M* tartaric acid, 0.5 *M* sulphuric acid and 1.2 *M* ammonium sulphate.

A sample of the alloy is first leached with sodium hydroxide and then the titanium is extracted from the residue with sulphuric acid. The solution, after neutralisation and the addition of appropriate amounts of tartaric and sulphuric acids, gives a well-formed polarographic wave, the height of which is directly proportional to the concentration of titanium.

When applied to a wide range of standard samples from several laboratories, the method gave results in excellent agreement with the certified values.

TITANIUM in aluminium-base alloys, as indeed in other substances, is perhaps most often determined by the absorptiometric method with hydrogen peroxide; although with improved instrumentation for rapid control work the spectrochemical method is more common than it was formerly.¹ If appropriate facilities are at hand, spectrochemical methods are faster than absorptiometric ones and their precision is satisfactory; especially is this true with direct reading spectrometers. The absorptiometric method suffers from the disadvantage of interference from elements that give coloured solutions (iron, nickel and chromium), from elements that form coloured complexes with hydrogen peroxide (vanadium and molybdenum), as well as from substances that bleach the colour given by titanium (fluoride, phosphate, alkali sulphates and citric acid). All these interferences can be overcome, but not always conveniently.

A polarographic method might be expected to be subject to less interference than the absorptiometric method and, because of the successful polarographic determination in this laboratory of titanium in rocks and minerals² and in steels and nickel-base alloys³ in an acid tartrate medium, it was decided to study the application of such a method to the analysis

of aluminium-base alloys. The results of the investigation are given in this paper. Although the polarographic determination of titanium in aluminium does not appear to have been studied previously, the polarograph has been applied to the determination of other elements in aluminium and its alloys, *e.g.*, antimony, copper, indium, iron, lead, manganese, nickel, sodium, tin, and zinc (see review by Stross⁴).

OUTLINE OF METHOD

Elements that give rise to waves at potentials less negative than does titanium may constitute an interference if they are present at concentrations appreciably higher than that of the titanium. In an acid tartrate medium iron and copper are among such elements.

Although low concentrations of aluminium do not interfere significantly with the determination of titanium in this supporting electrolyte,² we have found that a high concentration of aluminium relative to that of titanium, such as is found in aluminium alloys, causes a pronounced reduction in the diffusion current of titanium. For example, when the molar ratio $[Al^{+++}]/[Ti^{++++}]$ was 170, the height of the wave for titanium was 15 per cent. lower than that for the same concentration of titanium in the absence of aluminium. Potts⁵ and Adams⁶ have also reported such an interference of aluminium with the polarographic determination of titanium, and Kolthoff and Matsuyama⁷ reported interferences of aluminium in the polarographic determination of several elements in aluminium-base alloys. For the accurate polarographic determination of titanium, it is accordingly necessary to separate, beforehand, the aluminium from the titanium.

One method of separating aluminium from titanium consists in precipitating the titanium from a sulphuric acid solution of the alloy with cupferron. The cupferron precipitate can be ignited and the titanium extracted with sulphuric acid. After adjustment of the acidity and addition of tartaric acid, the solution can be polarographed and the wave for titanium recorded. We have studied such a method, and attained good accuracy. The procedure is, however, more lengthy than the one adopted, in which aluminium is removed by leaching a sample of the alloy with sodium hydroxide. We have found that the titanium is quantitatively retained in the residue that remains after leaching. The residue is treated with sulphuric acid to dissolve the titanium, the acidity is adjusted, tartaric acid added, and the solution polarographed. That the extraction of titanium from the residue is quantitative was established by igniting extracted residues (from alloys of high copper and widely differing titanium contents), fusing with potassium pyrosulphate, treating with sulphuric acid, and testing for titanium by means of sensitive colorimetric reagents (hydrogen peroxide, Chromotropic acid); all such tests were negative.

Normally a wave due to copper can be recorded, which precedes and is well separated from the wave due to titanium. In this, our experience differed from that of Potts⁵ who reported that, in acid tartrate medium, copper produced a wave at the same potential as titanium. Under the conditions of the analysis only a part of the copper is removed from the residue when the titanium is extracted, and there is insufficient copper in the final solution to cause interference, even when analysing alloys of high copper content (9 per cent.). The successful determination of titanium in an aluminium alloy containing 1.4 per cent. of iron, as well as the results of experiments with prepared solutions containing iron and titanium, show that iron, at the concentrations normally encountered in aluminium alloys, does not constitute an interference. If tin should be present at significant concentration in the solution being polarographed, interference would be expected because one of the tin^{II} waves would coalesce with the wave for titanium (the other wave given by tin^{II} would precede the wave for titanium, and very likely coalesce with the wave for copper). Although tin is known to be present in some of our standard samples, there is in the data no evidence of interference from this element; possibly the bulk of the tin is removed in the leaching of the alloy with sodium hydroxide.

METHOD

APPARATUS—

An Heyrovský polarograph* was used in this investigation. The capillary was cut from the special tubing supplied for this purpose by the makers, and was cleaned, when necessary, by immersing it in hot nitric acid while the mercury was flowing.⁸

The *m* and *t* values of the capillary in the supporting electrolyte (*M* tartaric acid, 0.5 *M* sulphuric acid, 1.2 *M* ammonium sulphate) were determined at $25.0 \pm 0.1^\circ C$ by the method

* A Model XI polarograph made by E. H. Sargent & Co., Chicago, Ill., U.S.A.

of Lingane and Kolthoff.⁹ At an applied potential of -0.30 volt against the saturated calomel electrode, the drop time, t , was 5.07 seconds, the rate of flow of mercury, m , was 1.357 mg per second, and $m/t^{\frac{1}{2}}$ was 1.606 mg[†] sec.^{-†} The variation of $m/t^{\frac{1}{2}}$ with applied potential was in close agreement with the relative values given by Kolthoff and Orlemann.¹⁰

An H type of polarographic cell similar to that described by Lingane and Laitinen¹¹ was used; one arm of the cell contained the saturated calomel reference electrode.

REAGENTS—

Purify the mercury for the dropping-mercury electrode by bubbling it through 10 to 15 per cent. nitric acid for 10 hours, wash it several times with water, and then distil twice *in vacuo*. Test all the reagents (colorimetrically and polarographically) for the presence of titanium. None was detected in our experiments.

PROCEDURE—

With the galvanometer sensitivity that we chose, concentrations of titanium in the final solution of from 0.005 to 0.07 mg per ml ($1.0 \times 10^{-4}M$ to $1.4 \times 10^{-3}M$) could be measured easily. We preferred a concentration in the range of 0.02 to 0.06 mg per ml; for our alloys, with the concentration of titanium in all but one in the range 0.1 to 0.3 per cent, such final concentrations (in a volume of 100 ml) were given by a 2-g sample.

Accurately weigh about 2 g of sample and treat it with 30 ml of a $6.5 M$ solution of sodium hydroxide, adding the alkali in small, 1 to 2-ml, portions to avoid too vigorous a reaction. When the reaction has subsided, add water to make the volume about 100 ml. Heat the mixture and filter it through Whatman No. 52 filter-paper. Wash the residue twice with a hot $0.25 M$ solution of sodium hydroxide and then with water; discard the filtrate and washings. Heat the residue on the paper with 26 to 27 ml of a hot $4.5 M$ solution of sulphuric acid to dissolve the titanium, and then wash thoroughly with water. Neutralise the combined acid solution and washings to litmus with a $15 M$ solution of ammonium hydroxide and then add 25 ml of a $2.0 M$ solution of sulphuric acid and 15.0 g of anhydrous tartaric acid. Dilute the solution to 100.0 ml and mix thoroughly. These operations give a solution that is M with respect to tartaric acid, $0.50 M$ to sulphuric acid, and $1.20 M$ to ammonium sulphate—a supporting electrolyte that has proved useful in other work in this laboratory on the polarographic determination of titanium.^{2,3}

Transfer a portion of the solution to the polarographic cell, bubble nitrogen, which has been purified by passing it through an alkaline solution of potassium pyrogallate and one of distilled water, through it for 15 minutes, and polarograph it at $25.0 \pm 0.1^\circ C$ from 0.0 to -1.0 volt against the saturated calomel electrode. The galvanometer sensitivity, at the setting $R = 10$ on our instrument, was 2.80×10^{-2} microampere per mm. Polarograph each solution 4 times and measure each of the 4 polarograms, which are recorded photographically on Kodabromide E-2 paper, twice by the slope-intercept method.

Assess the amount of titanium with the help of a straight-line calibration curve relating the concentration of titanium to wave-height. The calibration was carried out in our experiments with solutions prepared from standard sample No. 154 (titanium dioxide) of the National Bureau of Standards and which contained $1.2 M$ ammonium sulphate, $0.5 M$ sulphuric acid and M tartaric acid.

RESULTS

ACCURACY—

Values for titanium obtained by this polarographic method are shown in Table I in comparison with values obtained by other methods for a variety of aluminium-base alloys. The certified value for the sample from the National Bureau of Standards is the average of determinations in nine laboratories (the spread is between 0.15 and 0.17 per cent of titanium), all by the absorptiometric method with hydrogen peroxide. The certified values for the samples obtained from the three companies listed were determined with great care in the laboratories of these companies by the absorptiometric and spectrographic methods. The samples from the Aluminum Company of America and from Apex Smelting Company were supplied in disc form and were intended for use as standards for the spectrographic analysis of chill cast disc samples and not, as we have used them, as standards for a chemical method of analysis.

The agreement between the polarographic values and the certified values is good for almost all the alloys. The agreement is only fair for the alloy of highest titanium content (0.30 per cent.), but this is not surprising when it is borne in mind that appreciable segregation of titanium occurs in aluminium alloys containing this element at a concentration exceeding about 0.2 per cent.

PRECISION—

Each of the values given under "Individual Determinations" in Table I is an average value derived from 8 wave-height measurements (2 on each of the 4 polarograms recorded for each solution). The maximum deviation of any measurement from the average of the 8 was, with but 2 exceptions in the 41 determinations recorded in Table I, in the range of 1 to 8 per cent. of the average value, the average maximum deviation being 4.1 per cent. of the average value. This reproducibility is usual for the polarographic method.

The agreement between individual determinations on the same standard sample is set forth in Table I. The measure of precision shown in the last column of this table is that of the maximum deviation of an individual determination from the average. In most experiments this maximum deviation was less than 0.01 per cent.

TABLE I
COMPARISON OF POLAROGRAPHIC AND OTHER METHODS

Sample	Certified value of titanium, %	Polarographic values of titanium content		
		Individual determinations, %		Mean, %
<i>National Bureau of Standards</i> Aluminium-Silicon Alloy No. 87	0.16	0.167, 0.163, 0.166, 0.160,* 0.160,* 0.154*	0.162 ±	0.008
<i>Aluminium Laboratories Ltd.</i>				
Alcan 123 CAC	0.12	0.116, 0.121, 0.113, 0.107, 0.110*	0.113 ±	0.008
Alcan 123 CAE	0.15	0.148*	0.148	
Alcan 125 CAE	0.17	0.182, 0.162, 0.179	0.174 ±	0.012
Alcan 135 CAD	0.14	0.137, 0.121, 0.143, 0.136*	0.134 ±	0.013
Misc. Standard Sample	0.19	0.185, 0.179, 0.190, 0.176*	0.183 ±	0.007
<i>Aluminium Company of America</i>				
SA 409-H	0.30	0.268, 0.271, 0.264	0.268 ±	0.004
SA 896-J	0.18	0.180, 0.168, 0.178	0.175 ±	0.007
<i>Apex Smelting Company</i>				
D1633 D	0.19	0.196, 0.193, 0.197	0.195 ±	0.002
D1633 H	0.14	0.149, 0.155, 0.151	0.152 ±	0.003
D1633 R	0.16	0.161, 0.173, 0.174	0.169 ±	0.008
D1820 I	0.06	0.070, 0.069, 0.059	0.066 ±	0.007

*In these determinations the residue remaining after the leaching with sodium hydroxide was treated with hydrochloric acid and washed with water; bromine water was added to the acid solution, and then titanium was precipitated from the hydrochloric acid solution with sodium hydroxide; the mixture was boiled, filtered while hot, washed, and dissolved in sulphuric acid. In the other determinations the residue from the sodium hydroxide leaching was treated directly with sulphuric acid, as outlined in the procedure.

RANGE OF APPLICATION—

The method can be used in the analysis of aluminium-base alloys of various compositions. The copper content of our samples ranged from 0.01 to 9.5 per cent., the silicon content from 0.1 to 6.7 per cent., and other elements were present in the concentration ranges shown in Table II.

TABLE II
RANGE OF CONCENTRATIONS OF ELEMENTS IN SAMPLES ANALYSED

Cr, %	0.02-0.60	Ni, %	0.02-3.39
Cu, %	0.01-9.46	Pb, %	0.07-0.25
Fe, %	0.09-1.38	Si, %	0.10-6.65
Mg, %	0.01-1.90	Sn, %	0.04-0.31
Mn, %	0.01-1.11	Zn, %	0.05-1.95

The low and high values for titanium were 0.06 and 0.30 per cent. Higher concentrations are not normally encountered in wrought and casting alloys, but they could readily be determined by this method. With a galvanometer sensitivity ten times that used in this study, we have recorded a 40-mm wave given by a solution with a concentration of titanium of 0.0036 mg per ml ($7.5 \times 10^{-5} M$). With a 2-g sample it should thus be possible to determine titanium at a concentration below 0.01 per cent., and the method can be regarded as sufficiently sensitive to meet all reasonable demands.

We wish to express our thanks to the Defence Research Board of Canada and to the Research Council of Ontario for the grants-in-aid that allowed this study to be undertaken. We are grateful also to Mr. R. W. Callon (Aluminium Laboratories Limited, Arvida, Quebec), Mr. R. Raisig (Apex Smelting Company, Chicago, Illinois), and Mr. J. R. Churchill (Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pennsylvania), and to their organisations for providing standard samples and helpful information.

REFERENCES

1. Callon, R. W., and Charette, L. P., *Anal. Chem.*, 1951, **23**, 960.
2. Graham, R. P., and Maxwell, J. A., *Ibid.*, 1951, **23**, 1123.
3. Graham, R. P., Hitchen, A., and Maxwell, J. A., *Canad. J. Chem.*, 1952, **30**, 661.
4. Stross, W., *Analyst*, 1949, **74**, 285.
5. Potts, B. R., *Canad. J. Res., F*, 1950, **28**, 128.
6. Adams, D. F., *Anal. Chem.*, 1948, **20**, 891.
7. Kolthoff, I. M., and Matsuyama, G., *Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 615.
8. Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York, 1941, p. 243.
9. Lingane, J. J., and Kolthoff, I. M., *J. Amer. Chem. Soc.*, 1939, **61**, 825.
10. Kolthoff, I. M., and Orlemann, E. F., *Ibid.*, 1941, **63**, 2085.
11. Lingane, J. J., and Laitinen, H. A., *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 504.

DEPARTMENT OF CHEMISTRY
HAMILTON COLLEGE, MCMASTER UNIVERSITY
HAMILTON, ONTARIO, CANADA

March, 1952

Notes

THE DETERMINATION OF POTASSIUM IN SOIL EXTRACTS WITH A FLAME PHOTOMETER

THE formation of the National Agricultural Advisory Service in 1946 was immediately followed by a demand for soil analyses on a scale hitherto unknown in this country. The rapid colorimetric methods of determining potassium in soil extracts that were developed enabled two workers to carry out 750 estimations each week, the average time of each determination being about 3 minutes. To reduce the errors inherent in such methods, introduced by the monotony of repetitive manipulative work, a robust easily-operated flame photometer was sought.

Lundegardh¹ had developed a technique of general application; he measured spectrographically, the intensity of the spectral lines produced when solutions were introduced into a flame. Mitchell,² in this country, applied the Lundegardh method to the analysis of soils and showed that it could be used to evaluate the potassium, calcium, magnesium, manganese, and sodium status of soils. Jansen, Heyes and Richter³ developed a simpler apparatus with which the alkali metals could be estimated; a monochromator was used to isolate the required spectral lines, and a photocell to measure their intensity. Schuhknecht⁴ estimated potassium, using filters to isolate the red potassium wavelengths, and a phototube to measure their intensity. Baines, Richardson, Berry and Hood,⁵ using a combination of filters and a barrier layer photocell, developed an instrument with which Hald⁶ successfully estimated sodium and potassium in biological materials. Mitchell⁷ estimated potassium photometrically, with a 35-mm "EEL" selenium cell, or a Cintel GS 18 photocell or an R.C.A. 931A photomultiplier, connected to a power pack, used in conjunction with an infra-red image converter. An admirable general review of flame photometric methods up to 1949 has been given by Leyton.⁸

Commercial flame photometers for use in industry have been marketed in America by Perkin-Elmer and in Germany by Siemens and Zeiss, and descriptions of these instruments are given by Overman and Davis,⁹ and by Schmitt and Breitweiser.¹⁰ As no cheap commercial model was

available in this country in 1950, a simple instrument suitable for the determination of potassium was built in the laboratory.

THE APPARATUS—

The instrument consists essentially of four parts: the atomising unit, the burner, the filter system and the measuring system.

As the extractant used was Morgan's reagent, consisting of a 10 per cent. solution of sodium acetate in 0.5*N* acetic acid, a rigid all-glass atomiser, similar to that described by Brealey and Ross¹¹ and consisting of two concentric tubes sealed together, was used. The problem of corrosion was thus eliminated, and the rigidity gave maximum uniformity to the size of the droplets in the spray. A stream of air, at a constant pressure, was passed between the two tubes so that, as it passed over one end of the inner capillary tube, it drew up the liquid through the other end and dispersed it as a fine spray into a glass flask arranged to act as a trap for any large droplets. The fine uniform spray was carried on by the air into the flame.

The burner was made by fitting a porcelain top from a Meker burner into the end of a glass tube, which had a slight constriction to promote mixing of the gases. The air, carrying the fine spray, and Calor gas at constant pressure were introduced separately into the base of the tube; the Calor gas burnt with a steady flame above the porcelain.

The spectral lines of potassium at 7660 and 7690A were isolated by the use of the three filters; Wratten 88A (visually opaque), Chance ON.20 (heat-absorbing) and Chance ON.16. This combination of filters had been used successfully by Brealey and Ross¹¹ when determining potassium as an impurity in sodium salts, and was found to be effective in preventing interference from all elements likely to be encountered in soil work.

Robust ex-Government radio apparatus was used. A photomultiplier tube, of the type R.C.A. 931A, as described by Janes and Glover,¹² in which the photocurrent produced at the light-sensitive cathode is multiplied by secondary emission occurring at successive dynodes within the tube, was used in conjunction with an infra-red image converter. The latter consists of an evacuated tube with a cathode made by depositing an infra-red sensitive layer of silver caesium oxide on to a glass surface, and an anode of medium persistence willemite deposited on a thin glass plate. The electrons, which are emitted when red light falls on the photosensitive cathode of the infra-red image converter, are accelerated by the high voltage and bombard the willemite, which produces a green fluorescence to which the R.C.A. 931A is sensitive. The final output current was measured with a spot galvanometer, with full-scale sensitivity of 1 microampere, that was obtained from the Cambridge Instrument Co. The required voltages, 1500 volts for the infra-red image converter and 1000 volts for the photomultiplier tube, were obtained from mains voltage by using a transformer and the principle of the voltage doubler circuit developed by Cockcroft and Walton.¹³ Mains voltage fluctuation, which takes place when much electrical apparatus is in use in a laboratory, can be eliminated by the use of a voltage stabiliser.

APPLICATION OF THE FLAME PHOTOMETER TO EXAMINATION OF SOILS FOR AVAILABLE POTASH—

The available potash in each of 71 heavy, 94 medium and 69 light soils, classified as 66 permanent pastures, 44 temporary pastures, 79 arable and 45 horticultural soils, was determined colorimetrically with the flame photometer. Ten grams of each soil were shaken with 50 ml of Morgan's reagent, and the suspension was filtered through a Whatman No. 30 filter-paper. The potash in the filtrates was estimated in the flame photometer and also by precipitating the potassium as potassium silver cobaltinitrite and determining the amount of cobalt in the washed precipitate by developing the blue colour with ammonium thiocyanate. The available potash is usually expressed as the number of milligrams of potash (K_2O) extracted from 100 g of soil (parts per 100,000); satisfactory agricultural and horticultural soils normally give figures of 10 to 20 and 21 to 50 parts per 100,000, respectively.

COMPARISONS OF RESULTS OBTAINED BY THE TWO METHODS—

Of the soils examined, 92 per cent. gave results by the two methods that did not differ by more than 2 parts per 100,000 or more than 5 per cent., whilst 80 per cent. of the soils gave results that differed by 1 part per 100,000 or less. Of the remaining 8 per cent. (18 soils), nine soils gave a difference of 3 parts per 100,000; of the other nine, five were classified as high in available potash and no change in classification would have been brought about by taking either result. There were thus four soils with a difference of more than 3 parts per 100,000, where the classification depended on the method used. A change would have been made once from high to

satisfactory, twice from moderate to satisfactory, and once, with a difference of 4 parts per 100,000, from satisfactory to low.

I wish to thank those members of the laboratory staff who have carried out the thousands of analyses made with the instrument, and Mr. N. M. Morris, Ministry of Works, who greatly assisted with the construction and assembly of the component parts of the flame photometer.

REFERENCES

1. Lundegardh, H., "*Die Quantitative Spektralanalyse der Elemente*," Jena, Gustav Fischer, Part I, 1929; Part II, 1934.
2. Mitchell, R. L., *J. Soc. Chem. Ind.*, 1936, **55**, 267T.
3. Jansen, W. H., Heyes, J., and Richter, C., *Z. physik. Chem., A*, 1935, **174**, 291.
4. Schuhknecht, W., *Angew. Chem.*, 1937, **50**, 299.
5. Barnes, R. B., Richardson, D., Berry, J. W., and Hood, R. L., *Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 605.
6. Hald, P. M., *J. Biol. Chem.*, 1947, **167**, 499.
7. Mitchell, R. L., *Spectrochim. Acta*, 1950, **4**, 62.
8. Leyton, L., *Ann. Rep. Chem. Soc.*, 1948, **45**, 316.
9. Overman, R. R., and Davis, A. K., *J. Biol. Chem.*, 1947, **168**, 641.
10. Schmitt, L., and Breitweiser, W., *Bodenk. u. Pflernähr*, 1938, **9-10**, 750.
11. Brealey, L., and Ross, R. E., *Analyst*, 1951, **76**, 334.
12. Janes, R. B., and Glover, A. M., *R.C.A. Review*, 1941, **6**, 43.
13. Cockcroft, J. D., and Walton, E. T. S., *Proc. Roy. Soc., A*, 1932, **136**, 619.

WEST MIDLAND PROVINCE
NATIONAL AGRICULTURAL ADVISORY SERVICE
WOLVERHAMPTON

A. J. CAVELL
First submitted March, 1952
Amended June, 1952

THE DETERMINATION OF BERYLLIUM IN BERYL BY MEANS OF ETHYLENEDIAMINE TETRA-ACETIC ACID

DURING the last three years the commercial output of beryl in Southern Rhodesia has greatly increased, and its assay in this laboratory has become more frequent. In the past the oxine method¹ has been used to separate the beryllium from the elements precipitated by ammonium hydroxide after reducing the quantity of aluminium present by a sodium carbonate fusion. This method gives fairly satisfactory results, but is lengthy.

Přibil and Kucharský² have recently published a method for separating beryllium from aluminium and other elements, based upon the fact that the beryllium complex with ethylenediamine tetra-acetic acid is decomposed by ammonium hydroxide whereas the other elements form more stable complexes. As this appeared to possess advantages over the oxine method it was investigated.

PRELIMINARY OBSERVATIONS

Precipitation of beryllium hydroxide in the presence of ethylenediamine tetra-acetic acid—Přibil and Kucharský found that for the quantitative precipitation of beryllium hydroxide in the presence of ethylenediamine tetra-acetic acid, an excess of 15 to 20 ml of 14 per cent. ammonium hydroxide was required and that precipitation must take place at room temperature. Instead of adding a known excess of ammonium hydroxide, it was found more convenient during the present investigation to use a pH indicator. Low results were obtained by making the solution ammoniacal to phenol red (pH 8.0), or cresol red (pH 8.8), but at a pH of 9.6 (thymol blue) results were satisfactory. If the solution was filtered hot, large losses of beryllium occurred, but if it was allowed to stand at room temperature overnight before filtration, only a small amount of beryllium remained in the filtrate. A high concentration of ammonium salts was also found to be desirable. The quantity of beryllium oxide in the filtrate was estimated by a semi-quantitative spectrographic method. When 100 mg of beryllium oxide were precipitated, 0.5 to 1.0 mg was found in the filtrate. A small quantity of the hydroxide adhered tenaciously to the beaker; this could only be completely recovered by solution in hot dilute acid and re-precipitation with ammonium hydroxide. The addition of a few drops of Teepol reduced, but did not entirely prevent, adherence of the precipitate.

Separation from other elements—Beryl occurs in pegmatites and is associated with many other minerals, but only minerals with a similar specific gravity and appearance are likely to be found

in the ore after sorting. These are mainly quartz and felspar, but apatite, topaz and lithium minerals, such as spodumene and lepidolite, may also be present. Although tin and tantalum minerals are sometimes found with beryl, it is unlikely that they would occur in more than trace quantities in the sorted ore. Pure beryl has the theoretical composition: silica 67.0 per cent., aluminium oxide 19.0 per cent., and beryllium oxide 14.0 per cent. Therefore, if 1 g of sample is taken for analysis, provision must be made for separating up to 140 mg of beryllium oxide from about 200 mg of aluminium oxide. Small amounts of iron, phosphorus, manganese, chromium and titanium are also likely to be present.

Přibil and Kucharský found that aluminium, iron, lead, bismuth, copper, cadmium, zinc, manganese, nickel, cobalt and vanadium (in small amounts) formed stable complexes with ethylenediamine tetra-acetic acid and did not interfere. They also found that the chromium complex formed only on warming, and that titanium and phosphorus were precipitated with the beryllium. This was confirmed in the present investigation.

Provided a sufficiently large excess of ethylenediamine tetra-acetic acid was used, the separation of beryllium from iron, manganese, chromium, calcium, magnesium and aluminium was nearly complete. Up to approximately 2 mg of titania (TiO_2) could be present without interference, but when more was present, part of the titania was found with the beryllium oxide.

Decomposition of beryl and removal of silica—Sodium carbonate was a suitable flux; over a blast burner it decomposed the mineral rapidly. With this flux part of the beryllium was converted to the α -hydroxide,^{3,4} which is insoluble in dilute acids. It is, however, readily soluble in hot concentrated sulphuric acid, and it was convenient to dehydrate the silica in this solution by evaporating to fumes of the acid. Little beryllium was retained by the silica. The silica was dehydrated only once; part of that remaining was precipitated with the beryllium hydroxide, but this was largely removed by fusing the ignited beryllium oxide with sodium carbonate and leaching with water.⁵ This treatment served also to separate phosphorus and any aluminium. A small amount of platinum was dissolved from the crucible during the fusion, but the platinum remained with the beryllium oxide and was allowed for by weighing the crucible before the fusion. Spectrographic examination of the filtrates from sodium carbonate fusions showed that the loss of beryllium oxide was less than 0.5 mg.

METHOD

Mix 1 g of the finely ground sample with 4 g of sodium carbonate in a platinum crucible and fuse over a blast burner until decomposition is complete (about 15 minutes). Pour the melt on to a steel plate and, when cool, place the crucible and melt in a beaker containing 60 ml of diluted hydrochloric acid (1 + 1). Warm until the reaction ceases. Remove the crucible and lid, and clean them with a rubber-tipped glass rod. Add 30 ml of diluted sulphuric acid (1 + 1) and evaporate until fumes of this acid appear. Cool, add about 50 ml of water and 5 ml of concentrated hydrochloric acid and warm until all soluble salts are in solution. Filter through a Whatman No. 41 filter-paper containing pulp and wash with hot diluted hydrochloric acid (1 + 19). Ignite the silica precipitate and volatilise the silica with hydrofluoric acid in the usual way. Fuse the non-volatile residue with a little sodium pyrosulphate, dissolve the melt in water and add to the filtrate.

Add 40 ml of 10 per cent. w/v di-sodium ethylenediamine tetra-acetate and a few drops of thymol blue. Heat to about 80° C and add ammonium hydroxide until the indicator is deep blue. Allow the solution to cool overnight. Filter through a Whatman No. 40 filter-paper containing pulp, removing as much of the precipitate as possible from the beaker with a rubber-tipped glass rod. Dissolve the beryllium hydroxide remaining on the walls of the beaker with hot diluted hydrochloric acid (1 + 19), re-precipitate with ammonium hydroxide, cool, and add to the main bulk. Wash the precipitate about 15 times with cold 2 per cent. w/v ammonium chloride solution made alkaline to thymol blue. Dry the precipitate and ignite in a weighed platinum crucible.

Fuse the precipitate with 3 g of sodium carbonate for about 10 minutes over a blast burner. Leach with about 400 ml of hot water and filter through a Whatman No. 42 filter-paper containing pulp. Wash about 15 times with hot water. Ignite to constant weight at bright red heat in the previously weighed crucible that was used for the sodium carbonate fusion.

Fuse the beryllium oxide with sodium pyrosulphate until a clear melt is obtained. Dissolve in diluted sulphuric acid (1 + 19) and determine the titanium colorimetrically with hydrogen peroxide in the usual way.

RESULTS

As no satisfactory standards were available, the method was tested by adding beryllium oxide of known purity to a granite of the following percentage composition—silica 75.9, alumina 13.2, ferric oxide 0.3, ferrous oxide 1.1, magnesia 0.4, calcium oxide 1.0, sodium oxide 4.3, potassium oxide 3.4, titania 0.2, phosphorus pentoxide 0.05, manganous oxide 0.03, beryllium oxide less than 0.005 per cent. Sufficient alumina was added to bring the total alumina content up to approximately 200 mg.

TABLE I
RESULTS FOR MIXTURES OF GRANITE AND BERYLLIUM OXIDE

Granite taken, g	Alumina taken, g	Beryllium oxide taken, g	Beryllium oxide found,* g	ERROR, g
nil	0.07	0.1065	0.1071	+0.0006
1.0	0.07	0.1410	0.1402	-0.0008
1.0	0.07	0.1386	0.1387	+0.0001
1.0	0.07	0.1065	0.1071	+0.0006
1.0	0.07	0.0820	0.0809	-0.0011
1.0	0.07	0.0129	0.0133	+0.0004
1.0	0.07	0.0061	0.0058	-0.0003
1.0	0.07	nil	0.0007	+0.0007

* The figures have been corrected for the insoluble matter in 3 g of sodium carbonate.

A sample of transparent green beryl that was found to contain 13.0 per cent. of BeO by the oxine method gave results of 13.11, 13.10, 13.17 and 13.02 by the proposed method. For the last two determinations 0.5 g of sample was taken.

DISCUSSION OF RESULTS

Spectrographic examination of the final beryllium oxide precipitates given by the proposed method for commercial ores containing from 11 to 13 per cent. of beryllium oxide showed that the main impurity was silica; about 1 mg was present in each precipitate. Small quantities of iron, aluminium, platinum and sodium were also present. The accuracy of the method is therefore partly due to balanced errors, the beryllium oxide lost in the ammonium hydroxide precipitation and the sodium carbonate fusion being approximately balanced by the impurities in the final precipitate. The same criticism applies to the oxine method,⁶ but the results obtained by the proposed method are more consistent and can be reached more rapidly than by the oxine method.

The author thanks the Director of the Geological Survey for his permission to publish this note.

REFERENCES

1. Schoeller, W. R., and Powell, A. R., "The Analysis of Minerals and Ores of the Rarer Elements," Second Edition, Charles Griffin & Co. Ltd., London, 1940, p. 48.
2. Přibil, R., and Kucharský, J., *Coll. Trav. Chim. Tchechosl.*, 1950, **15**, 132.
3. Osborn, G. H., *Analyst*, 1947, **72**, 475.
4. Osborn, G. H., and Stross, W., *Metallurgia*, 1944, **30**, No. 175, 3.
5. Schoeller, W. R., and Powell, A. R., "The Analysis of Minerals and Ores of the Rarer Elements," Charles Griffin & Co. Ltd., London, 1940, p. 54.
6. Stevens, R. E., and Carron, M. K., *U.S. Geol. Surv. Bull. No. 950*, 1946, 91.

DEPARTMENT OF GEOLOGICAL SURVEY
SALISBURY
SOUTHERN RHODESIA

P. I. BREWER
April, 1952

Apparatus

AN APPARATUS FOR MICRO DISTILLATION

THE apparatus shown in Fig. 1 is designed to carry out micro distillation and vacuum micro distillation. In micro distillation it is desirable for the condensing surface to be as close to the evaporating liquid as possible, provided always that transfer of the liquid by any means other than evaporation and subsequent condensation cannot occur. Further, the amount of liquid that condenses and returns to the boiler towards the end of the distillation must be an absolute minimum. The apparatus described fulfils these requirements.

DESCRIPTION AND MODE OF USE—

The conical distillation tube can be made from a 15-mm \times 150-mm Pyrex test tube. It is provided with a side-arm, and a trace of glass powder is sintered into the extreme tip to promote regular boiling. The condenser and receiver unit consists of three parts, each made from 6-mm (outside diameter) Pyrex tubing. A is a right-angled piece of glass tubing that is drawn off so

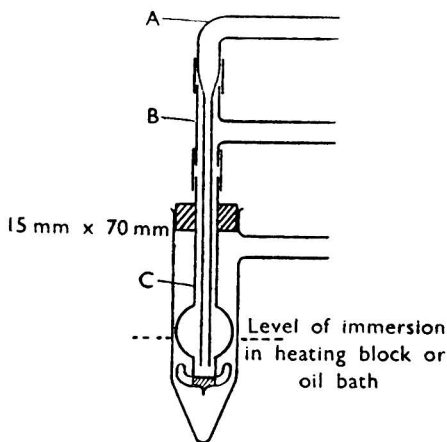


Fig. 1. Micro-distillation apparatus

as to reach to within a millimetre or so of the bottom of C. B is a T-piece with a short top section, 3 cm being a convenient length. Cooling water passes in through A and out through B. The part C is made by blowing two bulbs in a piece of glass tubing; the lower bulb is then collapsed as shown, so as to give a solid glass plug at the end of the tube. This leaves a partial vacuum inside the wall of the receiver; this is important since the under side must be cooled as little as possible during distillation. If water circulates inside the wall of the receiver owing to the glass plug not completely blocking the end of the tube, the liquid in the distillation tube will merely reflux from the bottom surface of C and no distillate will be collected. Further, C must be carefully annealed, otherwise, during distillation, a crack might develop on the inside of the receiver at the bottom, when the distillate would be drawn into the interior of the receiver wall by the partial vacuum. The diameter of the top bulb should be only a fraction less than the inside diameter of the distillation tube so that there is no chance for vapour to escape.

Finally, a glass "whisker," or better, a tiny piece of platinum wire, should be attached to the bottom of C so as to promote rapid drainage from the lower surface at the commencement of the distillation. If the apparatus is not required for vacuum distillation, A, B and C can be made together in one piece and held in the distillation tube by a split cork. For vacuum distillation, in which it is necessary to have a bung in C, it is preferable to have sections A, B and C separate. The tube A is rather fragile and the author has found it convenient to replace this by a metal tube of narrow bore.

When carrying out a distillation the outer tube should be inserted into the heating block or oil-bath to about the level shown, so that no condensation takes place on the wall of the distillation tube. At the commencement of distillation, some distillate will collect on the bottom of C, but

this should drain off rapidly. As the temperature of the under side of C rises, no further condensation will occur and the distillate will then collect in the receiver whence it can be removed by a capillary pipette. The temperature of the distillation can be measured by a fine thermocouple. The author uses a copper - constantan couple in conjunction with a sensitive voltmeter calibrated in hundredths of a volt. Such a couple is easy to make and gives a reasonable calibration curve.

The distillation process is confined to the bottom of the tube and no difficulty is therefore experienced in distilling liquids that attack cork or rubber. Acid chlorides and aromatic amines can be readily distilled without decomposition. Finally, the apparatus is inexpensive and reasonably easy to construct.

DEPARTMENT OF PURE AND APPLIED SCIENCE
INSTITUTE OF TECHNOLOGY
LOUGHBOROUGH
LEICESTERSHIRE

G. OLDHAM
April, 1952

The Analysis of Meat Products

METHOD RECOMMENDED BY THE SOCIETY OF PUBLIC ANALYSTS AND OTHER
ANALYTICAL CHEMISTS FOR THE ANALYSIS OF MEAT PRODUCTS
IN RELATION TO THE MEAT PRODUCTS ORDER, 1952

THE Meat Products Order, 1952, requires that certain canned meat products shall contain a minimum percentage of meat. As there exists uncertainty in some quarters as to the methods of analysis to be followed by analysts, the Analytical Methods Committee of the Society has accepted and adopted the following recommendations of a special Sub-Committee comprising representatives from industry, the Government Laboratory and Public Analysts.

For the purpose of the above Order, the meat content shall be determined by the method of Stubbs and More (*Analyst*, 1919, **44**, 125), as given in detail below.

The factors to be used for converting meat nitrogen into defatted meat are as follows—

Beef and mutton	100/3.4
Pork	100/3.6
*Mixed meat	100/3.5

* That is, pork and beef, and meat unspecified, *e.g.*, meat roll and luncheon meat.

When the filler consists of a wheat flour product, the nitrogen correction for the filler recommended by Stubbs and More shall be followed, but if the filler consists of potato starch no correction for nitrogen shall be made.

METHODS OF ANALYSIS

PREPARATION OF SAMPLE—

Prepare the sample by passing it at least twice through a mincing machine and then mixing rapidly in a mortar. If the product is a paste, mix in a mortar or on a slab.

DETERMINATION OF WATER—

Weigh 5 g of sample into a dried and weighed nickel or aluminium dish containing a small glass rod and 20 g of ignited sand. Mix the sample thoroughly with the sand and dry at 100° C to constant weight. Stir the mixture at intervals during the drying.

DETERMINATION OF FAT—

(A) Weigh 5 g of sample into a flat-bottomed dish containing a small glass rod and 10 g of ignited sand; mix thoroughly and dry on a steam-bath for 30 minutes. The mixture should be stirred at intervals (the residue from the moisture determination may be used if desired).

Macerate the cold residue with ether until the fat is dissolved. Filter the ethereal solution through a small filter into a tared flask. Wash the dish and filter with ether until they are free from fat, evaporate the ether and dry at 100° C to constant weight.

ALTERNATIVE METHOD FOR FAT—

(B) Weigh 5 g of the sample into a small flask, add 40 ml of diluted hydrochloric acid (1 volume of concentrated hydrochloric acid plus 2 volumes of water) and digest for 30 minutes at 50° to 60° C. Finally heat on a water-bath until the meat fibre has completely disintegrated. Remove the fat from the digest by three extractions with ether, wash the extracts with water, evaporate the ether and dry the fat at 100° C.

DETERMINATION OF NITROGEN—

Determine the nitrogen in the sample by the Kjeldahl method as described in the S.P.A. method for nitrogen in meat extract (*Analyst*, 1951, 76, 329) using 2.5 to 5.0 g of sample according to the proportion of meat in the material, with copper sulphate or mercuric oxide as the catalyst.

The percentage of nitrogen is converted to protein by multiplying by 6.25.

NOTE—As the nitrogen content of the material is of fundamental importance in the calculation of the meat content it is recommended that the efficiency of the ammonia distillation apparatus and the concentration of the standard acid should be checked by distillation of a weighed amount of dry ammonium sulphate of recognised analytical grade.

DETERMINATION OF ASH—

Weigh 5 g of sample into a tared platinum dish and incinerate it to a white ash at a temperature not exceeding 500° C.

If it is not possible to control the temperature, incinerate over a small flame to a white ash. After weighing the ash, determine its chlorine content. Determine the chlorine content of the original sample by the Volhard method and make an allowance for any sodium chloride lost during the ashing.

DETERMINATION OF STARCH—

Digest 20 g of the sample with 300 ml of 5 per cent. alcoholic potash solution on a water-bath until the meat and the fat have dissolved. Filter off the insoluble matter and wash the filter with alcoholic potash. Wash the insoluble matter from the filter-paper into a beaker with 200 ml of warm water. Add 40 ml of *N* aqueous potassium hydroxide solution and warm until the starch has dissolved. Cool the solution, transfer to a 250-ml graduated flask and make up to volume with water.

Transfer 50 ml of the solution to a beaker containing 300 ml of 90 per cent. by volume alcohol acidified with acetic acid (sufficient acid must be present to neutralise 8 ml of *N* potassium hydroxide). Stir well and allow the starch to settle, preferably overnight. Filter off the precipitated starch, wash it free from acid with 90 per cent. alcohol, wash with ether to remove alcohol and dry at 100° C. After weighing, incinerate and deduct the ash from the weight of the starch.

CALCULATIONS—

1. The sum of the percentages of water, fat, protein and ash deducted from 100 gives the percentage of dry carbohydrate and crude cellulose material.
2. From the total nitrogen deduct an amount equal to 2 per cent. of the dry carbohydrate plus crude cellulose for nitrogen associated with the carbohydrate and calculate the remainder to lean or defatted meat by means of the factors specified on page 543.
3. The total meat present is the sum of the fat and the lean meat.
4. If the filler is potato starch no correction should be made for nitrogen in the filler.
5. Calculate the approximate percentage of "cereal filler," containing 40 per cent. of its weight of water, by multiplying the percentage of carbohydrate by two.
6. The difference between 100 and the sum of the percentages of "cereal filler," salt and total meat gives the additional water; that is, water used in the preparation of the product other than natural moisture and water present in the filler.

The determined starch should agree with the carbohydrate figure obtained as a difference figure by the Stubbs and More method to within ± 2 per cent. If this is not so, the presence of substances such as milk-powder or soya flour is indicated.

Official Appointments

PUBLIC ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Food since the last record in *The Analyst* (1952, 77, 330).

<i>Public Analyst</i>			<i>Appointments</i>
CAREY, William Gordon	Borough of Wallsend.
ROBINS, Cecil Hancorn	Rural District of the Isles of Scilly.
WILLIAMS, Hugh Amphlett	Royal Borough of Kensington.

Ministry of Food and Ministry of Health

STATUTORY INSTRUMENT*

1952—No. 1481. The Public Health (Meat) (Amendment) Regulations, 1952. Price 2d.

These Regulations came into operation on August 31st, 1952, and amend the Public Health (Meat) Regulations, 1924 (S.R. & O., 1924, No. 1432), as amended, so as to extend to horses, asses and mules the application of Part II thereof, which relates to slaughter-houses and the slaughter of cattle, swine, sheep and goats for sale for human consumption and requires, inter alia, prior notice of slaughter to be given to the local authority.

Ministry of Food

STATUTORY INSTRUMENTS*

1952—No. 1619. The Meat Products (Amendment) Order, 1952. Price 2d.

This Order, which came into operation on September 7th, 1952, amends the Meat Products (No. 2) Order, 1952 (S.I. 1952, No. 1124; Analyst, 1952, 77, 442), by extending until December 31st, 1952, the operation of the Second and Third Schedules, which specify maximum prices and minimum meat contents for certain open pack meat products and canned meats, and by postponing until January 1st, 1953, the operation of the Fourth and Fifth Schedules, which provide for some amendments of prices and meat contents that would otherwise have come into operation on September 14th, 1952.

1952—No. 1652. The Feeding Stuffs (Manufacture) (Amendment) Order, 1952. Price 2d.

This Order, which came into operation on October 1st, 1952, amends the Feeding Stuffs (Manufacture) Order, 1952 (S.I., 1952, No. 375), by increasing the minimum albuminoids (protein) content of certain National compounds, as follows—

	Column 1	Column 2
Item No.		
No. 1	National Cattle Food No. 1	17
No. 2	National Cattle Food No. 2	18
No. 3	National Cattle Food No. 3	19
No. 4	National Cattle Food No. 4	16
No. 10	National Pig Food No. 1	17½
No. 12	National Poultry Food No. 1	17½
No. 13	National Poultry Food No. 1A	17½
No. 14	National Poultry Food No. 2	16½
No. 15	National Poultry Food No. 2A	16½
No. 16	National Poultry Food No. 3A	17½

* Obtainable from H.M. Stationery Office. Italics indicate changed wording.

1952—No. 1697. The Food Standards (Coffee Mixtures) Order, 1952. Price 2d.

This Order, which came into operation on September 21st, 1952, and should be read with the Food Standards (General Provisions) Order, 1944 (S.R. & O., 1944, No. 42; Analyst, 1944, 69, 49), as amended (S. R. & O., 1944, No. 654; Analyst, 1944, 69, 247), prescribes standards for coffee and chicory mixtures (including French coffee) and for coffee with fig flavour or fig seasoning (including Viennese coffee), as follows—

1. The standard for coffee and chicory mixtures, including French coffee, shall be as follows:—

Coffee and chicory mixtures, including French coffee, shall be mixtures of coffee and chicory only; each such mixture to contain not less than 51 per cent. by weight of pure coffee.

2. The standard for coffee with fig flavour or fig seasoning, including Viennese coffee, shall be as follows:—

Coffee with fig flavour or fig seasoning, including Viennese coffee, shall be a mixture of coffee and figs only; each such mixture to contain not less than 85 per cent. by weight of pure coffee.

ERRATUM: June (1952) issue, p. 330. Under "Ministry of Food," the number of the Labelling of Food (Amendment) Order, 1952, *should read* "1952—No. 549"; the number of the circular "Liqueur Chocolates" *should read* "2/52."

British Standards Institution

AMENDMENT SLIP

A PRINTED slip bearing Amendments to British Standards has been issued by the Institution as follows—
PD 1455—Amendment No. 1 (August, 1952) to B.S. 1752:1952. Sintered disk filters for laboratory use.

DRAFT SPECIFICATION

A FEW copies of the following draft specification, issued for comment only, are available to members of the Society, and can be obtained on application to the Secretary, Society of Public Analysts and Other Analytical Chemists, 7-8, Idol Lane, London, E.C.3.

Draft Specification prepared by Technical Committee P/169—Ampoules.

CO(P)3728—Draft B.S. for Ampoules (Revision of B.S.795).

Book Reviews

TEXTBOOK OF PHARMACOGNOSY. By T. E. WALLIS, D.Sc., F.R.I.C., Ph.C., F.L.S. Second Edition. Pp. xi + 556. London: J. & A. Churchill Ltd. 1951. Price 35s.

The first edition of this book was published in 1946, and at once established itself as the most authoritative work on crude drugs, and a worthy successor to Greenish's "Materia Medica." In the preface, Dr. Wallis claims that he has selected from the material available the most important items; as at some time herbalists have claimed therapeutic activity as a property of most wild plants, a drastic limitation was obviously necessary. Presumably the selection was made to satisfy students preparing for the examinations of the Pharmaceutical Society and it is a moot point whether the time is not now ripe to reject many of the drugs still retained. Pharmacognosy for the purposes of this book "includes all those materials which come legitimately within the purview of pharmacy," such as surgical dressings and articles used in carrying out pharmaceutical operations. *Per contra*, there appear to be a few important omissions of which, perhaps, that of pepper is the most surprising, especially as Dr. Wallis has published original work on this spice. Tea and cocoa are adequately dealt with and there are notes on lesser known caffeine-containing plants, but coffee is omitted. Tobacco too can scarcely be passed over in any account of drugs. Duboisia has become an important drug in commerce and its description should be added to those of the Solanaceae having the same alkaloidal constituents.

Most of the crude drugs dealt with are grouped on a morphological system, the various sections being dealt with in order of increasing microscopical complexity. Each chapter begins with a description of the plant organ in question, including definitions of the macroscopical and microscopical terms required, sometimes supplemented by drawings illustrating the more difficult points.

Under "Leaves" there are accounts of the stomatal index, palisade ratio and vein-islet number, which, with the lycopodium method for determination of adulterants in powdered materials (Wallis, *Analyst*, 1916, **41**, 357), has put the analysis of powdered drugs and spices on a firm quantitative basis. Microscopical descriptions are given for all the more important drugs, together with beautifully clear and careful drawings of sections of plants and details of powders made by Dr. and Mrs. Wallis.

In revising the book for this edition, the specific names of all plants mentioned, except *Hydnocarpus Wightiana*, have been printed with small initial letters, thus reversing a practice introduced by Linnaeus of using capital letters in certain circumstances. Your reviewer takes exception to this practice, which has apparently been introduced out of sheer laziness by some members of the younger generation of botanists of limited cultural outlook. Dr. Wallis is not of this company; unless and until the change is made by the appropriate International Botanical Committee, the names should be printed as they were coined by their authors. Many references have been added to the monographs in the revision. One of the few errors detected in reading the book occurs on p. 177, where Maplethorpe is spelt Mabelthorpe. The interpolation of new material on p. 506, paragraph 7, has left a sentence without a predicate. One hesitates to criticise the text against Dr. Wallis's authority, but here and there are statements one would like to comment on. As an example, the chemistry of ergot is left in this edition much as in the first, and from this the description of the B.P. Codex 1949 differs widely. As a parting shot, *Fucus vesiculosus* is reputed to reduce obesity; it is also used for fattening pigs, and serves as an example of a drug that should not be considered worth retaining.

Students working for the Royal Institute of Chemistry's Examination in Branch E will find this book and the author's "Practical Pharmacognosy" indispensable. The inclusion in a future revision of the items mentioned above will make the book more useful to them and to others; and to those whose student days are memories it will form a reference for facts not generally obtainable and a source of pleasure for desultory reading.

J. E. WOODHEAD

MEDICINAL CHEMISTRY, Vol. II. By ALFRED BURGER. Pp. xv + 579 - 1084. New York and London: Interscience Publishers Inc. 1951. Price \$10.00; 80s.

The first volume of this work was reviewed in *The Analyst* (1951, **76**, 674). The present volume contains chapters on hormones, antibiotics, chemotherapeutic synthetic drugs, anti-malarials, antitubercular agents, drugs used in tropical diseases, compounds of arsenic, antimony and bismuth, anthelmintics and antiseptics, amongst other subjects.

The statement as to the scope of the book made in the review of Volume I, applies also to Volume II, and it must be repeated that the book is almost devoid of data of direct value to the analyst. This, however, is not a criticism as, clearly, the author has not set out to provide such data, his chief interest being in synthetic chemistry and the relation of structure to pharmacological action. Within this range there is a large amount of information presented in a clear and readable manner.

The selection of material must have been a difficult matter, but on the whole it has been well done, although some of the data presented are only of interest to workers in a limited field. It is rather surprising that the synthesis of quinine has not been described. This is surely of great interest as an achievement, although not at present of any practical value.

Errors and misprints are few. The production of penicillin by surface culture or by the bran method is now only of academic interest. There is not always uniformity in the method of drawing graphic formulae. The two formulae for equilin (xxix-13) given on pp. 594 and 595 are not exactly the same. The genus from which ipecacuanha is derived is *Cephaelis* not *Cephoelis*.

Drug research in these days is not as much a matter of shooting at targets in the dark as it used to be. A few of the targets at the end of the range are becoming faintly illuminated, but with many others it is still a matter of guesswork where to train our sights. Professor Burger has compiled an admirable account of the shooting to date. It includes a few bull's-eyes and a number of shots on the target, but the number of misses is far, far greater.

N. EVERS

THE PHOSPHATIDES. By HAROLD WITTCOFF. American Chemical Monograph No. 112. Pp. xviii + 564. New York: Reinhold Publishing Corporation. London: Chapman & Hall Ltd. 1951. Price \$10.00; 80s.

This book fills a long-felt want in a special branch of chemistry, as it is the first book of an authoritative nature on the subject in English since MacLean's "Lecithin and Allied Substances" appeared in 1927. While several excellent books on fats have been published in this interval,

reliable information on phosphatides has been difficult to find. The nomenclature and classification of this widespread group has been a problem for many years, but the author now proposes a scheme embracing all known data, and one that he hopes will be sufficiently flexible to include the results of future research. Most of the individual lecithins reported have until recently been subsequently found to be mixtures, and it is probably fair to state that their properties were not accurately known until Lesuk and Anderson isolated a lecithin in a pure state in 1941 from *Cysticercus fasciolaris*. Channon and Chibnall had, however, previously isolated lipides in a comparatively pure state. Since then Baer and Kates have described a method of synthesis of both enantiomeric forms of fully saturated α -lecithins of undoubted purity. The extraction and determination of total phosphatides and the determination of individual phosphatides is indeed a problem, but the whole of the available knowledge on this difficult subject up to 1949 has been thoroughly sifted, and the most authoritative methods are briefly indicated. While phosphatides are very widely distributed in the animal and vegetable kingdoms, their amount is usually small, and reliable information is sparsely distributed in the literature. The author has, however, collected all the available data in the form of tables giving the phosphatide content of dairy products, egg yolks, the blood and organs of many animals and naturally occurring oils and fats. The main body of the book is of interest mainly to the biochemist and physiologist, but the final two chapters devoted to the manufacture and industrial uses of phosphatides are of more general interest. In view of their rapidly increasing use in commerce, many readers would have welcomed rather more information in this direction. Like all the monographs of the American Chemical Society, this book has a most comprehensive bibliography as well as the final author and subject indexes, and as a book of reference it will be indispensable to the specialist and research worker. J. KING

TRAITÉ DE MANIPULATION ET D'ANALYSE DES GAZ. By HENRI GUÉRIN. Pp. vi + 636. Paris: Masson et Cie. 1952. Price 4500 fr. (paper); 5100 fr. (cloth).

A new book on gas analysis in French is perhaps needed more by the French-speaking than by the English-speaking scientific world, which has already got books by Dennis, Lunge and Ambler, Altieri and others. Nevertheless, this book has a great deal to commend it.

The book is divided into five main sections: History (6 pages), Handling of Gases (136 pages), General Methods of Analysis (160 pages), Survey of Principal Gases (180 pages) and Applications of Analysis of Gases (195 pages). The author has been thorough and painstaking. The first section includes an interesting historical summary and a chronological list of publications on gas analysis. The second section deals with sampling, confining liquids, gas measurement, vacuum pumps, pressure measurement, joints, taps and the purification, storage and preparation of gases. Section III discusses methods of analysis, apparatus, separation and absorption of gases, absorption pipettes and wash bottles, and includes useful sub-sections on the determination of specific gravity and on the newer methods of gas analysis involving interferometry, mass spectrography, infra-red spectroscopy, polarography, magnetic susceptibility and adsorption. The fourth of the main sections is probably the most valuable. The physical and chemical properties of many gases and vapours—some of them unusual ones—are fully given, together with various methods of determination at various concentrations. The sub-section on oxygen, for example, covers 19 pages with a summary of all kinds of methods of analysis. The last section deals with methods of analysis of gases in various industries. The whole book is well printed and well illustrated. The author has included a very wide and up-to-date range of references, his author index covering 29 pages.

Some minor criticisms might be made. The Bone and Wheeler apparatus shown on p. 205 is almost obsolete in Great Britain, the most up-to-date American apparatus are not shown, some drawings are not well reproduced, micro gas analysis should be separated from the analysis of traces of gas colorimetrically and the sub-section on gas calorimetry is incomplete in its account of British practice. W. J. GOODERHAM

ELEKTROCHEMIE. THEORETISCHE GRUNDLAGEN UND ANWENDUNGEN. By GIULIO MILAZZO. Translated into German from Italian by W. Schwabl. Pp. xiii + 419. Vienna: Springer. 1952. Price 61s. 6d.

The widespread use of new electrical methods for the preparation, purification and analysis of inorganic and organic substances has created a demand by students and chemists for a textbook that will provide a reliable introduction to modern electrochemistry. The book, written in 1947 by Dr. G. Milazzo, professor of electrochemistry in the University of Rome, to meet such a demand in Italy, has now been translated into German and re-edited by Dr. W. Schwabl of Vienna.

Professor Milazzo has based his survey of electrochemistry on sound thermodynamic principles, but has rightly placed considerable emphasis on practical applications. Fundamental principles, electrical conductivity, electromotive force, analytical applications, metallurgical and non-metallurgical applications of electrolysis, electrolytic cells and the electrochemistry of colloids and of gases are discussed in turn. One hundred tables of electrochemical data are interspersed in the various chapters and are a valuable feature of the book. Each chapter contains a useful list of selected literature references.

The chapter on analytical applications surveys in the space of 43 pages the techniques used in conductivity and pH value measurements, potentiometric titrations, electrochemical and polarographic analyses and amperometric titrations. The usefulness of a table listing the polarographic half-wave potentials of about 200 organic substances is marred by the facts that for nearly half of the substances listed obsolete reduction potential values are quoted instead of half-wave potential values and that some of the potentials are referred to the normal and not to the saturated calomel electrode; reliable half-wave potential values are available (see P. Zuman, *Coll. Czech. Chem. Comm.*, 1950, 15, 1107) for nearly all the substances listed and there should be no difficulty in referring potentials to the saturated calomel electrode.

The book is well printed and the figures are exceptionally clear. Although it can be recommended to chemists requiring a sound introduction to modern electrochemistry, it is doubtful whether the German edition will find favour among English-speaking students. J. E. PAGE

STATISTICAL METHODS FOR CHEMISTS. By W. J. YOUDEN. Pp. x + 126. New York: John Wiley and Sons, Inc. London: Chapman and Hall Ltd. 1951. Price \$3.00; 24s.

Although several books are now available that seek to expound statistical methods for the benefit of the scientist who is not also a mathematician, they are almost without exception written with a genetical or agricultural background. The reasons are clear to anyone knowing the history of the development of statistics; but the chemist finds it difficult enough to learn how to do the special kinds of sums that constitute applied statistics without having to follow illustrative problems based on unfamiliar sciences with their own even more unfamiliar vocabulary. As far as I know, Youden's book is the first of its kind to have a definitely chemical setting, and it is certainly the first to have as its author one who has distinguished himself both as a chemist and as a statistician.

As was to be expected, mathematical theory and proofs have been largely omitted, stress being laid on explaining those statistical techniques most likely to be useful to the chemist, with an abundance of numerical examples based on chemical problems. An initial chapter on precision and accuracy, with special reference to small sets of data (very pertinent stuff, this), is followed by one on the measurement of precision, introducing the concept of confidence limits commendably early, and another on the estimation of errors. Next comes a most important chapter in which the topic of linear regression—without apparently using that technical term once!—is dealt with in such a way as to bring home to any chemist the value of the statistical approach to all problems involving the ratio of two quantities. The analysis of variance, and a discussion of interaction between components, is followed by three chapters on experimental design, the last of which explains the devices of confounding and of fractional replication very interestingly and clearly and suggests many new ideas for the design of complex chemical experiments.

It will be seen that much of the matter found in the genetical-agricultural books previously mentioned is missing; chi-squared, for instance, is mentioned briefly once, and distributions other than Normal not at all. This, in my opinion, is as it should be, for if chemists are to be induced to apply statistics to their work, they must be introduced to the subject by way of those techniques they can see have a direct bearing on the kinds of jobs they have to do, without distraction by discussion of others for which they never afterwards find a use. Practically all the tests given by Youden are variations of the t and F tests, and the only tables provided in the book are of these two functions and of squares. Yet the chemist who properly digests this book, and cannot only apply the techniques described therein in the situations to which they are applicable, but also refrain from doing so in the situations to which they are not, will have gone a surprisingly long way towards being his own statistician. It should be added that the author's lucid style, and the apposite examples he has chosen, make the road, if not easy—for the acquisition of an entirely new technique can never be quite that—at least free from serious fogs, snags, and uncertainties of direction.

The book has been attractively printed in the United States, on good quality paper, with a very praiseworthy absence of misprints. It is by no means expensive as books are to-day, and

can be confidently recommended not merely to chemists but to all who, to copy a phrase from the preface, "make measurements and interpret experiments." Apart from its undoubted merit as an introduction to statistics for scientists who know nothing of the subject but "would rather like to try," it will be found informative and thought-provoking even by those who have, or think they have, a competent familiarity with the subject.

ERIC C. WOOD

MILK TESTING. By J. G. DAVIS, D.Sc., Ph.D., F.R.I.C. Pp. 260. London: Dairy Industries Ltd. 1951. Price 15s.

Dr. Davis has once again rendered a real service to the laboratory workers of the dairy industry, this time by collecting together, in one volume of convenient size, "all the necessary information for the routine control of milk," raw, pasteurised or sterilised.

His sequence of chapters is entirely logical. He begins by emphasising the basic importance of sampling. This emphasis is more than justified, since there can be little doubt that one of the most frequent causes of the far too common anomalies on fat determinations in milk is still the failure to obtain a fair sample. It is sometimes difficult for the younger laboratory assistant to realise that the time and care spent on analysis may be worse than wasted—since they may give a spurious confidence in results—unless sampling has been methodically and effectively carried out.

Chapters follow on physical tests (cream line, freezing-point, refractive index), chemical tests (including details of recent additions and modifications to the old-established ones and some useful paragraphs on preservatives), biochemical tests, including phosphatase tests, and a wide selection of bacteriological tests, which are not only carefully described in detail but have their value assessed in terms that reflect the long experience of the author. In the concluding chapter, which maintains the high standard of usefulness of the earlier ones, Dr. Davis deals with the general organisation of the dairy control laboratory. Sections on laboratory records, costing, standard solutions, treatment of glassware and media equipment all provide information that it is most useful to have collected together in this convenient form. Finally, about the right number of references are given to original texts and papers and there is an adequate index.

There seem to be remarkably few printers' errors in the book, and few questionable statements. In Table 14, however, the relative accuracy of the clot-on-boiling test for keeping quality appears to be seriously under-estimated. Also Fig. 34 needs rather more care in drafting and some textual explanation.

After such a careful, complete and well-documented presentation of the technique of milk testing—in fact almost a model presentation—it comes as somewhat of a shock to find several pages of miscellaneous commercial advertisements jostling each other at the end of the volume. Surely the right place for these is in the trade journals, not in a textbook. In their place a few blank pages suitable for notes and additions would have been welcome.

This book will undoubtedly find its way into every responsible laboratory, whether a trade laboratory or not, dealing with milk analysis or milk quality control. It should also be of great value to students of dairying, in this country or abroad.

H. D. KAY

FURTHER LABORATORY AND WORKSHOP NOTES. Compiled and edited by RUTH LANG, Ph.D., A.Inst.P. Pp. xii + 290. London: Edward Arnold & Co. 1951. Price 28s.

A light-spot of diameter about 0.004 inches is required; a lamp placed behind a perforated diaphragm would seem to meet the situation. But how can the spot be made visible at a wide angle? Such problems, with solutions both neat and simple, have appeared for many years past as Laboratory and Workshop Notes in the *Journal of Scientific Instruments*. A selection of these Notes, compiled and edited by Dr. Lang, was published in book form in 1949 (for review, see *Analyst*, 1950, 75, 115), thus providing an opportunity for many elegant devices and techniques to become more widely known. The favourable reception of the first volume has now brought about the welcome appearance of a second selection of notes, likewise under the editorship of Dr. Lang. As before, royalties from the sale of the book are to be placed to the credit of the Benevolent Fund of the Institute of Physics.

Most of the 124 Notes selected appeared originally in the journal from 1946 onwards. Classification is in seven sections: graphs and drawings; optical devices and techniques; devices for liquids and gases; heat, thermometry and furnaces; laboratory and workshop tools, processes and devices; vacuum and pressure techniques and devices; electrical devices and ancillary equipment and techniques. Some of the devices dealt with are extremely simple. Mr. F. Stafford's solution

to the light-spot problem mentioned above, Professor Hartridge's most effective method of connecting many wires to one terminal, and the preparation of extremely thin specimen tubes described by Professor Ubbelohde, are good examples. In addition, there are many interesting descriptions of the necessarily more complex solutions to some really tough problems, such as accurate metering of solutions at low rates of flow.

Longer Notes, on such topics as care of thermometers, machining of plastics, construction of laboratory furnaces, preparation and use of instrument suspensions and control of humidity by salt solutions, are also included. The last-mentioned Note contains extensive tables giving the percentage relative humidities of a large number of saturated salt solutions at temperatures up to 100° C.

The whole work is excellently printed and illustrated and makes interesting reading. Thereafter, it and its predecessor will be reached for whenever knotty problems arise. To this end a full list of contents and an adequate subject index are wisely included. J. T. Strock

EXPERIMENTAL SPECTROSCOPY. By RALPH A. SAWYER, Ph.D., Sc.D. Second Edition. Pp. x + 358. London: Chapman & Hall Ltd. 1951. Price 30s.

This is the second edition of a text that appeared originally in 1944. To be fair, it must be stated at the outset that it is not a working text for the general analyst in search of details of spectrographic procedures. In fact, three or four pages on the applications of infra-red spectroscopy and a short chapter on emission spectroscopy cover all the material of direct analytical interest.

For the advanced student, however, and for the research worker using spectroscopic procedures, it is a valuable reference book. The theory, use and adjustment of both prism and grating instruments are given detailed attention, and chapters are also devoted to determination of wavelength and the determination of spectral intensity—the spectroscopist's "what is it" and "how much."

Lack of attention to certain topics is offset by reference to other recent texts that give more detailed treatment—which explains, for example, why absorption spectrophotometry is completely ignored. References are also provided to most of the original published work, even as far back as the early papers of Herschel, Wollaston and Fraunhofer in the first years of the nineteenth century.

To sum up, this is not a text for the analyst, but is strongly recommended to spectroscopists. B. S. COOPER

ORGANIC SYNTHESSES. Volume 31. Edited by R. S. SCHREIBER. Pp. vi + 122. New York: John Wiley & Sons Inc. London: Chapman & Hall Ltd. 1951. Price \$2.75; 22s.

Perhaps the most interesting feature of the second contribution towards the fourth collective volume is that eight of the forty-one main items were contributed from sources other than American; India supplies 2-hydroxy-5-methoxyacetophenone, while from Great Britain come ethyl pyruvate, triethyl phosphite and diisopropyl methylphosphonate, *p*-bromo- and *p*-ethoxyphenylurea, *o*-chlorophenylcyanamide and the thiourea from which it is made. On the whole, the structures of the compounds are relatively simple; apart from *O*-methylcaprolactim and the lactones coumalic acid and α -acetyl- δ -chloro- γ -valerolactone, the heterocyclic group is represented only by 3:5-dimethylpyrazole, 2-formylthiophen and benzfurazan oxide.

The halogenated compounds present are 1:6-di-iodohexane, tetra(bromomethyl)methane, 4:4'-dibromodiphenyl and iodocyclohexane; with these may be associated acetobromamide and 2-chloroethyldimethylamine. A chloro-compound from earlier times is used as a source of tetraphenylethylene. Nitration procedures lead to 2:6-dinitroaniline and 9-nitroanthracene; 1-*p*-nitrophenylbuta-1:3-diene is obtained indirectly.

2:2:6:6-Tetra(hydroxymethyl)cyclohexanol is the only representative of alcohols but the four carbonyl compounds are divided equally—on the one hand *p*-aminobenzaldehyde and syringaldehyde, on the other laurone and methyl cyclopropyl ketone. Ring-opening leads to δ -acetylvaleric acid and $\beta\beta$ -dimethylglutaric acid; *o*-veratraldehyde is used to prepare 2:3-dimethoxycinnamic acid as well as ethyl α -acetyl- β -2:3-dimethoxyphenylpropionate. Other acids described are cinnamylsuccinic, 4:4':6:6'-tetrachlorodiphenic and thiolacetic.

Two unsaturated nitriles are included, *viz.*, triphenylacrylonitrile and cyclohex-1-enylacetonitrile. Phenylchlorophosphine, 1:6-diisocyanatohexane and NN'-diphenylbenzamidine constitute the miscellaneous residue.

As is customary, some of the preparations include separate, but here unnamed, intermediates and, in at least ten instances, it is indicated that the procedure described may readily be applied more widely. B. A. ELLIS

Publications Received

- FOOD SCIENCE. A SYMPOSIUM ON QUALITY AND PRESERVATION OF FOODS. Edited by E. C. BATE-SMITH, M.Sc., Ph.D. Pp. xvii + 319. Cambridge University Press. 1952. Price 40s.
- TABLES FOR THE ANALYSIS OF BETA SPECTRA. National Bureau of Standards Applied Mathematics Series 13. Pp. iii + 61. Washington: U.S. Government Printing Office for U.S. Department of Commerce. 1952. Price 35 cents.
- QUANTITATIVE CHEMICAL ANALYSIS. By CHARLES W. FOULK, HARVEY V. MOYER and WILLIAM M. MACNEVIN. Pp. ix + 484. New York and London: McGraw-Hill Book Co. Inc. 1952. Price \$5.00; 42s. 6d.
- THE PHYSICAL CHEMISTRY OF SURFACE FILMS. By WILLIAM D. HARKINS. Pp. xvi + 413. New York: Reinhold Publishing Corporation. London: Chapman & Hall Ltd. 1952. Price \$10.00; 80s.
- PAPER CHROMATOGRAPHY (A LABORATORY MANUAL). By RICHARD J. BLOCK, RAYMOND LESTRANGE and GUNTER ZWEIG. Pp. x + 195. New York: Academic Press Inc. London: Academic Books Ltd. 1952. Price \$4.50; 36s.
- REPORTS ON THE PROGRESS OF APPLIED CHEMISTRY. Vol. XXXVI. Edited by F. CLARK. Pp. 878. London: The Society of Chemical Industry. 1951. Price 40s.
- CONCISE PHYSICAL CHEMISTRY (FOR INTERMEDIATE STUDENTS). By J. E. WYNFIELD RHODES, B.Sc., Ph.D., F.R.I.C., F.G.S. Pp. xv + 196. London: English Universities Press Ltd. 1952. Price 12s. 6d.
- ANTIBIOTICS: A SURVEY OF THEIR PROPERTIES AND USES. Published by direction of the Council of the Pharmaceutical Society of Great Britain. Second Edition. Pp. ix + 290. London: The Pharmaceutical Press. 1952. Price 25s.

THE DISTILLERS CO. LTD. seek to fill the following appointments vacant in South Africa. (1) **ANALYST** to carry out general chemical analyses, organic and inorganic, and laboratory work in connection with the development of new projects and investigation of plant problems. (2) **ORGANIC CHEMIST** to do research work on processes and investigate production problems of organic chemicals, particularly concerning lacquers, solvents, organic acids and also some synthetic work. Applicants must have a University Degree in Chemistry, or equivalent, and be between 26 and 32 years of age. They should have at least 5 years' appropriate industrial experience. Salary will be £700-£1,000 p.a., depending on qualifications and experience. Successful applicants will have a period of training in this country. Apply: Staff Manager, Distillers Co. Ltd., 21, St. James' Square, London, S.W.1.

ALBRIGHT & WILSON LIMITED (Chemical Manufacturers), have a vacancy for a graduate chemist for work comprising analytical investigation and research into analytical methods at the Company's factory at Barry, South Wales. The qualifications desired are a degree in Chemistry, together with knowledge of investigational methods and experience of analytical research. Age 25-30. Salary according to age, qualifications and experience. Bonus is payable and a non-contributory pension scheme is in operation. Apply to the Appointments Officer, Albright & Wilson Limited, Oldbury, Birmingham.

ASSISTANT ORGANIC RESEARCH CHEMIST required by heavy chemical manufacturers in East Anglia. Preferably one with industrial research experience to develop new processes to the pilot plant stage. Salary according to ability and experience. Write (quoting Ad. 723) giving full details to Box No. 3822, THE ANALYST, 47, Gresham Street, London, E.C.2.

MAGNESIUM ELEKTRON LTD. have vacancies for experienced Analytical Chemists of degree or A.R.I.C. standard. Work covers wide range of inorganic materials connected with several research projects. Salary according to qualifications and experience, but not below £500 p.a.; 5-day week and pension scheme. Written applications with full details of age, education, experience and positions held to Secretary, Magnesium Elektron Ltd., Clifton Junction, nr. Manchester.

NATIONAL COAL BOARD NORTH-WESTERN DIVISION

APPLICATIONS are invited for the post of Scientist, Grade III, at the Central Laboratory, Shade House, Bolton Road, Pendlebury, Manchester. The appointment will be within the salary scale £445 × 25 = £845, and the commencing salary will be in accordance with qualifications and experience. Candidates should possess a first or second class honours degree in physics, and preference will be given to applicants possessing a knowledge of electronics, workshop practice and general physics. The successful candidate will be required to undergo a medical examination in connection with the Board's Superannuation Scheme. Applications, giving full particulars of age, education, qualifications and experience (with dates), should be sent to the Divisional Establishment Officer, National Coal Board, North-Western Division, 40, Portland Street, Manchester, 1, within fourteen days of this advertisement.

LAPORTE CHEMICALS, LUTON, require graduate wishing to specialise in analytical chemistry, age preferably under thirty. The work will cover the development of analytical methods, particularly from a physico chemical standpoint. Apply, giving full particulars, to the Research Manager.

BRITISH ELECTRICITY AUTHORITY MIDLANDS DIVISION

ASSISTANT CHEMIST is required in the Analytical Section of the Divisional Laboratory, Birmingham. N.J.B. service conditions, superannuable appointment, salary in accordance with Schedule C, Grade 5, commencing in the range £629 to £765, ultimately rising to £834 per annum. Applicants should possess a university degree or A.R.I.C. and be thoroughly experienced in general analytical chemistry, particularly relating to water, fuel, and oil and should be capable of carrying out analysis of complex materials and development of analytical methods. Application forms available from the Establishments Officer, 53, Wake Green Road, Moseley, Birmingham, 13, to be completed and returned by 28th October, 1962. F. W. LAWTON, Divisional Controller.

C.A.V. LIMITED require to appoint immediately a qualified Metallurgist to lead section of Metallurgical Laboratory on production problems and new developments. Candidates should be L.I.M. or equivalent and must have had some industrial experience in the heat treatment and use of alloy steels. Salary in the range £600-£700 according to age and experience. The appointment will include participation in a pension scheme. Applications should be addressed to The Personnel Manager, C.A.V. Ltd., Acton, London, W.3.

C.A.V. LIMITED require competent Metallographer for general duties in their Laboratories. Applicants should have some experience with ferrous and non-ferrous materials as used in the precision engineering industry. Female applicants will be considered. Good salary varying according to age and ability. Staff Pension Fund. Opportunities for completing studies. 5-day week. Applications should be addressed to The Personnel Manager, C.A.V. Ltd., Acton, London, W.3.

A CHEMIST required for general analytic and research laboratory engaged in investigations into water and effluent treatment. Pension Scheme in operation. Five-day week; permanent and progressive position. All letters treated in strict confidence. Apply in writing in first instance stating age, experience and salary required, to The Personnel Manager, John Thompson Limited, Etingshall, Wolverhampton.

ADMIRALTY VICTUALLING DEPARTMENT require Temporary Assistant Technical Examining Officers at Risley, near Warrington, or in London, but must be willing to serve elsewhere in U.K. if required. Must be British born subjects and have either 1st or 2nd Class Honours degree (with Chemistry as principal subject) or hold A.R.I.C. or F.R.I.C. Post-graduate experience with any of following stores an advantage: (1) Provisions; (2) Clothing; (3) Mess-Gear (tableware, cooking utensils, etc.). Salary within £600-£900 (slightly lower in provinces). Successful applicants may compete for established posts. Form from M. of L. and N.S. Technical and Scientific Register (K), Almack House, 26, King Street, London, S.W.1, quoting F.421/52A.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, Dye-stuffs Division, has vacancies in the Division Analytical Department for chemists (men) with an Honours Degree or A.R.I.C. and post-graduate analytical or research experience. Age below 30. Salary in accordance with training and experience. Applications in writing to Staff Department, Hexagon House, Blackley, Manchester, 9. Ref. D.A.D.

HER MAJESTY'S COLONIAL RESEARCH SERVICE EAST AFRICA HIGH COMMISSION

APPLICATIONS are invited from male candidates for the post of Biochemist in the East African Tsetse and Trypanosomiasis Research and Reclamation Organisation. Salary (according to qualifications and experience) in the scale £750-£950 per annum plus Overseas Research Allowance of between £135 and £220 per annum. Cost of Living allowance is also payable at the rate of 25% on basic salary plus Overseas Research allowance (subject to a maximum of £250 per annum). Outfit allowance. Free passages are provided on appointment and on leave up to the cost of three adult fares. Superannuation is provided under the Colonial Superannuation scheme. Quarters provided at a rental of 10% of basic salary. Candidates, between 25 and 45, must possess a B.Sc. (Honours) degree and preference will be given to those with two years' post-graduate research. Duties will be to carry out research on animal and insect physiology in connection with trypanosomiasis investigations in East Africa. Application forms can be obtained from the Director of Recruitment (Colonial Service), Colonial Office, Sanctuary Buildings, Great Smith Street, London, S.W.1 (quoting reference No. 27106/63/52).

GLAXO LABORATORIES LIMITED, Barnard Castle, require a qualified Analyst for their Analytical Laboratory. The work involves the analytical control of a wide range of antibiotic products, together with the supervision of the analytical work of a number of junior assistants. Previous experience in the pharmaceutical industry is desirable. Commencing salary according to qualifications and experience, but not less than £485 per annum with participation in the Company's Superannuation and Incentive Schemes. Applications should be addressed to the Senior Personnel Officer, Glaxo Laboratories Ltd., Greenford, Middlesex.

CITY OF PORTSMOUTH PUBLIC ANALYST'S DEPARTMENT APPOINTMENT OF ASSISTANT ANALYST

APPLICATIONS are invited for the above-mentioned appointment from candidates with B.Sc. or A.R.I.C. qualification. Salary £555 rising to £645 by annual increments of £15. The candidate's qualifications and experience will be taken into account in determining the initial salary to be offered. The successful candidate will be required to pass a medical examination. Applications, stating age, qualifications and experience and accompanied by the names of three referees, should be addressed to the undersigned not later than 25th October.

V. BLANCHARD, Town Clerk,
City Council Chambers,
1, Clarence Parade, Southsea.

ARMSTRONG SIDDELEY MOTORS have a vacancy for a Physical Chemist to act as senior Laboratory Assistant on gas analysis. The work is concerned with the chemistry of combustion problems and is to do with gas turbine engines. Degree or Higher National Certificate is necessary. This is important super priority work. Reply in the first instance to Reference ACK, Personnel Manager, Armstrong Siddeley Motors, Coventry
(continued overleaf)

SOUTHERN RHODESIA GOVERNMENT
VACANCY—ANALYTICAL CHEMIST—DEPARTMENT
OF HEALTH

APPLICATIONS are invited from males under the age of 40 years, and holders of at least the B.Sc. degree in Chemistry, for appointment in the Government Analyst's Laboratory, Salisbury. The work of this Laboratory includes the analysis of waters, foods and drugs, dairy produce and certain clinical specimens; toxicology, forensic chemistry; and general miscellaneous analyses. Salary scale: £468 × £66 to £600 × £34 to £668 × £33 to £800 × £100 to £900 × £40 to £1,140 per annum, plus a cost of living allowance varying between £127 and £279 per annum and, when applicable, children's and marriage allowance. If the successful applicant holds the M.Sc., A.R.I.C. or equivalent qualifications in Chemistry, the commencing salary on this scale will be £600 per annum. Additional increments, but not exceeding four, may be granted in recognition of previous experience. Further particulars and application forms may be obtained on written application to the Secretary, Rhodesia House, 429, Strand, London, W.C.2, with whom applications should be lodged not later than the 31st October, 1952.

HER MAJESTY'S COLONIAL SERVICE
ST. VINCENT, WINDWARD ISLANDS

A VACANCY exists for an Arrowroot Processing Chemist (27106/62/52) in St. Vincent. The appointment is on contract/gratuity terms for two years with a fixed salary of £1,220 per annum. A temporary cost of living allowance of £80 per annum is also payable. Gratuity at the rate of £37 10s. 0d. for each completed three months' satisfactory service. Quarters are provided at a rental of £100 per annum; free passages for officer and family, not exceeding five persons, on appointment and on satisfactory completion of engagement; leave on full salary at the rate of one week for each completed three months' service at end of engagement. Candidates must possess a degree in Chemistry and have had experience in starch technology. Duties entail thorough investigation of: all phases of processing arrowroot; the starch content and its extraction from the rhizome; the stage in growth when rhizome should be harvested. The officer would also be responsible for the supervision of such central factories as may be erected. Intending candidates should apply in writing to The Director of Recruitment (Colonial Service), Colonial Office, Sanctuary Buildings, Great Smith Street, London, S.W.1, giving brief details of their age, qualifications and experience. They should mention this paper and quote the reference number (27106/62/52).

CROWN AGENTS FOR THE COLONIES

LABORATORY TECHNICIAN required by the Colonial Insecticide Research Department, Tanganyika, for one tour of 24–36 months in the first instance. Salary (including present temporary allowance of 25%) in scale £687 a year rising to £1,050. Outfit allowance £30. Free passages and liberal leave on full salary. Superannuation Scheme. National Health Service Superannuation rights may be preserved. Candidates must have had experience in an analytical chemical laboratory. Apply at once by letter stating age, full names in block letters and full particulars of qualifications and experience and mentioning this paper to the Crown Agents for the Colonies, 4, Millbank, London, S.W.1, quoting on letter M.28081.G. The Crown Agents cannot undertake to acknowledge all applications and will communicate only with applicants selected for further consideration.

UNITED KINGDOM OF LIBYA

APPLICATIONS are invited for the appointment of Government Chemist under the Provincial Administration of Tripolitania. Would be required to act as Adviser and Consultant, if necessary (a) to the Government on any industrial chemical products or processes or any mineral deposits or natural resources which may be of national interest, (b) on behalf of the Government to industrial firms producing or using vegetable oils, soaps and by-products, canning of fish, food, etc., wines, coals, mineral oils, petrols, alcohols, etc.; and the performance of routine Government and municipal analytical chemical work which normally covers water, alcohols, wines, foods, flours, etc., industrial products both chemical and medicinal, and chemical analysis of wine and toxic substances. Candidates should hold Associateship or Fellowship of the Institute of Chemistry and preferably a degree in Science as well. Experience in the laboratory of a public analyst, consulting chemist or under the Government Chemist would be an advantage. Salary £900 × £30–£1,050 per annum, plus tax free Foreign Service Allowance £130–£530 per annum, according to individual circumstances. Salary not liable to U.K. income tax (Schedule E) but liable to local tax (at present 8%). Appointment subject to medical fitness. Initial contract 3 years. Age limit between 30 and 50 years. Home leave 72 days for each two years of resident service plus local leave 18 days annually. Passages for officials and their families at Government expense. Application forms from Foreign Office (A.A.T.), 17, Carlton House Terrace, London, S.W.1, should be completed and returned within ten days of the appearance of this advertisement.

JUST PUBLISHED

THE EXTRA PHARMACOPŒIA
(MARTINDALE)

Volume I 23rd Edition

During the eleven years that have passed since the last edition of Volume I was published there have been more important additions to *materia medica* than in any similar previous period. This new edition, completely rewritten and re-set, provides up to date information on the thousands of drugs used in medical practice. It supplies the most complete guide available on "ethical" proprietaries and to preparations in foreign pharmacopœias.

Every new national pharmacopœia which has been published since the last edition has been examined and suitable references from each are included. Comparisons are made between the British Pharmacopœia, the United States Pharmacopœia and the International Pharmacopœia, so that buyers and users of drugs will be made aware of points of contact and difference. The book has a larger page size and more pages than any previous edition.

Pages xxii + 1352

Price 55s.

Postage 1s.

Remittance with order is requested

THE PHARMACEUTICAL PRESS, 17, Bloomsbury Square, London, W.C.1
(Publishers of the British Pharmaceutical Codex)

WEIGHING THE ELEMENTS



*Symbol Al. Atomic Number 13
Atomic Weight 27.1*

IT is strange that aluminium, estimated to form one-thirteenth part of the earth's crust (only oxygen and silicon are more abundant) has but recently come to be used extensively by man in his everyday life. Its climb to favour has been so rapid that now it is a commonplace in everything about us, from aeroplanes to domestic utensils.

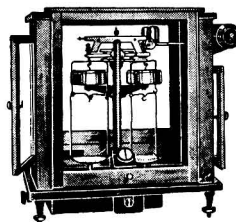
Its affinity for oxygen, one of its greatest properties, is manifest in such precious stones as rubies and sapphires. Corundum, too, is an oxide of aluminium. Produced synthetically, it looms largely in the development of the modern analytical balance.

For it was STANTON who in 1947 pioneered the use of synthetic sapphire (corundum) planes as opposed to agate which it has largely replaced because of its superior hardness.

We of STANTON take a modest pride in our achievements in developing balances worthy of modern researchers and technologists. Every instrument bearing the name of STANTON, wherever in the world it may serve the cause of science, is as near the craftsman's ideal of perfection as human hands can contrive.

You can rely on STANTON—
Built by BRITISH craftsmen

*The STANTON Semi-Automatic Aperiodic Balance—
Model AD2 with a capacity of 200g. and a sensitivity of
0.1mg. completely eliminates the use of fraction weights below
1g. by means of the auto-loading device. The beam comes
to rest in approx. 15.20 secs. Ideal for general analytical work
where the time-saving factor is important.*



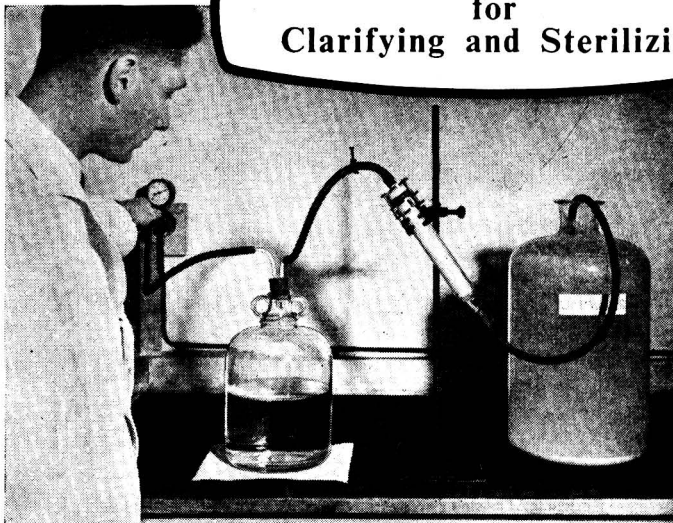
Write for our literature



STANTON PRECISION BALANCES

Stanton Instruments Ltd., 119 Oxford Street, London, W.1 Tel. Gerrard 7533/4

CERAMIC FILTERS for Clarifying and Sterilizing



Removing calcium carbonate and excess lime from a saturated solution, using a Doulton F10 filter candle.

For the removal of gross impurities from medicinal or other solutions and for the sterilization of heat-labile preparations, Doulton filters offer important advantages. These include:

- Robustness, and resistance to sudden pressure changes.
- Suitability for use with positive or negative pressure.
- Chemical inertness, guarding against filtrate contamination.
- Ability to withstand repeated autoclaving.
- Provision of filtrates of optical clarity.
- Easily tested by the 'bubbling pressure test'
- Available in fast and medium grades for clarifying; fast, medium and slow grades for sterilizing.

Write for Catalogue No. 10 to Dept. AJ, Industrial Ceramics Division,
Doulton & Co. Ltd., Doulton House, Albert Embankment, London, S.E.1

Royal **DOULTON** FILTERS

Colorimetric analysis



For the rapid and accurate determination of colour density in liquid samples, the EEL Portable Colorimeter is without question the most efficient and economical photoelectric device of its kind available. Simplicity of operation enables routine tests to be accurately determined by untrained personnel, yet the EEL Portable Colorimeter is unsurpassed in the hands of the experienced physicist or chemist. Its applications are countless and it is widely used in Biochemistry, Metallurgy, Agricultural Research, etc. It is supplied to many Government Departments and is a robust, accurate device capable of many years trouble-free service. You are invited to apply for full details of this economical instrument.

THE



Portable Colorimeter
a product of

EVANS ELECTROSELENIUM LTD.

SALES DIVISION 347

HARLOW

ESSEX

TINSLEY

Single unit — Ink recording
POLAROGRAPH

For rapid and accurate micro-chemical analysis

- ★ Completely undamped waves and high precision damping
- ★ 34 current ranges, multi-speed potentiometer and counter current
- ★ Analysis of Metals, Inorganic and Organic substances
- ★ Simultaneous estimations of several constituents on one Polarogram

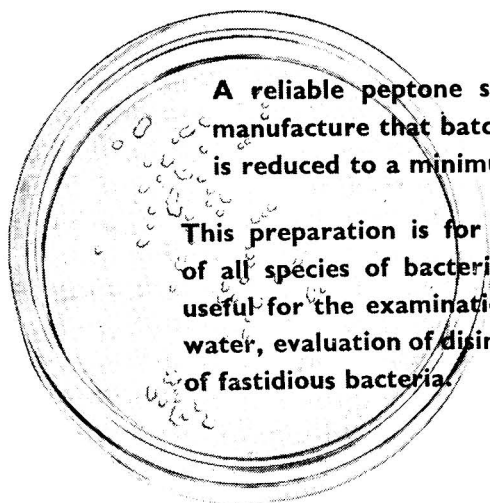
A comprehensive advisory service on methods is available without obligation.

Please write for Leaflet A.A

TINSLEY (INDUSTRIAL INSTRUMENTS) LIMITED
NORTH CIRCULAR ROAD, LONDON, N.W.10. ° ELGAr 6081

'OXOID'

Bacteriological Peptone



A reliable peptone so controlled during manufacture that batch to batch variation is reduced to a minimum.

This preparation is for the general culture of all species of bacteria. It is particularly useful for the examination of foodstuffs and water, evaluation of disinfectants and culture of fastidious bacteria.

Other 'OXOID' Laboratory

Preparations include :—

Agar-Agar
 Bacteriological Yeast Extract
 Desiccated Ox Bile
 Bile Salts
 'Lab-Lemco'



Desiccated Ox Heart
 Mycological Peptone
 Bacteriological Liver Extract

OXO Ltd. (Medical Dept.) Thames House, London, E.C.4

Telephone: **CEN**tral 9781



pH METER AND MILLIVOLTMETER

*Mains operated — but virtually
immune to supply variations.*

This instrument can be used to speed up any industrial process dependent upon acidity or alkalinity, thus reducing labour or production costs. Operation is extremely simple and a series of readings can be taken by an unskilled operator with rapidity and ease.

All accessories including electrodes and buffer tablets are stored in a compartment within the instrument. The operating instructions are lucid and in simple language. Please write for descriptive leaflet, quoting A.11054.

OUTSTANDING FEATURES

★ Mains Operated ★ Direct Reading ★ Automatic Temperature Compensation ★ Full Range 0-14 pH ★ Can be used with any electrode assembly ★ Operates external meters, recorders, process controllers ★ Electrode fully protected ★ Ideal for Redox-Millivolt measurements

SCIENTIFIC  INSTRUMENTS

W. G. PYE & CO. LTD., GRANTA WORKS, CAMBRIDGE, ENGLAND

THE IDEAL SWABBING MATERIAL CALGITEX

ALGINATE BACTERIOLOGICAL WOOL

SOLUBLE, STERILIZABLE, *with no bactericidal or bacteriostatic effect*

Soluble in solutions of sodium salts to give neutral solutions, thus permitting high recovery of organisms. Comparative tests¹ have shown that for staphylococci the recovery of known inocula was 50% using cotton wool and 90% using alginate wool; with *B. coli* the recoveries were 67% and 90%. Particularly suitable for diagnostic work and for hygienic control in the food processing and distributing industries².

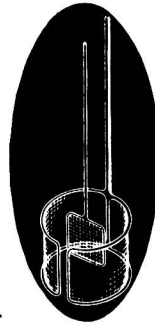
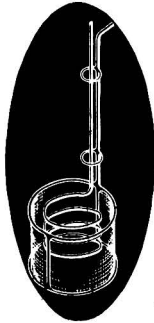
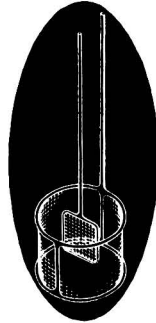
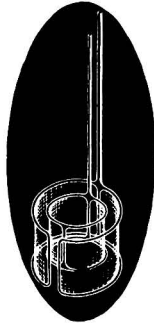
**Note: Calgitex Alginate Bacteriological Wool is 100% alginate—
NOT a cotton fibre impregnated with alginate.**

Refs: 1. Higgins, M. Monthly Bull. Min. of Health & Pub. Health Lab. Service, Feb. 1950 p. 49. 2. Higgins, M. & Hobbs, B. ibid, p. 38.

Calgitex Alginate Bacteriological Wool is available in tubes containing sufficient for approximately 50 swabs. Price 3s. 6d. per tube.

Full technical information gladly supplied from sole suppliers: . . .

MEDICAL ALGINATES LIMITED WADSWORTH ROAD, PERIVALE, MIDDLESEX



As you like it

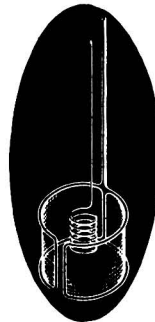
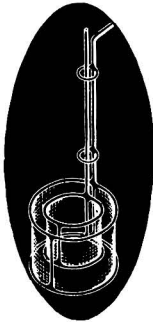
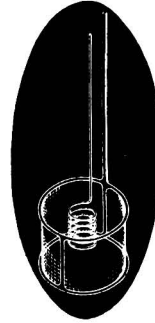
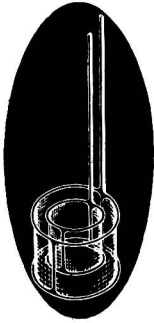
Platinum electrodes for
electromechanical analysis

The use of platinum in electrochemical technique is based on its complete resistance to chemical and electrolytic attack. Platinum electrodes remain absolutely constant in weight and the deposited metal may be easily removed after each determination.

Johnson Matthey publication 1720, from which these examples of various electrode combinations are taken, discusses impartially the various considerations influencing choice of electrodes, and gives full details of the standard JMC patterns available. Copies are free on request.

Specialised products of

Johnson 
Matthey



JOHNSON, MATTHEY & CO., LIMITED
HATTON GARDEN, LONDON, E.C.1.

Telephone : Holborn 9277

BIRMINGHAM : Vittoria Street, Birmingham 1.

JOHNSONS OF HENDON
ARE MANUFACTURERS OF

LITMUS
▪
CUDBEAR
▪
ORCEIN

Enquiries are invited

JOHNSONS OF HENDON LTD.
LONDON, N.W.4
Established 1743

PITMAN "Microbiology"

Series:

**The Microbiological
Assay of the Vitamin
B-Complex and Amino
Acids**

By E. C. BARTON-WRIGHT, D.Sc., F.R.I.C.

An entirely new study of this branch of biochemical analysis. Each assay is described in detail so that the procedure is clear to the beginner. Cultural details for the organisms used in the assays, and directions for the preparation of stock solutions, are given in the Appendices, and there are useful bibliographies at the conclusion of each chapter. 18s. net.

PITMAN, *Parker Street, Kingsway, London, W.C.2*

EACH 1952 SUBSCRIBER TO
ANALYTICAL CHEMISTRY

receives through his
January and February issues
the
FOURTH ANNUAL REVIEW
of
ANALYTICAL CHEMISTRY

featuring

LIGHT ABSORPTION SPECTROMETRY
INFRARED SPECTROMETRY
ULTRAVIOLET ABSORPTION SPECTROMETRY
X-RAY ABSORPTION
X-RAY DIFFRACTION
EMISSION SPECTROSCOPY
MASS SPECTROMETRY
ORGANIC POLAROGRAPHY
ACID-BASE TITRATIONS IN
NONAQUEOUS SOLVENTS
AMPEROMETRIC TITRATIONS
CHROMATOGRAPHY AND ANALOGOUS
DIFFERENTIAL MIGRATION METHODS
DISTILLATION
ION EXCHANGE
EXTRACTION
ORGANIC MICROCHEMISTRY
INORGANIC MICROCHEMISTRY
FLUORIMETRIC ANALYSIS
ELECTROANALYSIS
INORGANIC GRAVIMETRIC ANALYSIS
INORGANIC VOLUMETRIC ANALYSIS
VOLUMETRIC ANALYTICAL METHODS FOR
ORGANIC COMPOUNDS
CHARACTERIZATION OF
ORGANIC COMPOUNDS
EXPERIMENTAL STATISTICS
BIOCHEMICAL ANALYSIS
COATINGS
FOOD
SOLID AND GASEOUS FUELS
FERROUS METALLURGY
NONFERROUS METALLURGY
PETROLEUM
PHARMACEUTICALS AND NATURAL DRUGS
NATURAL AND SYNTHETIC RUBBERS
WATER ANALYSIS

EACH MONTHLY ISSUE CONTAINS
OVER 150 PAGES AND FROM
35 TO 50 TECHNICAL PAPERS

Annual subscription price and
foreign postage..... \$5.20

Order from the
AMERICAN CHEMICAL SOCIETY
1155 Sixteenth Street, N.W.,
Washington 6, D.C., U.S.A.
or
W. HEFFER & SONS, LTD.
Booksellers
Cambridge, England

THE ANALYST

THE JOURNAL OF
THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

PUBLICATION COMMITTEE

Chairman: J. R. Nicholls, C.B.E. *Members:* N. L. Allport, A. J. Amos, A. L. Bacharach, R. C. Chirnside, B. S. Cooper, L. Eynon, D. C. Garratt, J. Haslam, S. Ernest Melling, G. H. Osborn, J. E. Page, W. H. Simmons, A. A. Smales, George Taylor, O.B.E., L. S. Theobald, Eric Voelcker, C. Whalley, E. C. Wood, G. H. Wyatt.

President of the Society: J. R. Nicholls, C.B.E.

Hon. Secretary of the Society:
K. A. Williams

Secretary:
Miss D. V. Wilson

Hon. Treasurer of the Society:
J. H. Hamence

Editor: F. L. Okell, F.R.I.C.

Assistant Editor: J. B. Attrill, M.A.

CONTENTS

	<i>Page</i>
Editorial	
International Congress, Oxford, 1952	497
Proceedings of the Society of Public Analysts and Other Analytical Chemists	
North of England Section	498
Biological Methods Group	498
Original Papers	
The Chemical Composition of Milk Between 1900 and 1950 J. G. Davis	499
A Nomogram for the Calculation of Urinary 17-Ketosteroids E. R. Cook and Margaret E. Rooks	525
The Determination of Small Amounts of Calcium in Plant Material A. C. Mason	529
The Polarographic Determination of Titanium in Aluminium Alloys R. P. Graham and A. Hitchen	533
Notes	
The Determination of Potassium in Soil Extracts with a Flame Photometer—A. J. Cavell	537
The Determination of Beryllium in Beryl by Means of Ethylenediamine Tetra-Acetic Acid—P. I. Brewer	539
Apparatus	
An Apparatus for Micro Distillation—G. Oldham	542
The Analysis of Meat Products	543
Official Appointments	545
Ministry of Food and Ministry of Health	545
Ministry of Food	545
British Standards Institution	546
Book Reviews	546
Publications Received	552