Volume 68
No. 808, Pages 199—232

July, 1943

THE ANALYST

The Journal of
The Society of Public Analysts
and other Analytical Chemists

Publication Committee

Chairman: J. R. NICHOLLS, D.Sc., F.I.C.

N. L. ALLPORT, F.I.C.
F. W. F. ARNAUD, F.I.C.
A. L. BACHARACH, M.A., F.I.C.
R. C. CHIRNSIDE, F.I.C.
H. E. COX, D.Sc., Ph.D., F.I.C.
BERNARD DYER, D.Sc., F.I.C.
F. W. EDWARDS, F.I.C.
B. S. EVANS, M.B.E., M.C., D.Sc., F.I.C.
E. HINKS, M.B.E., B.Sc., F.I.C.
E. B. HUGHES, D.Sc., F.I.C.
D. W. KENT-JONES, B.Sc., Ph.D., F.I.C.
S. ERNEST MELLING, F.I.C.
G. W. MONIER-WILLIAMS, O.B.E., M.C., Ph.D., F.I.C.
A. MORE, I.S.O., A.R.C.S., A.R.T.C., F.I.C.
W. H. SIMMONS, B.Sc., F.I.C.
ERIC VOELCKER, A.R.C.S., F.I.C.
K. A. WILLIAMS, B.Sc., F.I.C.

Hon. Secretary:
L. EYNON, B.Sc., F.I.C.
7-8, Idol Lane, E.C.3

Hon. Treasurer:
G. TAYLOR, F.I.C.
Peek House, 20, Eastcheap, E.C.3

Editor: C. AINSWORTH MITCHELL, D.Sc., M.A., F.I.C.
16, Blomfield Road, London, W.9

Secretary and Assistant Editor: J. H. LANE, B.Sc., F.I.C.
7-8, Idol Lane, E.C.3

Abstractors

S. G. CLARKE, D.Sc., Ph.D., A.I.C.
B. S. COOPER, B.Sc., F.Inst.P.
E. B. DAW, B.Sc., A.I.C.
J. GRANT, Ph.D., M.Sc., F.I.C.
A. O. JONES, M.A., F.I.C.
J. W. MATTHEWS, Ph.D., F.I.C.
E. M. POPE, B.Sc.
F. A. ROBINSON, M.Sc.Tech., F.I.C.
W. R. SCHOELLER, Ph.D., F.I.C.
D. R. WOOD, F.I.C.

Published for the Society by
W. HEFFER & SONS LTD., Cambridge, England

IMPORTANT NOTICE TO SUBSCRIBERS
(*Other than Members of the Society*).

All Subscriptions and renewals to the Journal should be sent through a Bookseller or direct to
W. HEFFER & SONS LTD., CAMBRIDGE, ENGLAND.

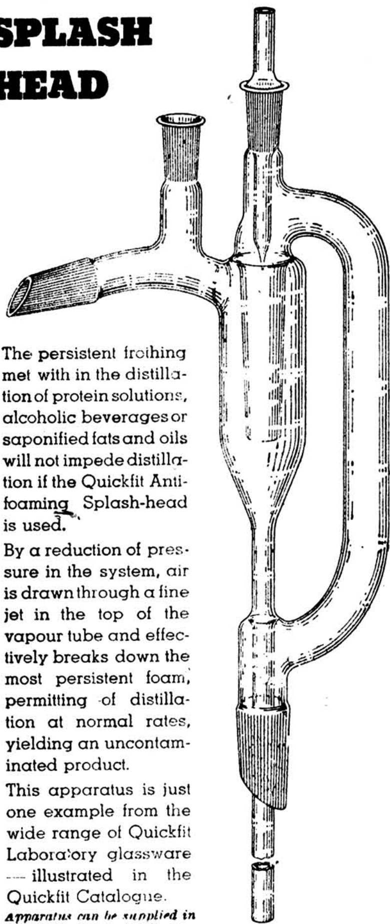
Price 3/6; or to Subscribers in advance, post free, 35/- per annum.

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

Entered as Second Class at New York, U.S.A., Post Office
Printed in England

QUICKFIT DOES IT BETTER—

ANTI-FOAMING SPLASH HEAD



The persistent frothing met with in the distillation of protein solutions, alcoholic beverages or saponified fats and oils will not impede distillation if the Quickfit Anti-foaming Splash-head is used.

By a reduction of pressure in the system, air is drawn through a fine jet in the top of the vapour tube and effectively breaks down the most persistent foam, permitting of distillation at normal rates, yielding an uncontaminated product.

This apparatus is just one example from the wide range of Quickfit Laboratory glassware — illustrated in the Quickfit Catalogue.

Apparatus can be supplied in Pyrex, Phoenix or Hysil glass.

QUICKFIT

LABORATORY GLASSWARE WITH STANDARD INTERCHANGEABLE GROUND GLASS JOINTS

QUICKFIT & QUARTZ LTD

TRIPLEX WORKS, KING'S NORTON, BIRMINGHAM

London Office: 1 *Albemarle Street, W.*1

Phone Regent 8171

Ample Supplies now Available!

It is free from contaminating organisms and toxic by-products.

It contains no fermentable carbohydrate.

Unlike many of the older peptones it provides in saline solution *alone* a complete medium for a wide variety of bacteria.

With the addition of dextrose, a saline solution produces an excellent growth of pneumococci, hæmolytic streptococci, and organisms of the coli typhoid and welchii groups.

No serum need be added when it is used for typing streptococci for the fermentation reactions.

It conforms to the requirements of the Indol test.

Potent diphtheria, tetanus, welchii and other toxins can be obtained with media containing this peptone.

It has low copper and iron content.

Bacteriological Peptone (Evans) is issued in 5 and 8-oz. amber bottles with bakelite screw caps.

Prices and full details will be sent on application to :—
London: *Home Medical Dept., Bartholomew Close, E.C.1*
Liverpool: *Home Medical Dept., Speke, Liverpool, 19*

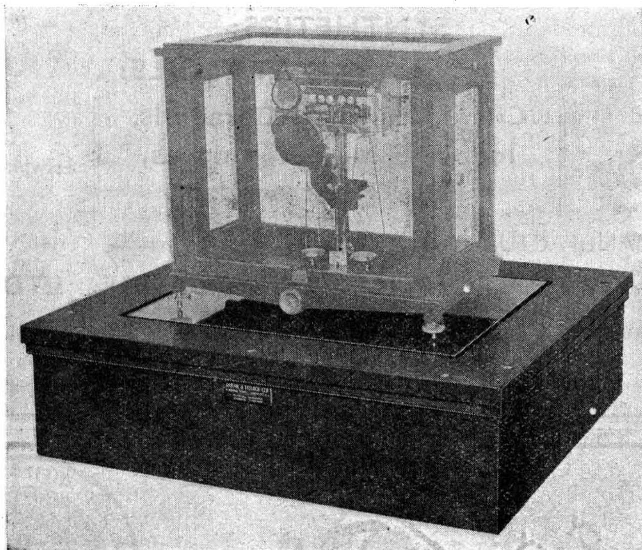
MEDICAL EVANS RESEARCH

Made at The Evans Biological Institute, by
EVANS SONS LESCHER AND WEBB, LTD.
LIVERPOOL AND LONDON

M33

THE G & T ANTI-VIBRATION BALANCE TABLE

Solves the most obstinate problem of balance vibration



Balance vibration is a very troublesome problem. It is especially acute in many war factories where, to save time in the transit of samples, the laboratory is installed in the works. Cases are known where the vibration is so severe as to cause fractional weights of small denomination to jump out of the pan.

The G & T Anti-Vibration Balance Table has been successful even under these conditions. It is applicable to any instrument in any situation where vibration is experienced—severe or mild, of high or low frequency, intermittent or continuous.

Leaflet GT1338A on application

GRIFFIN and TATLOCK Ltd

LONDON	MANCHESTER	GLASGOW	EDINBURGH
Kemble St., W.C.2	19 Cheetham Hill Rd., 4	45 Renfrew St., C.2	7 Teviot Place, 1

Established as Scientific Instrument Makers in 1826

REIGATE BRAND

Registered Trade Mark

NATURAL ISOLATES:
ESSENTIAL OILS:
SYNTHETICS:
FLOWER OILS:

'Phone
Reigate 2242

Citral, Eugenol, Geraniols,
Ionones, Methyl Ionones,
Hydroxycitronellal

Grams
Esswhite, Reigate

SOLE MANUFACTURERS:—

WHITE, TOMKINS & COURAGE, LTD
REIGATE, SURREY

Established 1841

FOR ACCURACY AND RAPIDITY
WHATMAN High Grade FILTER PAPERS
ARE ENTIRELY DEPENDABLE

Each grade is distinctively labelled

STOCKED BY LABORATORY FURNISHERS THROUGHOUT THE WORLD

IN SEALED BOXES

THE WHATMAN range covers all requirements of the chemist in every branch of industry and research.

In the event of difficulty in obtaining supplies, free samples, or copy of our descriptive booklet and price list, please write the Sole Sales Representatives:

H. REEVE ANGEL & COMPANY, LTD.
9, BRIDEWELL PLACE, LONDON, E.C.4.

Made only by
W. & R. BALSTON, Ltd.
KENT

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

PUBLIC ANALYSTS AND OFFICIAL AGRICULTURAL ANALYSTS COMMITTEE

THE members of this Committee are as follows: F. W. F. Arnaud, W. G. Carey, H. E. Cox (*Chairman*), B. Dyer, R. H. Ellis, J. Evans, L. Eynon, J. G. A. Griffiths, J. W. Hawley, E. Hinks, G. Hogan, E. B. Hughes, A. R. Jamieson, L. H. Lampitt, A. Lees, C. H. Manley, J. B. McKean, S. E. Melling, G. W. Monier-Williams, M. H. Pearson, W. H. Roberts, S. G. E. Stevens, C. J. H. Stock, J. R. Stubbs, R. W. Sutton, G. Taylor and E. Voelcker (*Hon. Secretary*).

This Committee has been authorised to invite other Public Analyst members of the Society to any of its meetings at which matters of sufficient general interest to Public Analysts are proposed for consideration. The Hon. Secretary of the Committee is Mr. E. Voelcker, 1, Tudor Street, London, E.C.4, to whom all communications should be addressed.

Obituary

ADOLPH JAFFÉ

ADOLPH JAFFÉ, who was elected a Fellow of the Institute of Chemistry in 1926, and had been a member of this Society since 1903, died at his home on March 20th at the age of 68. He was actively engaged in his practice as a consulting and analytical chemist, and his sudden death from a heart attack came as a great shock to his family and numerous friends.

Jaffé had been associated for over fifty years with his brother-in-law, Frederic William Richardson, Public Analyst for the West Riding of Yorkshire and the City of Bradford. In their early days they did a considerable amount of original work together and published papers on sugar, glycerin, olive oil, soap, gas analysis, etc. Of late, however, the demands of the practice had left little time for private investigation.

Jaffé had a most interesting life, filled with a variety of pursuits. For several years he was a member of the West Yorkshire Dragoons. Many will recall his great understanding of horses and remember the borzoi wolf hounds which accompanied him on walks. Fond of cycling, as a member of the Yorkshire Cycling Club he won a number of medals and cups for long-distance speed. He was also an expert swimmer, and more than once this saved him in his canoeing adventures on the English rivers. Outdoor life always appealed to him, and he spent his spare time camping in the Lake District and, before the war, touring on the Continent.

Music and literature were his recreations, and his loss will be felt locally, as he was one of the promoters of the Bradford Philharmonic, a founder member of the Bradford Music Club, and a regular supporter of all concerts in the district.

He leaves a widow, a married son, a daughter and four grandchildren.

F. W. M. JAFFÉ

HERBERT STANLEY REDGROVE

BY the sudden death of Herbert Stanley Redgrove, on March 13th, at the relatively early age of 56, the Society loses a member who had a wide range of interests and an original outlook.

Redgrove was educated privately and at the Regent Street Polytechnic, London. He took his B.Sc. (Lond.) in 1908, and was elected A.I.C. in 1922 and F.I.C. in 1931. He joined our Society in 1935. After taking his degree he returned to the Regent Street Polytechnic as a lecturer on mathematics and chemistry, and later held similar posts at West Ham Technical Institute and elsewhere. Meanwhile he contributed numerous articles to the scientific and technical press on a variety of themes and especially, in later

years, on perfumery and cosmetics, in the study of which he had specialised. He also published several books on these subjects, the best known of which, "*Hair Dyes and Hair Dyeing*," now in its third edition, was reviewed in THE ANALYST (1939, **64**, 637).

He was, however, perhaps best known for his writings on alchemy. Early in his scientific career he was associated with Professor John Ferguson and others in forming the Alchemical Society and was appointed editor of its journal; that Society was one of the many killed by the last war. Redgrove's book on "*Alchemy: Ancient and Modern*," first published in 1912, is an excellent survey, which brings out clearly the connection between the old alchemical doctrines and the conceptions of modern chemistry. He also published several books in which he attempted to establish a relationship between psychical ideas and modern science, notably "*A Mathematical Theory of Spirit*" (1912), "*Matter, Spirit and the Cosmos*," and "*Purpose and Transcendentalism*" (1920). His latest work, "*Joseph Glanvil and Psychical Research in the Seventeenth Century*," written in collaboration with I. M. L. Redgrove, is in the press.

Redgrove's personality was imprinted on everything that he undertook. Thus, he had definite views on education, and visited Russia with the official educational delegation in 1926. Again, while originally he had taken up field botany as a hobby, and had acquired an almost complete collection of British plants, this occupation led to an intensive study of medicinal plants, and he became a strong advocate for their cultivation in this country.

In addition to the circle of intimate friends who mourn him, many who knew him only professionally will miss seeing and talking to him at meetings and listening to his vigorous remarks in the discussions.

EDITOR

Notes on the Composition of Some Varieties of Onions

BY J. G. SHERRATT, B.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, October* 10, 1942)

THE composition of onions has not attracted much attention from chemists in this country, and authoritative information regarding the influence of climate, soil, variety, maturity and similar factors is not readily available. The following analyses of a few varieties of onions may therefore be helpful to those analysts who only occasionally have to examine onion-containing preparations, although their value is limited by the fact that all the samples, being grown within a comparatively small area in the North West of England, have been subject to similar climatic influences. The varieties of onions included James Keeping, Ailsa Craig, Nuneham Park, Bedfordshire Champion, Up-to-date, Brown Globe, and three samples of unknown origin and history.

ANALYTICAL METHODS.—The analyses refer only to the edible portions, the roots, stem and outer pigmented skin having been rejected. The prepared samples were shredded on a suet grater (with precautions to avoid loss of juice), and moisture and fibre were determined on suitable portions of the pulp. Determinations of sol. constituents were made in a soln. prepared by filtering a suspension of 50 g of the pulp, previously made up to 500 ml with recently boiled, cooled distilled water. To avoid decomposition the analyses were made with the minimum of delay.

Acidity.—All the samples gave a positive reaction for citric acid by the pentabromo-acetone test[1]; titratable acidity was calculated as $C_3H_4(OH)(COOH)_3.H_2O$.

Reducing Sugars in the extract were determined gravimetrically with Fehling's solution after neutralising acidity and then pptng. proteins with copper sulphate. *Non-reducing Sugars* were determined similarly in an aliquot portion of the extract after inversion with 5 ml of hydrochloric acid at 69–71° C. for 5 min.

Volatile Oxidisable Sulphur was determined by an arbitrary method, which gives reproducible results only when attention is paid to all the following details:—Wash 50 g of grated onion pulp into an 800-ml flask with 400 ml of 1% v/v *o*-phosphoric acid. Add 0·1 g of powdered pumice and boil under reflux for 2 hr. in an atmosphere of carbon dioxide. Cool and leave overnight, avoiding access of air. Next day, distil 300 ml of the liquid, collecting the distillate in 20 ml of sat. bromine water. A current of carbon dioxide should be maintained in the apparatus during distillation, and the receiving end of the

condenser should dip below the surface of the bromine water. Add 1 ml of conc. hydrochloric acid to the distillate and evaporate on a hot plate until the excess bromine is removed. Precipitate sulphates from the boiling liquid with barium chloride soln., and, after deduction of a blank, calculate as p.p.m. of sulphur.

Lead Number.—In fresh onions the "lead number" was determined on 100 ml of the extract. From dried onion powder an extract was made from 25 g suspended in water and made to 500 ml and filtered. To 50 ml of this extract (100 ml with fresh onions) add 50 ml of 2% w/v lead acetate soln., make up the mixture to 250 ml and filter. Boil 50 ml of the filtrate and titrate sol. lead with a 1% w/v soln. of ammonium molybdate, using tannin as external indicator. Titrate similarly a blank containing an equiv. quantity of lead acetate. From the difference between the two results calculate the lead number, *i.e.*, the number of ml of 2% lead acetate soln. pptd. by 10 g of onion sample.

The results of the analyses are given in the following tables.

TABLE I.—COMPOSITION OF FRESH ONIONS

	Number of samples	Number of varieties	Max.	Min.	Aver.
Loss on drying at 100° C., %	6	3	92·1	88·9	91
Crude fibre, %	6	3	0·7	0·4	0·5
Sol. solids: total, %	16	7	9·0	6·36	7·4
mineral, %	16	7	0·70	0·48	0·56
organic, %	16	7	8·36	5·89	7·07
Ratio $\frac{\text{Sol. organic}}{\text{Sol. mineral}}$	16	7	$\frac{17}{1}$	$\frac{11}{1}$	$\frac{12}{1}$
Sol. ash: $Ca_3(PO_4)_2$ (% of ash)	4	4	50	41	—
Cl, %	3	2	0·028	0·025	—
Fe_2O_3%	2	2	0·0006	0·0003	—
SO_3	10	5	present in traces		
Acidity (as citric acid), %	10	5	0·45	0·23	0·39
Reducing sugar (as dextrose), %	8	5	4·8	0·0	2·9
Non-reducing sugar (as sucrose), %	8	5	4·0	0·4	2·8
Sol. N × 6·25, %	7	5	1·31	0·98	1·10
Volatile sulphur, p.p.m.	10	5	106	86	93

TABLE II.—INFLUENCE OF SEASON (VARIETY: JAMES KEEPING)

	1940 Ripe	1941 Unripe	1941 Ripe	1942 Ripe
Total sol. solids, %	6·1	7·26	8·96	6·4
Mineral sol. solids, %	0·52	0·61	0·60	0·50
Organic sol. solids, %	5·58	6·65	8·36	5·90
Acidity (citric), %	0·38	0·38	0·42	0·23
Volatile sulphur, p.p.m.	90	86	96	88

TABLE III.—TWO VARIETIES GROWN IN ADJACENT PLOTS. SEASON 1941

	"James Keeping"	"Up-to-date"
Sol. solids, %	8·96	8·62
Sol. mineral solids, %	0·60	0·48
Sol. organic solids, %	8·36	8·14
Acidity (as citric acid), %	0·42	0·30
Volatile sulphur, p.p.m.	96	105

TABLE IV.—DRIED ONION POWDER (IMPORTED)

	%		%
Moisture	9·0	Sol. solids	77·8
Oil	1·0	Sol. ash	1·8
N × 6·25	6·8	Sol. organic	76·0
Crude fibre	3·4	Reducing sugars	
Ash	3·2	(as dextrose)	9·7
Acidity	1·6	(as maltose)	18·8
Diff.	75·0	Non-reducing sugars (as sucrose)	52·6
	100·0	Volatile sulphur, p.p.m.	5·75
		Lead number	30

DISCUSSION OF RESULTS.—Onions appear to consist of *ca.* water, 88–92; fibre, 0·5; sol. nitrogen ≡ *ca.* 1% of protein; sugars, 6–9; acid (as citric acid), 0·2–0·5; sol. ash, 0·5–0·8%. There are traces of volatile organic sulphides, and it is to these that the pungency of onions is mainly due.[5]

In the examination of commercial preparations containing onions, no one component or value can be relied upon to afford a sound basis for judgment, but a reasonably close approximation to the amount of onion present can often be made by careful consideration of some or all of the data mentioned above, due allowance being made, of course, for the influence of components of "non-onion" constituents of a mixture. The figures that are regarded as most generally useful in assessing the value of commercial liquid preparations purporting to contain onion extractives are acidity, sol. organic and mineral solids, ratio of sol. organic to sol. mineral matter, percentage of sugars, volatile oxidisable sulphur and, qualitatively, the presence of phosphate in the soluble ash.

Acidity.—This being of a low order, its value for calculating the onion % in a commercial extract is limited if the preparation has been made with water of high carbonate hardness, The determination of acidity is useful in the analysis of "onion juice" and also in the examination of mixtures of cereals and onion powder.

The ratio of organic to mineral extractives is high in genuine onions and only in very dil. preparations will the mineral solids contributed by a saline water seriously affect this characteristic. If there is sufficient of the sample, assistance may be obtained from a determination of sol. phosphate. In genuine onion extracts made with distilled water, phosphates, calc. as $Ca_3(PO_4)_2$, contribute 40 to 50% of the sol. ash.

Volatile oxidisable sulphur[2,3,5] is present in all onions. Unfortunately, it is not specific, since synthetic oil of garlic and other organic sulphides respond to the test. The figures relating to sulphur can only be used to calculate the approx. % of onion in a mixture if other sulphide-containing substances are known to be absent. Moreover, the ultimate concn. of volatile sulphur in onions is low and, unless the proportion of onion in relation to other components of a mixture is substantial, the quantity of sample required to provide reliable results may not be available. These considerations seriously limit the value of the determination of volatile sulphur in commercial liquid preparations of onion.

Influence of Drying.—It is probable that some of the organic sulphides of fresh onions will be lost during drying and that the ratio of sulphur to total solid matters will thereby be reduced. Enough sulphur remains in dried onion, however, to afford useful indications in the examination of mixtures of powdered onion and cereals and of "Sage and Onion Stuffing." Authentic specimens of dried onion are difficult to obtain, and information as to the extent of variation of the volatile sulphur content that may be expected in commercial samples is not yet available. Nevertheless, the determination of volatile sulphur in mixtures is of value, at least in relation to questions of pungency.

"Sage and Onion Stuffing."—Many commercial samples consist of bread with a little powdered onion and dried sage, and their analyses present considerable difficulty, owing to the presence of titratable acidity, maltose, dextrin, sol. nitrogenous bodies and phosphates in bread. Hence criteria that have been found useful in the examination of liquid preparations are not applicable to "Stuffing." Qualitative evidence of the presence of dried onion may be afforded by the microscope, and some assistance may also be obtained from a knowledge of the volatile sulphur content. Subject to the reservation that comparatively few samples have as yet been investigated, it appears that the lead number may also be helpful in this connection. Hinton has shown[4] that for fruit the "lead number" is in fact a measure of certain fruit acids, notably citric and malic acids. He has also demonstrated that lactic acid (which is present in bread) does not ppt. lead from solns. of lead acetate. As the acidity of onions is mainly due to citric acid, it is suggested that the determination of the lead number on an aqueous extract of "Stuffing" offers means of arriving at the approx. proportion of onion present. In experimental mixtures, containing respectively 4 and 6% of powdered onion with bread and a trace of dried sage, a satisfactory estimate of the proportion of onion was calculated from the lead number of extracts of the mixtures, it being assumed that a lead number of **31** represented 100% of onion powder. Approx. correct estimations were also made on similar lines with artificial mixtures of powdered onion and wheat flour.

REFERENCES

1. Elsdon, G. D., and Lees, A., ANALYST, 1933, **58**, 328.
2. Chapman, A. C., *id.*, 1922, **47**, 204.
3. Dyer, B., Taylor, G., and Hamence, J. H., *id.*, 1941, **66**, 9.
4. Hinton, C. L., *id.*, 1934, **59**, 248.
5. Platenius, H., and Knott, J. E., *J. Agric. Sci.*, 1941, **62**, 371; Abst., ANALYST, 1941, **66**, 389.

46, LEGH STREET, WARRINGTON

October, 1942

A Process for the Analysis of Tungsten Carbide Tips*

By B. S. EVANS, M.C., M.B.E., D.Sc., F.I.C., and F. W. BOX, B.Sc.

The tips in question consist essentially of a sintered mass of tungsten carbide in a matrix of cobalt or occasionally some other metal. To the extreme hardness, which is their main property, may be joined great toughness, with a suitable proportion of matrix; in that event it may be almost impossible to reduce them to a state approaching powder or, occasionally, even to subdivide them at all except by cutting (with a diamond wheel). It is therefore very desirable to have a process of analysis which does not rely on a fine state of division of the sample for the initial attack; also, even with a brittle material, the great hardness causes serious contamination with iron when the material is crushed in a steel mortar. The obvious method of attack, *i.e.*, by nitric and hydrofluoric acids in a platinum basin, is valid for these substances but, when the sample consists, say, of a single lump, it may be very protracted, taking several days for completion; also, of course, it does not permit determination of silicon. The process given below does not use hydrofluoric acid in the initial attack; it is available for samples in relatively large lumps; it avoids the ammonia separation of iron from cobalt,[1] the somewhat difficult pptn. of cobalt sulphide and the pptn. of nickel glyoxime in presence of preponderating amounts of $Co^{\cdot\cdot}$ ions,[2] whilst allowing the complete analysis (excluding carbon) to be carried out on a single sample; it introduces no iron and provides for the determination of silicon.

General Principles.—Initial attack is by fusion, with potassium pyrosulphate; this generally needs repeating 2 or 3 times, with intermediate burning of the residue. The solution of the melt in strong oxalic acid soln. leaves only crude silica insoluble. Tungsten is separated and determined by the methods of Schoeller, Lambie, etc.; titanium and iron are pptd. by cupferron and subsequently separated by Schoeller's method; cobalt and nickel are pptd. together as cobalticyanides and afterwards separated by Evans's method.

Process.—Place the weighed sample in a large silica crucible and add a few g of potassium bisulphate; cover the crucible with a platinum basin placed upright (not inverted) upon it and made to fit as closely as possible and put a small Bunsen flame below it so that fusion may begin at a low temp. As fusion proceeds raise the temp. at intervals until, after about ½ hr., the full force of the burner is used. Attack, with effervescence, is fairly violent at the outset, the practical cessation of effervescence marking the end of effective fusion; a single fusion very rarely produces complete attack. Allow the crucible to cool (the melt will probably be dark blue when hot and pink when cold, owing to the cobalt), introduce a few g of oxalic acid crystals and about half fill it with hot water, rinsing-in the bottom of the platinum basin at the same time; dissolve the melt by heating and, if necessary, further treatment with oxalic acid and water and then filter it into a beaker, washing the residue with hot water. Reserve the filtrate, return the filter and residue to the silica crucible, and burn off. If the residue is whitish or free from metallic-looking particles, transfer it to a platinum dish and eliminate the silica† by treatment in the usual manner with sulphuric and hydrofluoric acids; if, as is probable, the residue appears to contain unattacked material, repeat the fusion, etc., exactly as before, adding the oxalic filtrate to the former one. Again repeat this cycle until the residue is ready for sulphuric and hydrofluoric acid treatment, fuse the residue from this with a little bisulphate, take up with hot water, and add the soln. to the bulk of the combined filtrates. Two or three fusions are generally necessary. The silicon has now been eliminated and the rest of the material should be in solution; add sulphuric (5 ml conc.) and nitric (approx. 20 ml conc.) acids to the soln. and then boil down and evaporate to "fuming" to destroy the oxalic acid. Take up the residue, after cooling, with dil. (5%) nitric acid, boil and allow to settle. Filter off the pptd. tungstic oxide and wash thoroughly with dil. sulphuric acid containing potassium bisulphate; reserve the filtrate and continue the washing with ammonium nitrate soln. (5%) to remove potassium bisulphate; reject these latter washings and reserve the filter and precipitate (crude WO_3). Treat the reserved filtrate with excess of sodium hydroxide and hydrogen

---

* Communication from Armaments Research Department, formerly Research Department, Woolwich.

† For the determination of silicon it is best to use a separate sample attacked in a platinum dish. In presence of niobium this treatment must be replaced by burning off the pulp and fusion with pyrophosphate.

peroxide, boil for 10 min. and filter off the pptd. cobalt, nickel, iron and titanium, washing the ppt. with hot sodium chloride soln. (5%) and reserving it, and treating the filtrate by Lambie's method[3] for recovery of residual tungsten. Add the ppt. of residual tungsten thus obtained to the main tungsten ppt. and burn both off together in a weighed platinum dish; treat the residue with hydrofluoric and sulphuric acids and re-ignite. At this stage there are:—(*a*) A burnt-off residue of tungstic oxide containing some of the titanium and traces of iron, etc., (*b*) a ppt. containing the main bulk of the cobalt, iron and nickel and the remainder of the titanium.

Purification of the Tungstic Oxide (Powell, Schoeller and Jahn's method[7]).—Fuse the crude tungstic oxide with sodium carbonate; disintegrate the melt with a hot soln. of 10 g of sodium hydroxide in 50 ml of water, transfer the soln. and disintegrated solid to a nickel dish, rinsing in with 50 ml of water. Leave until cold, filter and wash the residue with half-saturated sodium chloride soln., reserving both filter and filtrate. Add phenolphthalein to the filtrate and just discharge the colour with dil. hydrochloric acid; then leave on the steam-bath, just discharging the red colour with dil. hydrochloric acid from time to time. When the titanium has flocculated filter it off and wash with half-saturated sodium chloride solution; then pulp the filter, together with that containing the residue from the sodium hydroxide treatment, with dil. hydrochloric acid, heat and filter off the pulp, washing with hot water. Ppt. the iron and titanium in the filtrate with ammonia, filter off the ppt., wash, ignite, and weigh the residue. This weight, deducted from that of the crude tungsten ppt., gives the WO_3 obtained from the weight of sample taken. This residue, containing iron and titanium, is reserved.

Precipitate containing Iron, Titanium, Cobalt and Nickel.—Transfer the filter and ppt. to a beaker, add 40 ml of dil. (1 : 1) hydrochloric acid, boil and filter off the pulp, washing with hot water up to a bulk of 200 ml. Cool, add 6% cupferron soln. until pptn. seems complete (white ppt. on further addition). Allow to settle, filter and wash the ppt. (iron and titanium) with dil. (2%) hydrochloric acid containing a little cupferron; reserve the filtrate (cobalt and nickel) and ignite the ppt. in a weighed platinum or silica crucible. The weight of the residue + the weight of the reserved residue from the purification of the tungsten gives the total iron and titanium oxides obtained from the sample taken. Add the residue obtained from the purification of the tungsten to the residue just weighed, fuse with potassium pyrosulphate, and dissolve the melt in hot water. If the titanium is present only as a trace, determine it colorimetrically in this soln. in the usual way and deduct the titanium oxide thus obtained from the total residue, the remainder being ferric oxide, from which the amount of iron is calculated. If the titanium is more than a trace, add citric acid to the soln., make ammoniacal and pass hydrogen sulphide to ppt. the iron; heat to boiling, digest, filter and wash the ppt. with a soln. containing 5% of ammonium chloride and 5% of ammonia.

Dissolve the iron sulphide ppt. in hot dil. *aqua regia*, wash the filter with hot water and re-ppt. the iron in the filtrate (which should now be free from titanium) with ammonia. The iron ppt. can be dealt with by any of the usual methods. The titanium can be determined as a difference figure, subtracting the ferric oxide from the weight of mixed oxides, or it can be positively determined in the filtrate from the iron sulphide by boiling off the ammonium sulphide, neutralising with hydrochloric acid and adding an excess of 10% of the total bulk, and pptng. with cupferron as before. This ppt., after filtration and washing as before, is burnt off and weighed as TiO_2.

Cobalt and Nickel Filtrate reserved from first Cupferron Precipitation (Evans's method[4]).—Add 20 ml of 10% potassium cobalticyanide soln., stir in a little pulp and allow to settle. Filter off the ppt. on close-packed pulp and wash with 5% sodium chloride soln. Transfer the filter to a beaker and treat with 100 ml of 5% sodium hydroxide soln. and 10 ml of hydrogen peroxide (20 vol.); heat to boiling and filter off the pulp with the pptd. nickel and cobalt hydroxides on a small pulp filter. Wash thoroughly with 5% sodium chloride soln., then re-transfer the filter to a beaker and dissolve the nickel and cobalt hydroxides by boiling with a mixture of dil. (1 : 1) hydrochloric acid and a little sulphurous acid. Filter off the pulp, wash well with hot water and evaporate the filtrate until crystallisation begins; dilute to about 100 ml, add 20 ml of 20% ammonium chloride soln. and ammonia in excess, then 5 ml of 10% potassium cyanide soln., followed by a few drops of hydrogen peroxide (20 vol.); boil for about 5 min. to convert the cobalt into cobalticyanide. Slightly cool the liquid, add 10 ml of dil. (1 : 1) ammonia and 10 ml of hydrogen peroxide (20 vol.)

and boil gently for 10 min. This treatment converts the whole of the nickel cyanide complex into Ni¨ and destroys the excess cyanide while leaving the cobalticyanide untouched. If necessary, add a little more ammonia until the odour is perceptible, add 0·5 g of solid dimethyl glyoxime, boil for 1–2 min. and completely cool. Filter off the pptd. nickel glyoxime and wash with cold water; determine the nickel in the ppt. by any of the usual methods; reserve the filtrate.

Cobalt.—Neutralise the reserved filtrate with hydrochloric acid and add 20 ml in excess, then add excess of 20% cupric chloride soln. and heat to boiling, stir in a little pulp and allow to settle until cool. Filter off the pptd. copper cobalticyanide and wash with dil. (5%) hydrochloric acid containing 1% of cupric chloride. Transfer the filter to a beaker, add 5 ml of sulphuric acid (conc.) and 20 ml of nitric acid (conc.) and boil down, with a cover-glass on, until the residual organic matter chars; then add nitric acid in repeated small amounts, with intermediate boiling down to charring until the organic matter is completely destroyed. This is shown by the liquid becoming and remaining blue, with no tendency to develop a brown tint, even after strongly "fuming" for several min. Cool, take up with 100 ml of water, heat to boiling, cool and ppt. the copper by passing hydrogen sulphide. Filter off the copper sulphide and wash it with sodium chloride soln., boil the hydrogen sulphide out of the filtrate, and determine the cobalt by any preferred method (*e.g.*, precipitating with sodium hydroxide and hydrogen peroxide, filtering, washing once or twice with dil. potassium nitrate soln., dissolving in a minimum of dil. nitric acid containing a few drops of sulphurous acid, washing with hot water, boiling, cooling and finishing volumetrically).[5]

Niobium and Tantalum.—Niobium is occasionally present as a constituent of these materials. If present, niobium and tantalum follow the titanium throughout the process and the three metals must be separated by the processes published by Schoeller and his collaborators.[6,7,8] If titanium is only present as a trace it should be determined colorimetrically and corrected for.

*Carbon.**—If the sample can be crushed to pass a 60–mesh sieve, it can be burnt as with steel. If it is uncrushable, pieces are flattened as thin as possible, 0·5 g is mixed with 2 g of electrolytic iron, and the sample is burnt as usual at 1100° C.; it is then withdrawn from the furnace, ground in an agate mortar and re-burnt. This process is repeated, if necessary, until all the sample is reduced to a fine powder.

As it was impracticable to test this method on synthetic samples, it was tested on a single sample of a commercial product which did not contain titanium, varying amounts of titanium being added to the soln. obtained after fusion and the weights taken adjusted to correspond with 10%, 8%, 5% and 2% of titanium respectively. The titanium was added in the form of titanium potassium oxalate. The per cent. results obtained were as follows:—

	Original sample	10% Ti	8% Ti	5% Ti	2% Ti
Carbon	4·50	4·05	4·14	4·27	4·41
Silicon	0·24	0·19	0·22	0·22	0·23
Tungsten	85·39	76·96	78·67	81·21	83·68
Iron	0·32	0·36	0·38	0·34	0·33
Nickel	0·09	0·08	0·08	0·09	0·08
Cobalt	8·93	7·90	8·28	8·51	8·75
Titanium	—	10·02	7·99	4·95	2·10
	99·47	99·56	99·76	99·59	99·58

If these results are calculated back to the weight of original sample (ignoring titanium) they give, per cent.

	Original sample	10% Ti	8% Ti	5% Ti	2% Ti
Carbon	4·50	4·50	4·50	4·50	4·50
Silicon	0·24	0·21	0·24	0·23	0·23
Tungsten	85·39	85·51	85·49	85·49	85·38
Iron	0·32	0·40	0·41	0·36	0·34
Nickel	0·09	0·09	0·09	0·09	0·08
Cobalt	8·93	8·78	9·00	8·95	8·93
	99·47	99·49	99·73	99·62	99·46

* Unpublished communication from Mr. A. T. Etheridge.

The following points about these figures must be noted:—(*a*) It was manifestly impossible to determine carbon on the mixed samples; the carbon figures in the tables therefore are calculated from the value obtained on the original sample. (*b*) The original method did not include hydrofluoric acid treatment of the tungstic oxide; the many analyses done on a variety of samples by this method invariably gave slightly high results (approx. 101%). As this does not occur with hydrofluoric acid treatment, it is presumably due to silica derived from the glassware. (*c*) The sample to which titanium was added had been ground in an iron mortar subsequent to the original analysis; the slight iron contamination resulting is reflected in the figures.

Thanks are due to the Director of Scientific Research for permission to publish this paper.

REFERENCES

1. Swift, E., and Barton, R., *J. Amer. Chem. Soc.*, 1932, **54**, 2220.
2. Feigl, F., and Kapulitras, H. J., *Z. anal. Chem.*, 1930, **82**, 417.
3. Lambie, D. A., ANALYST, 1939, **64**, 484.
4. Evans, B. S., *id.*, 1943, **68**, 67.
5. —— *id.*, 1937, **62**, 366.
6. Schoeller, W. R., *id.*, 1932, **57**, 750.
7. Powell, A. R., Schoeller, W. R., and Jahn, C., *id.*, 1935, **60**, 506.
8. Schoeller, W. R., "*The Analytical Chemistry of Tantalum and Niobium.*" London: Chapman & Hall, 1937.

February, 1943

The Rapid Photometric Determination of Copper in Ferrous Materials

BY F. W. HAYWOOD, B.SC., PH.D., F.I.C., AND A. A. R. WOOD

As accepted methods for determining copper in ferrous materials are somewhat tedious, it was thought that a rapid and accurate absorptiometric method would prove of value. The Spekker photoelectric absorptiometer has proved an accurate instrument.[1,2,3] Furthermore, the colour produced in the reaction of cupric ions with sodium diethyldithiocarbamate[4] was found stable under specific conditions. From an experimental study of the reaction the technique outlined below was developed.

DISCUSSION OF METHOD.—The ferrous alloy is dissolved in a mixture of sulphuric and phosphoric acids, and the colour due to copper is produced in an ammoniacal soln. by addition of sodium diethyldithiocarbamate, a suitable colloid being used to prevent pptn. of the complex; the colour is permanent for 3 hrs. Other common elements in ferrous materials found to interfere are ferrous and ferric iron, chromium, nickel and cobalt; the effect of the last element was ignored, as cobalt is rarely present intentionally in copper-bearing steels and cast irons; metals of the iron group are suppressed by adding ammonium citrate and ammonia after oxidation of the soln. with nitric acid. Excess of ammonium citrate is required to produce a constant minimum iron colour, allowed for by a blank reading on the absorptiometer. Under the conditions cited, nickel produces a greenish-yellow colour or turbidity and various attempts to suppress this were unsuccessful. It was proved that excess of dimethylglyoxime did not affect the formation of the copper complex. Nickel was separated as the dimethylglyoxime compound in slightly ammoniacal soln., but excess of ammonia is required to separate the copper salts quantitatively from this ppt.

REAGENTS.—(1) "*Spekker*" *Acid.*[1]—Make up 150 ml of phosphoric acid (sp.gr. 1·75, A.R.) and 150 ml of sulphuric acid (sp.gr. 1·84, A.R.) to 1 litre with water. (2) *Nitric acid.*—Sp.gr. 1·20, A.R. (3) *Ammonium citrate.*—Add 500 ml of ammonia (sp.gr. 0·880) to 500 g of citric acid (A.R.) until solution is complete, and then add 250 ml of water. (4) *Ammonium hydroxide.*—Dilute 200 ml of ammonia (sp.gr. 0·880) to 1 litre. (5) *Colloid.*—Dissolve 1·0 g of gum acacia in 100 ml of hot water and make up to 200 ml with water. (6) *Sodium diethyldithiocarbamate.*—Dissolve 0·50 g in 250 ml of water; store in a bottle of dark glass. (7) *Dimethylglyoxime.*—Dissolve 1·0 g in 100 ml of industrial spirit. (8) *Copper.*—Hilger's spectroscopically pure copper.

PROCEDURE.—*Copper percentage* 0–1% *and* 0–5%.—For alloys containing up to 1% of copper, take 1 g of the alloy; for higher concns. take proportionately less. Add 40 ml of "Spekker" acid and heat to dissolve, oxidise with 5 ml of nitric acid and boil to complete solution and expel nitrous fumes. "Fume" down, if necessary, to decompose carbides, cool to room temp. and make up to 100 ml with water. Two slightly different alternative procedures are provided, *viz.*, for steels containing nickel and those without nickel.

(A) *Steels not containing nickel.*—Take two 5-ml aliquot portions of the above soln. and colour as follows:—

(i) *Blank solution.*—Add 10 ml of ammonium citrate soln., 10 ml of ammonium hydroxide soln. and 10 ml of gum acacia soln. and make up to 100 ml with water.

(ii) *Colour solution.*—Add 10 ml of ammonium citrate soln. 10 ml of ammonium hydroxide soln., 10 ml of gum acacia soln. and 40 ml of water. Shake well, then add 10 ml of sodium diethyldithiocarbamate soln., and finally make up to 100 ml with water.

Measure the absorption of these solns. on the Spekker photoelectric absorptiometer, using 2-cm cells, Ilford Spectrum Blue filters No. 602, and a water-to-water setting[1] of 1·0. The difference between (i) and (ii) represents the colour due to copper and is read off on the appropriate calibration graph.

(B) *Steels containing nickel.*—Take two 5-ml aliquot portions of the original soln. and colour as follows:

(i) *Blank solution.*—Exactly as in (A) above.

(ii) *Colour solution.*—Add 10 ml of ammonium citrate soln., 10 ml of ammonium hydroxide soln. and 30 ml of water. Then add 2·5 ml of dimethylglyoxime for every 5% of nickel present in the steel originally and warm at *ca.* 70° C. for 15 min. Add 5 ml of ammonia (sp.gr. 0·880), filter through a Whatman 41 filter-paper and wash with 20–25 ml of warm water. Cool the filtrate and add 10 ml of gum acacia soln. and 10 ml of sodium diethyldithiocarbamate soln. and make up to 100 ml with water.

Measure the absorption of these solns. as described above under (A).

Copper percentage 0–0·25%.—For the determination of copper in ferrous alloys in which the copper concn. does not exceed 0·25%, a slightly different procedure is necessary. Dissolve the steel sample (1 g) and treat the soln. as described for steels containing 0–1% of copper. Take two 10-ml aliquot portions and colour as follows:

(i) *Blank solution.*—Add 20 ml of ammonium citrate soln., 20 ml of ammonium hydroxide soln. and 10 ml of gum acacia soln. and make up to 100 ml with water.

(ii) *Colour solution.*—Add 20 ml of ammonium citrate soln., 20 ml of ammonium hydroxide soln. and 10 ml of gum acacia soln. and shake well; then add 10 ml of sodium diethyldithiocarbamate soln., and make up to 100 ml with water.

Measure the absorption of these solns., using 4-cm cells, Ilford Spectrum Blue filters No. 602 and a water-to-water setting of 1·0. Remove nickel, if present, as previously described, but adding 5 ml of dimethylglyoxime soln. for every 5% of nickel present in the steel.

The full procedures given for steels apply equally to cast irons, except that, after boiling to dissolve carbides and expelling nitrous fumes, any residual graphite is filtered off in a sintered glass funnel and the soln. is then made up to 100 ml with water.

CALIBRATION GRAPH.—(*a*) *Copper percentage* 0–1% *and* 0–5%.—Dissolve 0·50 g of spectroscopically pure copper in 30 ml of nitric acid (sp.gr. 1·20), boil to expel nitrous fumes and make up to 1 litre with water. Dilute 50 ml of this soln. to 500 ml. Run from a burette 1 ml, 2 ml, 3 ml, etc., up to 10 ml of this soln.; to each vol. add 2 ml of "Spekker" acid and colour the soln. as previously described under (A) (ii). At the same time make a blank determination on the normal reagents used, *i.e.*, excluding the copper soln., and check these periodically. Measure the absorption of these solns. on the absorptiometer, using 2-cm cells as described above.

(*b*) *Copper percentage* 0–0·25%.—Dilute 25 ml of the original copper soln. to 500 ml. Run from a burette 1 ml, 2 ml, 3 ml, etc., up to 10 ml, of this soln., and to each vol. add 4 ml of "Spekker" acid; colour the soln. as previously described. Make a corresponding blank determination and check the solns. periodically. Measure the absorption of the solns. in 4-cm cells.

Calibration graphs thus constructed are practically linear.

RESULTS.—The methods described were applied to a wide variety of steels and cast irons. Representative results are given in Table I.

TABLE I

Ferrous alloy	Percentage composition Cu	Ni	Cr	Mn	Copper by absorptiometric method No Ni separation	Nickel separated
Austenitic cast iron* (No. 173)	4·73	13·45	3·97	1·01	——	4·73
White cast iron	0·93	—	0·04	0·49	0·92	—
Grey cast iron	0·82	—	0·09	0·77	0·82	—
Carbon steel A	0·34	—	0·87	0·87	0·33	—
„ „ B *No. 213) ..	0·12	0·24	0·029	0·72	—	0·117
„ „ C *(No. 215) ..	0·08	0·10	0·02	0·42	—	0·075
„ „ D *(No. 154) ..	0·03	0·27	0·013	0·527	—	0·033
Stainless steel *(No. 209) ..	0·034	8·36	18·71	0·38	—	0·030

*British Chemical Standards.

The accuracy of the results obtained by the absorptiometric method was of the same order as by the standard gravimetric and volumetric methods of analysis for copper in ferrous alloys. An examination of all the results obtained showed that by the method devised the order of accuracy was ±0·003% for alloys containing up to 0·25%, and ±0·01% for alloys containing up to 1%.

SUMMARY.—A method has been worked out and applied to the determination of copper in ferrous alloys by measurement of the absorption of the golden colour produced in the interaction of copper salts and sodium diethyldithiocarbamate. Under the conditions described, nickel is the only common interfering element; its interference has been overcome by the rapid removal of nickel salts with dimethylglyoxime. Whilst the order of addition of the reagents is critical, the amount added need only be within 10% of the volumes prescribed.

The method discussed is rapid, accurate and suitable for routine work; a complete determination on a steel or cast iron containing nickel can be effected in 15–20 min. after initial solution. This method can be satisfactorily fitted into the latest composite method for steels given by Vaughan.[3]

The work here described has been carried out in the laboratory of the Wild–Barfield Electric Furnaces, Ltd., and we wish to thank the directors for permission to publish it.

REFERENCES

1. Vaughan, E. J., "*The Use of the Spekker Photoelectric Absorptiometer in Metallurgical Analysis.*" Monograph published by The Institute of Chemistry, 1941.
2. British Aluminium Co., Ltd., "*Analysis of Aluminium and its Alloys*, 1941.
3. Vaughan, E. J., "*Further Advances in the Use of the Spekker Photoelectric Absorptiometer in Metallurgical Analysis.*" Monograph published by The Institute of Chemistry, 1942.
4. Callan, T., and Henderson, J. A. R., ANALYST, 1929, 54, 650.

RESEARCH DEPARTMENT, WILD-BARFIELD ELECTRIC FURNACES, LTD.
WATFORD, HERTS.

November, 1942

The Determination of Small Amounts of Aluminium in Water by means of Haematoxylin

BY G. U. HOUGHTON, M.Sc., F.I.C.

AT waterworks where aluminium compounds are used in the purification of the supply it is often necessary to determine the residual alumina at the various stages of treatment. The method must be one of high sensitivity, since the amount of aluminium to be determined will normally be less than 1 p.p.m., and for routine control purposes it should be capable of direct application without preliminary concentration or separation of interfering substances. The aurine tricarboxylate method worked out by Lampitt and Sylvester[1] was primarily devised for foodstuffs and mainly for amounts of aluminium above 1 p.p.m., which is likely to be the upper limit of concn. to be determined in water treatment. The very minute amount of aluminium present as impurity in the reagent sodium hydroxide used (*e.g.*, 0·005% in AnalaR NaOH) is a further drawback, and a very rigid control of

*p*H appears to be necessary to prevent fading of the lake. For these reasons attention has been concentrated on the haematoxylin method. This method, as described by Hatfield,[2] has been widely used, and is given by the American Public Health Association[3] as a "non-standard" one for use in waterworks control. The sample is treated successively with sat. ammonium carbonate and neutral aqueous haematoxylin solns. and left for 15 min. for the lake to form. The soln. is then slightly acidified with acetic acid and the colours are matched against aluminium standards prepared in distilled water. Although this simple procedure sometimes works well, it has several disadvantages.

Difficulties with the Haematoxylin Method.—Two of the reagents, sat. ammonium carbonate and neutral haematoxylin solns., are somewhat unstable. The colour change up to 0·4 p.p.m. is from orange to dark brown and is not very satisfactory for matching; moreover, the colours are so dense above 0·15 p.p.m. that comparisons have to be made by viewing through the sides of the tubes.

There are also difficulties with interfering substances. In particular, calcium and magnesium salts modify the colour of the aluminium lake and, if calcium equiv. to more than 100 p.p.m. of $CaCO_3$ is present, considerable errors are introduced when the sample is matched against standards prepared in distilled water. Hatfield stated that iron in amounts over 0·1–0·2 p.p.m. interferes, but unless the amount exceeded 1 p.p.m., he did not regard the interference as serious. Expts. during the present investigation have indicated that even 0·2 p.p.m. of ferric iron cannot be neglected, more especially if the amount of aluminium to be determined is of the same order. Small quantities of manganese, although of less common occurrence, may also interfere. Traces of copper also vitiate the results, and this may be of importance where coagulation of a supply follows the use of copper sulphate as an algicide. The work of Brockman[4] indicated that under such conditions any residual copper would be co-pptd. with the alumina floc and that none would remain after filtration. The water, after coagulation but before filtration, may, however, contain appreciable amounts of copper, probably adsorbed on particles of floc, and such copper may interfere in the determination of residual alumina at this stage of treatment. While it is doubtful if more than 0·2–0·3 p.p.m. of copper would ever be encountered in this way, even this amount may modify the haematoxylin colour.

Difficulties with interfering ions are partly overcome if the standards used in matching can be prepared from the actual raw water before coagulation. This, however, is not always possible, *e.g.*, if the raw water is turbid. Hatfield, who was primarily concerned with filtered water, suggested that, if other ions interfered, the standards be prepared in raw water which had been filtered through a Berkefeld filter, but obviously the use of distilled water for the standards is more convenient.

Development of Modified Procedure.—It was soon found, when testing coagulated but unfiltered waters, that reliable results could only be obtained if the sample was first slightly acidified so as to dissolve any particles of alumina floc.

In the present work the haematoxylin soln. was prepared by dissolving the dyestuff in very dil. hydrochloric acid. This acid reagent was found to be much more stable and resistant to oxidation than the neutral soln. usually employed; it retains its sensitivity for at least 2 months.

Hatfield showed that the optimum *p*H for aluminium lake formation is about 8·3, but he preferred to match the colours after a final acidification, which lowered the *p*H to 4·5. It would appear, however, that at such a low final *p*H there is some risk of destroying part of the lake already formed under optimum conditions in the first stage of the test. In the proposed modification the final *p*H of the soln. is *ca.* 6·8, and, although the final colour then develops rather slowly, once formed it is very stable, and an improved colour change is obtained at the lower aluminium concns.

Preliminary expts. with hard waters also showed the advantage of carrying out lake formation in presence of excess ammonium acetate. Pptn. of any calcium carbonate was thereby avoided and the interference of the hardness salts was markedly less, although addition of some sodium carbonate was necessary to raise the *p*H of the solution sufficiently for full lake formation. Unfortunately the test was still found to be very sensitive to traces of iron and copper, and, to inhibit the effect of these metals, part of the sodium carbonate was replaced by cyanide. The following procedure was finally adopted:

Reagents.—(1) *Haematoxylin solution.*—Dissolve 0·1 g of the pure dyestuff* in

* In the present work the B.D.H. "S.S." product was used.

100 ml of $N/200$ hydrochloric acid at b.p. Cool and saturate with chloroform to prevent mould formation. It is preferable to keep the soln. in the dark. (2) *Ammonium acetate soln.*—Dissolve 80 g of ammonium acetate (AnalaR) in 200 ml of water; filter if necessary. (3) *Sodium carbonate and cyanide soln.*—Dissolve 10·0 g of sodium carbonate (AnalaR) with 10·0 g of potassium cyanide (AnalaR) in 200 ml of water. (4) *Dilute acetic acid.*—Dilute 20 ml of glacial acid to 200 ml. (5) *Standard aluminium solution.*—(i) Stock solution (1 ml $\equiv$ 0·025 mg Al). Dissolve 0·420 g of ammonium alum (AnalaR) in 1 litre of water containing 10 ml of conc. hydrochloric acid. This soln. is preferably standardised gravimetrically. (ii) Dilute solution (1 ml $\equiv$ 0·0025 mg Al). Prepare before use by dilution of the stock soln. One ml of the dil. soln. added to 24 ml of water gives an Al concn. of 0·1 p.p.m. (6) *Hydrochloric acid.*—$N/2$ soln.

METHOD.—Acidify 25 ml of the well-shaken sample in a 100-ml Nessler tube with 0·5 ml of $N/2$ hydrochloric acid. Add 10 ml of the ammonium acetate soln. and then 2 ml of the carbonate and cyanide soln., mix and leave for 5 min. Next add 1 ml of haematoxylin soln. and again mix well. After 10 min. add 2 ml of the dil. acetic acid and mix. After 20 min. match the final colours against aluminium standards prepared with distilled water.

If iron or manganese is present, it is advisable that the distilled water used in preparing the aluminium standards should contain these metals in amounts equiv. to those in the sample. If iron, manganese and copper are absent, the 5 min. standing period before addition of the haematoxylin may be omitted.

Colour Changes.—If aluminium is absent, the colour of the soln. after addition of the haematoxylin will become purple-red; in presence of aluminium this colour is changed by the pure blue of the lake, giving a violet colour or some other tint having red and blue components. Hence the colour of the soln. at this stage gives a good indication of the aluminium content and shows if appropriate standards have been chosen. After the final acidification and standing period the increments of blue in the colour change are, however, much better defined and accurate matching is possible. The final colour of the soln. varies in presence of aluminium from a pale brownish-yellow, through grey at about 0·1 p.p.m. of Al, to a brilliant blue at 0·5 p.p.m. Above 0·5 p.p.m. the blue colour is very intense, so that samples expected to contain more than this amount of aluminium should be diluted before testing; in many instances this will also be advantageous, since there will then be a corresponding decrease in the concn. of any interfering ions.

The method will detect as little as 0·02 p.p.m. of aluminium in 25 ml of water.

TOLERANCE TO INTERFERING SUBSTANCES.—To ascertain the effect of calcium and magnesium, the colours produced from aluminium concns. down to 0·05 p.p.m. in distilled water were compared with those obtained in dil. solns. of calcium chloride and magnesium sulphate. The indications were that calcium equiv. to 300 p.p.m. of $CaCO_3$ and magnesium equiv. to 150 p.p.m. of $CaCO_3$ were without effect.

The cyanide is of great value in suppressing interference from iron, so that the colour increments due to aluminium are clearly apparent. It was found, however, that even 0·2 p.p.m. of iron or manganese still slightly modified the colour of the aluminium lake, and for this reason it is advisable that, as an additional safeguard, the standards should have an iron or manganese content equiv. to that of the sample. Copper in a concn. of less than 0·5 p.p.m. did not cause difficulties.

In expts. with other substances likely to interfere it was found that the colour of the lake was unaffected by 0·8 p.p.m. of phosphate (P_2O_5) or 0·7 p.p.m. of free chlorine. Fluoride in quantities up to 1·0 p.p.m. (as F) causes no difficulty, but with 5 p.p.m. there is slight interference. Since the vol. of sample tested is only 25 ml, and since the sample will probably be one that has been decolorised by the coagulation, the effect of any natural colouring matter will usually be negligible.

RESULTS.—The procedure described has proved satisfactory in the control of the coagulation at a large waterworks where a hard river water is treated. The Table shows the results of some tests made to check the accuracy of the method at this works. For this purpose a stock soln. of "Aluminoferric" was standardised gravimetrically, and known dilutions were added to the filtrate from a battery of mechanical filters; in certain tests a known amount of ferric iron was also added. The aluminium in the "dosed" samples was then determined, with the results shown. The filtrate had a hardness of 280 p.p.m. as $CaCO_3$, nearly all due to calcium, and its colour was 15 units A.P.H.A. The haematoxylin

soln. used was more than two months old. Only in Expts. 6 and 11 was the amount of aluminium added known to the operator.

Expt. No.	Aluminium (Al) added (p.p.m.)	Iron (Fe^{III}) added (p.p.m.)	Aluminium found (p.p.m.)
1	0·225	0	0·20
2	0·30	0	0·28
3	0·625	0	0·60
4	0·69	0	0·70
5	0·13	0·50	0·11
6	0·475	0·50	0·48
7	0·09	0·75	0·08
8	0·225	0·75	0·21
9	0·62	0·75	0·62
10	0·435	0·75	0·48
11	0·13	0·75	0·12

SUMMARY.—A procedure is described for the determination of small amounts of aluminium in water by means of haematoxylin. Compared with the well-known Hatfield method, the procedure has the advantage that more stable reagents are employed and that a better colour change is obtained; it is also less affected by hardness salts and by traces of iron and copper. My thanks are due to Dr. E. V. Suckling for his interest in this work and also to Mr. A. S. Davison, B.Sc., for his assistance.

REFERENCES

1. Lampitt, L. H., and Sylvester, N. D., ANALYST, 1932, **57**, 418.
2. Hatfield, W. D., *Ind. Eng. Chem.*, 1924, **16**, 233.
3. "*Standard Methods for the Examination of Water and Sewage.*" American Public Health Association, 8th Edn., 1936, p. 225.
4. Brockman, C. J., *Ind. Eng. Chem.*, 1933, **25**, 1402.

LABORATORY, SOUTH ESSEX WATERWORKS CO.
LANGHAM, COLCHESTER

December, 1942

Notes

THE MICRO-ANALYSIS OF BORACITE

THE following methods sufficed to determine the nature of a 0·1-g specimen suspected to be boracite ($6MgO.MgCl_2.8B_2O_3$?). Operations involving distillation of the boron or boiling of the soln. were avoided, carbon dioxide being removed by aeration with a stream of CO_2-free air as in Sumuleanu and Botezatu's micro-aeration method for the determination of boron in mineral waters (*Mikrochem.*, 1936, **21**, 75).

BORON.—Fuse 0·01 g of the powdered mineral at as low a temp. as possible with 0·05–0·1 g of sodium potassium carbonate mixture in a platinum micro crucible, digest the melt with warm water, filter by means of a micro filter-stick (paper pulp), wash lightly with 1% sodium carbonate soln., transfer the paper pulp and any adherent matter back to the platinum crucible, moisten with two drops of 10% sodium carbonate soln., ignite to destroy the paper, again fuse with sodium potassium carbonate mixture, leach, and filter. Evaporate the combined alkaline filtrates to dryness in a small platinum basin, dissolve the residue in 2–3 ml of water, add a small drop of aq. methyl orange soln. (0·02%), acidify by gradual addition of *N* hydrochloric acid, and add 10 drops in excess. Transfer the soln. to a 30 ml narrow beaker, thereby bringing the total vol. of the liquid to about 10 ml, and pass a brisk stream of CO_2-free air (about 10 bubbles per sec.) through the soln. for 30 min. While continuing the aeration, gradually run in *N* sodium hydroxide followed by *N*/10 sodium hydroxide until the soln. remains just acid. Continue the aeration, and, after 15 min., complete the neutralisation to methyl orange by using *N*/50 sodium hydroxide (the NaOH solns. should be substantially free from carbonate). Add a small drop of 1% alcoholic phenolphthalein soln., and 1 ml of 10% mannitol soln., continue aeration, and, after 15 min., titrate with carbonate-free *N*/50 sodium hydroxide (more dilute alkali may be used for smaller quantities of boron). If the titration is carried to within a few drops of the end-point, and the aeration is then allowed to continue for *ca.* 5 min. before finally completing the titration, the presence of a little carbonate in the *N*/50 sodium hydroxide should not affect the accuracy of the boron determination. After completion of the titration, add a further quantity of mannitol soln. to ensure that the correct end-point has been reached. Make a blank determination on the reagents, this also serving as a check on the efficiency of CO_2 removal. A control determination of a mixture containing 0·00190 g of B_2O_3 as boric acid gave 0·00187 g of B_2O_3.

MAGNESIUM, ETC.—As the powdered mineral is not completely destroyed by acid treatment, fuse 0·01 g with sodium carbonate, acidify with hydrochloric acid, and remove boron by repeated evaporations with methyl alcohol. Remove silica, iron, etc., by applying micro-technique to the usual methods. Ppt. magnesium as phosphate, together with any small quantities of calcium and manganese in the mineral, and, after ignition and weighing, examine the ppt. spectrographically for calcium, manganese and aluminimum, making the necessary corrections to arrive at the true figure for MgO. Correct for $Fe_2O_3+Al_2O_3$ obtained gravimetrically, by adding to it the small quantity of Al_2O_3 determined spectrographically in the $Mg_2P_2O_7$.

CHLORINE.—Determine by micro-fusion with sodium potassium carbonate mixture, leaching, filtering, acidification of the filtrate, and pptn. as silver chloride.

The following figures were obtained:—SiO_2, 0·5; total $Fe_2O_3 + Al_2O_3$, 2·3; MnO trace; CaO, 0·2; MgO, 31·0; B_2O_3, 60; Cl, 8·6%. Total, less O for Cl, 100·6%. Calculations based on the analysis gave the following atomic ratios:—Mg : B : Cl = 7·1 : 16 : 2·2.

All the determinations were carried out in duplicate, and it seems probable that the mineral, as supplied, did actually contain excess of $MgCl_2$.

These notes are published by permission of The Government Chemist and the Director of The Geological Survey and Museum.

C. O. HARVEY

CHEMICAL LABORATORY, GEOLOGICAL SURVEY AND MUSEUM
LONDON, S.W.7

March, 1943

THE FIRST CHEMICAL REAGENT

IN a previous communication[1] an attempt was made to sketch the early development of Pliny's reagent[2] for the detection of iron in verdigris by the use of papyrus soaked in a soln. of gall-nuts. Later, papyrus was replaced by parchment,[3] filter-paper,[4] cottonwool,[5] woollen or cotton rag,[6] and wood shavings and splinters,[7] each material being soaked in either aqueous[8] or alcoholic[9] solns. Preference was given, however, to powdered galls[10] for the analysis of aqueous solns.[11] Brandt[12] directed attention to the reliability of the gall-nut test; it was also used for the detection of iron in the ash of blood,[13] sera,[14] urine,[15] faeces,[16] drugs,[17] and sputum.[18] Although the Prussian blue test for iron was discovered so far back as 1704 by Diesbach,[19] it was never favoured as a test in water analysis; Cranz[20] published the results of a comparative test with Pliny's and Diesbach's reagents which led him to prefer the former. Thus Pliny has given us a test which has survived for 2000 years and is still in use in vinegar works for the detection of iron in vinegar.

In the following expts. 0·1% aqueous solns. of anhydrous ferric ammonium oxalate and Mitchell's glucose-free gallotannin[21] were used. The ancient papyrus was first soaked in water containing a few drops of hydrogen peroxide so as to bleach it; the parchment, vellum and goldbeater's skin were also soaked in water before use. The vegetable fibres were used without and with a mordant (aluminium acetate). As will be seen below, the mordanted vegetable materials reacted better than the unmordanted. The modification suggested by Hardy and Warneford,[22] who use Collodin (acetylcellulose), for the goldbeater's skin test is thus shown to be less reliable than the original test. In each expt. the material was first soaked for 24 hrs. in the gallotannin soln. and then for a further 24 hrs. in the iron soln.

Material	Date	Author	Result
Ancient papyrus	60 A.D.[23]	Pliny	++
Modern papyrus	—	—	++
Mordanted ancient papyrus ..	—	—	+++
Mordanted modern papyrus ..	—	—	+++
Parchment	1572	unknown	+++
Vellum	—	—	+++
Filter-paper	1822	Rüde	+
Mordanted filter-paper	—	—	+++
Cottonwool	1562	Paracelsus	D
Mordanted cottonwool	—	—	+++
Woollen rag	1512	Salzmann	+++
Cotton rag	1512	Salzmann	D
Mordanted cotton rag	—	—	+++
Wooden splinters	1604	Libavius	0
Mordanted wood splinters	—	—	D
Goldbeater skin	1909	Nierenstein and Tryon[24]	+++
Filter-paper soaked in gelatin ..	1943	Nierenstein	+++

+++ indicates a very strong reaction; ++ a good reaction; + a positive reaction; D doubtful; 0 no reaction.

In the last-named test, which is new, filter-paper is soaked in a 1% soln. of perfectly white gelatin for 24 hrs., and then dried and cut in strips.

The references given below show the first and the last that I have noticed in each instance.

REFERENCES

1. Nierenstein, M., *Isis*, 1931, **16**, 439.
2. *Hist. nat.*, XXXI, 11; see also Kopp, H., *Geschichte der Chemie*, 1843, **2**, 51; Bailey, K. C., "*The Elder Pliny's Chapters on Chemical Subjects*," 1932, **2**, 51; Nierenstein, M., "*The Natural Organic Tannins*," 1934, 291.
3. "*Auriferae artis*," 1572, p. 157; Dollfuss, J., *Chem. Annal.*, 1787, **10**, 147.
4. Rüde, G. W., "*Chemisches Probier Kabinet*," 1822, 57; Mandelin, C., *Pharm. Z. Russland*, 1882, **22**, 321.
5. Paracelsus, "*Bäderbüchlein*," 1562; Liborius, H., *Sitz.-Ber. d. Dorpater Naturf.-Ges.*, 1880, **5**, 277.
6. Salzmann, T. R., "*Zehn Bücher von kalten, warmen, mineralischen u. metallischen Wassern*," 1512, 17, 157; Pfeil, T., "*Chemische Beiträge zur Pomologie*," 1880, Diss., Dorpat.
7. Libavius, A., "*Praxisalchymiae*," 1604, 127; Dragendorff, N., *Sitz-Ber. d. Dorpater Naturf.-Ges.*, 1889, **8**, 78.
8. *Theatrum chemicum*, 1613, **1**, 173, 322; 1622, **4**, 127, 157, 193; 1641, **6**, 179; Dragendorff, N., *Sitz.-Ber. d. Dorpater Naturf.-Ges.*, 1884, **7**, 134.
9. Bergman, J. "*De Analyse Acquarum*," 1778; "*Farmacopea Venozolana*," 1928, 475–479.
10. Boyle, Robert, "*Collected Works*," 1744, **4**, 231.
11. Salzmann, T. R., "*Zehn Bücher von kalten, warmen, mineralischen u. metallischen Wassern*," 1512; "*Farmacopea Venozolana*," 1928, 475–479.
12. Brandt, C. C., *Acta lit. et scient.*, 1723, **3**, 39; Schwartz, V., *Pharm. Z. Russland*, 1880, **19**, 97.

13. von Eller, C. F. J. L., *Hist. de l'Acad. de Berlin*, 1751, **2**, 17; Rees, G. O., *"On the Analysis of Blood and Urine,"* 1846.
14. Berzelius, T., *"Überblick über die Zusammensetzung der thierischen Flüssigkeiten,"* 1814; Dragendorff, N., *Pharm. Z. Russland*, 1878, **17**, 97.
15. Surun, A., *"Nouv. Élém. de Physiologie pathologique,"* 1824; Kuhn, S. V., *Med. et chir. Trans.*, 1836, **47**, 12.
16. Kuntz, A., *J. der Chem., Physik u. Min.*, 1804, **11**, 459; Dragendorff, N., *Pharm. Z. Russland*, 1884, **23**, 329, 377.
17. Wauters, P. E., *"Repertorium remediorum,"* 1810; Wanklyn, T. A., and Chapman, E. J., *"Water Analysis,"* 1874.
18. Hollmann, S. C., *"De mechanismo et usu respiratorium,"* 1768; Usher, C., *J. d. Pathologie*, 1812, **5**, 1.
19. Darmstaedter, L., *"Handbuch zur Geschichte d. Naturwissenschaften,"* 1908, 161.
20. Cranz, T. W., *Chem. Annalen*, 1795, **26**, 127.
21. Mitchell, C. A., ANALYST, 1923, **48**, 7.
22. Hardy, F., and Warneford, L. H., *Ind. Eng. Chem.*, 1925, **17**, 49.
23. According to Jöcher, C. G. (*Allgemeines Gelehrten-Lexikon*, 1751, **3**, 1632), Pliny wrote his *"Natural History"* at the age of 37. As he was born in 23 A.D., he thus wrote it in 60 A.D.
24. Nierenstein, M., and Tryon, I., ANALYST, 1942, **67**, 389.

M. NIERENSTEIN

THE UNIVERSITY, BRISTOL

March, 1943

NOTE ON THE ANALYSIS OF OXYGEN AND CARBON DIOXIDE RESUSCITATION GAS MIXTURES

A GASEOUS mixture of oxygen (*ca.* 93%) and carbon dioxide (*ca.* 7%) is used therapeutically for resuscitation purposes. Hitherto, in this laboratory, the Hempel gas analysis apparatus without absorption bulbs has been used for the examination of such mixtures. The technique described by Frederick for the examination of commercial oxygen[1] has been followed, alkaline pyrogallol soln. being used for absorption of oxygen plus carbon dioxide and then, on a further sample, saturated caustic potash soln. for absorption of carbon dioxide. The method is quite satisfactory when only one sample is to be examined but is rather tedious for the examination of several in succession, owing to the necessity for thorough cleansing of the Hempel burette after each absorption.

By combining the Hempel process of carbon dioxide absorption with the improved copper and ammonia method of oxygen absorption, and using the Frederick apparatus,[2] the time needed for the analysis of such mixtures has been greatly curtailed.

The modified procedure is as follows. First use the Hempel apparatus to determine the % of carbon dioxide present, oxygen and a small amount of inert gas (mainly nitrogen) remaining unabsorbed in the burette. Next fill the capillary tube at the top of the burette with dilute ammonia soln. (1 : 1), using a Pasteur pipette fitted with a teat. Tilt the Hempel burette over and connect the capillary tube by means of a short stout piece of rubber tubing to the inlet tube of the copper and ammonia oxygen apparatus. By manipulation of the necessary taps and the slow raising of the Hempel levelling tube transfer the gas to the burette of the oxygen apparatus, taking care that the caustic soln., much diluted by admixture with water from the levelling tube, does not enter the body of the oxygen apparatus. At the appropriate moment close the tap controlling the influx of gas and disconnect the Hempel burette. Then absorb oxygen from the gas mixture in the burette of the oxygen apparatus by the normal procedure. In this way the determination of oxygen, carbon dioxide and inert gas is carried out on a single 100-ml sample.

The process may be applied to the analysis of mixtures of carbon dioxide and oxygen of widely varying proportions.

REFERENCES

1. Frederick, R. C., ANALYST, 1927, **52**, 401.
2. —— *id.*, 1935, **60**, 581.

W. R. SMITH

LABORATORY
ROYAL NAVAL MEDICAL SCHOOL

May, 1943

Official Appointments

THE following amendments to the list of Public Analysts appointed by Local Authorities with the approval of the Ministry of Health were notified by the Ministry on June 26th, 1943.

Authority.	*Public Analyst*
St. Pancras Metropolitan Borough	CHARLES HARCOURT WORDSWORTH (Deputy)
St. Helens County Borough	EDMUND GARDNER WILLIAMS (Deputy)
Holborn Metropolitan Borough	CHARLES HARCOURT WORDSWORTH (Deputy)
Mitcham Borough	EDWARD HINKS DANIEL DONALD MOIR (Deputy)
Sheffield County Borough	HUGH CHILDS (Deputy) (until April 28th, 1944)
Finsbury Metropolitan Borough	CHARLES HARCOURT WORDSWORTH (Deputy)
Scunthorpe Borough	HUGH CHILDS (Deputy)
St. Marylebone Metropolitan Borough	THOMAS McLACHLAN
Guildford Borough	DANIEL DONALD MOIR (Deputy)
Brighton County Borough	REGINALD FRANK WRIGHT
Worthing Borough	REGINALD FRANK WRIGHT
Eastbourne County Borough	REGINALD FRANK WRIGHT
Hove Borough	REGINALD FRANK WRIGHT
West Sussex County	REGINALD FRANK WRIGHT

Ministry of Food

STATUTORY RULES AND ORDERS*

1942—No. 2549. Order dated December 15, 1942, amending the Feeding Stuffs (Maximum Prices) Order, 1942. Price 2d.

Twenty amendments are made to the Principal Order as amended (S.R. & O., 1942, Nos. 1669 *and* 2127). *They include (a) "Animal proteins (including dried blood) and licensed concentrates" replace "Fish meal, meat meal and meat and bone meal" in Table of Contents, Part E. (b) "Licensed Mixer" and "National Priority Pigeon Mixture" are defined as in S.R. & O.*, 1941, *No.* 82). (*c*) *In Art.* 1 "Wheat by-products" means any by-products obtained in the production of flour by milling and includes millers' offals and wheat offals, both as defined in Part II, Schedule IV of the Fertilisers and Feeding Stuffs Act, 1926, as amended; and fine wheatfeed, straight run bran, coarse bran, fine bran, pollards, middlings, and wheat germ.

(*d*) *For Art.* 5 *the following Article is substituted*: "For the avoidance of doubt it is hereby declared that the basic price of any specified feeding stuff applies to that feeding stuff when damaged or reconditioned, unless a separate basic price for that feeding stuff when damaged or reconditioned is prescribed."

(*e*) *A sub-par (dd) relating to the basis of sale (gross or net) is inserted.*

(*f*) Art. 9. The provisions of this Order shall not apply—(*a*) to the purchase or sale of (i) any specified feeding stuff, compound or mixture intended for human consumption, for use as seed or as a medicine or condiment, or for such industrial purposes as are authorised under any Order for the time being in force made under the Defence (General) Regulations, 1939, prohibiting such use except when so authorised; (ii) any compound or mixture for feeding to dogs, cats or birds (other than poultry); (iii) any wheat by-product for which a price is prescribed by the Flour (Control and Prices) Order, 1941, or any Order amending or replacing that Order; (iv) any kitchen waste for which a max. price is prescribed by the Kitchen Waste (Max. Prices) (No. 1) Order, 1942, as amended; (v) National Priority Pigeon Mixture. (*b*) to the purchase by or sale to a licensed mixer of any feeding stuff for the manufacture of National Priority Pigeon Mixture.

(*g*) *Schedule I of this Order is substituted for Schedule I of the former Order.* (*h*) *Entries* 20 *and* 83 *are deleted from* Schedule II. (*i*) *In Col.* 1 *of Schedule II the following entry is substituted for entry* 23:

"23. Wheat by-products (home produced) other than (*a*) wheat germ, and (*b*) straight run bran derived from white wheat."

(*j*) *In Col.* 1, *Schedule II, the following are substituted entries*:

"90. Dried grains, other varieties and qualities. 91. Malt culms or malt screenings. 91A. Kiln dust or rock culms or other by-products of the manufacture of malt other than malt culms or malt screenings."

(*k*) *In Schedule II the heading Part E is given as in* (*a*) *above.*

(*l*) *In Schedule II, after entry* 151, *the following entries are inserted.*

"151A. Feeding dried blood.	The basic price per ton gross less 10/-.	12	7/6 for each complete 1% albuminoid content.
151B. Licensed concentrates.	The basic price per ton gross less 10/-.	12	The price per ton, on a sale to a consumer, specified in the manufacturer's licence granted under the Feeding Stuffs (Regulation of Manufacture) Order, 1942."

(*m*) *Schedule II of the Order is substituted for Schedule III of the former Order.*

(*n*) *In par.* 1, *Schedule IV, the words "(other than a compound or concentrate) consisting solely" are substituted for "(other than a compound)."*

Details are given of the method of arriving at the basic price of any mixture (other than a compound or concentrate) not referred to in par. 1 *of this Schedule.*

Schedule I gives a Table of Ingredients of Compounds and Concentrates.

PART A—COMPOUNDS.—(1) Any of the following or any product thereof, or any by-product thereof which contains not more than 16% by weight of fibre.—Barley, Beans, Dried grain (including distillery dreg), Dried potato products, Locust beans, Maize, Malt culms (including rock culms and culm dust), Non-millable wheat (including non-millable reconditioned wheat), Oats, Peas, Rye, Tares.

(2) Any cake or extracted meal produced from one or more of the following or any meal produced from any such cake.—Coconut (copra), Cottonseed, Groundnut, Hempseed, Linseed, Palm kernels, Sesame seed (including tilseed, gingelly seed and niger seed), Soya beans, Sunflower-seed.

(3) Feeding meat meal (including feeding meat and bone meal and feeding dried blood), Fish meal, Licensed concentrates, Molasses, Rice bran (including rice meal and rice offals), Whale meat meal (including whale meat and bone meal), Wheat by-products other than wheat germ.

---

* A summary of some recent Orders. Italics signify changed wording. H.M. Stationery Office, 1943.

PART B.—CONCENTRATES.*—Any of the following.—Cod liver oil, Feeding dried blood, Dried milk (whole, separated or buttermilk), Dried whey, Dried yeast, Feeding meat meal (including feeding meat and bone meal), Groundnut meal, Dried liver meal, Soya bean cake meal, Whale meat meal (including whale meat and bone meal), Wheat germ.

1042—No. 546. The Fish (Distribution) Order. Dated April 8, 1943. Price 2d.

In this Order "Fillet" means fish from which all guts, bones, head, tail and fins have been removed and, in the case of haddock and whiting includes block fillet, provided that, for the purposes of this definition—(*a*) where such fish includes any flaps the small bones therein need not be removed; (*b*) dogfish flaps sold separately shall not be regarded as fillets.

"Block fillet" means fish from which all guts, bones and head have been removed but which has not been severed down the middle of the back, provided that where such fish includes flaps the small bones therein need not be removed for the purposes of this definition.

"Fish" is defined as in S.R. & O., 1943, *No.* 497 (ANALYST, 1943, 184) *except that the definition excludes herrings, pilchards, sprats, mackerel and horse mackerel, and it includes any part of a fish.*

— No. 608. The Starch and Dextrine (Control) Order. Dated April 16, 1943. Price 1d.

The supply or obtaining of starch or dextrine, or their use, otherwise than for domestic purposes, are prohibited except under licence.

"Dextrine" includes soluble starch, thin boiling starch and the substance known as "British gum."

"Starch" means (i) starch made from maize, potatoes, rice, rye or wheat (including any wheat product); (ii) flour or starch made from sago or tapioca (including cassava, manioc, mandioca and any similar tapioca plant); (iii) arrowroot.

— No. 625. Order, dated April 22, 1943, amending the Flour Order, 1943. Price 1d.

Numerous amendments to the Principal Order (*S.R. & O.*, 1943, *No.* 11, *cf.* ANALYST, 1943, 113) *are made. Thus, inter alia,*

In par. 1 (*Art.* 1) "Export" in relation to flour does not include shipment at a port in the United Kingdom for consumption as ships' stores on board the vessel in which the flour is so shipped.

In par. 1 (*Art.* 1) *after the definition of "Speciality flour" the following definition is inserted:*—" 'W flour' means (i) any flour which by the terms of a licence granted under Art. 3 of this Order authorising the production of the flour is authorised to be so described; or (ii) any flour the prescribed price of which for the purpose of Part I of Schedule I to this Order is the same as the prescribed price of national flour, and which, in so far as it is obtained from wheat, is of an extraction higher than 85%."

The words "other than 'W flour'" are to be inserted after "speciality flour" in Art. 21 *and Schedule I.*

Another amendment deals with the size of containers in which flour (other than semolina) may be packed for sale otherwise than in bulk.

Conditions are prescribed for the pre-packing of semolina.

For par. 3 *of Art.* 20 *the following par. is substituted:*

"No person shall in the course of any trade or business use semolina in the production of—(*a*) bread; (*b*) biscuits as defined in the Biscuits (Maximum Retail Prices) Order, 1942, as amended; (*c*) cake as defined in the Cake and Confectionery (Control and Maximum Prices) Order, 1942, as amended; (*d*) any manufactured product containing meat; (*e*) any meat or fish paste as defined in the Meat Products and Cooked Meat (Control and Maximum Prices) Order, 1942."

Except under licence Canadian Springs flour may not be used for any purpose.

— No. 629. Order, dated April 23, 1943, amending the Cereal Fillers (Control and Maximum Prices) Order, 1943. Price 1d.

The principal Order (*S.R. & O.*, 1943, *No.* 545) *is amended by inserting the following Article after Art.* 10:

"10A. This Order shall not apply to any cereal filler the manufacture of which has been or may be authorised by or on behalf of the Minister under the Food Substitutes (Control) Order, 1941, as amended, the Soya Flour (Control and Maximum Prices) Order, 1942, or the Manufactured and Pre-packed Foods (Control) Order, 1942, as amended."

— No. 638. The Soap Substitutes (Labelling and Prices) Order, 1943. Dated April 27, 1943. Price 1d.

In this Order "Soap substitute" means any substance, preparation or product, offered or purporting to be capable of being used as a substitute for soap or for the purposes for which soap is used, or (not being a mechanical appliance) as an article the use of which will result in a saving of soap, but does not include any detergent substance such as washing soda, ammonia or benzine, sold under its ordinary name or description.

Except under licence, no label shall be affixed to any soap substitute or the wrapper or container thereof. The Minister's licence does not warrant the quality or fitness for any particular purpose, or the weight or measure, of any soap substitute. It is prohibited to alter, deface or render illegible any statement upon an authorised label; but it shall be a defence in any proceedings for infringement of this regulation for the defendant to prove (*a*) *that the soap substitute was in his possession for a purpose other than sale; or* (*b*) *that he acted without intent to deceive.*

Erratum.—On p. 16 (January issue), in line 2 of the definition of "Sweetening tablet," for "not more" *read* "not less" than 0·09 grain of saccharin. (*Cf.* ANALYST, 1942, **67**, 261.)

---

* No compound or concentrate may be manufactured for sale or prepared for sale except in accordance with the provisions of the Feeding Stuffs (Regulation of Manufacture) Order, 1942, as amended, the Feeding Stuffs (Control) (Northern Ireland) Order, 1941, or any other Order for the time being in force made by the Minister providing for the control of feeding stuffs.

Ministry of Health

MILK AND DAIRIES, ENGLAND

Provisional Regulations, dated May 21, 1943, made by the Minister of Health under the Food and Drugs Act, 1938. Price 1d.

As any considerable extension of the use of steam for sterilising dairy equipment is impracticable, the Milk and Dairies Order, 1926, *is amended to permit the use of standard solutions of sodium hypochlorite for this purpose. The regulations do not abrogate the provisions in Art.* 21 (i) *of the Milk and Dairies Order,* 1926, *relating to cleansing and scalding of milk vessels, etc., with boiling water or steam. No oxidising or preservative agent other than solns. of sodium hypochlorite approved by the Minister of Agriculture and Fisheries may be used, and all trace of such soln. shall be removed before any cleansed vessel, lid or appliance is brought into contact with milk.*

Circular 2819. Milk and Dairies Regulations, 1926—1943. Cleansing of Dairy Equipment.

The Provisional Regulations (supra) are explained. The Ministry of Agriculture and Fisheries will require that, when despatched from the manufacturer's premises, the sodium hypochlorite soln. shall have a total available chlorine content of 9–12% *w/w plus or minus* 0·5%, *and that directions as to date of despatch, manner of storing and latest date for use shall appear on the label. Approved solns. must also contain not less than* 0·7% *of sodium chlorate to act as "detector" should sodium hypochlorite solns. obtain access to the milk.*

Joint Announcement by the Ministries of Agriculture and Food

COCOA AND CHOCOLATE RESIDUES, INCLUDING COCOA SHELL, FOR STOCK FEEDING

EXPERIENCE has shown that cocoa and chocolate residues, including cocoa shell, are suitable for feeding to adult cattle whether dairy or fattening, provided that the daily ration does not contain more than 2 lbs. of this material. This does not mean that cocoa and chocolate residues, including cocoa shell, are suitable feeding stuffs for other classes of livestock. In fact, in the case of pigs, poultry and calves, they are definitely detrimental and the cumulative effect of the consumption of even limited quantities may be serious. Cocoa residues are sold for inclusion in cattle foods to the extent of 2½% for feeding to adult cattle only.

Notes from the Reports of Public Analysts

The Editor would be glad to receive Reports containing matter of special interest

CITY AND COUNTY OF KINGSTON UPON HULL: REPORT FOR 1ST QUARTER, 1943

CANNED SOUP.—A sample, labelled "Highly Concentrated," contained only 7·7% instead of not less than 12% of solids as required by the Canned Meat and Canned Soup (Control and Max. Prices) Order, 1941. Also, the label did not bear the statement required by Art. 6 (*c*) of that Order. The Ministry of Food was notified.

ONION EXTRACT.—The sample was labelled "Extract of Onions. A high concentration of the goodness of onions," and the carton bore the words "Genuine Onion Juice." There was only about 1% of onion juice present. The vendor was cautioned.

SOFT DRINKS.—Samples of "Fruit Cup" and of "Sparkling Special" contained 0·08 and 0·014% w/v of citric acid respectively. According to the standards agreed by the Soft Drinks Industry (War Time) Association these drinks should have contained not less than 0·14 and 0·047% of citric acid respectively. A sample of "Limeade" contained 0·85% of sucrose and 0·024% of saccharin, whereas, according to the above standards "Limeade" should contain 1·12% of sucrose and 0·012% of saccharin. These are fixed, not minimum standards. Cautions were issued.

D. J. T. BAGNALL

Legal Notes

The Editor would be glad to receive particulars of cases with points of special legal or scientific interest

PASTEURISED MILK NOT AS DESCRIBED

MCHUGH *v.* T. P. FLOWER, LTD.

MCHUGH *v.* J. COPSON & SON

ON March 3, 1943, summonses, brought by the Chief Sanitary Inspector of Leicester against two firms for selling pasteurised milk not of the nature, substance and quality demanded, were heard at the City of Leicester Petty Sessions.

In the first case, against T. P. Flower, Ltd., the certificate of the Public Analyst (Mr. F. C. Bullock) stated that the sample was not genuine pasteurised milk. The phosphatase B test gave a reading of 35·0 Lovibond blue units, whereas genuine pasteurised milk should give a reading not exceeding 2·3. Hence, there was either a considerable error in pasteurisation or admission of raw unpasteurised milk to the sample. The defendants pleaded not guilty, but, after the case for the prosecution had been outlined, withdrew this plea. They were fined £5.

In the case of J. Copson & Son the certificate of the Public Analyst stated that the phosphatase B test gave a reading of 7·0 Lovibond blue units. The Magistrates fined the defendants £5.

There was a second summons against T. P. Flower, Ltd., heard on the same day. The Public Analyst's certificate stated that the phosphatase B test gave a reading of 10·4 Lovibond units. A fine of £5 was

imposed. The defendants pleaded that the by-pass fitted to their pasteurisation plant was defective, and that they were unable to obtain a fresh part. This defect allowed partly pasteurised milk to pass through, which would otherwise have been rejected. The Magistrates held that in the circumstances the milk should not have been described as pasteurised.

In all three cases the samples, labelled "Pasteurised Milk," were taken by a sampling officer, in the normal course of his duties, from roundsmen employed by the two defendants to deliver bottled milk.

Bibliography of Metals in Foods and Biological Materials

VI. BISMUTH

(*Concluded from page* 117)

POUZERGUES. Urinary Elimination of Bismuth after Injection of Bismuth Preparations. *Ann. Inst. Pasteur*, 1934, **53**, 535; Abst., *B.C.A.*, 1935, 119A.

POUZERGUES. Urinary Elimination of Bismuth. *Presse méd.*, 1934, **42**, 1923; Abst., *C.A.*, 1935, **29**, 1508. (Kidneys cannot eliminate more than 2 mg of Bi per kg in 24 hrs. without damage.)

PROBST. Spectro-Analytical Detection of Bismuth in Tissue and Determination of Mercury in Urine. *Arch. exp. Path. Pharm.*, 1933, **169**, 119; Abst., *B.C.A.*, 1933, 423A.

RAIZISS, SEVERAC and MOETSCH. Toxicity of various Compounds of Bismuth used in the Treatment of Syphilis. *J. Chemotherapy*, 1934, **10**, 77; Abst., *C.A.*, 1934, **28**, 2411. (K, Bi tartrate and Bi salicylate among least toxic. Doses up to 80 mg per kg body weight tolerated intramuscularly.)

SAEMUNDSSON. Excretion of Bismuth in the Urine and Transfer to the Cerebrospinal Fluid. *Acta psychiat. (Kopenhagen)*, 1935, **10**, 151; Abst., *C.A.*, 1937, **31**, 8018.

SANTI. Bismuth in the Cure of Syphilis. *Boll. Chim-farm.*, 1938, **77**, 665; Abst., *B.C.A.*, 1939, 189AIII.

SÄUFERLIN. Atypical Bismuth Poisoning. Contribution to the Pharmacodynamics and Toxicology of Bismuth. *Dermatol. Wochschr.*, 1935, **100**, 729; Abst., *C.A.*, 1936, **30**, 4565. (Bi apt to be stored in diseased tissue.)

SCHMITZ, ECKHARDT and SCHWIENHORST. Elimination of Bismuth in the Urine after the Use of Spirobismol soluble. *Dermatol. Wochschr.*, 1937, **104**, 237; Abst., *C.A.*, 1937, **31**, 4398.

SCHOLTZ and CHANEY. Tissue Concentration of Bismuth in Man. *Amer. J. Syphilis*, 1939, **23**, 759; Abst., *C.A.*, 1940, **34**, 2921.

SEREFIS. Bismuth Poisoning. *Med. Klinik.*, 1934, **30**, 968; Abst., *B.C.A.*, 1935, 398A. (Chronic poisoning from the oral administration of Bi salts frequently resembles that due to Pb or Hg.)

SEREFIS. Resorption of Bismuth from the Gastro-Intestinal Canal. *Deut. med. Woch.*, 1934, **60**, 1237; Abst., *B.C.A.*, 1935, 657A.

SEREFIS. Resorption Conditions for Bismuth and its Value in Oral Therapy of Syphilis. *Arch. Dermatol. Syphilol.*, 1934, **171**, 1; Abst., *C.A.*, 1936, **30**, 2261.

SOLLMANN, COLE and HENDERSON. Clinical Excretion of Bismuth. II. Urinary Excretion of Bismuth after Clinical Intramuscular Injections of Sodium Iodobismuthite and Sodium Bismuth Thioglycollate. *Amer. J. Syphilis*, 1937, **21**, 480; Abst., *C.A.*, 1938, **32**, 235.

SOLLMANN, COLE and HENDERSON. Clinical Excretion of Bismuth. V. Excretion of Sobisminol and some other Bismuth Preparations for Oral Administration. *Arch. Dermatol. Syphilol.*, 1938, **37**, 993; Abst., *C.A.*, 1938, **32**, 7128.

SOLLMANN and HENDERSON. Bismuth Studies. VI. Bismuth Absorption from the Site of Injection in Dogs. *Amer. J. Syphilis*, 1938, **22**, 286; Abst., *C.A.*, 1938, **32**, 4652.

SONDERN, PUGH, KALICH, TANN and WIEGAND. Potassium Bismuth Saccharate. II. Toxicity, Absorption and Distribution after Intramuscular Injection. *J. Amer. Pharm. Assoc.*, 1940, **29**, 346; Abst., *C.A.*, 1940, **34**, 7436.

SPROULL and GETTLER. Photoelectric Determination of Bismuth in Biological Materials. *Ind. Eng. Chem. Anal. Ed.*, 1941, **13**, 462; Abst., *C.A.*, 1941, **35**, 5922. (Bi determined by measurement of yellow Bi iodide complex in acid solution in presence of sulphite.)

STEADMAN and THOMPSON. Spectrochemical Determination of Bismuth in Biological Material. *J. Biol. Chem.*, 1941, **138**, 611; ANALYST, 1941, **66**, 386.

STEIN. Action of a Soluble Complex Bismuth Salt in Trypanosome Infections. *Z. Immunitäts.*, 1933, **78**, 489; Abst., *C.A.*, 1933, **27**, 5411. (Bi derivative of Na 2.6-dimercaptoisonicotinate has some therapeutic action in mice.)

STOCKTON. Actions of Diuretic Drugs and Changes in Metabolites in Oedematous Patients. *Arch. Internal. Med.*, 1936, **58**, 891; Abst., *C.A.*, 1937, **31**, 1095. (Bi Na tartrate acts directly on the tissues and causes mobilisation of chlorine and water.)

STOROEV. Pharmacology of Bismuth. Effect of Bismuth on the Reactions of the Vegetative Nervous System. *Bull. biol. méd. exptl. U.S.S.R.*, 1937, **3**, 310; Abst., *C.A.*, 1939, **33**, 8811.

STOROZHEV. Pharmacology of Bismuth. Effect on the Reactions of the Vegetative Nervous System. *Arch. sci. biol. (U.S.S.R.)*, 1937, **46**, No. 2, 29; Abst., *C.A.*, 1939, **23**, 6442.

STRATTON. Absorption and Elimination of Bismuth after Oral Administration to Rabbits. *Amer. J. Syphilis*, 1938, **22**, 728; Abst., *C.A.*, 1939, **33**, 733.

SÜMEGI and PUTNOKY. Experimental Poisoning with Heavy Metals. *Arch. Gewerbepath. Gewerbehyg.*, 1939, **9**, 566; Abst., *C.A.*, 1940, **34**, 2933. (Bi caused minimum damage to liver and kidneys.)

TAUBER and CLARKE. Daily Peroral Administration of Soluble Bismuth to Experimental Animals. *J. invest. Dermatol.*, 1938, **1**, 191; Abst., *B.C.A.*, 1939, 90AIII.

THIRY. Chemotherapy of Spontaneous and Induced Leptospirosis in White Mice. *Compt. rend. Soc. Biol.*, 1933, **114**, 172; Abst., *C.A.*, 1934, **28**, 527. (Effects of some compounds of Bi, As, Sb, and Au studied.)

THOMAS. Clinical Evaluation of Oral Bismuth Therapy in Early Infections of Syphilis in the Female. *Amer. J. Syphilis*, 1937, **21**, 513; Abst., *C.A.*, 1938, **32**, 236.

THOMPSON, ICHNIOWSKI and ROBERTS. Adsorption, Distribution and Excretion of Injectable Bismuth Preparations. *Amer. J. Syphilis*, 1933, **17**, 205; Abst., *B.C.A.*, 1934, 447A.
THURMON and BENOTTI. Excretion of Bismuth in the Urine of Patients Treated with Bismuth Ethyl Camphorate. *Arch. Dermatol. Syphilol.*, 1940, **42**, 1073; Abst., *C.A.*, 1941, **35**, 1509.
TOMMASO. Absorption and Excretion of Injected Bismuth. *Semana. méd.* (*Buenos Aires*), 1932, II, 940; Abst., *C.A.*, 1933, **27**, 137. (Absorption of Bi preparations studied by radiography.)
TOMPSETT. Determination of Bismuth in Biological Materials. ANALYST, 1938, **63**, 250. (Bi extracted from product of wet combustion with ether after addition of sodium diethyldithiocarbamate and determined with thiourea after destruction of organic matter.)
TREVISINI. Investigations on Bismuth Poisoning. *Sperimentale*, 1937, **91**, 193; Abst., *C.A.*, 1938, **32**, 245.
WHITRIDGE. Changes in the Long Bones of Newborn Infants following the Administration of Bismuth during Pregnancy. *Amer. J. Syphilis*, 1940, **24**, 223; Abst., *C.A.*, 1940, **34**, 4432.
ZEPALOVA. Quantitative Determination of Bismuth in Urine. *Lab. Prakt.* (*U.S.S.R.*), 1939, No. 6, 24; Abst., *C.A.*, 1939, **33**, 8654. (Method based on formation of yellow complex compound of Bi with I.)
ZLATAROV and PENCHEVA. Effect of Heavy Metals on Enzymes. III. Effect of Complex Bismuth Compounds on Proteolytic Enzymes. *Ann. univ. Sofia II, Faculté phys-math.*, 1934, **30**, No. 2, 203; Abst., *C.A.*, 1935, **29**, 4036. (Bi compounds retard action.)

J. H. SINGER

The Iron and Steel Institute

FIRST REPORT OF THE MARINE CORROSION SUB-COMMITTEE*

A DETAILED account is given of investigations of the forms, rates and mechanism of corrosion and fouling, with the ultimate object of establishing improved formulae for compositions for protecting ships' bottoms. Observations are also made on the results of raft-tests on proprietary paints.

CONSTITUTION OF PROPRIETARY PAINTS.—Samples were submitted by 23 firms, and the Sub-Committee added some of their own for the test schemes. Resin-oil media were used in more than half the compositions submitted. Bitumen was present in 16% and chlorinated rubber in 4%. Red iron oxide and zinc oxide were the chief pigments (in 80%). The toxin contents (based on Cu, Hg and As_2O_3) ranged from 5 to 51%. A few compositions also contained organic toxins. The average toxin content of all the samples was: Cu, 12·4; Hg, 4·8; As_2O_3, 5·3%. From a survey of these results it appears that there is much divergence of opinion as to the most suitable composition, especially as regards medium and pigmentation; the toxin content is largely determined by the selling price. Pronounced differences in consistency were observed from one sample to another, and stress is laid by the Sub-Committee on the desirability of establishing a more uniform standard in this respect.

Performance under raft-test conditions varied greatly; the worst of the painting systems broke down within a few weeks when applied to new or even to repainted steel, whilst the durability of the best exceeded 1 year.

TOXIC INDEX.—This is the aggregate % w/v of copper, mercury and arsenic in the anti-fouling composition, the mercury content being multiplied by 2; arsenic (as As_2O_3) is almost ineffective, but in these tests a weighting factor of 1/3 was assumed. Several marked deviations from this correlation were attributed to the presence of organic toxins in the compositions. The tests indicated that under the experimental conditions at Caernarvon a toxic index of at least 30 would be needed. This would correspond to 15% of Hg as mercury compounds or 30% of Cu as copper compounds, or an equiv. mixture, with the reservation that it is doubtful whether mercury can completely replace copper.

PROTECTIVE PROPERTIES.—These varied as greatly as the anti-fouling properties; the best painting schemes were but slightly affected after a year's immersion, whereas the worst suffered severe corrosion after only a few weeks. This variation was shown by the results for the adhesion of the paints and loss in weight on exposure. The depth of pitting in gaps in the coating ranged from 0·007 to 0·080 in.; this showed that paints promote pitting to different extents in bare areas of the steel. For temporary protective treatment, boiled linseed oil was the most effective, whilst mineral oil had practically no effect in preventing rusting. It is important, however, that temporary protection should be compatible with the final painting scheme. In one expt. the scheme was affected both by the boiled linseed oil film and by a protective coat of red iron oxide paint (in ordinary oil medium); on the other hand, a temporary film of thin red lead paint proved satisfactory.

Preliminary tests on special preparations formulated by the Paint Research Station (Dr. L. A. Jordan) indicated that coumarone can be substituted with advantage for rosin, and lanolin for linseed oil in protective compositions. On the other hand, for anti-fouling purposes, a rosin/coal-tar pitch/leaded-stand-oil medium proved superior to all substitute media tested.

CORROSION RATES OF IRON.—The results of all tests have indicated that there is little difference in the corrosion rates of the common irons or steels when immersed in sea water; such differences as there are will be eliminated when the surfaces are covered with paint. It is probable that the rate of corrosion of a bare steel is determined by the rate at which oxygen reaches the surface. The fact that the rust under a marine growth is black indicates that this rate of supply is insufficient to promote the max. corrosion rate. Fouling, also, possibly interferes with the diffusion of oxygen to the steel surface.

FOULING ORGANISMS.—These include (i) marine bacteria, which secrete a slimy film differing in properties when formed on surfaces of different degrees of toxicity; (ii) young spores of seaweeds; (iii) diatoms; (iv) larval forms of sessile marine animals. The earliest stage of fouling is a bacterial or diatom slime which forms on all anti-fouling paints exposed in the sea.

Measurement of Slime Formation.—A quantitative method has been based on staining the slime film with methylene blue, and subsequently leaching out the absorbed colour and estimating the dyestuff

* A Report to the Corrosion Committee, a Joint Committee of The Iron and Steel Institute and The British Iron and Steel Federation, reporting to the Iron and Steel Industrial Research Council. Paper No. 9/1943. Pp. 82.

colorimetrically. By the technique, which is also applicable to painted surfaces, it is possible to estimate accurately the amount of slime formation within 24–48 hrs. after immersion. The toxicity of the surface can thus be determined within a very short period, and, since the seasonal effect is much less pronounced for slime formation than for fouling, the tests can be applied all the year round.

The Diatom Flora.—By plotting the amount of slime formed on test panels against the toxic index of the applied paints, it is possible to estimate the toxicity of the surface immersed in sea water long before any visible signs of plant or animal fouling appear, *i.e.*, in a week or two instead of a year. As some diatoms reproduce at all seasons, it should also be possible to use this method at all times of year.

ANTI-FOULING COMPOSITIONS.—Expts. indicated that against weeds mercury was almost twice as effective as copper, and against animals, especially barnacles, 3 times as effective; arsenic (as As_2O_3) was as ineffective against barnacle fouling as against weeds. *Laminaria* (the large brown oarweed) and *Ulva* (sea lettuce) were very sensitive to metallic poisons, whilst red seaweeds were somewhat less so. *Schizonema* (a colonial diatom) and *Ectocarpus* (a small fluffy brown seaweed) were much more resistant. The effect of a constant weight of different copper toxins is determined principally by their copper content; thus copper bronze and cuprous oxide are more effective than copper thiocyanate or Paris green.

About 100 organic compounds, *e.g.*, as used in insecticides and fungicides, have been tested on marine organisms. In sea-water cultures many of these have proved at least as toxic as copper, but, with a few promising exceptions, when incorporated in paint films they proved less effective. The equilibrium between the poisons in the paint film and in the adjacent sea water probably plays a part in the anti-fouling efficacy. Methods have been developed for the micro-determination of copper and mercury in sea water, and chemical studies of the rate of leaching of ionic copper and mercury and also of organic compounds from the paint films are in progress.

British Standards Institution

BRITISH STANDARD SPECIFICATION FOR FLOW MEASUREMENT

B.S. No. 1042.—1943

HITHERTO in this country there has been no authoritative reference standard for the measurement of flow, such as have been formulated by Germany, Italy, U.S.A., and the International Federation of Standardising Associations.

The Code for Flow Measurement, now published, is the outcome of the work of a Committee appointed in 1938, and whilst full consideration has been given to foreign standards, the Code represents current British practice. It deals fully with the conditions governing the design, installation and use of standard pressure-difference devices, so as to obtain consistent and generally acceptable results within a specified tolerance from commercial instruments. The "secondary devices" or flow meters are not discussed, since, if all the relevant rules of the Code are followed, the slight additional correction to tolerance required for any flowmeter under given conditions can easily be established by a manometric check.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Solanine, Glycoside of the Potato. I. Its Isolation and Determination. II. Its Distribution in the Potato Plant. L. H. Lampitt, H. S. Rooke, J. H. Bushill and E. M. Jackson. (*J. Soc. Chem. Ind.*, 1943, **62**, 20–24; 48–51.)—I.—In view of conflicting statements in the literature, the properties of solanine were re-examined, and a method of estimation was devised. Solanine was isolated by the method of Pfankuch (*Biochem. Z.*, 1937, **295**, 44) from sprouting potatoes, and the crude material was purified by redissolving in acetic acid, filtering and repptng. with ammonia; after repeating this process 4 times the substance was extracted with hot amyl alcohol and isolated from the extract by concn. and treatment with ammonia; after recrystallisation from ethyl alcohol, it had m.p. 280° C. with slight decomposition after shrinking in a characteristic manner at 235° C. It gave a purplish-red colour with sulphuric acid and formaldehyde. On hydrolysis with 2·5 *N* hydrochloric acid in a boiling water-bath for 1 hr. solanine yielded the aglycone, solanidine, m.p. 210° C. The reactions of solanine and solanidine are summarised in the following table:

ALKALOIDAL AND OTHER COLOUR REACTIONS

	Solanine	Solanidine
	(Using solid material)	
Conc. H_2SO_4, warmed.	Yellow→red.	Yellow→brown.
Erdmann reagent.	Yellow	Yellow.
Fröhde reagent, warmed.	Yellow→brown.	Yellow→brown.
Ethylsulphuric acid	Cherry-red	Cherry-red
Resorcinol in glacial acetic acid H_2SO_4, warmed.	Wine-red→darker and browner →blood-red→brownish-red.	Yellow→orange→red→browner with green fluorescence.
Vanillin in glacial acetic acid and H_2SO_4, cold.	Brown ring at junction of liquids, purple colour in acetic acid layer.	
Ditto, warmed.	Yellow → brownish yellow → reddish-brown → blood-red → brown.	Yellow → orange-red → red → brownish-red → dark-brown → black.
	(Using dilute sulphuric acid solution)	
Iodine in KI soln.	No precipitate.	Precipitate.
Mayer reagent	,, ,,	,,
Picric acid.	,, ,,	,,
Tannic acid	Turbidity.	,,
Phosphomolybdic acid	Precipitate.	,,

The colour reaction with sulphuric acid and formaldehyde had previously been used by Pfankuch for estimating solanine plus solanidine, and the method was studied with a view to further improvement. It was found that the colour had max. absorption at $570m\mu$, but that matching could more easily be carried out at $530m\mu$. At this wavelength the extinction coefficient was directly proportional to the concn. The colour reached max. intensity after about 30 min. and then remained constant; a time of 90 min. was selected as being most convenient for measuring the colour. Solanine alone can be estimated by measurement of the increase in reducing power after acid hydrolysis, which is complete after 60 min. heating.[3] The extraction of solanine from potatoes was also investigated. Minced potato tissue was extracted first with acidified 96% alcohol and then with successive quantities of 64% alcohol. It was found that three extractions in all were adequate. The values given in the literature for the solubility of solanine in ammoniacal soln. were found to be excessive; a value of 0·2 mg per 100 ml was actually obtained. Solanine added to minced potato was recovered to the extent of 95%. *Recommended procedure.*—(1) *Extraction.*—To samples of minced material (up to 150 g) add 150 ml of 96% v/v ethyl alcohol and then 3 ml of glacial acetic acid. Leave for 18 hrs. with occasional shaking, filter, extract the residue twice with 150 ml of 64% alcohol, and concentrate the combined extracts under reduced pressure to 50 ml. Add 5 g of sodium sulphate and warm the mixture for 30 min. Cool, add 2 ml of 20% sulphuric acid and filter off the flocculent ppt. so formed. Wash this residue with 10 ml of water and make the combined filtrate and washings alkaline with conc. ammonia. Leave overnight, filter, wash the ppt. with 10 ml of 2% ammonia and measure the vol. of filtrate plus washings. Dissolve the ppt. in 15 ml of 1% sulphuric acid and dilute to 25 ml. (2) *Colorimetric Determination of Solanine plus Solanidine.*—Transfer 2·5 ml of this soln. to a small, dry flask, cool in ice and add, with vigorous shaking, 5 ml of conc. sulphuric acid dropwise, and then after 1 min. 2·5 ml of 1% formaldehyde, also drop by drop. Leave for 90 min. at room temp. and measure the extinction coefficient in a Zeiss photometer, using filter S53 and a 1-cm cell. Calculate the concn. of solanine plus solanidine by reference to a calibration curve and add a correction (0·2 mg per 100 ml) for the solanine left in the ammoniacal solution. (3) *Hydrolysis Method of Estimating Solanine.*—Put 5 ml of the soln. into each of two 25-ml graduated flasks and add 5 N hydrochloric acid to give a concn. of 2·5% of hydrochloric acid. Immediately neutralise one soln. with 5 N sodium hydroxide (methyl orange) and dilute to 25 ml. Heat the second soln. for 1 hr. in a boiling-water bath and then similarly neutralise and dilute. Estimate the reducing power of 10 ml samples of each of the solns. by the Hanes–Hagedorn–Jensen method as modified by Hulme and Narain (*Biochem. J.*, 1931, **25**, 1051). Calculate the solanine content by reference to a calibration curve and make due allowance for the solubility of solanine as before. The method can be applied to the estimation of solanine in other parts of the potato besides the tuber, fibrous parts being minced in the frozen state prior to extraction with 96% alcohol, and leaves and flowers extracted with 45% instead of 64% alcohol.

II.—In view of the claims made by various workers on the toxicity of certain potatoes reputed to contain an abnormal amount of solanine, it was decided to investigate the distribution of the glycoside in the potato plant, using the method outlined in the preceding abstract. Solanine determinations were made on the skin (scrapings), peelings, flesh and eyes of the tubers. Very little solanine was found in the flesh, most being found in the skin and in the eyes. Sprouts contained much greater quantities than either peel or eyes and, unlike the rest of the tuber, they contained notable quantities of solanidine. Observations on potatoes during storage indicated that the solanine content of the eyes at first increases, then, as the sprouts developed, decreases, whilst that of the flesh remains unchanged throughout. The content of the peel and flesh was found to decrease when the potatoes developed sprouts in the dark at 30° or 4° C., but little change occurred at room temp. in daylight or ultra-violet light. A decrease in the solanine content of the whole tuber occurred when these were stored in the dark at 4° C., where little or no sprouting occurred, whereas under other conditions of storage the amount of solanine increased. Considerable differences were found in the solanine content of different varieties of potato. The solanine contents of various parts of the potato plant were also estimated. By far the highest concn. was found in the flowers, and this increased as the plant matured; the other parts of the plant showed a decrease in solanine content as the plant matured, except the stolons and tubers, which showed a slight increase. No free solanidine occurred in any part of the plant. When potato haulms were stored, the solanine content decreased with storage at 1° C., but remained constant at −25° C., although at this temperature it increased in the stem. The solanine contents of different parts of the potato plant, as determined by the colorimetric method, are summarised in the following table:

	Original material (mg per 100 g)	Calc. on dry solids
Skin (2–3% of tubers)	30–64	106–270
Peel (10–12% of tubers)	15	66
Peel, including eye (1/8 in. disc)	30	130
Peel, excluding eye (1/8 in. disc)	19	83
Flesh	1·2–10	6–40
Whole potato	7·5	27
Sprouts (formed during irradiation of tuber)	420–730	565–4070
Flower	215–415	1580–3540
Leaf	55, 60	506, 620
Stem of haulm	2·3–3·3	25–55

F. A. R.

Rapid Determination of Starch. An Index to Maturity in Starchy Vegetables. J. P. Nielsen. (*Ind. Eng. Chem. Anal. Ed.*, 1943, **15**, 176–179.)—Disintegrate a 100-g sample of the fresh, frozen or canned vegetable with an equal wt. of water (preferably in a Waring blendor disintegrator running at full speed for 3–4 min.). Weigh 2 (±0·01) g of the product directly into a 50-ml beaker, add 2 ml of water, and then exactly 2·7 ml of 72% perchloric acid slowly, with thorough stirring, to avoid local high concns.; stir occasionally for 10 min. Dilute to 25 or 50 ml (according to the starch content), allow the mixture to settle in a test-tube, and add to 1 ml of the supernatant liquid, 6 ml of water, 1 drop of phenolphthalein indicator soln., sufficient 6 N sodium hydroxide

soln. to produce a pink colour, and 2 *N* acetic acid until the colour disappears. Add 2·5 ml of this acid in excess, and then 0·5 ml of 10% potassium iodide and (from a pipette) 5 ml of 0·01 *N* potassium iodate solns. After 5 min. dilute to 25 or 50 ml according as the soln. is pale or dark bluish-green. Match the colour in a photoelectric colorimeter fitted with a red filter (640–700$m\mu$), and set its zero for a blank test containing the reagents only; if the liquid is turbid before the colour is developed, a correction should be applied by discharging the blue colour (after it has been matched) with a few drops of 0·1 *N* sodium thiosulphate and matching the residual turbid soln. against water. Standardise the apparatus against solns. containing known amounts of starch, preferably 0–3 mg per 50 ml for depths of soln. of *ca.* 1·25 cm. The starch should be prepared from raw unblanched material similar to that being analysed. Disintegrate the material as described, separate the fibrous constituents by washing the pulp on a 100 to 200-mesh screen, and stir the material passing through with a large vol. of water. Allow the suspension to settle, decant off the water, and repeat this procedure until the sediment of starch is free from extraneous material. Then wash it in succession with alcohol and ether, and dry it at 70–80° C. for 30 min.; this starch should be sufficiently pure, but if there is any doubt, check analyses should be made. The effects of variations in the perchloric acid concn. and of filtration of the suspension are recorded; the latter procedure involves a risk of absorption of starch by the paper, but a centrifuge may be used. Expts. with maize, lima beans, soya beans and peas showed that no interfering substances which might give a similar colour were present, and, consequently, the usual preliminary extraction of sugars (which interfere in methods involving hydrolysis) with alcohol is unnecessary; if the red filter is used, the error due to any dextrins present in such materials is much less than in a method involving hydrolysis in which dextrins are not first removed. Expts. with samples of lima and soya beans to which had been added 0–49·3 mg of potato starch after their true starch contents had been determined, showed recoveries of 97·4–98·6%. A good correlation was obtained between the starch contents of 50 samples of frozen lima beans and the grading obtained organoleptically and by flotation in 20% brine. Graphs also show the relationship between the starch contents and the tenderometer readings for raw peas. A single sample can be examined in this way in 20–30 min.; or 40–50 samples in 8 hr. There is no special hazard from the perchloric acid if the above direction are observed (*cf.* Pucher and Vickery, *id.*, 1936, **8**, 927). J. G.

Biochemical

Chromatography as a Means of Separating Amino Acids. J. L. Wachtel and H. G. Cassidy. (*J. Amer. Chem. Soc.*, 1943, **65**, 665–668.)—A mixture of 37·87 mg of glycine, 66·52 mg of *dl*-leucine, 58·25 mg of *dl*-phenylalanine and 10·12 mg of *l*-tyrosine in 10 ml of aqueous soln. was separated chromatographically on two 2-cm diam. adsorption columns, A and B, containing respectively 1·4 g of charcoal and 3 g of pulped filter-paper, and 2·6 g of charcoal and 4 g of pulped filter-paper. Column A separated rapidly the less well adsorbed glycine and leucine from the more strongly adsorbed phenylalanine and tyrosine, and also separated more slowly the last two. The glycine and leucine were collected together in one fraction of percolate, after which Column A was developed with 5% aq. acetone until phenylalanine began to appear in the percolate. The column of adsorbate was then extruded and cut into 5 equal sections, each of which was eluted with 225 ml of freshly prepared 5% aq. ethyl acetate, the eluates being made up to 250 ml for analysis. The mixed glycine-leucine fraction from Column A was concentrated *in vacuo* to about 20 ml and applied to Column B. Details of the progress of the separations are given in a table. The recoveries were: glycine 37·89 mg, leucine 67·34 mg, tyrosine 8·61 mg, and phenylalanine 49·10 mg. The glycine and leucine recovered probably contained some inorganic material dissolved from the charcoal. Some tyrosine and phenylalanine were lost, probably by decomposition. E. M. P.

Colour Reaction for Methionine. L. H. Sofin, H. Rosenblum and R. C. Schultz. (*J. Biol. Chem.*, 1943, **147**, 557–559.)—Methionine is sometimes present in *l*-leucine as an impurity. It can be detected by the formation of a yellow colour with a sat. soln. of anhydrous cupric sulphate in conc. sulphuric acid. The reagent contains *ca.* 1 mg of copper sulphate per ml, the amount varying somewhat with the strength of the sulphuric acid; it is prepared by warming a slight excess of anhydrous cupric sulphate with conc. sulphuric acid, cooling to room temp., and allowing to settle. The min. detectable concn. of methionine is 0·1 mg per ml of the reagent. Place 100 mg of the sample of *l*-leucine in a small test-tube, add 1 ml of reagent and stir. If no colour is produced, less than 0·1% of methionine is present. As the yellow colour produced by methionine is intensified by leucine, the former can only be estimated satisfactorily if the standard contains an equiv. amount of leucine; for this purpose the synthetic amino acid can be used with advantage. Prepare a series of standards containing up to 2·0 mg of methionine per ml and add to each 100 mg of *dl*-leucine, and then sufficient reagent to make the final volume 1·0 ml. Compare the colour of the unknown with that of the standards. As the reagent reacts with halides, chlorides should first be converted to sulphates. The only amino acids, other than methionine, which give colours are tryptophan and tyrosine. The absence of these substances should therefore be established by other reagents before testing for methionine. F. A. R.

Colorimetric Estimation of Serine. M. J. Boyd and M. A. Logan. (*J. Biol. Chem.*, 1942, **146**, 279–287.)—The methods previously available for the estimation of serine in amino acid mixtures are not applicable in presence of cysteine, but satisfactory results can be obtained by treatment with periodic acid, followed by colorimetric estimation of the formaldehyde thus formed with chromotropic acid (1 : 8-dihydroxy-naphthalene-3 : 6-disulphonic acid), a reagent which produces no colour with acetaldehyde. The method is also more rapid than the dimedon pptn. method, being completed in a few min. Put 1 to 5 mg of serine and 3 drops of methyl red into a 300-ml Kjeldahl flask. Add 4 ml of 25% potassium arsenite soln. and 2·5–2·8 ml of 0·5 *M* periodic acid, the last 0·5 ml being added, drop by drop, with shaking, until the mixture is acid to methyl red. Add a little talc and dilute to 70 ml. Attach the flask to a vertical condenser with the end dipping in water contained in a

receiver, and distil the contents of the flask until only 5 ml remain, giving the flask an occasional shake to rinse down the sides. Dilute the distillate to 100 ml, pipette 5 ml of standard formaldehyde soln. (15μg per ml) into a 1 × 8-in. test-tube, graduated at 50 ml, and transfer a portion of the distillate, containing 50–100μg of formaldehyde, to a similar tube. Add to each, 0·5 ml of 0·01 *M* chromotropic acid (dissolve 0·9 g in 25 ml of water, add 50 mg of stannous chloride, shake and centrifuge until clear), and dilute to 17 ml. Cool in ice, add, with shaking, 10 ml of conc. sulphuric acid during 40–45 sec., and dilute to the mark by allowing conc. sulphuric acid to flow down the centre of the tube. Heat for 10 min. in boiling water, cool to room temp. and compare the colours in the two tubes in paraffined or all-glass cups within 1 hr.; 1μg of serine ≡ 3·5μg of formaldehyde. The colour is proportional to the concn. of formaldehyde within 2%, provided that the unknown does not differ by more than 50% from a standard containing 1·5μg per ml. The recovery of added serine was 99% of the theoretical. Threonine had no effect on the yield, but cysteine appeared to be converted spontaneously into serine on standing. The presence of carbohydrates may also interfere, as these yield formaldehyde with periodic acid, and sugars must therefore be converted into other compounds by a preliminary hydrolysis. Glucosamine also interferes, and the error thereby introduced may be serious in the estimation of serine in mucoids. F. A. R.

Field Test for the Estimation of Peroxidase. W. B. Davis. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 952–953.)—Blanching by heat is an essential operation in the dehydration of many vegetables, but attempts to define the degree of heating involved in terms of the extent of the inactivation of oxidising enzymes have proved unsatisfactory. The following method has the advantages of improved accuracy, it can be applied to vegetables which give coloured extracts, and it is sufficiently simple and rapid for field use. Since peroxidase has some thermal stability it is preferred as an indicator to catalase and other enzymes, which are too readily affected by heat. Finely divide 25 g of the sample in 140 ml of a reagent containing 20 ml of 2% sol. starch soln., 10 ml of 0·1 *N* sodium thiosulphate, 4·5 g of potassium iodide, and 0·2 *N* acetate buffer (*p*H, 4·7) to make a total vol. of 1 litre; this reagent is stable for 24 hr. Filter through 4 thicknesses of cheese-cloth, squeezing the cloth as dry as possible by hand, and dilute the filtrate to 200 ml with the reagent. To a 50-ml aliquot part of the mixed extract add 1 ml of 0·9% hydrogen peroxide (prepared by diluting a pure 30% soln. containing no stabiliser) from a quick-delivery pipette. Note the time when the pipette is half empty, and again when the colour first begins to turn blue-black; the reciprocal of this val. is a measure of the enzyme activity. The reaction measures the catalytic oxidation of the iodide by the peroxide (due to the peroxidase), with the liberation of iodine (*cf.* Jayle, *Compt. rend. Soc. Biol.*, 1938, **128**, 1074). Since variations in the amounts of ascorbic acid present in vegetables due to blanching or dehydration may affect the results by reason of the active reducing properties of this substance, the relatively large quantity of sodium thiosulphate specified must be used. In the few instances where this is inconvenient the decrease in naturally-occurring reducing substances may be found by titration with iodine soln., or a correction may be obtained by measuring the reaction time without addition of the thiosulphate. Data are tabulated for purple cabbage, mustard greens, beets and carrots at various stages of blanching, before and after drying, for intervals up to 5, 4, 20 and 6 min., respectively. They show that the destruction of the peroxidase is progressive and changes over a wide range of blanching; the degree of blanching, therefore, is readily defined, even when it has been overdone (*e.g.*, cabbage heated for 5 min. required 570 and 295 sec. to reach the end-point before and after drying, respectively). A reaction time for the dehydrated material which is less than that for the freshly-blanched material (*e.g.*, with cabbage extract) may indicate loss of ascorbic acid or regeneration of the enzyme. The test does not purport to determine the correct amount of blanching for a particular vegetable, but only to show when a predetermined amount has been attained. J. G.

Simplified Photelometric Estimation of Trigonelline. S. W. Fox, E. W. McNeill and H. Field, Jr. (*J. Biol. Chem.*, 1943, **147**, 645–650.) A large proportion of nicotinic acid is excreted in the form of the betaine, trigonelline, and a satisfactory method of estimating this substance is therefore essential in studies on nutrition. A method is described in which the trigonelline is hydrolysed with alkali, and the nicotinic acid so formed is estimated with cyanogen bromide and dianisidine. To make the method applicable to urine, methyl alcohol, which produces a homogeneous solution, is used. Under these conditions the photometric intensity/concn. curve is approx. a straight line. Put 2·50 ml of urine into each of two 125-ml conical flasks, and add 2·50 ml of water to one and 1·0 ml of standard trigonelline soln. plus 1·50 ml of water to the other. Add 1·5 ml of methyl alcohol and 5·0 ml of 4% sodium hydroxide soln. to each, heat under reflux for 30 min. with condensers protected by soda-lime tubes, cool and transfer the contents to 50-ml volumetric flasks, and add 5 ml of water to each. Rinse the conical flasks with methyl alcohol and add the washings to the volumetric flasks. Adjust the soln. to *p*H 8·0 with conc. hydrochloric acid and dilute to 50·0 ml with methyl alcohol. Transfer two 9-ml portions to two photelometer tubes and add 1·0 ml of dianisidine soln. (dissolve 2 g of recrystallised dianisidine in 100 ml of acetone and 300 ml of 1·8% hydrochloric acid) to one of the tubes and 1·0 ml of 1·8% hydrochloric acid to the other. Measure the colour at 10-min. intervals, using filter 520 until the max. intensity is reached. A blank can be prepared from the diluted, treated urine without added dianisidine. The aver. % deviation of three groups of 4 analyses were respectively ±4·7, ±3·9 and ±8·0. Of the substances tested, only glucose interfered with the estimation, but serious errors due to the presence of glucose are only likely to be encountered in the analysis of foodstuffs and in the examination of diabetic urine. F. A. R.

Chemical Determination of Nicotinic Acid in Plant Materials. E. B. Hale, G. K. Davis and H. R. Baldwin. (*J. Biol. Chem.*, 1942, **146**, 553–563.)—An examination was made of the validity of various methods of extraction and hydrolysis for avoiding non-specific reactions in the estimation of nicotinic acid in plants. It was assumed that the most satisfactory method would

result in the lowest possible chemical values, and these were checked by comparison with the results of microbiological assay. Aqueous extraction of plant materials was complete within 45 min., and nicotinic acid derivatives were completely hydrolysed by N sodium hydroxide within 5 min. and by 2 N acid in 30 min. The results differed, however, according to whether the sample was hydrolysed directly with acid or with alkali, or whether hydrolysis was carried out on the aqueous extract. With seeds and seed products, alkaline hydrolysis of an aqueous extract gave the lowest value, direct alkaline hydrolysis gave higher values, and acid hydrolysis (whether of the material or of the extract) gave extremely high values. With the forage part of the plants, direct or indirect acid hydrolysis gave the lowest values, even lower than those obtained when the samples were not hydrolysed at all. On the basis of these observations the following method was devised:—Add water to a sample (0·5–1·5 g) of the plant material in a Pyrex test-tube graduated at 15 ml, and heat in boiling water for 45 min. Cool, make up to vol. and centrifuge. *Seed portion.*—Pipette 5 ml of aqueous extract into a 200-mm ignition tube and add 1 ml of 20% sodium hydroxide soln. Heat in boiling water for 5–10 min., cool, add 40 ml of ethyl alcohol, centrifuge and decant into another ignition tube graduated at 50 ml. Add 1 ml of 5% sodium bicarbonate soln., and acidify to *p*H 6 with conc. hydrochloric acid from a micro-burette, using phenolphthalein as internal, and brom-thymol blue as external, indicator. Make up to vol. with alcohol. *Forage portion.*—Pipette 5 ml of the aqueous extract into an ignition tube, add 1 ml of conc. hydrochloric acid and heat in boiling water for 30 min. Treat as above, using sodium hydroxide to bring the solution to *p*H 6. *Colour development.*—Pipette three 10-ml portions of the neutralised extracts into test-tubes, using tube A for measuring the residual colour, B for the nicotinic acid content and C for the standard. Put 0·1 ml of alcohol containing 10μg of nicotinic acid in tube C, immerse the three tubes in water at 70–80° C. and, after 10 min., add 3 ml of 4% cyanogen bromide soln. to B and C and 5 ml of 1·2 N hydrochloric acid to A. After a further 5 min. cool the tubes and add 2 ml of *p*-aminoacetophenone solution (5 g in 30 ml of conc. hydrochloric acid, diluted to 100 ml with water) to B and C. Immediately place in the dark and after 5 min., but within 30–45 min., measure the colour in a photoelectric colorimeter with a 420$m\mu$ filter. The amount of nicotinic acid (μg) in tube B is given by the expression $\frac{B-A}{C-B} \times 10$. Duplicate values agreed within ±3·5% for seeds and ±5% for the forage parts of the plant. The microbiological values varied slightly with the method of extraction, N sodium hydroxide extraction giving higher values than simple aqueous extraction. The microbiological values obtained by extraction with alkali, however, agreed well with those obtained by extracting seeds with alkali or by extracting the forage parts with acid, the difference seldom exceeding ±4%. F. A. R.

Chromogenic Reagent for Vitamin C Determinations. R. A. Koenig, T. L. Schiefelbusch and C. R. Johnson. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 181–182.)—To prepare the reagent, dilute a soln. containing 1·76 g of ferrous ammonium sulphate ($6H_2O$) and 10 ml of 1% sulphur dioxide soln. to 800 ml, and stir-in 2·50 g of αα′-dipyridyl until solution is complete. Boil to complete the reaction, cool and dilute the soln. of ferrodipyridyl to 1000 ml; this serves as a stable stock soln. for the preparation of the ferridipyridyl reagent as follows:—Titrate 200 ml at 80° C. with a soln. prepared by dissolving 40 g of ceric sulphate in 500 ml of water containing 28 ml of 36N sulphuric acid, filtering and diluting to 1000 ml; the end-point is a sharp change in colour from red to yellow, and *ca.* 11 ml of the ceric soln. are required. Then back-titrate with the sulphur dioxide soln. until the colour is pink, adjust the *p*H to 3·6 (using a *p*H meter) with 4–6 N ammonia prepared by bubbling the anhyd. gas through distilled water, but avoid an excess, which may ppt. ferric hydroxide. Dilute the soln. to 400 ml, and on the following day decant off the supernatant liquid from any ppt. This liquid is the reagent, but, if necessary, a little sulphur dioxide should be added from time to time to maintain the presence of a little ferrodipyridyl, the effect of which on the results is eliminated by making a blank determination (*vide infra*) every 2–3 days. For the determination, add the ammonia soln. to a portion of sample containing not more than 0·40 mg of ascorbic acid in the min. vol. of water, and a piece of Congo red paper. When the colour of the paper is similar to that of another piece in a buffer soln. of *p*H 3·6 add 10 ml of a buffer soln. prepared by dissolving 10·00 g of recryst. sodium acetate ($3H_2O$) in 1000 ml of 6·0% v/v glacial acetic acid and adjusting the *p*H to 3·6 by addition of acid or salt. Then add 20 ml of reagent, heat the soln. at 70–80° C. for at least 25 min., cool and dilute it to exactly 100 ml; to economise reagent, the above quantities may all be halved or quartered; if the soln. is turbid it should be passed through a Pyrex glass or platinum filter crucible or centrifuged, before the colour is developed. Alternatively, the colour may be allowed to develop at room temp. in 12–48 hrs., after which the suspended matter is separated by decantation. In either event the vitamin is oxidised to threonic and oxalic acids. When the colour is constant, match it colorimetrically or, preferably, make transmission readings at 28–32 ° C. (*e.g.*, with a Coleman 10–S–30 spectrophotometer) for the wavelength 510$m\mu$, a soln. containing 5 ml of buffer soln. and 10 ml of reagent in 50 ml being used as a reference standard. Use the median value found to read the result from a graph obtained by the calibration of the instrument with pure cryst. ascorbic acid. Such a graph is best represented by a straight line joining the points ($T = 100·0$, $C = 0·000$) and ($T = 10·0$, $C = 0·400$), where T is the % transmission relative to the blank (plotted on a log scale), and C is the ascorbic acid concn. in mg per 100 ml (plotted on an arithmetical scale). The line for oxidation to the dehydroascorbic acid stage passes through the point ($T = 10·0$, $C = 0·80$), but it is less well-established. The method has been used satisfactorily to assay commercial ascorbic acid, citrus fruit juices and dried foods. Large and small concns. of arsenious acid, formaldehyde, acetaldehyde, methyl alcohol or formic acid do not interfere with either the hot or cold modification, and 0·4 mg of oxalic acid ($2H_2O$), or 200 mg of citric acid, per 100 ml have little or no effect, even at 80° C. Sulphur dioxide reduces the reagent rapidly, but in small concns. it does not produce equiv. quantities of ferrodipyridyl under the conditions described. The error of the method is 0·5–2%, which is usually less than may arise from other sources (*e.g.*, sampling errors, oxidation of the vitamin). Since oxidation can occur in 2 stages,

it may be possible to determine vitamin C in presence of other interfering substances by suitable control of the temp., time and concn. of reagent.

J. G.

Winter Sources of Vitamin C. H. W. Crowe and E. A. M. Bradford. (*Nature*, 1943, **151**, 505.)—Comparisons of the ascorbic acid contents (titration with 2·6-dichlorophenolindophenol) of watercress as purchased, and of small hardy plants collected in Feb. and March are presented:—Australian cress (*Lepidum sativum*?), 148; American cress (*Barbarea verna*), 108; Italian corn salad (*Valerianella eriocarpa*), 93; Nüsslisalat (*V. olitoria*) from Switzerland, 55 and 84; watercress (*Nasturtium officinale*), 37 and 54 mg per 100 g of fresh material. The Nüsslisalat and Italian corn salad gave positive responses to the growth of *Lactobacillus casei* ϵ in the Snell and Strong test for riboflavin; they do not require special methods of culture, and can be grown in odd corners of small gardens; since they lack the pungency of the cresses, they could be eaten in larger quantities so as to give an increased vitamin intake.

J. G.

Photometric Determination of Reduced and Total Ascorbic Acid. M. Hochberg, D. Melnick and B. L. Oser. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 182–188.)—The photocolorimetric methods of Bessey (*J. Biol. Chem.*, 1938, **126**, 771) and of Evelyn, Malloy and Rosen (ANALYST, 1939, **64**, 213) involving titration with 2.6-dichlorophenolindophenol, with slight modifications, are recommended. Evidence is provided showing the necessity for including dehydroascorbic acid in the determination of the vitamin C. The dependence of the reaction time on the concn. of ascorbic acid is shown graphically, and the reduction of the dye by the vitamin is shown to be a reaction of the second order; the rate constant at 25° C. and *p*H 3·5 is 0·099 ± 0·015. A nomogram is provided for the determination of the ascorbic acid content from the residual photometric densities of the dye after reaction times of 5 and 10 sec. The photometric method is much more specific than the visual method, and it also enables determinations to be made on extracts containing small amounts of ascorbic acid, even in presence of relatively large amounts of other substances which reduce the dye. It has been used successfully for the analysis of urine before and after administration of test doses, but it is always important to determine the dehydroascorbic acid initially present in certain substances, and that produced in others when proper analytical precautions have not been taken (*cf.* Harris and Olliver, *id.*, 1942, **67**, 302). The method of "reversed titration" (*i.e.*, titrating the dye with the sample) is not recommended (see, however, Harris and Olliver, *loc. cit.*), because many of the interfering substances in the latter are thereby added to the former at an early stage of the reaction, and have ample opportunity for reacting with it; in the ordinary procedure, however, the dye is accounted for as soon as it is added by the rapidly-reacting ascorbic acid. The question of the reaction time before the true end-point is reached is still controversial, since reaction with the ascorbic acid may be incomplete after 5 sec., whilst after 30 sec. many interfering substances may react. The interfering effects of hydrogen sulphide, pyruvic acid, quinone and 2-methyl-1.4-naphthoquinone were investigated from this point of view. Pyruvic acid did not interfere with the photometric method, and the concns. of the other substances normally found in biological materials are insufficient to cause serious interference, even when hydrogen sulphide reduction has been used. The visual method may, however, be used safely for the routine testing of pharmaceutical products, so long as it is previously established that interfering compounds are absent. A special pipette to add exactly 5 ml of the extract of the sample to the dye soln. in less than 1 sec. is described.

J. G.

Ascorbic Acid Content of Sweet Peppers. V. A. Beckley and V. A. Notley. (*J. Soc. Chem. Ind.*, 1943, **62**, 14–16.)—The sweet peppers, or non-pungent forms of *Capsicum annum*, are rich in ascorbic acid, Hungarian paprika being richer than pimento and bell pepper. The ascorbic acid content increases with ripening of the fruit and is highest when the fruit ripens under warm, dry conditions. Analysis of paprika fruits gave the following results:

Parts	Ascorbic acid mg 100 g			Distribution %		
Pericarp	326	383	254	87·7	92·3	91·5
Placentae	153	145	106	12·0	7·3	8·1
Seeds	12	21	10	0·3	0·4	0·4

When roughly ground, the paprika pericarp, which is non-pungent and palatable, is a suitable source of ascorbic acid to add to rations. Drying is simple, and extensive plant is not required, but the ascorbic acid content of artificially dried paprika (*a*) is greater than of sun-dried (*b*), *e.g.*, material containing from 332 to 407 mg/100 g gave dry products containing (*a*) 1708 to 2067 mg/100 g; loss 7·8 to 23·3% and (*b*) 1028 to 1450 mg/100 g; loss 34·6 to 42·4% of ascorbic acid. Drying is quickest, results are highest and the products are crisp for grinding in a mill when the material is first cut into thin strips. Blanching sweet peppers before drying reduced the ascorbic acid content of dried product from 1716 to 310 mg/100 g. To prevent rapid loss of ascorbic acid, the ground product must be stored under completely dry airtight conditions; no loss then occurs in 6 months.

E. B. D.

Ascorbic Acid in Mashed Potatoes. G. N. Jenkins. (*Nature*, 1943, **151**, 473.)—Half of a representative sample of medium-sized potatoes, boiled whole, was mashed, and both portions were placed in water-heated double pans for *ca.* 2 hrs. at 80–85° C., samples being removed at intervals for the determination of ascorbic acid by titration with 2.6-dichlorophenolindophenol; the losses in wt. due to evaporation were insignificant. Values obtained after 0, 20, 60 and 135 min. were, respectively:—Boiled and whole, 5·4, 4·0, 2·5, 0·9; boiled and mashed, 5·0, 1·8, 0·5, 0·4; whole potatoes, boiled and kept at room temp., 5·4, —, —, 4·3 mg per 100 g. The results show that mashing causes no immediate loss of ascorbic acid, but considerably accelerates the rate of loss during subsequent heating, and that whole, cold potatoes lose little of their ascorbic acid. It appears to be preferable to cool and re-heat potatoes when necessary, rather than to keep them hot for long periods. It was also found that during 3 hrs. at room temp. the loss of ascorbic acid in mashed potatoes was greater than in whole potatoes. The above conclusions were confirmed, in general, by expts. under canteen catering conditions. The differences between vegetables kept hot in small portions and in bulk are, however, variable, although all of a small order. Mashed potatoes lost more ascorbic acid in bulk, whilst cabbage and whole potatoes incurred a

greater degree of oxidation in small helpings; in general, however, it does not greatly matter whether the vegetables are served or left in bulk during the time they are kept hot. Mashing on the large scale should be as rapid as possible; when a hand method (taking *ca.* 10 min.) was used, the value fell from 10·5 to 6·9 mg per 100 g. J. G.

Comparison of Procedures for Removal of Lipid Material from Bones of Chicks. I. Motzok, D. C. Hill, S. J. Slinger and F. N. Marcellus. (*J. Assoc. Off. Agr. Chem.*, 1942, **25**, 965–969.)—In the tentative method of the A.O.A.C. for the biological assay of vitamin D ("*Methods of Analysis,*" 1940, 371) the criterion of response is the ash content of the dry fat-free bone. For the removal of lipoid material, 95% ethanol followed by dry ethyl ether is recommended. To investigate various extraction procedures, comparisons were made with paired right and left tibiae of White Leghorn chicks fed on the A.O.A.C. ration. In a preliminary study 89 pairs of bones from 3-week-old chicks receiving 15 units of vitamin D per 100 g of feed were used. The right tibiae were extracted for 25 hr. with 95% ethanol alone, with 2 changes of alcohol in the last 5 hr., and the left tibiae were further extracted with ether for 20 hr. The treatment with ether resulted in the extraction of a considerably larger amount of lipoid matter, but had no effect on the absolute ash content of the bones, the wide difference in the % ash (34·7 and 40·9) being attributable entirely to the additional removal of fat by ether treatment. The effect of boiling the bones with 95% ethanol for 20 hr. followed by extraction in Soxhlet extractors for another 20 hr. was compared with the results of the regular alcohol and ether extraction. Five groups of *ca.* 17 chicks each, receiving 4·44, 10, 15, 22·5 and 33·75 unit levels of vitamin D respectively, were used, and the fat extracted in each extraction period was weighed and, after the final extraction, the ash of the bone was determined. The first procedure removed less lipoid material (4·31 g) than the second procedure (6·44 g). The total ash contents of the two sets were almost identical, but the % ash varied correspondingly with the fat material extracted. To determine the effect of drying the bones *in vacuo*, 40 pairs from 5-week-old chicks fed at a 10-unit level of vitamin D were dried at 75° C and 7 mm of mercury. All the bones were boiled with alcohol for 16 hr. and extracted in an extractor for 4 hr. With one set continuous extraction with alcohol was continued for 160 hr.; the other set was extracted with ether for 80 hr. The fat removed during successive 20-hr. stages and the ash were determined for both sets, and similar expts. were made in which vacuum drying was followed by the regular A.O.A.C. procedure for extraction. Drying the bones had no effect upon the solvent power of hot alcohol but caused a decrease both in the total amount of fat extracted by alcohol and ether and in its rate of extraction. From all the expts. it is concluded that the ethanol and ether extraction procedure of the A.O.A.C. gives the most nearly complete and most rapid extraction of fat material. The work of Dustman (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 469), who found that ether used after 95% ethanol removed only small amounts of extractives, is not confirmed. A. O. J.

Bacteriological

Bacteriological and Physical Changes occurring in Frozen Eggs. R. Schneiter, M. T. Bartram and H. A. Lepper. (*J. Assoc. Off. Agr. Chem.*, 1943, **26**, 172–182.)—The experimental material consisted of 30-lb. cans of liquid egg, prepared, frozen, shipped and stored under the usual commercial conditions. Samples for bacteriological examination were taken immediately after the cans were filled, and all the cans were frozen at −10 to −14° F., with the exception of one set which was slow-frozen at 0° F. The cans were re-sampled 60 hrs. after freezing by drilling out representative portions. After storage at +5° to −13° F. for *ca.* 3 months the cans were sent with a commercial shipment from Kansas City to Washington, D.C. Recording thermometers indicated a range of temp. of 24°–32° F. during the journey. Samples were taken immediately after arrival, and the material was placed in commercial cold storage at 0° to −5° F. After *ca.* 1 month some of the cans were thawed by exposure to sunshine (80°–100° F.) for 6 hrs. and storage overnight at 64° F., the temp. of the stirred product ranging from 37° to 46° F. The eggs were sampled, re-frozen and again sampled. After another year's storage some of the material was thawed and sampled in the same manner, and the procedure was repeated in 5 and 6 years. All samples taken for bacteriological examination were subjected to total plate counts on dextrose agar with incubation at 25°–32° C. and at 37° C. for 72 hrs. Coliform types were determined by lactose broth presumptive tests with partial confirmation with Levine's eosin, methylene blue and agar medium. Examinations for haemolytic staphylococci and streptococci (veal-blood-agar medium) and for anaerobes (alkaline cooked meat medium) gave results of no apparent significance. In the initial examination of unfrozen material, the highest grade product made from selected fresh, uncracked, clean eggs gave counts from less than 10,000 to 30,000 per g, with coliform types never present in dilutions greater than 1 : 1,000. With the product that included weak and slightly cracked eggs, the counts were slightly higher, and not more than 300,000 for the product containing white or yolks only, but up to 2,000,000 for the product from whole eggs, the initial freezing of which had been delayed. Material including washed and cracked eggs gave variable counts, and material from whole eggs with variable proportions of "rots" was putrid and gave correspondingly high counts. After storage and shipment the product of highest quality showed no change except a slightly decreased count. In other material increased counts were observed, especially in those of high initial count, but there was no change in odour. In thawed samples the eggs generally showed slight increase in bacterial content, but the counts did not exceed 24 times their original value, and after re-freezing they returned to the levels found in the third examination. After a year's storage, continued decreases in bacterial content were observed in first-grade material, whether previously thawed and replaced in storage or continuously in storage. Samples of somewhat lower quality showed some decrease in count, but some of the material previously thawed was putrid, and most of that of originally low quality showed increase in bacterial content. After thawing, increases up to 5-fold were observed in the best product, but the count returned to its original level after re-freezing. In second-grade yolk samples the counts increased 10-fold during thawing and re-freezing, and the odour was strong or slightly putrid. The remaining grades all showed higher counts. In all these examinations the coliform content followed roughly the total count and is

thus shown to be a good index of quality. After 5 and 6 years' storage the products contained large ice crystals and had a leathery texture, but the edibility after thawing was not affected. The product of second-grade whole eggs, the initial freezing of which had been delayed, and of lower grades containing "rots" presented a disintegrated appearance and had a strong or putrid odour. The bacterial count of the first-grade product underwent little change between the first and fifth year, and the egg whites in the first and second grades were almost free from bacteria (less than 10 per g). This was undoubtedly due to presence of bactericidal lysozyme in the egg white. Some of the lower-grade products had decreased in count to the level of the highest grade and were not an unsatisfactory product in spite of high counts and strong odour during the first year. Eggs that had been held in the churn before being canned and frozen reflected this abuse in 6 years. It is concluded that frozen eggs of good quality can withstand at least 2 thawings and re-freezings without significant change, that eggs of poor quality must be frozen rapidly and maintained in the frozen condition and that, even after 6 years, the bacterial count is an index of original quality. A. O. J.

Estimation of Rope Spores in Wheaten Flour and other Products. E. Barton-Wright. (*J. Soc. Chem. Ind.*, 1943, **62**, 33–36.)—A re-investigation of the rope-causative bacteria in bread is recorded. It is considered that these organisms belong to the *Bacillus subtilis* and not to *B. mesentericus* group, from which they may be distinguished by ability to reduce nitrates, to quicken action upon proteins, to form diastase and to hydrolyse starch, and by features of growth on solid media. Two main methods for the quantitative estimation of spores previously described are criticised and the following method is recommended:—To 100 ml of 1% sterile saline in a w.m. stoppered bottle are added 10 g of freshly ignited silver sand and 32 g of flour, and the whole is vigorously shaken for 2–4 min. Ten ml are pipetted into a small sterile bottle containing 10 ml of sterile saline soln. and this is shaken for 1 min.; from this another 2-fold dilution is made in the same way and so on until 9 dilutions of the primary suspension are obtained. One ml from each, including the primary suspension, is pipetted into each of 5 tubes of nutrient broth, the 50 tubes are then heated in a steam steriliser for 30 min. (timed from the free issue of steam), and incubated at 37° C. for 48 hrs., after which they are examined for grey-white pellicle formation on the surface of the broth. A useful table, constructed by H. W. Norton, of the Galton Laboratory, University College, London, is given for calculating the probable number of spores statistically from the results obtained. D. R. W.

Forensic

Modification of Widmark's Method for the Determination of Alcohol in Blood. R. M. du Pan. (*Helv. Chim. Acta*, 1943, **26**, 531–536.)—In Widmark's method (*Biochem. Z.*, 1922, **131**, 473) the procedure is as follows:—Draw a sample of blood (0·1 ml) into an S-shaped, wax-lined capillary tube and weigh the tube on a torsion balance. Blow the blood into the small cup attached to the stopper of a specially constructed Erlenmeyer flask and re-weigh the tube to obtain the wt. of blood in the cup. The flask contains exactly 1 ml of a soln. of 2·5 g of potassium dichromate in a litre of conc. sulphuric acid, and a similar flask with the same amount of reagent is used for a blank determination. Heat the tightly stoppered flasks at 60° C. in a water-bath for 2 hrs. and cool quickly. Treat the liquid in each flask with 25 ml of water and 1 ml of 5% potassium iodide soln., and titrate the liberated iodine with $N/100$ sodium thiosulphate, using starch indicator. The difference in titre of the two liquids is a measure of the alcohol oxidised to acetic acid by the dichromate soln.; 1 ml of $N/100$ sodium thiosulphate $\equiv 113\mu g$ of alcohol. The following simplified modification of the method was found to be equally precise. Transfer a sample of blood (1 ml), drawn from the finger, to a tube containing sodium fluoride to prevent coagulation. By means of an accurate pipette place 0·1 ml of blood in the cup of the Erlenmeyer flask, which contains 1 ml of a soln. of 1 g of potassium dichromate in 25% sulphuric acid. Rinse the pipette into the cup with a little water. The procedure is then as previously described, but the titrations are made with $N/200$ sodium thiosulphate; 1 ml $\equiv 56{\cdot}5\mu g$ of alcohol. To ascertain the wt. of blood used, the sp.gr. is taken to be 1·05. Expts. showed that with prolonged heating the soln. of potassium dichromate in 25% sulphuric acid is more stable than the corresponding soln. used by Widmark. It has the additional advantage of being more fluid. No loss of precision results from not using waxed capillary tubes, the torsion balance and Widmark's special pipette for measuring the potassium dichromate soln. Immediately before the determination, the Erlenmeyer flasks should be filled with acid potassium dichromate soln., heated on the water-bath for 30 min. and rinsed well with water; they should not be dried. A. O. J.

Organic

Determination of Furfural. I. J. Duncan. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 162–164.)—The method of Stillings and Browning (ANALYST, 1940, **65**, 663) is improved in respect of the rate of development and stability of the colour as follows:—To the sample of pentose, pentosan or plant material (furfural content, 1–15 mg) in a 500-ml two-necked round-bottomed flask add sufficient water and hydrochloric acid to produce 200–225 ml of *ca.* 18·5% hydrochloric acid. Insert a steam-delivery tube in one neck, so as to reach almost to the bottom of the flask, and steam-distil so that the temp. is at 105–106° C. at the inlet of the other neck, which connects the flask to a condenser. Collect the distillate, which should pass through a small filter as it comes from the condenser, in a 1000-ml flask. If the vol. of the liquid in the flask is reduced to *ca.* 75 ml., remove the steam-tube and add sufficient of the acid to restore the original vol. Distillation is complete when a few drops of distillate no longer give a colour in 10 min. with an equal vol. of glacial acetic acid containing 2·5 ml of aniline per 25 ml (2–2·5 hr.). Dilute the distillate to the mark, make 10-ml aliquot portions just alkaline to phenolphthalein with sodium hydroxide soln., in 50-ml flasks, and add 5 ml of a soln. containing *ca.* 0·12 g of oxalic acid and 0·25 g of disodium hydrogen phosphate (as accelerator and stabiliser for the colour). Dilute the soln. to *ca.* 25 ml, add 25 ml of a cool, freshly-prepared mixture of 22·5 ml of glacial acetic acid and 2·5 ml of freshly distilled aniline, and dilute to the 50-ml mark. After 45–60 min. in a bath at 20° C., in

the dark, match the colour of the soln. against that produced from a standard soln. of furfural. A photo-electric colorimeter calibrated in terms of the standard soln., is preferred. With pentoses and plant materials the method of steam-distillation described gave higher yields than when phosphoric acid was used in the flask; when 12% of hydrochloric acid was used the rate of removal of the furfural was halved, but xylose gave the same furfural yields with 12–24% of this acid. The method is not affected by methyl furfural or hydroxymethyl furfural, and the distillates from alfalfa and sweet clover produced coloured solns. very similar to those obtained from pure furfural (as shown by the spectrophotometric curves), indicating that no appreciable amounts of interfering substances were present in these materials. The titration-method of Hughes and Acree (ANALYST, 1934, **59**, 430) consistently gave higher results than the colorimetric method with distillates from sugars, alfalfa and sweet clover, and it is believed that this is due to the presence in their distillates of reducing substances other than furfural. J. G.

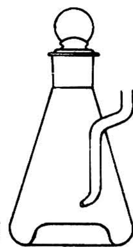
Colour Test for some Highly Reactive Organometallic Compounds. H. Gilman and L. A. Woods. (*J. Amer. Chem. Soc.*, 1943, **65**, 33–34.)—The reaction between benzylamine and highly reactive RM types forms the basis of a test which supplements those previously described (*J. Amer. Chem. Soc.*, 1925, **47**, 2002; 1940, **62**, 1847; 1941, **63**, 839). The procedure is as follows: Add 1 ml of the organometallic soln., without shaking, to 0·5 ml of an approx. molar solution of benzylamine (or dibenzylamine) in dry light petroleum free from unsat. compounds (b.p. 60–68°C. was used generally). The appearance of a cherry red colour in a few sec. is a positive test. If the RM solution is quite dilute the colour may fade in a few min. The shade depends to some extent on the concn. of the RM solution. Keep the benzylamine in a stoppered bottle. In sensitivity tests, 1 ml of a 0·020 molar *n*-butyllithium solution and 0·5 ml of 1·0 molar benzylamine solution gave a negative test, whilst 2 ml of the RM soln. with the same quantity of reagent gave a positive test.

E. M. P.

Inorganic

A Remarkable Indicator. G. Schwarzenbach. (*Helv. Chim. Acta*, 1943, **26**, 418–424.)—It is shown that 5-pyridinium-glutaconedialdehyde-perchlorate, which is colourless in acid and red in alkaline soln., is the only indicator so far known which reacts with two hydroxyl ions in one stage, and its colour change takes place within the range of one *p*H unit. The indicator has a very small salt error, and practically no alcohol error up to a concn. of *ca.* 60% of alcohol. The colour change takes place at about *p*H 12–13. W. R. S.

Simplified Technique in the use of Liquid Amalgam Reductors. G. F. Smith and L. T. Kurtz. (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 854–855.)—A rapid and simple method by which liquid amalgam reducing agents may be separated from reduced soln. by the introduction of a layer of carbon tetrachloride preparatory to oxidimetric determination is described. For reductions which do not require a neutral atmosphere, a 250–500-ml Erlenmeyer flask with a ground-glass stopper is all that is required, but when an oxygen-free atmosphere is necessary a special flask (see diagram) is needed. The liquid amalgams are prepared according to Someya (*Z. anorg. Chem.*, 1924, 1927). Experimental procedures for iron (using *e.g.*, *N*/10 ferric ammonium sulphate) and titanium determinations are given in detail, but the technique can be generally applied. *Iron.*—Place 25 ml of sat. zinc amalgam, 100 ml of 1 : 6 sulphuric acid and 25 ml of ferric alum soln. in a glass-stoppered Erlenmeyer flask, replace the stopper and shake vigorously for 2 min. Remove the stopper, rinse down the sides of the flask and add 30–50 ml of carbon tetrachloride. The carbon tetrachloride (sp.gr. 1·6) separates the amalgam layer from the soln. to be analysed. With a mechanical stirrer swirl the top layer so that the carbon tetrachloride is not appreciably disturbed and titrate with *N*/10 ceric sulphate, using ferroin as indicator [presumably *o*-phenanthroline.—ABSTRACTOR]. In presence of air the results are slightly low. This can be overcome by the introduction of carbon dioxide either from a cylinder or by adding 0·5 g of sodium bicarbonate to the acid soln. before shaking the flask for the reduction. The cause of these low results in the absence of carbon dioxide is as yet unknown. *Iron and Titanium.*—The same procedure can be applied to a mixture of ferric alum and titanic sulphate solns., using the special flask shown in the diagram. Having added solns. and amalgam, fill the flask with carbon dioxide through the side arm, replace the stopper, close the side arm and shake the flask for 2 min. Remove stoppers, rinse down the flask walls, and add carbon tetrachloride as before. Pass carbon dioxide rapidly through the side arm and titrate with *N*/10 ceric sulphate, using methylene blue as indicator. Add 1–2 drops of ferroin and complete the titration of ferrous iron.



C. F. P.

Analysis of Bolivian Tin Concentrates. S. Kallmann. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 166–174.)—A useful detailed description of reliable methods for the determination of tin and impurities (lead, copper, bismuth, antimony, arsenic, zinc, sulphur). Acid decomposition for the determination of copper is shown to give low results; the ore must be decomposed by fusion with sodium peroxide and carbonate (8 : 4). For the determination of bismuth, 5–10 g of ore is fused with litharge, soda, borax, and flour in a clay crucible, and the bismuth is determined in the resulting lead buttons. W. R. S.

Determination of Zinc in Aluminium Alloys. A. Cohen. (*Helv. Chim. Acta*, 1943, **26**, 75–88.)—*Rapid Electrolytic Method.*—Add 15 ml of 25% sodium hydroxide soln. to a 1-g sample of drillings in a 150-ml beaker. Cool if necessary. When gas evolution has died down, add a little water and boil gently for 6–10 min. Cool and dilute with about 80 ml of water. Filter off the residue, wash twice with dil. sodium hydroxide soln., and discard the residue. To the filtrate add 1–2 ml of 50% tartaric acid soln. and deposit the zinc electrolytically on a rapidly rotating coppered cathode; zinc is determined from the increase in weight of the cathode. A correction is required for zinc remaining undissolved in the residue from the alkali attack. As a result of tests on a wide variety of aluminium alloys varying in content of zinc and other constituents it was found that the correction

depends principally on the zinc content; the following additions % should be made to the zinc found: 0·05–0·14%, nil; 0·15–0·24%, 0·01; 0·25–0·30, 0·02; 0·31–5·00, 0·1; 5·01–6·00, 0·5; 6·01–7·00, 0·55; 7·01–9·00, 0·60; 9·01–12·00, 0·70; 12·01–20·00, 0·80; 20·01–30·00, 0·9; 30·01–50·00, 1·00. The process should be carried out in a room free from fumes of ammonia or ammonium salts to avoid any chance of solution of copper from the residue. Tests were carried out on a recent process of K. Steinhauser (*Aluminium*, 1942, **24**, 176), which involves alkali attack on the alloy, acidification of the liquid and addition of hydrogen peroxide to dissolve the residue; copper is pptd. with hydrazine sulphate and zinc is deposited electrolytically from alkaline soln. This process was found to be inaccurate with alloys containing lead, which escaped complete pptn. with the copper and co-deposited with the zinc. *Zinc Mercury Thiocyanate Pptn. Method.*—Dissolve, as far as possible, 5 g of drillings in 200 ml of 1 : 3 sulphuric acid and 0·8 ml of conc. hydrochloric acid; add 5–10 ml of conc. hydrogen peroxide soln. to dissolve metallic residue, and boil to destroy excess. Dilute to 250 ml and electrolyse to remove copper. Add 40 ml of conc. sulphuric acid, dilute to 400 ml, cool and add, with stirring, 25 ml of reagent soln. (54 g of mercuric chloride and 70 g of ammonium thiocyanate per litre; 5 ml required per 0·05 g of zinc). After 1 hr. (or 12 hrs. if small amounts of zinc are present) filter off the ppt., wash with a mixture of 50 ml of reagent and 25 ml of 1 : 3 sulphuric acid per litre, ash the filter and ignite the residual impure zinc oxide. Extract the residue by heating, with 10 ml of 25% sodium hydroxide soln., dilute to 100 ml and filter. The bulk of the zinc is now in the filtrate as zincate, but some remains in the ppt. The residue on the filter is therefore dissolved in 5 ml of 1 : 3 sulphuric acid with addition of a few drops of hydrogen peroxide; neutralise the liquid with 25% sodium hydroxide soln., add 8 ml in excess, boil to ppt. manganese, cool, dilute and filter. A small amount of hydrazine sulphate should be added during the boiling to prevent solution of traces of copper, which may be present at this stage through copper not having been completely deposited in the earlier electrolysis. Add to the combined alkaline solns. 1–2 ml of 50% tartaric acid, and deposit zinc electrolytically on a coppered rotating cathode and weigh. It is important in the zinc mercury thiocyanate pptn. that the sulphuric acid concn. should be sufficiently high, *viz.*, *ca.* 25% v/v; with too little acid present the pptn. is slow and incomplete. This pptn. affords a separation of zinc from the bulk of the nickel, cobalt and manganese present. S. G. C.

Determination of Zinc in Magnesium Alloys. A. Cohen. (*Helv. Chim. Acta*, 1943, **26**, 89–91.)—The process employs pptn. of zinc as zinc mercury thiocyanate on the lines of that developed by the author for zinc in aluminium alloys (*cf.* preceding abstract). Dissolve, as far as possible, 1 g of alloy drillings in 25 ml of 25% v/v sulphuric acid. Boil for 10 min. if considerable amounts of copper are present, and filter while hot. Cool, add 15 ml of conc. sulphuric acid and dilute to 140 ml. Cool and add 15 ml of reagent (54 g. of mercuric chloride and 70 g of ammonium thiocyanate per litre), which is sufficient for pptn. of 0·1 g of zinc. After 1 hr. filter off the ppt., ash the filter and ignite the residue, which yields impure zinc oxide. Extract the residue by heating with 10 ml of 25% sodium hydroxide soln. If small amounts of copper are present at this stage, add a little hydrazine sulphate and heat for 10 min. Dilute, filter off any residue, and wash with dil. sodium hydroxide soln. Add to the filtrate 1–2 ml of 50% tartaric acid soln. and deposit zinc electrolytically on a rotating coppered cathode. S. G. C.

Determination of Ferrous Oxide in Chromite. G. E. Seil. (*Ind. Eng. Chem.*, *Anal. Ed.*, 1943, **15**, 189–192.)—Chromite reacts quantitatively with sulphuric acid in phosphoric acid at 350° C. in an atmosphere of carbon dioxide under reduced pressure: $2Cr_2O_3.FeO + 10H_2SO_4 = 2Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + 10H_2O + SO_2$. The evolved sulphur dioxide is absorbed in a soln. of dichromate, the excess of which is determined. The apparatus is elaborate, and reference should be made to the original for full particulars and working details. The ore, which is crushed to pass a 325-mesh, must be free from other reducing substances (carbides, sulphides, metallics); if necessary, it may be calcined at about 500° C. without appreciable oxidation of the ferrous oxide. Weigh 0·5 g of ore into a round-bottomed 200-ml flask containing 20 ml of 85% phosphoric, and 5 ml of strong sulphuric, acid. The inlet tube of the flask is connected with a supply of purest carbon dioxide (from bicarbonate), the exit tube with a train of two cooled receivers containing 25 ml of a 0·1 *N* dichromate soln. in 5% sulphuric acid, a splash trap, Bunsen valve, and a pump maintaining reduced pressure at *ca.* 680 mm of mercury during the operation. The reaction flask rests on an electrically heated air-bath provided with thermometer, rheostat, and ammeter. After the acid mixture has become anhydrous the ore dissolves in 35–90 min. When the sulphur dioxide has been swept into the receivers by the carbon dioxide, the contents are transferred to a flask and titrated with iodide and thiosulphate. A blank should be run. The residual acid soln. may be used for the determination of chromium after oxidation with persulphate. W. R. S.

Critical Study of Reagents for the Detection of Cerium. P. Wenger and R. Duckert. (*Helv. Chim. Acta*, 1942, **25**, 1547–1552.)—The following are reagents which are recommended:—*Phosphomolybdic acid* (Komarowsky and Korenmann, *Mikrochem.*, 1932, **12**, 211).—Used in 10% aqueous soln., it gives a blue colour or ppt. with cerous salts in neutral or alkaline soln. The sensitivity is 0·5μg in 1 drop on a tile or spot on filter-paper. Iron^{II}, cobalt^{II} and manganese^{II} interfere; the rare earths do not react. *Benzidine or o-Toluidine* (Feigl, *Österr. Chem. Ztg.*, 1919, **22**, 124; Kuhlberg, *Zavodskayalab.*, 1938, **7**, 905). Used as 0·05% soln. in 10% acetic acid, it gives a blue colour with ceric salts in neutral sodium acetate soln. The sensitivity is 1·5μg in 0·1 ml on a tile or 0·5μg in 1 drop on a filter paper, and 1μg in 1 ml in a test-tube. Copper, silver, thallium, manganese and ferric ions give a similar reaction; gold interferes; rare earths do not react. *Ammonium Anthranilate* (Schemjakin and Belokon, *C.r. Acad. Sci. U.S.S.R.*, 1938, **18**, 275).—Used as 5% aqueous soln. (or 5% alcoholic soln. of anthranilic acid), it gives a brownish-red colour or ppt. with ceric salts in strongly acid or neutral soln. The sensitivity is 5μg in 0·1 ml on a tile, or 0·5μg in 2 ml in a test-tube. Thorium, zirconium, praseodymium, neodymium and cerous salts do not react.

Tetramethyldiamino-4-4′-triphenylmethane (leuco malachite green) (Kuhlberg, *Mikrochem.*, 1936, **21**,

35).—Used as a 0·1% soln., in 40% acetic acid neutralised with *N* sodium hydroxide soln., it gives a bluish-green colour with ceric salts in neutral soln. The sensitivity is 0·03μg in 1 drop on filter-paper. Gold, thallium, thorium, cobalt and manganese interfere. Rare earths do not react. *Sodium Carbonate* (Behrens-Kley, "*Mikrochem. Analyse,*" 1915, p. 127).—The white ppt. given by cerous or ceric ions on addition of solid sodium carbonate is useful as a microscopic reaction. The sensitivity is 0·05μg in 1 drop. Lead, thorium and the alkaline earths gave a similar ppt.

The following reagents which have been proposed from time to time are not recommended as they are either too general, not sensitive or give similar reactions with rare earths—sodium sulphate, caesium chloride, formic acid, oxalic acid, ammoniacal hydrogen peroxide, ammonium molybdate, ammonium succinate and hydrogen peroxide, pyrocatechol and sodium thiosulphate, quinalizarine, pyrogallol, morphine, ammonium tartrate and hydrogen peroxide, gallic acid and sodium sulphite, methylene blue, brucine, *o*-hydroxyquinoline, ammonium salicylate, ammonium naphthionate, phenyl alanine, dimethylglyoxime and a ferrous salt, sulphanilic acid, *o*-phenanthroline ferrous ion, diphenylamine plus metaphosphoric acid plus chromic acid plus arsenious acid, tannin, carminic acid, cochenille, sodium *p*-aminophenylarsinate. S. G. C.

Rare-Earth Fractionation by Zeolite Action. R. G. Russell and D. W. Pearce. (*J. Amer. Chem. Soc.*, 1943, **65**, 595–600.)—Preliminary work, which is being continued, indicates that fractionation of a rare-earth mixture by zeolite action is feasible. The rare earths can enter the zeolite lattice, and, if the base exchange material is in excess, they are completely removed from solution. If not, the exchange-material exhibits a preference for rare earths of smaller ionic radius. This decreases from lanthanum to lutecium, yttrium being intermediate between dysprosium and holmium. The technique consists in passing a neutral rare-earth nitrate soln. through a tall column of a synthetic zeolite (*e.g.*, crystallite). The ions for which the lattice has greater affinity are held in the upper part of the column, the others passing further down. As fresh soln. drips in at the top, the more loosely held ions tend to be displaced. The filtrate issuing at the base of the column is fractionally collected. Controlled regeneration of the washed zeolite by strong sodium chloride soln. and fractional collection of the "regenerate" also gives head fractions showing an accumulation of the more readily removable ions. Hence a 2-fold fractionation takes place; first by the action of the rare-earth soln. upon the zeolite, then by regeneration of the zeolite by means of brine. The various fractions obtained in each series are suitably combined and re-treated. The ceria earths accumulate in the filtrates, the yttria earths in the "regenerates." The relative concn. of the individual earths in the mixture under treatment may possibly affect the course of the fractionation. W. R. S.

Determination of Lithium as Periodate. L. B. Rogers and E. R. Caley. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 209–211.)—Dissolve 24 g of potassium hydroxide in 100 ml of water, cool, add 10 g of potassium metaperiodate. Keep in the dark in a paraffined container. To 1 ml of test soln. add 1 ml of reagent; 0·0005 g of lithium gives a ppt. within 1 min. in the cold. At 70° C. a distinct ppt. is obtained with 0·0001 g. In chloride soln. 0·05 g of sodium or ammonium or 0·1 g of potassium gives no ppt. under these conditions. Other metals must be absent. The common anions do not interfere. Acid solns. should be neutralised with potassium hydroxide. When produced in the cold the ppt. is finely divided; slowly pptd. at 70° C. it is coarser. It is soluble in water, acids, and weak alkalis. As pptd. from strongly alkaline soln. it retains considerable alkali. No stoichiometric relation was found in the Li : I ratio, which varied from 4·37 to 4·70. The authors regard the ppt. as "a mixture of lithium periodates" [more probably it is lithium periodate in which potassium partly replaces lithium.—ABSTRACTOR]. It cannot be used for gravimetric work, but may serve for a rapid empirical volumetric method. Treat the soln. (2 ml), free from ammonium, at 70° C. with 2 ml of reagent, added at the rate of 1 drop in 5 sec. If a heavy ppt. forms, add another 3 ml of reagent in the same manner. Set aside for 20 min. at 60°–70° C., filter on a moderately thick asbestos paid in a Gooch crucible, wash with four 2-ml portions of 3 to 5 *N* potassium hydroxide added slowly from a pipette. If more than 0·02 g of sodium is present, carry out the pptn. in the cold. Transfer ppt. and pad to a 250-ml beaker, dissolve in 5 ml of *N* sulphuric acid, add potassium iodide and titrate with thiosulphate standardised against a pure lithium salt which is submitted to exactly the same procedure. W. R. S.

Determination of Iodate in Presence of Bromate and Chlorate. I. M. Kolthoff and D. N. Hume. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 174–175.)—At *p*H 5 the reaction between iodide and bromate is negligible during the time required for titration; at *p*H 4 the rate of reaction is more rapid. Iodide and iodate react readily at *p*H 4–5. Treat the soln. (25–50 ml; 2–3 milli-equiv. of iodate) with 2 g of solid potassium biphthalate (*p*H 4); swirl until dissolved, add 3 g of potassium iodide, set aside for 3 min., and titrate the iodine with 0·1 *N* thiosulphate. A fourfold excess of bromate or chlorate does not interfere, but the iodate concn. should be determined by a preliminary titration serving as a guide for the addition of biphthalate in the above ratio. W. R. S.

Physical Methods, Apparatus, etc.

Dispersion of Pigments and Fillers for Microscopical Examination. L. B. Miller. (*Paper Trade J.*, 1943, **116**, *T.A.P.P.I. Sect.*, 9–12.)—The object of the technique described is to prevent the aggregation which occurs, especially between particles of different sizes, in the preparation of slides of powdered materials for microscopical examination. The dispersion medium used for dense particles of considerable structural strength is: amyl acetate, 82; ether, 6; abs. alcohol, 4; purified thin-flake pyroxylin ("Parlodion)," 1·94 g. For fragile particles slower evaporation is desirable, and a suitable medium is: amyl acetate, 80; ether, 4; abs. alcohol, 6; butyl alcohol, 2; pyroxylin, 1·94 g. The solvents should have a high degree of purity; the pyroxylin dissolves slowly in the mixture if it is agitated occasionally over a period of some days. Dry the powder thoroughly at 220° F., or at as high a temp. as is permissible, and place a speck of it on the microscope slide. Place 2 drops of the medium on it

from a medicine dropper, and disperse it by rubbing with a small spatula. Tilt the slide, guide the dispersion to one corner by means of a spatula, and allow one drop only of it to fall on to the surface of distilled water (free from bubbles) in a beaker. The dispersion spreads at once into a thin film, and the completion of evaporation (after about 2 min.) is indicated by the disappearance of the surface gloss. Isolate the portion of the film to be examined by cutting away the adjacent portions, and remove it from the water on a horizontal glass slide which is submerged and then lifted up underneath it; when the film is clear of the water, run a knife along the edge of the slide to remove any surplus portions. Remove most of the water from between the film and slide and from their surfaces by touching the composite edge of both film and slide with absorbent paper, and dry the film thoroughly in an air-current at a temp. not exceeding 130° F. Such slides remain satisfactory for several hrs., or if stored in a desiccator, for several days. To prepare a permanent slide, place 1 drop of a 60% soln. of Clarite (a synthetic resin) in toluene on the film, dip the edge of a cover glass (15 mm square) in the soln., and lower it slowly on to the preparation so as to exclude air-bubbles; press the cover glass down firmly, and set the slide aside in a horizontal position for 2 days. Particles passing a 100-mesh but retained on a 200-mesh screen may require a higher ratio of dispersion medium to powder, and a larger surface area of water than described above; a gentle blowing action on the film when it is first formed may then also be helpful in preventing clumping. Fragile particles (*e.g.*, of diatomaceous earth) are dispersed by means of a needle, rubbing being avoided, and the second dispersion medium is then preferable. Photomicrographs (× 100–1000) illustrating the results obtainable are reproduced. J. G.

Photochemical Stability of Papers. H. F Launer and W. K. Wilson. (*Paper Trade J.*, 1943, **116**, *T.A.P.P.I. Sect.*, 78–86.)—Papers were irradiated at 58% R.H. with a carbon arc, through filters which eliminated infra-red rays and ultraviolet rays of wavelengths less than 330$m\mu$; the effects of temp. were eliminated by holding the papers by suction against aluminium foil at *ca.* 30° C. The yellowing of papers containing no appreciable quantities of lignin was found to be produced by heat or ageing, but not by light; the papers were bleached by light, even when they contained lignin and were tested in an atmosphere of nitrogen, or when they had been browned by scorching, or yellowed by heating at 100° C., or by age (250 years old). Absence of oxygen inhibited but did not completely prevent photochemical deterioration, but the effects of moisture varied with the nature of the fibrous constituents present. Papers containing lignified fibres were very unstable to light, but printer's ink had a protective effect on all papers. Irradiation rendered papers less stable subsequently to natural ageing in the dark. The following decreasing order of photochemical activity was found for the fibrous constituents of the papers:—New rags, refined sulphite wood pulp, old rags, soda wood, ordinary sulphite wood pulps, newsprint. The stability to light of new rag papers was more seriously decreased by the use of excessive rosin and alum than was that of old rag papers or of papers containing sulphite and/or soda wood pulps. The effect of rosin alone, however, was small when the acidity was low. The light stability of newsprint was improved considerably after neutralisation with sodium bicarbonate soln. On the other hand, the *p*H was found to be one of the most important factors influencing the stability to heat of all papers. J. G.

Reviews

Soil and Plant Analysis. By C. S. Piper, D.Sc. Pp. xiv + 368. W.E.A.A. Bookroom, The University, Adelaide. 1942. Price 15s. 9d. net post free (Australian currency).

This monograph is a laboratory manual of the methods in use at the Waite Agricultural Research Institute for the examination of soils and the determination of the inorganic constituents of plants. No claim is made that it covers the whole ground of soil examination, but it is claimed that the methods put forward have been found particularly valuable for the examination of soils collected from all parts of Australia and therefore have the value of general purpose methods as distinct from methods limited to certain types of soil. The association of the analysis of plants with the examination of soils is presented as a logical development of the study of the soil, which has for its ultimate purpose the assessment of fertility, such analysis being particularly valuable in respect of the availability of trace elements and in connection with many animal nutrition problems associated with deficiency diseases. Unfortunately the author has found it impracticable to include in this monograph biological methods of soil examination, such as the well known Neubauer, Mitscherlich and *Aspergillus* methods. This impracticability is perhaps a little difficult to understand, seeing that a biological method for the determination of Permanent Wilting Point, using seedlings grown from sunflower seeds, is given with full working details.

The book is divided into two parts: the first, dealing with the examination of soils in 244 pages, is divided into 14 chapters, and the second, dealing with the analysis of plant constituents and covering 124 pages, is divided into 4 chapters. The plan followed in each chapter is the presentation of a preliminary outline of the purpose and theoretical considerations of the methods indicated in the chapter, followed by brief but sufficiently precise working details. Chapters calling for particular mention are those on Mechanical Analysis,

Hydrogen Ion Concentration, Single Value Soil Constants, Exchangeable Ions and Exchange Capacity, Trace Elements and Methods for the Ashing of Plant Materials. With regard to methods of Mechanical Analysis, the standardisations effected by the International Society of Soil Science up to the date of the most recent Congress are collated; a valuable comparison table is set out for the purpose of bringing laboratory records and data into line, together with a series of factors correlating times and temperatures of sedimentation. Dithizone is the chief weapon of attack for determining "trace elements," but a timely and necessary warning note is sounded as to the rigid conditions required in the use of this reagent to ensure accurate differential results. Under the heading of "Exchangeable Ions" some of us will, no doubt, regret the disappearance of the phrase "Base Exchange," although its replacement by "Cation Exchange" may be scientifically preferable; even more will regret the disappearance, among others, of many useful and well established methods such as Hutchinson and MacLennan's "Lime Requirement" and Dyer's "1 per cent. Citric Acid Extraction," from which many useful data have accumulated over the years during which they have been accepted as standard methods of procedure. The chapter devoted to preparation of the ash of plant materials,—so seemingly simple an operation yet meaning so much—may possibly be regarded as one of the most valuable in the book, including as it does full working details for all methods of dry and wet ashing, with a comprehensive consideration of the many snags and pitfalls that await the unwary.

The science of pedology grows rapidly and methods of examination must change with the times. Dr. Piper has introduced in his monograph a resumé of the methods used by the Waite Institute, and this obviously implies that the selection has been chosen from the newer methods that have attained reliability and reproducibility. This enhances the value of the book, which will be welcomed as an outstanding addition to the soil books at present available, whether considered as a bench working book or as a book of reference or as both.

GEORGE TAYLOR

TEXTILE FIBER ATLAS. By W. VON BERGEN and W. KRAUSS. Pp. 68. New York: American Wool Handbook Co. 1942. 4$.

This useful book is probably unique. No other atlas of the kind exists, so far as we know, save that of Herzog which, having been published so long ago as 1908, could not contain all the modern synthetics that are so well treated in this volume. There are 24 black and white plates with 38 pages of text, in which the characteristics of all kinds of fibres are described in detail. Much importance is attached to accurate measurement, not only in longitudinal and surface views but in cross sections; much reliance is placed on these measurements, and the authors give a very attractive Kodachrome plate showing a detailed analysis of a piece of woollen suiting by their methods. The fibres dealt with include many types of wool, hair, fur, silks, cottons, kapok, bast, sisal, flax, raphia, and many varieties of rayon, prolons, synthons, including nylon and vinyon, and mineral fibres, such as asbestos and glass. No other work covers so wide a range.

The descriptions are concise and accurately draw attention to the salient diagnostic features; indeed, it is surprising that synthetic fibres, such as prolons, can be so differentiated by the microscope. The book will become indispensable to all who have to deal with fibrous materials, and it is commended to analysts who examine textiles or fur. H. E. COX

SPOT-TESTS FOR THE IDENTIFICATION OF CERTAIN METALLIC COATINGS AND OF CERTAIN METALS IN BULK. B. S. EVANS, M.C., M.B.E., D.Sc., F.I.C., and D. G. HIGGS. Pp. 24. Cambridge: W. Heffer & Sons Ltd. 1943. Price 3s. 6d.*

Many analytical chemists engaged in metallurgical work have come to regard THE ANALYST as the proper vehicle for papers on metallurgical analysis. It is fitting, therefore, that this latest and valuable contribution of Dr. B. S. Evans to the metallurgical industry should have been made available so quickly, conveniently and cheaply under the auspices of the Society. Its publication is not only opportune but will serve also to remind "other analytical chemists" how large a share they have in the interests and activities of the Society.

The purpose of the booklet is set out in the first sentence: "It is frequently necessary to identify the metal (or alloy) which has been used as a coating on another metal; in addition to this, one is occasionally asked for a rough sorting test which will enable ingots,

* Special price to members of the Society 2s. 6d. pre-paid, on application to the EDITOR.

billets or bars of metal which have become accidentally mixed in bulk to be identified on the spot without the vast labour of dismantling piles of stock material running into many tons, prior to individual chemical analysis."

The authors have evolved a scheme of tests in which the chemical reactions used to classify or identify any metallic surface take place and are observed in the drop of reagent placed on that surface. Nineteen such reagents are listed and after each follows a table showing the responses of the various metals. The first six tables may be used in grouping the metals, Tables 7–18 give tests which are more nearly specific and Table 19 may be used for confirming earlier indications. Table 20 is an index or key to the preceding tables, and the results of the tests are indicated under three headings: "D," a distinctive test for the metal in question, "+," a positive reaction which is not distinctive, "—," a faint, very slow, or negative reaction.

The apparatus required is simple; a few lengths of glass tubing and rod and some rings cut from the tubing. These can be made to adhere to the metal surface by lightly smearing the ground end with vaseline and they act as a container for the drop of test solution. The technique for testing single metal coatings and metals in bulk is fully described and there are later sections in which it is shown how, by some modification of the tests, some alloy coatings and alloys in bulk may be brought within the scope of the scheme.

In devising and presenting this scheme the authors have performed a service whose value in present circumstances cannot be too highly estimated. But they may, incidentally, have done something more. For those who believe, with Dr. Evans, that there are still some avenues of research open in inorganic chemistry in general, and in inorganic analysis in particular, a number of sign posts have been erected.

Having in mind that the book may have to stand rough usage it should be added that it is well bound in stiff serviceable covers. R. C. CHIRNSIDE

Papers for Publication in THE ANALYST

THE Editor welcomes Papers and Notes for insertion in THE ANALYST, whether from members of the Society or non-members. They are submitted to the Publication Committee, who decide on their suitability for insertion or otherwise.

Authors and prospective authors are reminded that, owing to the paper shortage, all contributions to the journal must be condensed as far as possible.

The Publication Committee have recently issued a circular containing Advice to Authors on the writing of Papers for THE ANALYST. This can be obtained on application to the Secretary, Society of Public Analysts and Other Analytical Chemists, 7–8, Idol Lane, London, E.C.3. All Papers submitted will be expected to conform to the recommendations there laid down and any that do not may be returned for amendment or rejected.

Society of Public Analysts and Other Analytical Chemists

ANALYTICAL METHODS COMMITTEE

The following Reports may be obtained direct from the Editor of THE ANALYST, 16, Blomfield Road, London, W.9 (**not through Trade Agents**), at the price of 1s. 6d. each to Members of the Society, 2s. each to non-Members. Remittance must accompany the order, and be made payable to "The Society of Public Analysts."

The Reichert-Polenske-Kirschner Process. *One Report.* **Sub-Committee on Dirt in Milk.** *One Report.*

Milk Products Sub-Committee. *Four Reports.*—(1) and (2) Analysis of Condensed Milks. (3) Analysis of Sweetened Condensed Milk, etc. (4) Determination of Water, of Total Solids and of Fat in Dried Milk.

Essential Oil Sub-Committee. *Thirteen Reports.*—(1) Estimation of Cineole in (*a*) Cajuput and Eucalyptus Oils. (2) and (3) Physical Constants. (4) Acetylisable Constants in Essential Oils. (5) Phenols in Essential Oils. (6) Citral in Lemon Oil. (7) Determination of Solubilities. (8) Cineole in (*b*) Camphor Oil and (*c*) Other Oils. (9) Carvone and Menthone. (10) Citronellal. (11) Aldehydes other than Citronellal. (12) Ascaridole. (13) Determination of Esters.

Sub-Committee on the Determination of Arsenic, Lead, etc. *Three Reports.*—(1) Arsenic. (2) Lead. (3) Copper.

Sub-Committee on the Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soap. *Five Reports.*—(1) Unsaponifiable Matter in Oils and Fats. (2) Unsaponified Fat in Soap. (3) Free Alkali in Soaps. (4) Free Alkali and Silica in Silicated Soaps. (5) Rosin in Soaps.

Poisons Sub-Committee. *Three Reports.*—(1) Assay of Lobelia. (2) Assay of Gelsemium. (3) Assay of Aconite.

Spectrophotometric Terms and Symbols. *One Report.*

Also:—**Bibliography of Heavy Metals in Food & Biological Material** (1929-1933). Price : Members 2s ; Non-Members 3s. prepaid

TECHNICAL AND GENERAL BOOKS

We specialise in the supply of scientific and technical books, new and second-hand, English and Foreign. Inquiries for new and second-hand books will be dealt with both intelligently and promptly.

Wanted to purchase complete sets or long runs of:
AMERICAN CHEMICAL ABSTRACTS; AMERICAN CHEMICAL SOC. JOURNAL; ANALYST, Vols. 1—10, or any CHEMICAL SOC. JOURNAL; CHEMICAL REVIEWS; FARADAY SOC. TRANSACTIONS; and many scientific journals and books generally.

W. HEFFER & SONS LTD., CAMBRIDGE, ENGLAND

CHELSEA POLYTECHNIC

MANRESA ROAD, LONDON, S.W.3

Principal: F. J. HARLOW, M.B.E., Ph.D., B.Sc.
Head of Chemistry Department:
J. C. CROCKER, M.A., D.Sc., F.I.C.

A course of lectures and practical work on

THE CHEMISTRY AND MICROSCOPY OF FOOD, DRUGS AND WATER

will be given by D. C. GARRATT, Ph.D., F.I.C., September to July, 1943–4.

The Course is based on the Syllabus of the Examination for the Fellowship of the Royal Institute of Chemistry (Branch E), and includes the Analysis and Microscopy of Food, Drugs and Water; Toxicological Analysis; Acts and Regulations relating to Food, Drugs and Poisons.

Lecturers will be in attendance on SATURDAY afternoon, September 4th, 2–4 p.m., to advise Students.

Full particulars may be obtained on application to the Principal.

UNIVERSITY OF MANCHESTER

Faculty of Technology

Particulars of Degree Courses in General Chemical Technology, Chemical Engineering, Metallurgy and Assaying, Fermentation Processes (including Brewing) Foodstuffs, Fuels, Colouring Matters, and Electro-Chemistry, and of the Post-Graduate Diploma Course in Chemical Engineering, will be supplied on request by the Registrar, College of Technology, Manchester, 1.

BUREAU OF ANALYSED SAMPLES, Ltd.

Send for New List just issued of

ANALYTICALLY STANDARDIZED SAMPLES

Now ready: 0·3% Lead Steel No. 212 (free-cutting) Complete Analysis.

Nr. Markington, Harrogate, Eng.

"ANALOID" (reg'd.)

SYSTEM of RAPID ANALYSIS

for determining by use of compressed reagents

P, Mn, Cr, V in STEEL & IRON
Cu in BRASS, BRONZE, etc.
CaO in LIMESTONE, CEMENT, SLAGS
A WAR-TIME NECESSITY

Send for descriptive booklet 163A to

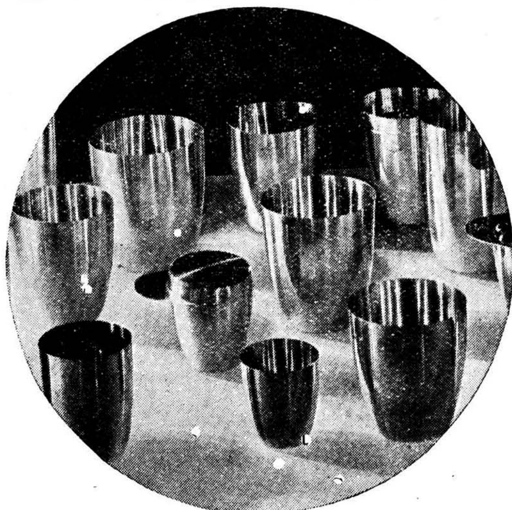
RIDSDALE & CO., LTD.
Nr. Markington, Harrogate, Eng.

B.D.H. LABORATORY CHEMICALS

A new edition of the B.D.H. Catalogue of Laboratory Chemicals has been published. Because of the need for economy in the use of paper, the number of copies available is limited, but chemists to whom a currently priced catalogue of supplies is essential are invited to apply for a copy.

THE BRITISH DRUG HOUSES LTD., LONDON, N.1

SAVE PRECIOUS TIME-USE PRECIOUS METALS



Every Chemist in a well-equipped laboratory has realised the advantages and economies obtained from the use of platinum apparatus.

JMC
PLATINUM CRUCIBLES
AND DISHES

are of sturdy construction, give accurate determinations, enjoy long life, and may usually be repaired and remodelled as new after many years of trustworthy service.

Publication No. 45 gives details of JMC Platinum Crucibles and Dishes. No. 47 provides much helpful information on the use and maintenance of Platinum Laboratory Apparatus. Copies free upon request.

JOHNSON, MATTHEY & CO., LIMITED

HEAD OFFICE

73/83 HATTON GARDEN, LONDON, E.C.1

REAGENT FUSED ALUMINA

NOW AVAILABLE FOR COMBUSTION BOATS FOR CARBON DETERMINATIONS

This new product is used for protecting combustion boats in carbon combustion and replaces material formerly imported.

Type REHT has carbon less than 0.0015%
„ RE „ „ of the order of 0.005%
Fineness numbers of both types are 30, 60, 90.

THE THERMAL SYNDICATE LTD.

WALLSEND, NORTHUMBERLAND, ENGLAND

LONDON OFFICE—12-14, OLD PYE STREET, S.W.1.

Something very New and Neat

THE T & M "COLD SPIRAL" CONDENSER

In this new type the usual annular space between two cooled walls contains a spiral tube through which the cooling water also circulates

This spiral fits the gap so that all gases rising into the condenser have to follow the spiral all the way up the condenser. This ensures that the gases are scrubbed more vigorously than usual by the cold surfaces

MULTIPLE SURFACE FOR VERTICAL USE ONLY

Ascending gases cannot escape without scrubbing on water-cooled walls

FAR MORE EFFICIENT THAN NORMAL DOUBLE SURFACE TYPES

These Condensers can be supplied with standard joints if required

—FOR—"*Service to Science*"

TOWNSON & MERCER LIMITED

390 Sydenham Road, Croydon

TELEPHONE - THORNTON HEATH 3851 (5 LINES)
TELEGRAMS - - - - - - - TOWNSON, CROYDON

Volume 68 July, 1943
No. 808, Pages 199—232

Contents

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

PAGE

Public Analysts and Official Agricultural Analysts Committee 199

Obituary: Adolph Jaffé and Herbert Stanley Redgrove 199

Notes on the Composition of Some Varieties of Onions.—J. G. Sherratt, B.Sc., F.I.C. 200

A Process for the Analysis of Tungsten Carbide Tips.—B. S. Evans, M.C., M.B.E., D.Sc., F.I.C., and F. W. Box, B.Sc. 203

The Rapid Photometric Determination of Copper in Ferrous Materials.—F. W. Haywood, B.Sc., Ph.D., F.I.C., and A. A. R. Wood 206

The Determination of Small Amounts of Aluminium in Water by means of Haematoxylin.—G. U. Houghton, M.Sc., F.I.C. 208

Notes.—The Micro-analysis of Boracite; The First Chemical Reagent; Note on the Analysis of Oxygen and Carbon Dioxide Resuscitation Gas Mixtures 211

Official Appointments 213

Ministry of Food.—Statutory Rules and Orders 214

Ministry of Health.—Milk and Dairies, England 216

Joint Announcement by the Ministries of Agriculture and Food —Cocoa and Chocolate Residues, including Cocoa Shell, for Stock Feeding 216

Notes from the Reports of Public Analysts 216

Legal Notes 216

Bibliography of Metals in Foods and Biological Materials —VI Bismuth 217

The Iron and Steel Institute: First Report of the Marine Corrosion Sub-Committee 218

British Standards Institution: British Standard Specification for Flow Measurement 219

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs—

Solanine, Glycoside of the Potato. I. Its Isolation and Determination. II. Its Distribution in the Potato Plant.—L. H. Lampitt, H. S. Rooke, J. H. Bushill and E. M. Jackson 219
Rapid Determination of Starch. An Index to Maturity in Starchy Vegetables.—J. P. Nielsen .. 220

Biochemical—

Chromatography as a Means of Separating Amino Acids.—J. L. Wachtel and H. G. Cassidy 221
Colour Reaction for Methionine.—L. H. Sofin, H. Rosenblum and R. C. Schultz 221
Colorimetric Estimation of Serine.—M. J. Boyd and M. A. Logan 221
Field Test for the Estimation of Peroxidase.—W. B. Davis 222
Simplified Photelometric Estimation of Trigonelline.—S. W. Fox, E. W. McNeill and H. Field, Jr. 222
Chemical Determination of Nicotinic Acid in Plant Materials.—E. B. Hale, G. K. Davis and H. R. Baldwin 222
Chromogenic Reagent for Vitamin C Determinations.—R. A. Koenig, T. L. Schiefelbusch and C. R. Johnson 223
Winter Sources of Vitamin C.—H. W. Crowe and E. A. M. Bradford 224
Photometric Determination of Reduced and Total Ascorbic Acid.—M. Hochberg, D. Melnick and B. L. Oser 224
Ascorbic Acid Content of Sweet Peppers.—V. A. Beckley and V. A. Notley 224
Ascorbic Acid in Mashed Potatoes.—G. N. Jenkins 224
Comparison of Procedures for Removal of Lipid Material from Bones of Chicks.—I. Motzok, D. C. Hill, S. J. Slinger and H. N. Marcellus 225

Bacteriological—

Bacteriological and Physical Changes occurring in Frozen Eggs.—R. Schneiter, M. T. Bartram and H. A. Lepper 225
Estimation of Rope Spores in Wheaten Flour and other Products.—E. Barton-Wright 226

Forensic—

Modification of Widmark's Method for the Determination of Alcohol in Blood.—R. M. du Pan .. 226

Organic—

Determination of Furfural.—I. J. Duncan 226
Colour Test for some Highly Reactive Organometallic Compounds.—H. Gilman and L. A. Woods.. 227

Inorganic—

A Remarkable Indicator.—G. Schwarzenbach 227
Simplified Technique in the use of Liquid Amalgam Reductors.—G. F. Smith and L. T. Kurtz .. 227
Analysis of Bolivian Tin Concentrates.—S. Kallmann 227
Determination of Zinc in Aluminium Alloys.—A. Cohen 227
Determination of Zinc in Magnesium Alloys.—A. Cohen 228
Determination of Ferrous Oxide in Chromite.—G. E. Seil 228
Critical Study of Reagents for the Detection of Cerium.—P. Wenger and R. Duckert 228
Rare-Earth Fractionation by Zeolite Action.—R. G. Russell and D. W. Pearce 229
Determination of Lithium as Periodate.—L. B. Rogers and E. R. Caley 229
Determination of Iodate in Presence of Bromate and Chlorate.—I. Y. Kolthoff and D. N. Hume 229

Physical Methods, Apparatus, etc.—

Dispersion of Pigments and Fillers for Microscopical Examination.—L. B. Miller 229
Photochemical Stability of Papers.—H. F. Launer and W. K. Wilson 230

Reviews 230

Printed for the Society of Public Analysts by W. Heffer & Sons Ltd., Hills Road, Cambridge.
Communications to be addressed to the Editor, C. Ainsworth Mitchell, 16, Blomfield Road, LONDON, W.9.