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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, February 4th, the President, Dr. J. T. Dunn, being in the chair.

Certificates were read for the first time in favour of Cecil Chilvers, B.Sc., F.I.C., Jack Hubert Hamence, M.Sc., A.I.C., Cecil John House, B.Sc., A.R.C.Sc., F.I.C., and Henry George Rees, B.Sc., A.R.C.Sc., A.I.C.

Certificates were read for the second time in favour of Kenneth Bullock, M.Sc., Ph.D., and Frederick Cecil Hymas, B.Sc., A.I.C.

The following were elected Members of the Society:—Arthur Nicholls Ainsworth, B.Sc., Bertram Arthur Gough, William Henry Gough, M.Sc., A.I.C., and William Henry Shilling, B.Sc., A.I.C.

The following papers were read and discussed:—"Some Factors affecting the Solubility of Milk Powder," by L. H. Lampitt, D.Sc., F.I.C., and J. H. Bushill, M.Sc., A.I.C.; i, "The Determination of the Hydroxyl Content of Organic Compounds: Estimation of Castor Oil," ii, "The Determination of the Carbonyl and Aldehyde Content of Organic Compounds: Estimation of Phenylhydrazine," by S. Marks, M.Sc., A.I.C., and R. S. Morrell, Ph.D., F.I.C.; "Food Control in Holland," by A. van Raalte, D.Sc., and J. Straub; "The Determination of Small Quantities of Methane," by H. R. Ambler, B.Sc., F.I.C.; and "The Fatty Acids and Component Glycerides of Indian Ghee," by R. Bhattacharya, Ph.D., A.I.C., and T. P. Hilditch, D.Sc., F.I.C.

NORTH OF ENGLAND SECTION.

The Sixth General Annual Meeting of the Section was held in Manchester on February 14th, 1931. The attendance was thirty-four, and the Chairman (Mr. G. D. Elsdon) presided.

A resolution of sympathy with Mrs. Miller and family on the death of Mr. James Miller was passed. The financial statement for the past year was adopted. The following officers and committee were appointed:

Chairman, C. J. H. Stock; *Vice-Chairman,* J. Evans.

Committee, E. G. Jones, H. Haslam, H. Heap, A. Lees, A. R. Tankard, and J. Wood; *Honorary Auditors,* U. A. Coates and W. Marshall; *Hon. Secretary,* J. R. Stubbs.

The Chairman gave the Annual Address, and the following papers were read and discussed:—"The Rapid Quantitative Determination of Solid Saturated Fatty Acids," by Prof. T. P. Hilditch, F.I.C., and J. Priestman, Ph.D. (*Work done under the Analytical Investigation Scheme*); "A New Method for the Determination of Solid Unsaturated Fatty Acids," by L. V. Cocks, F.I.C., B. C. Christian, Ph.D., A.I.C., and G. Harding, F.I.C.

Death.

WITH regret we record the death, on January 30th, of James Miller, a Member of the Society since 1922.

Obituary.

EDWARD WILLIAM VOELCKER.

THE passing away, on November 22nd, of our Past President, Edward William Voelcker, has made another gap in the too rapidly lessening roll of the survivors of the "Old Brigade" of those who were intimately associated with the work of our Society in its earlier, as well as in its later, days.

He was the third of five sons of the late Dr. Augustus Voelcker, F.R.S., and was born on July 14th, 1857, at Cirencester, during the time when his distinguished father occupied the chair of chemistry in the once celebrated Royal Agricultural College, which was then the only academical seat of agricultural training.

In 1864, the pressure of his duties as consulting chemist to the Royal Agricultural Society of England led Dr. Voelcker to resign his professorship at Cirencester and to migrate to London, where, as they severally emerged from the preparatory educational stage, he placed his sons, including the subject of this memoir, in the well-known school attached to University College, London. The eldest brother, George, proceeded to the College itself, having chosen a medical career which, unhappily, was closed by early death after a brilliant studentship. The second son, our other Past President, Dr. J. A. Voelcker, also proceeded to University College, and subsequently to Giessen; while "E. W." or "Will" (as

E. W. Voelcker

Emery Walker Ltd. ph. sc.

his intimates affectionately and alternatively called him), having acquired an enthusiasm for chemistry under his then well-known chemical schoolmaster, Temple Orme, and having matriculated in the University of London, persuaded his father, in 1874, to allow him to go to the Royal School of Mines, where in due course in, 1877, he took his associateship, being awarded the De la Bêche Medal for proficiency in mining. His teachers there were Edward Frankland, Percy, Warrington Smyth and A. C. Ramsay, and among the best remembered of his college friends of those days were Arthur G. Phillips, George Seymour and Edgar Rathbone.

During the college vacations he used to frequent his father's laboratory in Salisbury Square, where he and the writer—who was then serving his pupilage—became from time to time fellow workers at the same bench, resulting in the foundation of a deep friendship which never waned during the fifty-five years that followed. After leaving the School of Mines he continued to work regularly in his father's laboratory, varying his experience as opportunities offered by visiting mines in various parts of England and Wales.

In 1879 he went on an exploratory trip on behalf of clients of his father to New Guinea, prospecting for phosphate deposits on various groups of islands adjacent to the north-east coast thereof, the chief group being that known as the Purdy Islands. He also spent some time in Australia, and after his return settled down as a permanent member of his father's staff. Shortly before his death, in 1884, Dr. Voelcker took the two sons into partnership, the elder brother, J. A. Voelcker, subsequently succeeding his father in the post of consulting chemist to the Royal Agricultural Society.

E. W. Voelcker joined our Society in 1889, and was elected a Member of Council in 1890. In 1894 he was chosen to succeed the late Charles Heaton in the office of Honorary Treasurer, and in this capacity his natural ability for finance became valuable to the Society, which not very long before had taken over the proprietorship of THE ANALYST, thus placing on the shoulders of the Treasurer more work and responsibility than devolved on his predecessor in earlier days, the duties of the office steadily increasing in exigency as the size and scope of our Journal developed. Voelcker continued to fill this office until 1910, when, after sixteen years of service, he was chosen to succeed our old friend, Mr. Tatlock (who it may be parenthetically remarked is still well and hearty in his ninety-fourth year) as President. Later on, from 1916 to 1920, during the absence on war service of his successor, Mr. Hinks, he again became our Acting Treasurer. In this connection it must be still further recorded that his willingness to place his ability for dealing with financial matters at the disposal of his professional brethren was not confined to the service rendered to our own Society, for he further earned our general gratitude by discharging, from 1918 to 1924, the still more onerous and complicated duties of the Honorary Treasurership of the Institute of Chemistry. On the Council of this latter body, in addition to his term of office as Treasurer, he served, in various periods, twenty-four years, including

two periods as Vice-President; while during five years he occupied the responsible office of Censor. During all this time, both in our own Society and in the Institute, he assiduously attended the constantly occurring meetings of the various committees on which so much of the spade work of such organisations necessarily devolves, and his conscientious attention to details, as well as the judgment of a well-balanced brain, will be long remembered by all those who had the satisfaction of serving with him. Apart, too, from his share in our corporate labours, many of us will have grateful personal recollection of wise advice always sympathetically given in cases of personal doubt or difficulty such as will occasionally arise in professional matters. His sense of right and wrong in matters of etiquette, as well as in matters of ethics, was always to be trusted.

His knowledge of general as well as of scientific matters was wide, and his mental ability such as might well have been devoted to original investigation; but he was modestly satisfied to leave in the hands of his brother the task of continuing the investigational work at Woburn and elsewhere entailed by successorship to the work of their father, restricting his chemical activity mainly to the everyday duties of the laboratory. That this involved no apathy or lack of grasp of the wider aspects of agricultural science was evidenced by the success with which he took over and carried on both the investigational work at Woburn and the multifarious advisory duties of consulting chemist to the Royal Agricultural Society during the time of Dr. Voelcker's absence in the service of the India Office on the tour which resulted in his memorable report of 1893, which formed the basis of the subsequent widespread development of Indian agricultural education. But it was with unconcealed relief that, on the return of Dr. Voelcker, he handed back to him the reins which he had temporarily held.

His first public appointments were those of Public Analyst for the Counties of Hereford and Northampton in 1894, and he subsequently became, with his brother, Joint Public Analyst for the Counties of Bucks. and Oxford and the Boroughs of Aylesbury and Banbury, being also Official Agricultural Analyst for Hereford and Northampton, and Deputy Agricultural Analyst for the Counties of Berks., Bucks., Northumberland, Oxford, the East Riding of Yorks., and the Isle of Ely. Some of these appointments he had recently resigned owing to failing health, being succeeded therein by his son and junior partner, Mr. Eric Voelcker, who, it is pleasant to realise, is carrying on the family chemical activity in the third generation.

"E. W." was much loved by those of his chemical brethren who were within the circle of his personal acquaintance, and it must be added that he was for very many years a popular member of the Savage Club. His favourite recreations were shooting and fishing, in both of which sports he was an adept.

He married in 1893 Jessie McCaskie, eldest daughter of Mr. R. Purvis Beattie, of Edinburgh, and leaves, including Mr. Eric Voelcker, three sons and one daughter.

BERNARD DYER.

The Determination of the Milk Proteins.

By GEORGE M. MOIR, M.Sc., Ph.D., A.I.C.,
Pedler Research Scholar of the Institute of Chemistry, 1928–1930.

(*Read at the Meeting, November* 5, 1930.)

III. PROPOSED MODIFIED METHOD FOR CASEIN.

On the basis of a series of experiments which have been carried out, the following modification is proposed of the acetic acid method for the analytical separation of casein from milk:

Into a weighed covered beaker (100–150 ml.) pipette 10 ml. of the well mixed sample and weigh again quickly. Dilute the milk with about 50 ml. (*Note* 1) of distilled water which has been first warmed to 40–42° C. (*Note* 2). Add at once 1·5 ml. of 1·67 *N* (10 per cent.) acetic acid (*Note* 3), and then stir gently by rotating the stirring rod four times in the beaker (*Note* 4). After allowing the beaker to stand about 20 minutes, add 4·5 ml. of 0·25 *N* sodium acetate solution (*Note* 5), and, after stirring gently (*Note* 4), leave for at least an hour. Filter through a 9 cm. No. 42 Whatman filter, which it is desirable to fold in the fluted way to facilitate the operation. Wash the precipitate with distilled water three times by decantation and follow by two further washings in which the precipitate is broken up and transferred to the paper (*Note* 6). Finally, rinse the rim of the filter paper with a fine stream of water. The filtration and the washing should be carried out without interruption, and subsequently the casein adhering to the beaker and stirring rod should not be allowed to dry before being washed out with the sulphuric acid that is required for the Kjeldahl digestion. For this purpose about 20 ml. of water are placed in the beaker and about 5–7 ml. of the strong acid carefully poured down the side. The heat generated by gentle mixing helps to dissolve the casein, which is usually completely removed after three such treatments (*Note* 7). The filter paper and casein are added to the Kjeldahl flask into which the washings from the beaker have been poured; the usual quantity of sodium or potassium sulphate and a little copper sulphate are added before commencing to heat the digestion flask. It is desirable to evaporate the water with a small flame, as frothing is liable to occur just before the last of the water is boiled off. During digestion some of the acids from the fat condense upon the neck of the flask and may subsequently cause trouble by frothing during the distillation. These can be destroyed if the flask is allowed to cool when digestion is nearly complete, and about 50 ml. of water are carefully added and mixed with the contents. The fatty material is washed down by the condensation of steam during evaporation of the water. The determination is completed in the usual way and the ammonia collected in 40 ml. of *N*/10 sulphuric acid to which a few drops of sodium alizarine-sulphonate (1 per cent.) indicator has been added. The excess of acid is measured by titration with *N*/10 sodium hydroxide solution until the brown colour first develops a pink shade. The results

must be corrected for a blank properly carried out (in this case on a single filter paper and the same quantities of the other reagents), and expressed as per cent. of casein *nitrogen*. It is better to state the results in this way than as casein because of the existence of a slight doubt about the conversion factor.

NOTES.—1. The amount of water for dilution need not be exactly measured but an excess is more desirable than a deficiency.

2. The warm water facilitates the gathering of the casein into a clot, leaving a clear filtrate. The temperature must not exceed by more than one or two degrees that prescribed or there will be a risk of coagulating soluble protein.

3. The acetic acid must be added first, followed by the acetate, otherwise an opalescent filtrate results. The filtrate ought to be clear and filtration fairly rapid, and one advantage of the method is that if these requirements are not attained the results must be viewed with suspicion. The use of acetic acid alone will usually give a clear filtrate, but the results will be low by 1–2 per cent.

4. Excessive stirring will detach fat globules from the casein and will also leave some of the latter in a finely divided state, so that a cloudy filtrate results. Sometimes this can be remedied by passing the first 15 or 20 ml. twice through the filter paper, but this, on occasion, causes the remainder of the filtration and washing to be very slow, and the results unreliable.

5. The sodium acetate solution may be made by weighing out A.R. crystals, but too much should not be made at once, as moulds grow very readily in it. The amounts of the reagents are chosen to bring 10 ml. of the diluted milk to *p*H 4·6, the isoelectric point of casein, and approximately this *p*H will be attained with most normal milks. Slight souring will not make much difference, but when the titratable acidity of 10 ml. of milk exceeds 2·5 ml. of *N*/9 sodium hydroxide solution (0·25 per cent. of lactic acid) it may be desirable to investigate the *p*H of the filtrate (or, alternatively, add to the milk sufficient alkali to bring the titratable acidity back to 0·25 per cent.). It must be remembered, however, that owing to the possibility of proteolysis, casein determinations in sour or clotted milk are liable to be low. Palmer (*Missouri Agr. Exp. Sta. Research Bull.* 34, 1919) has shown that the best preservative of the milk proteins is formaldehyde (1·5–2 ml. of 40 per cent. formalin per litre will keep the sample at 10° C.), but unfortunately this is liable to cause fat determinations to be slightly low.

6. I have made tests in which the casein precipitate was washed with an acetic acid and sodium acetate mixture of very low concentration, but of *p*H close to the isoelectric point of casein. The results scarcely differed from those obtained by washing the precipitate with water, so that it is doubtful whether the use of such a buffer solution should be recommended for this purpose.

7. Great care is necessary in this operation to avoid loss due to spurting of the acid during mixing, and also due to small pieces of casein which adhere to the stirring rod and the lip of the beaker. If the casein has become dry before rinsing out the beaker, its removal can be facilitated by moistening it with about 20 ml. of water containing 1 ml. of *N*/10 sodium hydroxide solution and allowing

the beaker to stand for 5 to 10 minutes before adding the first portion of acid. The alkali solution must not be warmed before adding the acid, or ammonia may be lost.

This paper represents part of the work carried out during my tenure of the Pedler Research Scholarship of the Institute of Chemistry, the assistance of which and the interest of the members of the Pedler Fund Committee are gratefully acknowledged. I wish to add my appreciation of the facilities made available to me at the National Institute for Research in Dairying, and especially of the valuable advice of the chief chemist, Capt. J. Golding.

(Part IV, "The Determination of Albumin and Globulin," will be published in the April issue.)

The Analysis and Composition of Vegetable Parchment used for Packing Dairy Products.

BY PAUL ARUP, M.Sc., F.I.C.

(*Read at the Meeting, November* 5, 1930.)

THE following instructions relating to Vegetable Parchment to be used for the packing of butter were issued by the Department of Agriculture in Dublin under the Dairy Produce Act, 1924 (Regulations under Part II, Order No. 1, 1925):—

The vegetable parchment paper to be used for lining and wrapping shall be white in colour and free from any weighting material such as gums or sugars, etc. The texture shall be even and free from blotches, pin-holes, particles of metal and untreated material, and shall be such that, when torn, there shall be no appearance of fibres on the torn edges.

WEIGHT.—For lining bulk packages, the vegetable parchment paper should weigh not less than 25 lb. per ream of 480 sheets, measuring 30 × 20 inches each.

For wrapping rolls, bricks and prints, the vegetable parchment paper should weigh not less than 18 lb. per ream of 480 sheets, measuring 30 × 20 inches.

PREPARATION OF VEGETABLE PARCHMENT PAPER.—The parchment paper cut to the requisite sizes must, the night before it is to be used, be placed in a strong wooden tub or other approved vessel free from odour, containing a saturated boiling solution of salt brine with some excess salt in the bottom of the tub or other vessel and be allowed to remain in the brine overnight.

The parchment paper should not be crushed when placing it in the brine, but should be rolled up so that it will present a smooth appearance when taken out. The packages should be carefully lined with the parchment paper so as to avoid wrinkles and bare spaces.

At the suggestion of Mr. A. Poole Wilson, Chief Inspector of Dairying in the Irish Free State, a detailed investigation was made of the chemical and physical properties of a number of samples of vegetable parchment commonly in use for the packing of butter, with a view to obtaining data which might make it possible to lay down more definite standards for this commodity.

The results of this investigation are contained in the table on p. 152. The first 23 samples, numbered from 1 to 15 inclusive, were obtained from manufacturers or their agents under the description of "vegetable parchment." Where letters are used after the numbers, the samples composing each group were of the same material, differing only in weight, and the bracketed results were obtained from

composite samples of the respective groups. The 18 samples, numbered 16 to 33 inclusive, were received for analysis from various creameries in the Irish Free State. Nos. 34 and 35 are samples of grease-proof paper, or imitation vegetable parchment, included for comparison.

METHODS OF ANALYSIS.

MOISTURE.—One grm. of the sample, cut into strips not exceeding $\frac{1}{8}$ inch wide, was weighed out in a stoppered weighing bottle (2" wide by 1" high) with straight side, and dried in a steam oven until constant in weight; the steam oven was fitted with air inlet and outlet, whereby there was a flow of ventilating air, preheated by passage through a tube in the body of the oven. Drying was completed within one hour.

ASH.—One grm. of the sample was incinerated in a platinum dish, precautions being taken to prevent loss of the very light ash through air currents. It was found advantageous to fold the parchment closely together before burning.

FOREIGN MATTER.—In many cases foreign matter would be detected by a careful inspection, and the presence of a number of substances is easily demonstrated by applying certain reagents to the surface of the paper. Thus *nitrogenous matter*, such as *glue, gelatin or casein*, is detected by applying Millon's reagent or a little powdered sucrose and concentrated sulphuric acid, the latter test giving a characteristic red colour in positive cases. In testing for *starch* by the application of iodine solution it should be noted that genuine vegetable parchments give a faint blue colour with iodine, owing to the presence of products produced by the action of the sulphuric acid used in the parchmentising process, on the cellulose. *Rosin* is tested for by boiling a few grms. of the paper with acetic anhydride and adding a few drops of concentrated sulphuric acid to the extract. *Ground-wood* is tested for by applying a 2 per cent. solution of phloroglucinol in a mixture of equal parts of concentrated hydrochloric acid and water to the paper. In the samples examined *free acid* was not present, and it was sufficient to test the aqueous extract of the sample with indicators such as methyl red and brom-phenol blue or methyl orange. *Sugars* are dealt with under a special heading below.

WATER-SOLUBLE EXTRACT.—To 5 grms. of the sample, taken from various sheets throughout the batch and cut into strips not more than $\frac{1}{4}$ inch broad and $2\frac{1}{2}$ inches long, were added 100 c.c. of distilled water in a 200 c.c. beaker flask which was kept on a steam bath for half an hour, the contents being stirred frequently. The water was then poured off through a filter into a tared basin in which it was evaporated to dryness on the steam bath. In the meantime the parchment strips were treated with a second portion of 100 c.c. of distilled water as before, and the process was carried on until four successive portions of 100 c.c. had been used for extraction and evaporated to dryness. A further 50 c.c. of water were used for washing out the filter and run into the basin so as to concentrate the extract near the centre of the basin, in order that solution in a small volume of water might be facilitated in the subsequent determination of reducing material.

When the residue had been dried as far as possible on the steam-bath it was further dried *in vacuo* until constant in weight; being slightly hygroscopic, it was

weighed as quickly as possible. In these investigations the dryings were carried out in a Mojonnier vacuum oven at 85–90° C. and 25 inches of vacuum; failing this, a vacuum desiccator could be employed.

REDUCING MATERIAL CALCULATED AS DEXTROSE.—The solid extract in the dish from the previous determination of extract was transferred to a 150 c.c. conical flask with 10 c.c. of hot water, used in three portions of 3 to 4 c.c. each, to allow of two rinsings. The reducing material was determined by iodimetric titration, as described by Hinton and Macara (ANALYST, 1924, **49**, 2). In all cases except that of sample No. 19, 10 c.c. of 0·05 *N* iodine solution were used, with proportionate amounts of alkali and acid. On adding the 10 c.c. of iodine solution and 2·5 c.c. of 0·25 *N* sodium hydroxide, the temperature of the mixture was adjusted to 17·5° C. as quickly as possible, the flask was closed with a rubber stopper and placed in a water bath at 17·5° C. for 10 minutes, after which the contents were acidified with 2·5 c.c. of *N* sulphuric acid and titrated with 0·05 *N* thiosulphate solution in the usual way. A blank was carried out under the same conditions. For the calculation it was assumed that 1·410 grms. of iodine represented 1 grm. of glucose; the results must be regarded as empirical, and used in a comparative sense. The question of the composition of the water-soluble extract is dealt with under a separate heading below, where it is shown that in genuine vegetable parchment the reducing action can by no means be considered to be due to glucose alone.

STRENGTH.—The figures in the table represent the bursting strength of the samples in lbs. per square inch, as determined by the Ashcroft paper tester; the column headed "wet" contains results of tests made on the samples immediately after immersion in water at 80° C. for 15 minutes, and that headed "dry" contains the results of tests on the corresponding samples before wetting. The column headed "Ratio per cent." shows the strength wet calculated as the percentage of the strength dry. In all cases the results represent the average of ten determinations on pieces cut from different sheets or parts of sheets.

WEIGHT.—This was determined by means of the "Pocket Gram Scale" (made by L. Schopper of Leipzig), which gives readings in grms. per square metre. As the figures represent the average of ten determinations in each case, the use of a direct reading scale saves a considerable amount of labour. A convenient scale for conversion of results into lbs. per ream of 480 sheets, measuring 20×30 inches, is made by R. Stewart & Co., of Glasgow.

SUPPORT OF MOULD GROWTH.—Experiments were made to ascertain how far the parchment would support the growth of mould under favourable conditions as regards moisture and temperature. Circles of the parchment, about 4″ in diameter, were placed in sterile 4½″ Petri dishes, and moistened with water containing a suspension of spores of *Penicillium* and *Cladosporium* species, these being among the most active moulds which produce rancidity. The dishes were incubated at 25° C. and examined from time to time, water being added when necessary, to keep the parchment moist but not flooded. A final judgment could be made after 14 days.

Results of Analyses.

The quantitative results are summarised in the accompanying table:

Table I.

No.	Description.	Water.	Ash.	Extract.	Reducing matter calculated as dextrose.	Reducing matter in extract.	Strength in lb. per sq. inch. Wet.	Dry.	Ratio.	Weight per ream.
		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.			Per Cent.	lbs.
1	Vegetable parchment	8·45	0·28	0·78	0·13	17·0	13	33	39	29
2	do.	—	—	0·78	0·14	18·0	8	22	36	18
3	do.	9·05	0·27	1·08	0·21	19·4	7	19	37	23
4A	Vegetable parchment First grade Pure rag	—	—	0·78	0·12	15·4	12	26	46	21
4B		—	—				14	28	50	25
4C		—	—				18	29	62	27
5A	Vegetable parchment Second grade	—	—	1·14	0·12	9·5	12	25	48	22
5B		—	—				12	23	52	25
6	Vegetable parchment	9·10	0·37	0·65	0·09	11·3	12	27	44	28
7A	"Real vegetable parchment"	8·32	0·29	0·66	0·09	13·7	7	20	35	19
7B							6	18	33	18
7C							9	21	43	21
7D							10	24	42	24
7E							15	30	50	29
7F							11	28	40	29
8	Vegetable parchment	—	—	0·83	0·08	9·6	9	28	32	25
9	do.	9·38	0·40	1·30	0·22	17·0	20	34	59	30
10	do.	8·75	0·35	1·42	0·17	12·1	15	24	62	23
11	do.	9·13	0·59	1·67	0·21	15·1	18	32	56	29
12	do.	8·75	0·34	0·70	0·16	22·9	10	19	53	19
13	do.	8·15	0·34	1·16	0·25	21·5	14	25	56	26
14	do.	8·60	0·28	1·14	0·21	18·4	9	16	50	16
15	do.	9·15	0·33	1·02	0·17	17·0	16	32	50	29
16	do.	9·16	0·25	0·86	0·12	14·0	13	25	52	28
17	do.	9·27	0·38	0·78	0·14	18·0	7	22	32	25
18	do.	9·08	0·26	0·85	0·14	16·5	16	29	55	30
19	do.	10·75	0·12	7·01	0·75	12·0	13	28	46	31
20	do.	—	—	0·60	0·13	21·7	15	32	47	29
21	do.	—	—	0·78	0·19	24·4	15	29	52	31
22	do.	—	—	0·70	0·11	15·7	10	29	34	31
23	do.	—	—	0·80	0·11	13·8	11	31	35	29
24	do.	9·69	0·29	0·75	0·12	16·0	19	31	61	27
25	do.	8·45	0·32	0·96	0·11	11·5	18	31	58	30
26	do.	8·95	0·40	1·05	0·13	12·4	14	30	47	30
27	do.	10·10	0·26	1·12	0·21	18·8	17	34	50	31
28	do.	11·70	0·26	0·84	0·20	23·8	22	35	63	30
29	do.	10·08	0·41	1·18	0·14	11·9	15	28	54	29
30	do.	9·06	0·40	1·30	0·12	9·2	17	29	59	29
31	do.	8·16	0·39	1·24	0·22	17·8	9	25	36	26
32	do.	8·97	0·40	1·18	0·20	17·0	16	30	53	28
33	do.	—	—	0·98	0·13	13·3	13	29	44	28
34	Greaseproof bleached	8·72	2·67	0·76	0·26	34·2	nil	29	nil	18
35	Greaseproof unbleached	8·37	0·93	0·47	0·17	36·2	nil	21	nil	18

The qualitative tests for *foreign materials* gave negative results in all cases. The exceptional sample, No. 19, gave a somewhat stronger colour with iodine than usual, but not sufficiently strong to indicate the presence of added starch.

Support of Mould Growth.—All the samples except No. 19, when tested in the manner described, showed a somewhat attenuated growth of mould. Sample No. 19, which contained far more carbohydrate material than the other samples, showed a vigorous growth.

The following table and account give particulars of simultaneous comparative tests for support of mould growth with six samples of parchment having different percentages of soluble extract:

Sample No.	22	24	16	10	11	19
Extract, per cent. ..	0·70	0·75	0·86	1·42	1·67	7·10

The samples were examined from time to time over a period of 14 days, using a low-power microscope where necessary. Sample No. 19 developed a visible mould growth in the course of 4–5 days, and long before the rest of the samples. Nos. 10 and 11 had developed less vigorous growths than No. 19 at the end of the 14 days. Nos. 22, 24 and 16 supported growth more sparingly than the rest, and microscopic examination especially showed that the mould hyphae were not nearly so plentiful as in Nos. 10 and 11. These experiments, therefore, show a definite connection between extract content and power to support mould growth.

It should, however, be emphasised that if a parchment has become heavily infected with mould spores through storage in an unsuitable place, it may easily develop mould spots under practical conditions of use, even if of satisfactory chemical composition. In such cases the parchment must be very thoroughly sterilised in boiling brine, because the mere presence of salt, even in high concentration, is not sufficient to check the growth of some of the common moulds, notably the *Cladosporium* species.

Discussion of Results.

Before discussing the above results in detail it may be of use to tabulate some previously published results in the following condensed form:

Table II.

Observers.	No. of samples.	Description of samples.	Water.	Ash.	Water-soluble extract.	Sugar.
			Per Cent.	Per Cent.	Per Cent.	Per Cent.
Burr and Wolff[1]	26	Commercial parchments	7·13 to 10·31	0·34 to 17·10		0 to 25·78
Burr, Wolff and Berberich[2]	58	do.	5·49 to 13·10	0·23 to 17·10	0·05 to 31·10	
Weiss[3]	40	Parchment and parchment substitutes	5·91 to 11·32	0·32 to 10·32	0·38 to 33·9	

[1] Analyst, 1910, **35**, 435. [2] Analyst, 1912, **37**, 465.

[3] *Z. Untersuch. Nahr. Genussm.*, 1923, **46**, 301.

On the basis of the results summarised in Table II, the following maximum standards were suggested by Burr, Wolff and Berberich, and adopted by the German Dairy Association:—Ash, 3; water-soluble extract, 8; sugar, 8 per cent.

It will be seen that the figures obtained in the present investigation point to a considerably higher standard of purity.

MOISTURE.—This varied from 8·15 to 11·70 per cent. As regards the four samples over 10 per cent., No. 19 was the exceptional sample, containing an excessive amount of water-soluble extract, whilst Nos. 27, 28 and 29 represented batches which were found to have been stored under unsuitable conditions. It is suggested that 10·0 per cent. would be a suitable maximum standard. Excessive moisture, such as would be occasioned by the presence of undue amounts of sugar or glycerin, would favour the growth of moulds. In general, it may be said that good vegetable parchments contain between 8·0 and 10 per cent. of moisture. An unduly low moisture content would probably be accompanied by a lack of pliability.

ASH.—The figures for vegetable parchment varied from 0·12 to 0·59 per cent., those for the greaseproof papers, especially the bleached sample, being considerably higher. As a maximum standard, the figure 0·45 per cent. may be tentatively suggested. The maximum value of 3·0 per cent., adopted in Germany, is intended to allow for the impregnation of the parchment with salt. It is claimed that this practice prevents mould growth on the parchment; and while this is no doubt quite true, it is considered better, from several points of view, to purchase a pure quality of parchment and to steep this in hot brine before use, as recommended in the instructions quoted at the beginning of the account of the present investigation. In this way the advantage of the sterilising effect of the hot brine is secured, while the procedure is to be recommended as being, on the whole, more systematic and amenable to control.

WATER-SOLUBLE EXTRACT.—For vegetable parchment, the figures vary from 0·65 to 7·01 per cent. If sample No. 19 is omitted, the variation is from 0·65 to 1·67 per cent. These figures show, on the whole, far less variation than those quoted in Table II, and it is obvious that the parchments under examination were far better in quality than the majority of those analysed by previous observers. As the water-soluble extract is capable of supporting mould growth, it will be argued that the paper should be washed free from this matter in the process of manufacture, but it is stated by the makers that such a course would result in lack of pliability in the product. It is, no doubt, the hygroscopic nature of the extract which enables it to impart suppleness to the parchment; the same reason underlies the occasional use of glycerin for this purpose.

An unduly high percentage of extract will cause the parchment to have a brownish tinge, as was seen in the case of sample No. 19, which contained 7·01 per cent. of extract. As the proportion of reducing sugar to the total extract in this sample came within the usual limits, it may be presumed that the excessive amount of extract was due, not to added sugar, but to products of the action of sulphuric

acid on cellulose formed in the parchmentising process and not removed by washing. In this case the aqueous extract was neutral, as usual. From the results quoted under "Support of Mould Growth" (p. 153), it is seen to be important that the water-soluble extract should be kept within moderate limits; and, judging from the general trend of the results, a maximum of 1·20 per cent. is suggested for this constituent.

REDUCING MATERIAL, CALCULATED AS DEXTROSE.—Excluding sample No. 19, the figures for vegetable parchment varied from 0·09 to 0·25 per cent. The percentage of reducing material in total extract varied from 9·2 to 24·4 per cent. It is suggested that these figures may be used as a basis for determining the presence of added glucose, 1 per cent. of which would raise the percentage to somewhere about 50; in most cases this figure would be exceeded.

From the results of the examination of the composition of the water-soluble extract, it is evident that only a relatively small amount of the reducing material in genuine vegetable parchment consists of dextrose; the major portion appears to be lignone or its decomposition products. The calculation to dextrose is, therefore, only made in order to have a standard for purposes of comparison, and because the object of the determination is largely to detect added glucose.

BURSTING STRENGTH.—As the Regulations quoted at the beginning of this paper prescribe 25 lbs. per ream as the minimum weight for the purpose of lining bulk packages, the bursting strength of the samples of this weight and over may be considered separately. The figures for this group vary from 22 to 35 lbs. per square inch; for 25 to 26 lbs. per ream the strength varied from 22 to 28 lbs. per square inch, and for 30 to 31 lbs. per ream from 29 to 35 lbs. per square inch. As regards the minimum value of 22 lbs. per square inch observed for sample No. 17, it will be noted that this is the only sample showing the strength, wet, to be under 33 per cent. of the strength, dry (*vide infra*), while sample No. 5B, which showed the comparatively low value of 23 lbs. per square inch, was supplied under the description of second grade. It is, therefore, suggested that 25 lbs. per square inch might fairly be adopted as a minimum for this class of parchment.

In the Regulations quoted at the beginning of this paper, the minimum weight of parchment for wrapping rolls, prints, bricks, etc., is 18 lbs. per ream. The strengths of samples from 18 to 24 lbs. per ream varied from 18 to 24 lbs. per square inch. For this class of paper it is suggested that 18 lbs. per square inch might be taken as a minimum.

The ratio of the strengths in the wet and dry states affords the most reliable criterion for genuine vegetable parchment, especially as it has a direct connection with practical conditions. It may be regarded as covering other tests, such as that of boiling with 10 per cent. sodium hydroxide solution for 15 minutes, after which the parchment should not have disintegrated, or that of observing the behaviour of the parchment on scorching with a small flame.

It will be noticed that the greaseproof papers break down entirely in the bursting-strength test after having been wetted.

The rule that the strength, wet, should be at least 33 per cent. of that dry, may safely be taken as a standard for genuine vegetable parchment, and it will be seen that all of the samples from 1 to 33 inclusive (41 in all), except two (Nos. 8 and 17), conform to this requirement, the two exceptions falling short by 1 per cent. It is understood that all weight and strength test results are averages of at least ten separate trials.

Composition of Water-Soluble Extract.

It was considered desirable to examine the general nature of the substances determined and examined in routine analyses as water-soluble extract in genuine vegetable parchment. Several quantities, each of 1 kilo., of sample No. 32, were extracted with hot distilled water on the steam-bath, the aqueous extract being concentrated by evaporation over steam. The extraction was not made quantitatively, as this would have involved the evaporation of inconveniently large amounts of water. The extract from 1 kilo. of parchment was concentrated to 100 c.c., treated with charcoal and filtered. To the filtrate were added 400 c.c. of 96 per cent. alcohol, which caused the precipitation of a white substance resembling dextrin; this was well washed with 90 per cent. spirit, filtered off and dried. One kilo. of parchment yielded 1·7 grms. of this substance.

The alcoholic filtrate was evaporated to dryness, and the residue was extracted with 95 per cent. alcohol; the alcoholic solution, on evaporation to dryness, yielded a brown solid, 1 grm. being obtained from 1 kilo. of parchment.

(A) Examination of Substance Precipitated by Alcohol.—This was a white amorphous substance with a slight greyish tinge, resembling dextrin, giving gummy solutions in water, which produced a purple coloration on the cautious addition of iodine. When the powder was stained with iodine solution, and viewed under the microscope, it showed two distinct localised colorations, *viz.* deep reddish brown and light purple. Staining with ferric ferricyanide and with aniline acetate solutions in a similar manner showed distinctly localised blue and red colorations, respectively. These indications point to the substance being a mixture of lignone and cellulose decomposition products, which supposition was borne out by the analytical data given below.

The solution gave a red coloration when warmed with phloroglucinol in hydrochloric acid solution; it reduced Fehling's solution, and in cold solution decolorised permanganate slowly. A 2 per cent. solution in water was laevo-rotatory, showing a specific rotation of $[\alpha]_D = -46{\cdot}6°$ (calculated on the substance, less ash). On heating this 2 per cent. solution with dilute hydrochloric acid on the steam bath it became dextro-rotatory, a constant value being obtained after one hour's heating with 10 per cent. of the concentrated acid or after 2 hours with 2 per cent. of acid. The figure attained was $[\alpha]_D = +25{\cdot}8°$ (calculated on the ash-free substance). This would correspond with the specific rotation of a mixture of dextrose and xylose, approximately in the proportion of one to four, assuming these two sugars to be the product of hydrolysis. The laevo-rotatory power of the original

substance may be assumed to be due to the predominance of a pentose-yielding complex.

On treatment of the hydrolysed material with phenylhydrazine in the usual way, a dark brown product was obtained, which after four crystallisations from alcohol yielded a small amount of crystalline material (m.pt. 206° C.), which was identified as glucosazone; this may represent either or all of the three sugars—dextrose, mannose or laevulose, as these have all been obtained from wood by various observers. (See "Power Alcohol," by Monier-Williams.)

The material gave the following results on analysis:—Ash, 18·47 (chiefly calcium sulphate with a little ferric oxide); sulphur, 3·56; pentosan (by Kröber's method), 58·1 per cent. (calculated on the material, less ash); methoxyl, nil; acetic acid (by distillation with dilute sulphuric acid), nil.

With regard to the sulphur content of 3·56 per cent., this was represented by 0·15 per cent. of sulphur in the original parchment. It was thought possible that carbohydrate sulphuric esters, such as described by Cross and Bevan ("Cellulose," 1918, p. 50), might be present, but this was negatived by the fact that aqueous extracts of parchments invariably remained neutral during evaporation (*p*H 4·6–5·2), while the material under consideration similarly remained neutral on boiling for 6 hours in 2 per cent. solution in water. The sulphur is, therefore, present as calcium sulphate.

The figures given under pentosan are based on the production of furfuraldehyde on distillation with 12 per cent. hydrochloric acid under the standard conditions of the Kröber method. The reducing properties of the original substance are to be expected from the known action of sulphuric acid on cellulose. (See Cross and Bevan, "Cellulose," 1918, p. 53.)

From the above observation it may be concluded that this material consists essentially of carbohydrate material, being a mixture of pentose- and hexose-yielding complexes, the former predominating. The lignone material which yields acetic acid and reduces permanganate instantaneously (see the following section) is absent.

(B) Examination of Substance Soluble in Alcohol.—This was a brown hygroscopic powder; it reduced Fehling's solution readily and also decolorised permanganate instantaneously in cold solution. On treatment with phenylhydrazine in the usual way, it behaved similarly to the material described under (A), the crude product yielding, after four crystallisations from alcohol, a small amount of glucosazone (m.pt. 206° C.). Polarimetric examination showed $[\alpha]_D = -22{\cdot}7°$ (calculated on the substance, less ash).

The following results were obtained on analysis:—Ash, 11·53; pentoses (by Kröber's method), 6·25; methoxyl, nil; and acetic acid (on distillation with dilute sulphuric acid), 31·30 per cent. (Pentoses and acetic acid were calculated on the substance, less ash.)

The determination of acetic acid was carried out as follows:—One grm. of the material was dissolved in 100 c.c. of recently boiled water and 40 c.c. of *N*

sulphuric acid; a little pumice was added, and the mixture was distilled in a Polenske apparatus. One hundred c.c. of distillate were collected and titrated with $N/10$ sodium hydroxide solution (phenolphthalein as indicator). Successive quantities of 100 c.c. of water were added to the mixture in the flask and distilled off until a constant blank value was obtained on titration. The sum of the titrations, with allowances for blanks, gave the total yield of acetic acid. The acid was identified as practically pure acetic acid (containing traces of formic acid) by the usual reactions and by an electrometric determination of the *p*H value of a solution of known titre obtained after evaporating the neutralised distillates to dryness, dissolving in water, acidifying and distilling as before.

The unsaturated nature of the material and its yield of acetic acid on hydrolysis are characteristic of lignone. (See "Researches on Cellulose," by Cross and Dorée.)

The methoxyl which might be expected to be present in this material has evidently been completely split off by the action of the strong sulphuric acid used in the parchmentising process. (*Cf.* Hägglund, *Chem. Ztg.*, 1919, **90**, 186.)

The comparatively small amount of furfuraldehyde obtained by the Kröber distillation process has been provisionally calculated as pentose. It may, however, be due to the presence of some of the material described under (A), which is also indicated by the laevorotation of the material and the fact that, when exhaustively extracted with alcohol, the rotation of the alcohol-soluble portion is found to be practically nil.

The examination of the water-soluble extract under headings (A) and (B) shows that it consists of decomposition products of lignocellulose. The analytical methods which have been adapted, mainly from the investigations of Cross and Bevan, Cross and Dorée, and Klason, may perhaps be found useful for purposes of analytical control. It may be pointed out that the reducing material determined by iodine titration in genuine vegetable parchment probably represents substances falling under at least three different headings—(1) Simple sugars; (2) complex carbohydrates; (3) unsaturated lignone material, which reduces permanganate far more readily than the sugars.

SUMMARY.—1. The following determinations were carried out on 41 samples of vegetable parchment and 2 samples of greaseproof paper:—Water, per cent.; ash, per cent.; water-soluble extract, per cent.; reducing material (as dextrose), per cent.; bursting strength wet and dry, and weight, in lbs. per ream. The samples were also examined as to their power to support mould growth. The methods adopted are described and the results are tabulated.

2. As the result of these determinations, the following additional standards are tentatively suggested:—Water, maximum 10·0 per cent.; ash, 0·45 per cent.; water-soluble extract, 1·30 per cent.; bursting strength (by Ashcroft tester), minimum 25 lbs. per square inch for parchments of 25 lbs. per ream, and 18 lbs. per sq. in. for 18 lbs. per ream. The strength immediately after wetting, as described, to be at least 33 per cent. of the strength of the unwetted sample.

3. The percentages of reducing material, as dextrose, in the water-soluble extract have been calculated as a guide to the detection of added sugar.

4. Certain standards adopted in Germany (*viz.* 8 per cent. of extract and 3 per cent. of ash), are considered far too high, being based on additions of sugar and salt, respectively. An unduly high content of extract renders the parchment particularly susceptible to attack by mould.

5. The water-soluble extract from genuine vegetable parchment was examined, and found to consist of decomposition products of lignocellulose. Methods by which they may be characterised have been adapted chiefly from the investigations of Cross and Bevan.

I wish to thank the Department of Agriculture, Irish Free State, for permission to publish this paper.

DEPARTMENT OF AGRICULTURE,
BUTTER TESTING STATION, DUBLIN.

DISCUSSION.

The PRESIDENT remarked that he was sure the very fact that so little literature could be found on this subject would make these results of great value. He then welcomed to the meeting Mr. Faber, representing the Danish Government, and an old member of the Society.

Mr. HARALD FABER, after thanking the Society for the kind invitation to be present to hear this very interesting paper, said that he had great pleasure in proposing a vote of thanks to Mr. Arup. He was really surprised at the number of interesting details which had been extracted from such a subject. The chief interest which, he believed, Mr. Arup had in mind was to find out what composition parchment paper for wrapping butter should have, so as to avoid the growth of mould upon it. That side of the question had been studied in Denmark to some extent, but not so thoroughly as in the work under discussion.

When he received the invitation to be present at this meeting, he (Mr. Faber) had written to the Chief Inspector in Copenhagen, Mr. T. Lohse, who had to deal with this subject, and who had kindly sent a few notes from which Mr. Faber abstracted the following:

When the Chief Inspector took over his duties he found parchment paper being used which sometimes contained as much as 25 per cent. of sugar. (Mr. Arup had found a similar kind of paper used in Germany.) This was very bad for use in connection with butter, as it induced mould to grow. He had also found paper containing as much as 10 per cent. of glycerin. (Mr. Faber here mentioned that in Denmark they issued a parchment paper with their National Brand for butter wrapping, and the Chief Inspector had control of the specifications for this paper.) He had, therefore, been able to stipulate that the paper must be free from sugar or dextrose, but he had at first allowed 3 per cent. of glycerin, because he had found that paper was easier to handle if it contained a certain amount of glycerin, and 3 per cent. did not seem to encourage the moulds. Later, however, he eliminated that also, and tried paper entirely free from glycerin, and no objection was taken to its use. Various papers were tested by wrapping them round butter and infecting them with spores, and it was found that paper free from glycerin or sugar was very resistant to mould growth. Mr. Lohse had had one peculiar experience with a particular kind of paper free

from sugar and glycerin, which was very apt to grow mould; he had come to the conclusion that the paper during manufacture, or very soon after, must have been infected with moulds, and when steeped in boiling water for some time and dried no mildew grew on it. It had recently been a practice, when packing margarine in parchment paper, to have it lined on the inside with a thin layer of paraffin wax. This would make it easier for the packer to handle, but it was more expensive, and offered no advantage, so far as resistance to mould growth was concerned; therefore, its use was not likely to spread. Most of the parchment paper used at present in the Danish dairies was derived from Belgian sources (as also, he believed, was that used in Ireland), but they had recently had an English paper from a mill in Kent which, on analysis, was found to be entirely free from sugars and glycerin, and was very good paper. They were trying to find other mills in this country where they could buy good parchment paper, as, naturally, when sending butter to England, they would like to be able to wrap it in English paper.

Mr. McLachlan asked whether Mr. Arup had made any attempt to determine metallic impurities in the papers.

Mr. W. Partridge said that he would only touch on the side issues of this paper. This was the second time recently that he had heard of attenuated moulds; the previous occasion was when G. Smith, working on the mycology of textile fabrics, was getting them in the mildew on yarns and cotton cloths. In Mr. Arup's selection of moulds to determine the readiness of mould growth, he had noticed that *Penicillium* and *Cladosporium* had been taken. He supposed that this was because they were both coloured and therefore easy to see. *Cladosporium* was a cold-store mould which grew on meat—did it grow on butter? (This was answered in the affirmative.) He remarked that had he been asked to choose a mould for this purpose he would have suggested *Fusarium*. He quite appreciated that Mr. Arup would prefer a coloured mould, which would show up on the white paper, otherwise *Oidium lactis* would seem to be the most suitable in this connection. He would also like to make a point regarding the suggestion that paper should be dipped in hot brine. Had Mr. Arup given any strength for this brine? His reason for asking this was that in the case of brine for pig's flesh it was supposed to contain 23–28 per cent. NaCl, but often by the time it was sold as bacon it had been through brine containing only 12–13 per cent. NaCl and a few million bacteria per c.c. If the Irish Government were going to stipulate for immersion in brine, they ought to state definitely that the brine should be discarded before the sodium chloride percentage fell below a certain number. Finally he remarked on the use of the word "dextrose," and queried whether the word "glucose" should have been used.

Mr. A. L. Bacharach called attention to a practical problem, arising especially over papers used for wrapping small packets intended for the retail market, namely, resistance to creasing. The several methods devised for measuring tensile strength did not give any information about the extent to which one could go in creasing or crushing a paper without breaking it. A method for rapidly measuring this, even approximately, would be very useful. Like the Danish authorities, he had found parchment paper from a Kent mill (presumably the same) quite satisfactory, though occasionally a sample exceeded the very low limit set for free acidity.

Mr. Arup, replying, thanked Mr. Faber for his very helpful remarks. It appeared that Mr. Faber's friend had been working along similar lines to those he himself had followed, and he hoped they would be able to get in touch with each other on the subject. He had not come across any glycerin; he would like to

know the method used for determining this. In connection with paper he queried whether, when speaking of freedom from sugar, one meant actually chemically free from all traces of sugar or not. According to statements by manufacturers, if the carbohydrate were completely washed out, the paper would be too brittle. He had chosen *Penicillium* and *Cladosporium* because they were the most common moulds. *Oidium* was colourless. With regard to the brine, one should use dry salt of reasonably pure quality; spores gathered on the surface of damp salt. He had included in his paper directions for making the brine. Regarding the reaction, all soluble extracts were neutral, ranging between methyl orange and methyl red. The word "dextrose" was used for the pure chemical compound, whereas "glucose" was applied to the commercial product. In reply to Mr. Bacharach, Mr. Arup said that attempts to avoid this had been made by specifying that the paper must be of a certain weight. There was not nearly so much creasing if pure vegetable parchment were used as was the case with the imitation grease-proof paper. He had never found any metallic impurities, such as might have been used for weighting the paper.

Replying to Mr. Bolton, he said that he was rather loath to lay down definite standards (though he had put forward suggestions), as there was so often a tendency to regard them as the ultimate perfection. Very little technical information could be obtained from the manufacturers, and one had to decide what would be a fair standard from the results at one's disposal.

The Fatty Acids and Component Glycerides of Indian Ghee.

By R. BHATTACHARYA, Ph.D., A.I.C., AND T. P. HILDITCH, D.Sc., F.I.C.

(*Read at the Meeting, February* 4, 1931.)

OWING to climatic and other factors it is difficult to preserve butter as such in good condition in India, and, moreover, it is not suited to Indian methods of cooking or sweetmeat making. Butter or cream is, therefore, almost universally clarified before sale, and is then known as ghee; when properly clarified, it has a pleasant odour and keeps indefinitely if stored in porous earthenware vessels, although rancidity develops in course of time when ghee is kept in glazed vessels or tins. Ghee is usually prepared from the milk of the cow or the buffalo; goat's milk, although considerably used in the Northern provinces, is not often churned for butter.

Ghee of the highest quality, clear white or yellow in colour and with a perfectly fresh butter-like flavour, is the subject of the present communication. This is generally prepared by collecting the thick layer of "skin" which forms when

boiled milk is left at a moderate warmth, and mashing and churning the accumulated layers, cold water being added towards the end as the fat rises. The buttermilk or whey is separated from the fat, which is very gently heated in an open pan, strained and stored.

The second quality ghee, which appears to be the pattern for most "ghee substitutes" imported into India, is underclarified, and in consequence soon develops its characteristic sharp rancid taste and peculiar flavour. It results either from the churning of fresh milk in open pitchers by means of a bamboo staff forked at the lower end and rotated by a twisted rope (a method dating back to the earliest Vedic period), or by curdling the milk with curd or lactic acid bacilli and then churning the curdled milk.

Two samples of buffalo and of cow ghee (first quality) have been investigated. In the first instance the fats had been prepared at a temperature not exceeding 40° C. from the milk of animals fed on a ration of dry grass and green millet with concentrates containing cotton-seed, sesamé-cake and lentil husks (Tur-chuni); the buffaloes were of Murrah breed, and the cows were three quarter Indian and one-quarter Ayrshire crossbred. These specimens are referred to as buffalo No. 1 and cow No. 1, and were, respectively, clear white and very pale cream in colour.

As the quantity of material was not sufficient for examination of the glyceride structure, further supplies were obtained, but these consisted of market samples from pasture-fed animals; the pasture-fed buffalo ghee (No. 2) was almost white, whilst the pasture-fed cow ghee (No. 2) was of a full yellow colour, and the odour of both was, again, perfectly fresh and free from rancidity. All the samples were kindly obtained for us by the Director of Industries, Central Provinces, Nagpur.

The general analytical characteristics of the ghees were as follows:

	Buffalo.		Cow.	
	No. 1.	No. 2.	No. 1.	No. 2.
Sap. equivalent	252·3	251·0	252·0	249·2
Iodine value	32·5	33·5	35·2	36·0
Reichert–Meissl value ..	28·0	30·9	25·2	26·0
Polenske value	1·4	2·2	1·4	1·9
Kirschner value	24·6	25·6	20·9	20·6
Refractive index, $n^{60°}_{D}$ ..	1·4467	1·4462	1·4475	1·4470

Composition of the Fatty Acids of the Four Specimens of Ghee.—The method employed was in all essentials identical with that which was described fully in the Analyst by one of us and E. E. Jones (1929, **54**, 75). The total mixed fatty acids from 250–500 grms. of fat were carefully distilled in steam for four or five hours, during which time about 3 litres of aqueous condensate were collected. The "steam-volatile acids" were worked up, as described in the earlier paper, but it has been found that very small quantities of unsaturated acid are

present in the steam-distillate and are left in the residue from the fractional distillation of the volatile acids. The iodine value of this residue is, therefore, determined, and the unsaturated acid calculated as oleic acid; the amount is too small appreciably to affect the accuracy of the oleic acid figure, but its recognition permits a more correct value for the mean equivalent of the saturated acids (usually caprylic and capric) in this particular residue (usually only 1·5–2·5 grms.) to be ascertained. The acids non-volatile in steam are resolved by the lead-salt-alcohol procedure into groups of "solid" and "liquid" acids, which are converted into the respective esters and fractionally distilled in the manner previously described.

A typical set of the complete experimental data is given for one fat; but, as these figures occupy considerable space, the analytical results as a whole are summarised in Table II, wherein will be found the calculated increments of each acid present in the "steam-volatile," "solid" and "liquid" groups of fatty acids.

Precise identification of the majority of the commonly-recognised butter acids was thought unnecessary, but the acids present in the residual fraction of the "solid" esters from buffalo ghee No. 1 were submited to fractional crystallisation from ethyl acetate and alcohol several times, when a specimen which melted at 74° C. was finally obtained, thus affording definite evidence of the presence of arachidic acid, or, at least, of an acid of higher molecular weight than stearic acid.

Table I.

Typical Experimental Data (Buffalo Ghee No. 2).

The ghee (250 grms.) yielded **14·1** grms. of steam-volatile and **216·5** grms. of non-steam-volatile acids; the latter were resolved by lead salt separation into "solid" acids (**56·7** per cent., iodine value **7·2**) and "liquid" acids (**43·3** per cent., iodine value **68·8**).

"Steam-volatile" Acids.

No.	Grms.	B.pt. °C.	Pressure.	Mean equivalent.	Acids. Butyric. Grms.	Caproic. Grms.	Caprylic. Grms.	Capric. Grms.	Oleic. Grms.
	In aqueous solution	..	..	..	1·65				
	In recovered ether	..	..	..	0·14				
1	14·0	35/ 85	Atmospheric		0·07				
2	7·3	85/ 90	,,		0·43				
3	0·58	90/157	,,		0·30				
4	1·32	157/161	,,		1·23				
5	2·31	161/165	,,	92·1	1·89	0·42			
6	2·84	165/170	,,	94·9	1·98	0·86			
7	0·70	170	,,	95·6	0·47	0·23			
8	2·86	119/140	Reduced	102·0	1·23	1·63			
9	1·54	Residue (iod. val. 14·4)		162·0			1·20	0·09	0·25
	Totals:				9·39	3·14	1·20	0·09	0·25

METHYL ESTERS OF "SOLID" ACIDS S.

Primary fractionation.

No.	Grms.	B.pt./ 1 mm. °C.	Saponi-fication equiva-lent.	Iodine value.
S1	29·62	40–144	258·7	2·1
S2	11·79	144–145	268·5	2·5
S3	12·22	145	270·5	5·8
S4	10·21	145–146	275·1	5·9
S5	10·82	146–150	278·6	8·7
S6	8·66	150–157	295·0	13·8
S7	9·29	157–161	295·4	17·6
S8	4·10	Residue	308·0	19·2
	96·71			

Refractionation (of S1).

No.	Grms.	B.pt./ 1 mm. °C.	Saponi-fication equiva-lent.	Iodine value.
S11	0·84	81–100	226·2	nil
S12	1·48	100–109	239·4	1·0
S13	2·28	109–118	245·5	0·9
S14	2·76	118–128	254·0	1·0
S15	5·09	128–129	255·6	0·8
S16	6·31	129–130	262·8	0·8
S17	4·63	130	271·7	2·9
S18	3·87	Residue	279·1	6·9
	27·26			

METHYL ESTERS OF "LIQUID" ACIDS L.

Primary fractionation.

No.	Grms.	B.pt./ 1 mm. °C.	Saponi-fication equiva-lent.	Iodine value.
L1	20·56	40–136		36·1
L2	7·39	136	277·6	71·1
L3	12·06	136–144	287·5	80·6
L4	9·94	144–146	288·4	88·3
L5	9·17	146–150	292·1	88·7
L6	8·18	150	295·4	93·2
L7	9·32	Residue	311·7	95·6
	76·62			

Refractionation (of L1).

No.	Grms.	B.pt./ 1 mm. °C.	Saponi-fication equiva-lent.	Iodine value.
L11	1·10	70	174·9	3·9
L12	1·34	70–75	188·1	7·6
L13	1·40	75– 95	196·6	8·5
L14	1·78	95–105	231·1	13·0
L15	3·29	105–120	237·2	23·8
L16	3·23	120–122	251·2	32·9
L17	1·74	122–133	268·3	35·0
L18	4·11	Residue	296·2	74·4
	17·99			

TABLE II.

Summarised Data for the Fatty Acids of Buffalo and Cow Ghee.

Acid.	Volatile acids. Grms.	Acids non-volatile in steam. "Solid" acids. Grms.	Acids non-volatile in steam. "Liquid" acids. Grms.	Total. Grms.	Per cent. (excluding unsaponifiable matter).
Buffalo Ghee No. 1.					
	29·8	263·0	178·7	471·5	
Butyric	18·6	—	—	18·6	3·9
Caproic	8·1	—	—	8·1	1·7
Caprylic	1·0	—	0·6	1·6	0·3
Capric	—	—	4·1	4·1	0·9
Lauric	1·8	0·4	7·3	9·5	2·0
Myristic	0·3	14·0	19·7	34·0	7·2
Palmitic	—	93·2	0·8	94·0	20·0
Stearic	—	114·9	—	114·9	24·4
Arachidic	—	12·6	—	12·6	2·7
Oleic	—	27·2	133·5	160·7	34·3
Linoleic	—	—	12·4	12·4	2·6
Unsaponifiable matter ..	—	0·7	0·3	1·0	—
Buffalo Ghee No. 2.					
	14·1	122·6	93·9	230·6	
Butyric	9·4	—	—	9·4	4·1
Caproic	3·1	—	—	3·1	1·4
Caprylic	1·2	—	0·9	2·1	0·9
Capric	0·1	—	3·9	4·0	1·7
Lauric	—	0·8	5·8	6·6	2·8
Myristic	—	14·4	8·9	23·3	10·1
Palmitic	—	70·8	0·8	71·6	31·1
Stearic	—	24·5	1·1	25·6	11·2
Arachidic	—	2·0	—	2·0	0·9
Oleic	0·3	10·1	65·9	76·3	33·2
Linoleic	—	—	6·0	6·0	2·6
Unsaponifiable matter ..	—	—	0·6	0·6	—
Cow Ghee No. 1.					
	28·4	244·9	206·1	479·4	
Butyric	15·6	—	—	15·6	3·3
Caproic	9·9	—	—	9·9	2·1
Caprylic	1·4	—	3·2	4·6	1·0
Capric	1·2	—	10·1	11·3	2·3
Lauric	—	1·0	16·9	17·9	3·7
Myristic	—	22·8	5·2	28·0	5·8
Palmitic	—	143·5	—	143·5	30·0
Stearic	—	53·6	—	53·6	11·2
Oleic	0·3	24·0	145·6	169·9	35·5
Linoleic	—	—	24·6	24·6	5·1
Unsaponifiable matter ..	—	—	0·5	0·5	—
Cow Ghee No. 2.					
	8·3	72·3	63·9	144·5	
Butyric	3·7	—	—	3·7	2·6
Caproic	2·8	—	—	2·8	1·9
Caprylic	0·8	—	1·2	2·0	1·4
Capric	0·8	—	4·3	5·1	3·6
Lauric	—	1·7	6·6	8·3	5·7
Myristic	—	13·2	2·1	15·3	10·6
Palmitic	—	41·8	0·2	42·0	29·1
Stearic	—	9·6	—	9·6	6·7
Oleic	0·2	6·0	42·9	49·1	34·0
Linoleic	—	—	6·4	6·4	4·4
Unsaponifiable matter ..	—	—	0·2	0·2	—

The figures for the unsaturated acids in cow ghee No. 1 are somewhat higher than are demanded by the iodine value of the original ghee, whilst the palmitic and stearic acid contents given for buffalo ghee No. 1 are markedly different from those of the three other samples; unfortunately, lack of material precluded us from repeating the analyses, as we should have preferred to do. In view of the definitely proven presence of arachidic acid in buffalo ghee No. 1, it may well be that the palmitic and stearic acid values given are not far removed from the truth; but there is almost certainly a small experimental error in the figures given for cow ghee No. 1 oleic and linoleic acids. Since, however, the rest of these respective analyses is, to the best of our knowledge, of the ordinary order of accuracy for this type of determination, and since detailed analyses of ghee fats are not numerous, we feel that, with these reservations, it is well to publish all four sets of results in order to give a general picture of the fatty acid components present in representative Indian ghees.

THE COMPONENT GLYCERIDES OF BUFFALO AND COW GHEE.—The same method was followed as in the former paper, namely, oxidation of the ghee (1 part) dissolved in acetone (10 parts) with finely-powdered potassium permanganate (4 parts), followed by isolation and purification of the fully-saturated glycerides, which alone are left unattacked. The composition of the fatty acids present in the fully-saturated glycerides was determined by the same means as were employed in the case of the original ghees, and the resulting data permit conclusions to be drawn as to the distribution of the saturated fatty acids in the fully-saturated and mixed saturated-unsaturated glycerides of the fats and as to the general composition of the mixed saturated-unsaturated glycerides.

For this part of the investigation the pasture-fed buffalo and cow ghee only were utilised, owing to shortage of material in the case of the other samples.

Buffalo Ghee No. 2.—Six hundred grms. of the buffalo ghee gave 213·2 grms. of crude fully-saturated glycerides (iodine value nil) which was still somewhat contaminated with acidic glyceride products of oxidation; the crude product (212·0 grms.) was further purified by boiling with dilute potassium carbonate solution, and then repeatedly with water (the aqueous and alkaline washings being extracted with ether), and yielded:

(*a*) 151·5 grms. completely neutral fat, sap. equiv. 233·5 (acid value nil);

(*b*) 36·7 grms. fat extracted by ether, sap. equiv. 225·2 (acid value 3·5);

(*c*) 17·5 grms. acidic material, sap. equiv. 199·0 (acid value 108·7).

Assuming that the acidic matter present in (*b*) has the same acid value as (*c*), the proportion of fully-saturated glycerides in the original fat is 32·3 per cent. Analysis of the acids present in the completely neutral product (*a*) gave results which are summed up in Table III.

TABLE III.

Acid.	Acids. Volatile acids. Grms.	Non-volatile in steam. Grms.	Total. Grms.	Per cent. (excluding unsaponifiable matter).
	12·6	125·8	138·4	
Butyric	7·7	—	7·7	5·6
Caproic	3·6	—	3·6	2·6
Caprylic	0·6	—	0·6	0·4
Capric	0·7	1·0	1·7	1·2
Lauric	—	5·5	5·5	4·0
Myristic	—	13·0	13·0	9·4
Palmitic	—	74·7	74·7	54·0
Stearic	—	29·5	29·5	21·3
Arachidic	—	2·1	2·1	1·5

Table IV shows the general composition of 100 parts of the glycerides of buffalo ghee No. 2, as indicated by the foregoing analyses.

TABLE IV.

Glyceryl residue.	Original ghee. 100	Fully-saturated glycerides. 32·3	Mixed saturated-unsaturated glycerides (by difference). 67·7	
Glyceryl residue ..	5·0	1·7	3·3	
				(Molecular ratios)
Butyric acid ..	3·9	1·7	2·2	25
Caproic ,, ..	1·3	0·8	0·5	4
Caprylic ,, ..	0·9	0·1	0·8	5
Capric ,, ..	1·6	0·4	1·2	7
Lauric ,, ..	2·7	1·2	1·5	8
Myristic ,, ..	9·6	2·9	6·7	30
Palmitic ,, ..	29·6	16·5	13·1	51
Stearic ,, ..	10·6	6·5	4·1	14
Arachidic ,, ..	0·8	0·5	0·3	1
Oleic ,, ..	31·5	—	31·5	112
Linoleic ,, ..	2·5	—	2·5	9

From these figures, and also from the saponification equivalent and proportion of the fully-saturated glycerides, together with the equivalent of the original ghee and the known proportion of unsaturated acids therein present, it follows that approximately 1·2 mols. of saturated acids are linked with 1 mol. of unsaturated acids in the form of saturated-unsaturated (+completely unsaturated) glycerides. Consequently, of 100 mols. of buffalo ghee No. 2, about 34 consist of fully-saturated glycerides, and about 42–54 of mono-unsaturated-disaturated glycerides, according as the amount of di-unsaturated-monosaturated glycerides lies between 24 and nil, and that of tri-unsaturated glycerides between nil and 12. The general structure of the buffalo ghee, allowing for its particular content of oleic and linoleic acids, is closely comparable with that of the cow butter fats recorded in the former paper; as in the latter, all the saturated acids are distributed more or less evenly throughout both the fully-saturated and the mixed saturated-unsaturated parts of the fat,

with perhaps a slight tendency for the lower fatty acids to be associated more with oleic than with palmitic or stearic acid.

Cow Ghee No. 2.—Six hundred grms. of the cow ghee gave **208·7** grms. of crude fully-saturated glycerides (iodine value nil), which, on further purification as previously described (p. 166), yielded:

(*a*) **166·7** grms. neutral fat, sap. equiv. **245·1** (acid value **1·7**);

(*b*) **28·0** grms. fat extracted by ether, sap. equiv. **236·9** (acid value **8·9**);

(*c*) **14·0** grms. acidic material, sap. equiv. **172·2** (acid value **121·5**).

Assuming that the acidic matter still present in (*b*) has the same acid value as (*c*), the proportion of fully-saturated glycerides in the original fat is **31·7** per cent.

Analysis of the acids present in the neutral product (*a*) gave the results summarised in Table V.

TABLE V.

Acid.	Volatile acids. Grms.	Acids non-volatile in steam. Grms.	Total. Grms.	Per Cent. (excluding unsaponifiable matter).
	8·9	96·5	105·4	
Butyric	4·7	—	4·7	4·4
Caproic	2·8	—	2·8	2·7
Caprylic	0·4	—	0·4	0·3
Capric	1·0	2·6	3·6	3·4
Lauric	—	5·8	5·8	5·5
Myristic	—	16·8	16·8	16·0
Palmitic	—	52·2	52·2	49·6
Stearic	—	19·1	19·1	18·1

Table VI shows the general composition of 100 parts of the glycerides of cow ghee No. 2, as indicated by the foregoing analyses.

TABLE VI.

	Original ghee. 100	Fully-saturated glycerides. 31·7	Mixed saturated-unsaturated glycerides (by difference). 68·3	
Glyceryl residue	5·1	1·6	3·4	
				(Molecular ratios)
Butyric acid ..	2·5	1·3	1·2	13
Caproic ,, ..	1·8	0·8	1·0	9
Caprylic ,, ..	1·3	0·1	1·2	8
Capric ,, ..	3·4	1·0	2·4	14
Lauric ,, ..	5·4	1·7	3·7	19
Myristic ,, ..	10·1	4·8	5·3	23
Palmitic ,, ..	27·6	14·9	12·7	50
Stearic ,, ..	6·3	5·5	0·8	3
Oleic ,, ..	32·3	—	32·3	114
Linoleic ,, ..	4·2	—	4·2	15

From these figures, or from the saponification equivalent and proportion of fully-saturated glycerides, together with the equivalent of the original ghee and the known proportion of unsaturated acids therein present, it follows that approximately 1·1 mols. of saturated acids are linked with 1 mol. of unsaturated acids in the form of saturated-unsaturated (+completely unsaturated) glycerides. So that, of 100 mols. of cow ghee No. 2, about 33 consist of fully-saturated glycerides, and about 38–53 of mono-unsaturated-disaturated glycerides, according as the amount of di-unsaturated-mono-saturated glycerides lies between 29 and nil, and that of tri-unsaturated glycerides between nil and 14. The general structure of the cow ghee is again similar in type to that of the New Zealand butter-fats dealt with in the previous paper, the saturated acids being for the most part more or less evenly distributed in both the fully-saturated and the mixed saturated-unsaturated glycerides of the fat.

Summary and Discussion of Results.

(i) General Analytical Characteristics and Detailed Fatty Acid Composition.—The two specimens of cow ghee, respectively from stall-fed and pasture-fed animals, have given figures which in each case lie within the limits of the eight New Zealand and English cow butter-fats which have been given by Hilditch and Jones (*loc. cit.*), and by Hilditch and Sleightholme (*Biochem. J.*, 1930, **24**, 1098). The Reichert–Meissl values and the observed percentages of butyric acid tend perhaps towards the lowest values obtained in the New Zealand and English series, whilst the oleic acid contents lie about half-way between the extreme values recorded for the latter series. Beyond this, the milk-fat of the Indian cow, judging from these two observations, would appear very closely to resemble that of English or New Zealand cattle. The amount of stearic acid (always a somewhat variable component) is higher in the fat from the stall-fed than in that from the pasture-fed sample, whilst the palmitic acid figure (29–30 per cent.) is of the order which seems to be specific both for cow butter-fats and beef tallows.

The corresponding specimens of buffalo ghee have given figures not greatly differing from those of cow butters, although certain features seem to be distinctive. There is definitely more butyric acid present than in the average cow butter-fat from any locality, and this is reflected in somewhat higher Reichert–Meissl and Kirschner values; the proportion of linoleic to oleic acid is lower than in cow milk-fats, and the mean unsaturation (iodine value) is also lower than for the average cow butter-fats. The most apparent difference in the milk-fats of the two types of animal seems, however, to lie in the increased amount of stearic acid, and the presence of small but definite amounts of arachidic acid, in buffalo as compared with cow butters; it is also probable that the proportion of palmitic acid is more variable in buffalo than in cow butters. It is, of course, not safe to generalise too far from the examination of only two specimens of buffalo ghee, but, on the other hand, it may be remarked that our experience of cow milk fats (ten specimens of which have now been submitted to detailed study by the present

methods) leads us to believe that, broadly speaking, the main characteristics of fatty acid composition are fairly well defined for a given species of animal, subject to minor variations caused by differences in climatic or feeding conditions.

(ii) GLYCERIDE STRUCTURE.—The present results merely reinforce our previous conclusion, that the glyceride structure of milk-fats, like that of tallows and other animal fats, is of the mixed "heterogeneous" type, and is determined by factors which are independent of the particular fatty acids present. We have recently shown (*Proc. Roy. Soc.*, 1930, **129**, *A*, 468) that the relationship between the fully-saturated glycerides present in such fats and the ratio of saturated to unsaturated acids in the mixed fatty acids thereof is closely similar to that in triglycerides prepared synthetically from glycerol by heating with excess of a mixture of saturated and unsaturated fatty acids.

The pasture-fed buffalo and cow ghee, which were investigated from this standpoint, conform with this generalisation, the proportions of fully-saturated glycerides present (respectively **32·3** per cent. and **31·7** per cent.) being those which would be expected from the mean unsaturation of each fat. There has been no evidence of segregation of any fatty acid into a simple triglyceride, and all the saturated fatty acids are found, in more or less the same distribution, in each part of the fat—fully-saturated and mixed saturated-unsaturated triglycerides. It is doubtful whether triolein is present in appreciable proportions, but tripalmitin or tristearin is only present, if at all, in very small amount, and there is no reason to suppose that the quantity of triolein will be much greater.

It may be repeated, finally, that the four fats studied in this work represent first quality Indian ghees equivalent in flavour and odour to the best European or Australasian butter-fats.

We wish to acknowledge the grant to one of us (R. B.) of a Research Scholarship by the Government of the Central Provinces of India during the course of this work, and to express our appreciation of the provision of the samples of ghee by the Director of Industries, Central Provinces, Nagpur.

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A New Method of Reduction of Tin and Antimony Prior to Titration.*

By B. S. EVANS, M.C., Ph.D., F.I.C.

Up to the present the agents in use for the reduction of tin to the stannous condition appear to be exclusively metals, no soluble reducing agent apparently being known, or, at any rate, used. A large number of metallic reducing agents have been tried with varying success, of which, perhaps, the best is lead (A. R. Powell, *J. Soc. Chem. Ind.*, 1918, **37**, 287T.). They, one and all, however, suffer from certain drawbacks which are inherent in their metallic condition, and of which the principal one is due to the fact that any metal which will reduce tin will also reduce certain other metals, notably antimony, to the metallic condition; this reduced antimony, if present in any amount, will not only completely obscure the end-point, but will also withdraw a certain proportion, too large to be neglected, of tin from solution (K. Järvinen, *Z. anal. Chem.*, 1923, **62**, 184; S. G. Clarke, Analyst, **1931**, 82). Some metals in use, *e.g.* zinc, reduce the tin itself to the metallic condition, necessitating re-solution, and the tin deposited on the reducing metal may hinder further reduction (Oesterheld and Honegger, *Helv. Chim. Acta*, **1919**, **2**, 398; Analyst, 1919, **44**, 359). Iron, which is very commonly used, has certain disadvantages, pointed out by K. Sandved (Analyst, **1927**, **52**, 2), and is, in addition, very liable to contain disturbing impurities; nickel has been stated to give very incomplete reduction (A. Jilek, *Chem. Listy*, **1923**, **17**, 223, 268, 295).

Hypophosphorous Acid as Reducing Agent.—In the course of an investigation into the reduction of antimony by hypophosphorous acid it was noted that whereas, alone, antimony gave correct figures on titration, in the presence of tin, the results were very much too high, pointing obviously to the partial reduction of the tin. More careful titrations, carried out in an atmosphere of carbon dioxide, however, failed to give the full figure for the tin, 0·05 grm. of tin giving a titration of 5·75 c.c. of $N/10$ iodine, instead of the theoretical 8·42 c.c. Various catalysts were tried, and successful reduction was accomplished by the addition of a trace of mercury to the reducing solution. The peculiar reducing properties of hypophosphorous acid make it unique as an analytical reducing agent; whereas in strongly acid (say, 1:1 conc. HCl) boiling solution it is capable, as has been seen, of reducing tin to the stannous condition, yet, in cold solution of one-fifth of this acid strength, its reducing power is so low that an iodine titration of, say, reduced tin can be carried out in it without any interference from the hypophosphorous acid, beyond a tendency towards slow fading

* Communication from the Research Department, Woolwich.

of the end-point. This being the case, a method was worked out on the following broad lines:

(*a*) The tin was reduced by boiling in a carbon dioxide atmosphere with a solution of sodium hypophosphite in hydrochloric acid (1:1) and a little mercuric chloride.

(*b*) The solution, after cooling, was diluted with 2½ times its volume of cooled boiled-out water containing citric acid, starch and potassium iodide.

(*c*) The resulting mixture was titrated with standard iodine solutions.

The tin solution from start to finish was kept in an atmosphere of carbon dioxide.

APPARATUS.—It should not be necessary at this time to insist on the desirability of conducting titrations of tin entirely in an inert atmosphere; this point has been stressed many times (*e.g.* by A. Boller, Diss. Zurich, 1915; K. Sandved, *loc. cit.*; S. G. Clarke, *loc. cit.*); and if, as is the case, the operation can be carried out as quickly and with very little more trouble than the direct titration in air, it seems obviously preferable to use a method which can be performed at one's leisure, which involves no "personal factor," and which employs the theoretical factor for calculation, rather than one which relies on standardisation against metallic tin as a method of correction for a host of errors, which are necessarily always varying with the conditions. The apparatus used in this work was that which I described in a former paper (ANALYST, 1927, **52**, 570), and, for convenience of reference, the description and figure are repeated here. The apparatus consists of a 750 c.c. Erlenmeyer flask, the mouth of which is closed by a three-holed rubber stopper carrying the following attachments:

(*a*) A leading tube, connected by about 2 feet of rubber tubing with a Kipp's apparatus delivering carbon dioxide, and passing down to within about ½ inch above the liquid in the flask.

(*b*) A small tapped funnel with its stem bent twice, so that the bulb of the funnel clears the burette, which is subsequently inserted in the third hole.

(*c*) A removable glass plug.

The reduction is carried out in the flask, the air being displaced by a stream of carbon dioxide, which passes in through the leading tube and out through the funnel, the tap of which is left open; the glass plug is left in position. When reduction is complete, the tap of the funnel is closed, that of the Kipp's apparatus fully opened, and the flask is cooled under pressure of the carbon dioxide in the Kipp's apparatus. When cool, the glass plug is removed, the tap of the Kipp's apparatus being simultaneously regulated to deliver a steady stream, and any desired reagent admitted through the tapped funnel, care being taken not to admit any air. Finally, a burette with a jet sufficiently long to pass completely through the stopper is inserted in the hole which carried the glass plug, and the titration is carried out. In the process described below the time of reduction (¼ hour)

is so short that it is very improbable that the air would be adequately removed from the apparatus; consequently, the following procedure was adopted:

The stopper is removed from the flask, which is then completely filled with water; the glass plug is removed from the stopper, which is allowed to fall by its own weight into the neck of the flask, and when the water overflows through the empty hole the glass plug is re-inserted. On then pressing the stopper home the water is forced up the leading tube, which it should completely fill; if it does not it is made to do so by gently blowing into the funnel, the tap being open; the tap of the Kipp's apparatus is partly opened to allow a rapid stream of carbon dioxide to pass through the rubber connecting tube, which is then attached to the water-filled leading tube, so that air is completely excluded from the system. The apparatus is next inverted over a sink, the tap of the funnel being left open and the water allowed to run out, its place being taken by carbon dioxide. When all the water has been expelled the tap of the funnel is turned off, and the apparatus is ready for use.

Description of Process.—It must be emphasised that the acid strength of the solution during the reduction must not be much below 1:1 hydrochloric acid. The solution of the tin in about 30 c.c. of dilute (1:1) hydrochloric acid is run into the funnel of the apparatus, 1 c.c. of saturated mercuric chloride solution is added, and the liquid run into the flask by withdrawing the glass plug and opening the tap, care being taken not to let the surface of the liquid fall below the tap. About 5 grms. of sodium hypophosphite are placed in the beaker which contained the tin solution and rinsed into the apparatus with successive quantities of hydrochloric acid (1:1) until the total volume in the flask is about 100 c.c., the last addition being allowed to run through the tap and to within about an inch from the end of the funnel stem; the plug is now re-inserted and the tap opened, when the remaining few drops of acid are blown up into the funnel and a stream of carbon dioxide passes through the apparatus. The flask is next placed on the hot plate and the liquid allowed to boil for 15 minutes; meanwhile, 250 c.c. of water, 20 c.c. of citric acid solution (100 grms. of citric acid dissolved in 200 c.c. of water), 10 c.c. of potassium iodide solution (4 per cent.), and a few c.c. of fresh starch solution are boiled for 10 minutes in a separate flask and then cooled. At the end of the 15 minutes' reduction the tap of the funnel of the apparatus is closed, the flask removed from the plate, and the tap of the Kipp's apparatus fully opened; the flask is now cooled, the place of the contracting vapour being taken by carbon dioxide from the Kipp's apparatus. The tap of the Kipp's apparatus having been partially closed, so that only a steady stream of bubbles will pass, the plug is withdrawn and the boiled-out water, containing citric acid, potassium iodide and starch, is run into the flask, the burette containing standard iodine is inserted into the hole formerly occupied by the plug, and the solution is titrated.

For calculating the amount of tin present the theoretical factor, 1 c.c. of $N/10$ iodine=0·005935 grm. of tin, is used. When $N/100$ iodine solution is employed,

a small blank, found experimentally, and representing the amount of iodine required to colour the starch, is deducted; for the present work the blank was found to be 0·2 c.c.

TEST RESULTS.—The following results were obtained with known amounts of tin in the form of stannic chloride:

Tin taken. Grm.	Titration. c.c.	Tin found. Grm.
0·0500	8·46 of $N/10$	0·0502
0·0400	6·72 ,,	0·0399
0·0300	5·02 ,,	0·0298
0·0200	3·48 ,,	0·0207
0·0100	1·74 ,,	0·0103
0·0050	8·6—0·2=8·4 of $N/100$	0·0050
0·0040	6·8—0·2=6·6 ,,	0·0039
0·0030	5·3—0·2=5·1 ,,	0·0030
0·0020	3·5—0·2=3·3 ,,	0·0020
0·0010	1·9—0·2=1·7 ,,	0·0010
Blank	0·2 ,,	

It was found that iron and copper must be separated and that nitric acid must be absent. These separations offer no great difficulty, and it is hoped shortly to publish a new method of effecting them. With regard to antimony, it was found that by increasing the amount of potassium iodide, accurate titrations of tin could be obtained in presence of a relatively large excess of antimony. The amount of potassium iodide used in the following experiments was 20 c.c. of 4 per cent. solution; larger amounts of antimony would probably require more:

Tin taken. Grm.	Antimony taken. Grm.	Titration. c.c. of $N/100$.	Tin found. Grm.
0·0050	0·0500	8·5—0·2=8·3	0·0049
0·0040	0·0500	7·0—0·2=6·8	0·0040
0·0030	0·0500	5·2—0·2=5·0	0·0030
0·0020	0·0500	3·6—0·2=3·4	0·0020
0·0010	0·0500	1·9—0·2=1·7	0·0010

ANTIMONY.—As might be expected, the reduction of antimonic salts takes place much more readily than that of stannic salts, no mercury catalyst is required, and only five minutes' boiling in an open flask are needed. The antimony, dissolved in 60 to 70 c.c. of hydrochloric acid (1:1), is boiled gently for five minutes, after the addition of 5 grms. of hypophosphite, and is then cooled, after which 20 c.c. of citric acid solution (100 grms. in 200 c.c. of water) and a fragment of litmus paper are added. It is diluted with 100 c.c. of water, made alkaline with ammonia, and then slightly acid with hydrochloric acid, and again completely cooled; sodium bicarbonate is now added in decided excess (the litmus paper should be blue, and further addition of bicarbonate should not cause liberation of any more gas), followed by starch solution, and the liquid titrated with standard iodine solution (addition of potassium iodide is undesirable),

1 c.c. of $N/10$ iodine = 0·00609 grm. of antimony.

Experiments carried out with known amounts of antimony gave the following results:

Antimony added. Grm.	Titration. c.c.	Antimony found. Grm.
0·1000	16·50—0·05=16·45 of $N/10$	0·1002
0·0900	14·80—0·05=14·75 ,,	0·0898
0·0800	13·20—0·05=13·15 ,,	0·0801
0·0700	11·60—0·05=11·55 ,,	0·0703
0·C600	9·95—0·05= 9·90 ,,	0·0603
0·0500	8·20—0·05= 8·15 ,,	0·0496
0·0400	6·60—0·05= 6·55 ,,	0·0399
0·0300	5·00—0·05= 4·95 ,,	0·0301
0·0200	3·30—0·05= 3·25 ,,	0·0198
0·0100	1·70—0·05= 1·65 ,,	0·0100
0·0060	10·15—0·40= 9·75 of $N/100$	0·0059
0·0040	7·00—0·40= 6·60 ,,	0·0040
0·0020	3·60—0·40= 3·20 ,,	0·0019
0·0010	2·00—0·40= 1·60 ,,	0·0010
0·0100	17·00—0·40=16·60 ,,	0·0100
0·0080	13·60—0·40=13·20 ,,	0·0079

As in the case of tin, the blank deducted from titrations was found by experiment.

Trials were made of the titration carried out in the presence of various other metals:

LEAD.—The only alteration made in the process was that **10** c.c. of dilute (1:3) sulphuric acid were added before reduction.

Antimony added. Grm.	Lead added. Grm.	Titration. c.c.	Antimony found. Grm.
0·0020	0·22	3·7 —0·4 = 3·3 of $N/100$	0·0020
0·0040	0·22	7·1 —0·4 = 6·7 ,,	0·0041
0·0200	0·22	3·38—0·05= 3·33 of $N/10$	0·0203
0·0400	0·22	6·66—0·05= 6·61 ,,	0·0403
0·1C00	0·22	16·42—0·05=16·37 ,,	0·0997

TIN, CADMIUM, AND BISMUTH.—The only alteration made was, that after dilution and addition of starch, and prior to the addition of citric acid and neutralisation, $N/10$ iodine was added in amount required to produce a blue colour lasting for a few seconds.* If this blue colour had not completely faded after the lapse of 3 or 4 minutes, the liquid was gently warmed until colourless. The citric acid was then added, followed by neutralisation, and the process finished as usual.

Antimony added. Grm.	Other metal added. Grm.	Titration. c.c.	Antimony found. Grm.
0·0010	0·20 Tin	2·2 —0·4 = 1·8 of $N/100$	0·0011
0·0020	0·20 ,,	3·7 —0·4 = 3·3 ,,	0·0020
0·0040	0·20 ,,	7·0 —0·4 = 6·6 ,,	0·0040
0·0200	0·20 ,,	3·33—0·05= 3·28 of $N/10$	0·0200
0·0400	0·20 ,,	6·66—0·05= 6·61 ,,	0·0403
0·1000	0·20 ,,	16·47—0·05=16·42 ,,	0·1000
0·0020	0·10 Cadmium	3·7 —0·4 = 3·3 of $N/100$	0·0020
0·0040	0·10 ,,	6·9 —0·4 = 6·5 ,,	0·0040
0·0200	0·10 ,,	3·28—0·05= 3·23 of $N/10$	0·0197
0·0400	0·10 ,,	6·56—0·05= 6·51 ,,	0·0396
0·1000	0·10 ,,	16·57—0·05=16·52 ,,	0·1006
0·0020	0·13 Bismuth	3·7 —0·4 = 3·3 of $N/100$	0·0020
0·0040	0·13 ,,	6·9 —0·4 = 6·5 ,,	0·0040
0·0400	0·13 ,,	6·66—0·05= 6·61 of $N/10$	0·0403

*It is desirable always to do this when tin is present as an impurity.

ARSENIC.—In this case the arsenic is precipitated in the form of element by the hypophosphorous acid; the following procedure was adopted:

The reduction was carried out in 30 c.c. of dilute (1:1) hydrochloric acid; the arsenic was filtered off and washed, first with 30 c.c. of dilute (1:1) hydrochloric acid, then once or twice with 5 per cent. ammonium chloride solution. The filtrate was neutralised, after addition of citric acid, as in the usual procedure, and titrated.

Antimony added. Grm.	Arsenic added. Grm.	Titration. c.c.	Antimony found. Grm.
0·0020	0·019	3·65—0·40= 3·25 of $N/100$	0·0020
0·0040	0·019	6·80—0·40= 6·40 ,,	0·0040
0·0200	0·019	3·30—0·05= 3·25 of $N/10$	0·0198
0·0400	0·019	6·60—0·05= 6·55 ,,	0·0399
0·1000	0·019	16·40—0·05=16·35 ,,	0·0996

If, as is usually the case, the antimony, prior to titration, has to be brought into solution from a precipitate containing sulphur (this applies to the antimony precipitated by hydrosulphite as well as to the sulphide, since the liquid used for washing the former contains hydrosulphite, B. S. Evans, ANALYST, 1929, **54**, 396), it is unsafe to effect this by treatment with bromine and hydrochloric acid, owing to the likelihood of formation of sulphur bromide, which causes bad end-points and very high results in the final titration. In such cases the precipitate can be dissolved by treatment of the filter in a beaker with 10 c.c. of 20 per cent. sodium hydroxide solution and 10 c.c. of hydrogen peroxide, warming slightly and stirring thoroughly and then making strongly acid with citric acid; in the presence of some other sulphides a little dilute sulphuric acid may also be required. When the precipitate has completely dissolved, the pulp is filtered off on a small pulp filter and washed with hot water. The filtrate is boiled down to about 30 c.c., an equal volume of hydrochloric acid added, and the solution transferred to a flask and rinsed in with sufficient dilute (1:1) hydrochloric acid to bring the total bulk up to 80 to 90 c.c. The reduction and titration are then carried out as usual, omitting the final addition of citric acid.

The following table shows results obtained from lead-antimony or lead-cadmium-antimony alloys, both by the Györy titration and by the present method, following precipitation of the antimony by hydrosulphite (B. S. Evans, *loc. cit.*):

Bromate* titration. (Antimony.) Per Cent.	Hypophosphite reduction followed by iodine titration. (Antimony.) Per Cent.
2·06, 2·08	2·09
0·54	0·53
0·20	0·20
3·06, 3·08	3·07
6·55	6·57
0·514	0·516
7·10	7·12
7·04	6·90

* S. G. Clarke's modification, to be published shortly.

The advantages of the method here described, as compared with the bromate titration, are three in number:

(*a*) Since *N*/100 iodine can be employed, considerably smaller amounts of antimony can be titrated.

(*b*) Since the reducing agent need not be removed, the boiling necessary to expel sulphur dioxide can be eliminated.

(*c*) Arsenic is automatically precipitated and can be simply filtered off.

With regard to (*c*), work to be published shortly by S. G. Clarke shows that it is practically impossible to eliminate arsenic by boiling down the hydrochloric acid solution, as directed in Rowell's modification of the Györy process, without at the same time losing an appreciable amount of antimony; if the drop adhering to the cover glass during solution of the metal in bromine hydrochloric acid is tested, antimony is always to be found in it. In this respect, therefore, the present method seems to be an advance.

Notes.

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

THE EXTRACTIVES OF WHISKEY.

THE amount of extractives in whiskey is usually a relatively minor matter, though it has acquired official recognition in the *United States Pharmacopoeia, X*, where *Spiritus Frumenti* is required to conform to the following test: that the weight of the residue from 20 c.c. should not exceed 0·10 grm., *i.e.* whiskey should not contain more than 0·50 per cent. (w/v) of total solids.

The matter would not be worth mention here were it not for a curious statement that has become dispersed in well-known literature without receiving contradiction. In *Aids to the Analysis of Food and Drugs*, 4th edition, 1918, it is stated that "the total solids rarely exceed 0·15 per cent." The same statement occurred in the second and third editions of the book. Squire's *Companion to the British Pharmacopoeia*, 19th edition, 1916, says "the amount of extractive matter rarely amounts to more than 100 grains per gallon, equivalent to about 0·15 per cent." It appears possible that both statements were originally derived from a passage that occurred on page 106 of the first edition of Allen's *Commercial Organic Analysis*, 1879, which lays it down that "the residue left on evaporating whiskey to dryness on the water-bath should not exceed 100 grains per gallon, and is usually much less."

Allen's limit for extractives in whiskey cannot be taken as representing results to be obtained to-day. I tabulate below the weight/volume figures for total solids obtained with forty-four samples of whiskey examined since 1926, and it will be seen that in 29, or roughly two-thirds, they exceed 0·15 per cent.

Range per cent. (Grm. per 100 c.c.)	Number of samples.
0·10 to 0·15	15
0·16 to 0·20	13
0·21 to 0·30	9
0·31 to 0·40	3
0·41 to 0·53	4
Total	44

The highest figure, namely 0·53 per cent., was yielded by an adulterated sample containing 60·02 per cent. of proof spirit. It may not be out of place to suggest that on some occasions, perhaps on this, whiskey is adulterated with sherry. As the duty per degree of alcohol in wine averages 2·2d., whilst whiskey pays 8·7d., a safe and profitable adulterant would appear to be to hand in sherry.

High figures for extractives in whiskey are no novelty. A. H. Church, in his book on *Food* in 1882, refers to a case: "A sample of so-called Scotch whiskey . . . was found to be rather impure, so far as fixed matter is concerned. The total residue from one pint amounted to 50 gr., 42 of which were sugar." Fifty grains per pint amounts to 0·57 per cent. w/v.

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THE ADDITION OF AMMONIUM SALTS TO VINEGAR.

SOME years ago certain foreign dealers were selling spurious vinegars, to which ammonium salts had been added in the correct proportion to give the analyst approximately the amount of nitrogen he would expect to find in a vinegar made from malt or from malted and unmalted grain. One of these preparations contained 60 per cent. of acetic acid, and, when diluted with eleven times its volume of water, it yielded a product containing 0·06 per cent. of nitrogen.

There has recently been a revival of this practice, and my attention has been drawn to a so-called malt vinegar which contained 0·05 per cent. of nitrogen, almost entirely derived from ammonium sulphate, presumably added in the expectation that an analyst would be unlikely to trouble about the nature of nitrogen in vinegar.

The following results, which I have obtained at various times, show that the ammoniacal nitrogen in a malt wort is usually less than a tenth of the total nitrogen, and it does not increase during acetification. It is usually rather less than the nitrogen derived from compounds "salted out" by zinc sulphate or

precipitated by bromine, and much less than the nitrogen in the compounds precipitable by phosphotungstic acid:

	Total nitrogen. Per Cent.	Precipitated by zinc sulphate. Per Cent.	Ammoniacal nitrogen. Per Cent.
Malt extract for brewing (sp. gr. 1·330)	0·42	0·098	0·021
Malt extract for brewing (sp.gr. 1·310)	0·79	—	0·032
Wort from barley malt (sp.gr. 1·077) ..	0·14	—	[1] 0·002
Vinegar from wort of sp.gr. 1·052 ..	0·12	0·015	[2] 0·015 } [1] 0·009 }
Medicinal malt extract	0·77	0·19	—
Malt extract for brewing (sp.gr. 1·333)	1·52	0·17	—
Commercial "malt" vinegar ..	0·089	0·008	0·007

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[1] Distilled with barium carbonate, after neutralisation with sodium hydroxide.
[2] Distilled with sodium hydroxide.

A SIMPLE CALCULATION OF THE LIMIT OF VALUE OF THE MICROSCOPICAL EXAMINATION OF MILK FOR TUBERCLE BACILLI.

LET us suppose that 100 c.c. of milk are centrifuged, and that the volume (V) of deposit is roughly measured; that films of the deposit are uniformly spread on cover-glass circles, (D) mm. in diameter, and that, after staining, the number (n) of tubercle bacilli per 100 fields is determined. The number (N) of tubercle bacilli per 100 c.c. of milk will be given by the equation

$$N = \frac{V}{v} \times \frac{D^2}{d^2} \times \frac{n}{100}$$

where v = the volume of deposit spread over the cover-glass circle, and d the diameter of the microscope field.

Of course, it is quite immaterial whether films are made on slides or cover-glass circles, the essential point being the volume of deposit per unit area. I find that v lies between 0·0025 and 0·005 c.c., say, 0·005 c.c., per cover-glass circle 19·05 mm. in diameter, and that with the microscope in use d=0·15 mm. Hence

$$N = \frac{V}{0{\cdot}005} \times \left(\frac{19{\cdot}05}{0{\cdot}15}\right)^2 \times \frac{n}{100}$$
$$= V \times 32{,}000 \times n.$$

V may vary from 0·2 c.c. to 30 c.c.

It is very obvious that unless N is very large, n will be very small, and it is only in cases of very advanced tubercular mastitis that n becomes a whole number. The reciprocal of n is of chief interest; this represents the number of times separate areas, each of 100 fields, must be examined in order to find 1 tubercle bacillus for any given values of N and V. It has been shown that a single tubercle bacillus can be detected biologically in 40 per cent. of trials, and two tubercle bacilli in 67 per cent. of trials.* One may reasonably assume, therefore, that 5 tubercle bacilli will be detected by the biological test.

* *The Prevention of Human Tuberculosis of Bovine Origin.* W. G. Savage, p. 131.

Taking an extreme example, and supposing that only 5 tubercle bacilli are present in 100 c.c. of milk, and taking a very moderate value for V = 0·5 c.c.

$$5 = 0{\cdot}5 \times 32{,}000 \times n = 16{,}000 \times n, \text{ or } \frac{1}{n} = 3{,}200.$$

The average time taken by three individual workers in this laboratory to view 100 fields is $2\frac{1}{4}$ minutes; on the average, therefore, one would have to spend $2\frac{1}{4} \times 3{,}200$ minutes, or 120 hours, in finding one tubercle bacillus, and an equal length of time in confirming the result; or, taking a less extreme case, and supposing 50 tubercle bacilli to be present in 100 c.c., one would have to search (on the average) for 12 hours. If we set a limit to our time of search and make this limit 36 minutes, all that we can claim, if we fail to find tubercle bacilli, is that (probably) less than 1000 are present per 100 c.c. of milk, provided V=0·5 c.c.; but if the milk has an abnormal cellular content, it will give a larger deposit, and the test will be proportionately less delicate. In an extreme case of milk, ropy with pus and giving a deposit of 25 c.c., one would only be able to say that less than 50,000 tubercle bacilli were present per 100 c.c. or 500 per c.c.

Without concentration, therefore (and none of the concentration methods hitherto proposed are really successful) the microscopical examination of milk for tubercle bacilli is limited to the detection of from 10 to 500 bacilli per c.c., or, excluding those cases with bulky deposits which are not characteristic of tubercular mastitis but of tubercular mastitis complicated by streptococcal mastitis, and confining our consideration to milk giving a deposit of not more than 2·5 c.c. per 100 c.c., the examination is limited to the detection of not less than 10 to 50 bacilli per c.c., and is about 500 times less sensitive than the biological method.

SOMERSET COUNTY LABORATORY. D. R. WOOD.

THE FREEZING-POINT METHOD FOR THE EXAMINATION OF COCOA BUTTER.

OWING to a misunderstanding, I omitted to mention in my paper on the Classification of Chocolate Fats (ANALYST, 1930, **55**, 477), that the standard solidification test there described was devised by Mr. H. R. Jensen, and that part of the experimental work cited in the paper was done while I was working in his laboratory.

A. G. AVENT.

Official Appointments.

THE Minister of Health has confirmed the following appointments:

ERIC VOELCKER, A.R.C.S., F.I.C., as Public Analyst for the County of Northampton (January 28, 1931).

J. A. VOELCKER, C.I.E., Ph.D., F.I.C., as Additional Public Analyst for the County of Northampton (January 28, 1931).

The Minister of Agriculture and Fisheries has confirmed the following appointments:

F. E. BULLOCK, F.I.C., as Agricultural Analyst for the County Borough of Leicester (February 6, 1931).

J. A. Voelcker, C.I.E., Ph.D., F.I.C., as Official Agricultural Analyst for the County of Northampton (February 4, 1931).

Eric Voelcker, A.R.C.S., F.I.C., as Deputy Agricultural Analyst for the County of Northampton (February 4, 1931); and as Deputy Agricultural Analyst for the County of Northumberland (February 18, 1931).

Legal Notes.

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

REFINED BORAX.

On January 10th, a co-operative society was summoned at Leicester for selling borax not of the nature, substance and quality demanded.

On analysis the sample was found to contain 60 parts of arsenic per million, whereas purified borax, according to the British Pharmacopoeia, should not contain more than 5 parts per million.

For the defence it was urged that purified borax is a medicinal preparation, but that refined borax is a commercial article used for domestic purposes. On the side of the packet were the words: "Finest Refined Borax," and there was also a notice that it was not to be taken internally, but only to be used for domestic purposes.

Evidence was given that to get a poisonous dose it would be necessary to take 5 lbs. of the borax.

The Magistrates dismissed the case.

EXCESS OF SULPHUR DIOXIDE IN CANDIED PEEL.

On January 14, a Sheffield wholesale firm was summoned at Cardiff for selling candied peel containing sulphur dioxide to the amount of 40 parts per million in excess of that permitted by the Public Health Regulations, 1927.

The solicitor, for the defence, submitted that the summons was wrongly worded, the defendants being charged with selling candied peel, whereas only lemon peel was supplied; but the Stipendiary held that the Regulation applied to any of the three peels—lemon, orange or citron.

The General Manager of the defendant firm stated that a different process was used with orange and citron than with lemon peel. As lemon peel would not stand the same heat as the other two peels, it was necessary to add additional glucose and sugar to it, and each of these ingredients contained sulphur dioxide.

The Stipendiary imposed a fine of 40s. and costs.

New Zealand.

SIXTY-THIRD ANNUAL REPORT OF THE DOMINION ANALYST.

THE Dominion Analyst (Mr. W. Donovan), in his Report for 1929, states that 5462 samples were examined in the Dominion Laboratory for the different Government Departments. Of the 3788 samples examined for the Health Department, 2789 were milks. In the Christchurch Branch Laboratory, 1288 samples of milk were analysed. Of these, 1003 were for the Metropolitan area; and as there are 600 milk dealers, the sampling control is regarded as quite inadequate. The sampling at the Dunedin Branch (735 milks) was also very inadequate.

MINERAL CONTAMINATION OF AERATED WATERS.—Of the 153 samples of soda water examined at Wellington, lead was present in at least 51 samples, copper (traces) in 2, and iron in 9. It was noticed that soda waters from Hastings and Lower Hutt, where the waters are hard, were practically free from lead. Many of the soda waters were discoloured by material extracted from the corks.

NEW ZEALAND WHALE OILS.—The following results were obtained in the analysis of three samples from Whekeniu, Picton:

Acid value	12·7	5·3	14·8
Saponification value ..	191·7	191·6	190·0
Iodine value	134·8	139·0	140·5
Refractive index at 40° C. ..	1·4655	1·4660	1·4662
Refractive index at 60° C. ..	1·4575	1·4585	1·4588
Specific gravity at 15°/15° C.	0·923	0·925	0·923

These oils differed from Antarctic whale oils in throwing down hardly any stearine when chilled.

Trinidad and Tobago.

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1929.

IN his Annual Report to the Legislative Council, the Government Analyst (Mr. H. S. Shrewsbury) states that 2760 samples were examined, including 935 milks, 862 aerated waters, 186 spirit compounds, 141 oils, and 88 butters. The percentage of adulterated food and drugs samples, which was 65·3 in 1891, and 32·5 in 1900, was 5·7, as compared with 5·8 in 1928.

CORROSION OF WATER PIPES.—In connection with the Island water scheme, 10 samples of earth from the route of the proposed pipe line were examined for corrosive properties, and, with the exception of those connected with the corrosion of existing pipe lines at Prince's Town, were found to be satisfactory. Samples of cast iron pipes at Prince's Town and soil in which they were embedded, were submitted by the Public Works Department. The pipes were very badly pitted, the holes having remarkably clearly defined edges. It appeared that the piping had been corroded by contact with moist fragments of selenite or gypsum in the soil.

TOXICOLOGICAL.—In 52 samples (compared with 24 in 1928) of post-mortem remains and stomach washings, five poisons were discovered, namely, cresylic disinfectant, aconite, arsenic, luminal and strychnine. This was the first case of luminal poisoning in the Colony.

POISONING OF COCONUT TREES.—In this unusual case, samples of coconut trees which had died in suspicious circumstances, were submitted for analysis. Holes had been bored into the trunks, and evidently a solution of sodium arsenite had been poured into these, as the wood surrounding the holes contained 1 per cent. of sodium arsenite.

LIME SKINS AS CATTLE FOOD.—A sample of lime skins (after extraction of oil and juice) was submitted for analysis to determine their suitability as cattle food. Analysis showed this might be a suitable cattle food, but feeding experiments are advisable.

HYDNOCARPUS OIL.—Twelve samples of hydnocarpus oil were submitted by the Surgeon-General. This oil is used in the treatment of leprosy at Chacachacare. These particular samples caused intense local pain on injection. After a lengthy investigation it was found that these samples contained three impurities, any one of which might have caused the trouble.

United States Department of Agriculture.

REVISED AND AMENDED DEFINITIONS AND STANDARDS FOR FOOD PRODUCTS.*

CORN SUGAR.

The definitions for food products in S.R.A., F.D. No. 2, and supplements thereto, were adopted prior to the departmental announcement of December 26, 1930, which reads as follows:

"Corn sugar (dextrose) when sold in packages must be labelled as such; when sold in bulk must be declared as such; but the use of pure refined corn sugar as an ingredient in the packing, preparation, or processing of any article of food in which sugar is a recognised element need not be declared upon the label of any such product.

"Nothing in this ruling shall be construed to permit the adulteration or imitation of any natural product, such as honey, by the addition of any sugar or other ingredient whatever."

The term "sugar," with or without the parenthetical expression "sucrose," as used in the definitions to designate the sweetening agent in manufactured food products, is to be interpreted, wherever necessary to effect the purpose of the foregoing decision, as including dextrose (pure, refined corn sugar).

* Food and Drug Administration. Service and Regulatory Announcements. Food and Drug, No. 2 (First Revision). Supplement No. 3. (Dec. 31st, 1930.)

Erratum: *Notes on the Thiocyanate Method of Estimating Iron*, by G. W. Leeper (ANALYST, 1930, **55**, 371): *For* "iron content," 6 lines from the end, *read* "phosphorus content."

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Indications of Glucose in Milk. C. H. Whitnah. (*J. Amer. Chem. Soc.*, 1931, **53**, 300–304.)—The optical rotation of milk is not, as a rule, altered by treatment with yeast, but the extra rotation imparted to milk by addition of 0·5 per cent. of glucose is completely removed by leaving 50 c.c. of the milk in contact with 3 grms. of yeast for an hour at 30° C. The yeast is prepared from bakers' yeast by washing and centrifuging five times, the final washing water being clear and free from reducing sugars. Fermentation of 275 samples of milk in this way, without added glucose, showed that the resulting decrease in rotation varied from zero in 20 cases to a value corresponding with 0·35 per cent. of glucose in the milk. No explanation is advanced for increases in rotation amounting to 0·01 to 0·07 per cent. observed with 11 other samples. The apparent presence of glucose seems to be independent of any other characteristics of the milk. T. H. P.

Retained Milk. O. Laxa. (*Ann. Falsificat.*, 1930, **23**, 609–610.)—Twelve cows in the month of August travelled by rail for 3 days, and were not milked till they arrived at the farm, and four of these then only yielded about 100 c.c. of milk. This milk resembled colostrum, and was white with a brown tint, and had a smell of burnt milk, attributed to the decomposition of the milk sugar. The milk contained water, 78·4; fat, 10·15; casein, 2·65; albumin and globulin, 0·0; albumoses and peptones, 2·92; amino acids, 1·78; milk sugar, 1·50; ash, 1·10; and undetermined substances, 1·50 per cent. D. G. H.

Determination of Starch in Cereal Products. C. W. Herd and D. W. Kent-Jones. (*J. Soc. Chem. Ind.*, 1931, **50**, 15–22T.)—The difficulties encountered in the application of the various hydrolytic methods proposed for the determination of starch in cereals are due mainly to the following causes: Acid acts on matter other than starch; prepared diastases vary in hydrolytic power and exert unknown action on the different components of the starch; malt diastase exhibits varying hydrolytic action on the hemicelluloses; and with barley diastase, in addition, it must be assumed that the amylose-maltose value for other starches is the same as for potato starch. A number of the best-known methods have been investigated, with results which suggest the following remarks:

Scheele and Svensson's method (*Tekn. Tidskr.*, see *Milling*, 1928, 518): The meaning of "diastase absolute" is not clear, but the use of 0·1 grm. of a good prepared diastase with 3 grms. of substance gave very low results, and even 0·5 grm. of the diastase gave lower results than other methods. The method is hence complicated by the necessity for determining the conditions for complete hydrolysis with each batch of enzyme. *Hartmann and Hillig's method* (ANALYST,

1927, **52**, 160): A satisfactory method could probably be based on preliminary treatment for 12 hours with pepsin and subsequent hydrolysis with prepared diastase, but the necessity of modifying the procedure for different deliveries and the lack of knowledge of the effects on the "hemicelluloses" render the method unsuitable for general use, and render it difficult for analysts to check the work of others.

Ling's Malt Extract Method (ANALYST, 1923, **48**, 29, 554).—This requires modification to facilitate the filtration and washing of the insoluble matter from the conversion liquid, and, with flours, 2 (not 5) grms. should be taken; the accuracy attained is only about ±1 per cent., but within this limit the method works well with wheats and flours.

Ling, Nanji and Harper's Barley Diastase Method (*J. Inst. Brew.*, 1924, **30**, 838).—Here the accuracy is within ±0·5 per cent., and the method seems satisfactory for wheats and flours, but takes longer; if the amylose-maltose figure for potato starch is accurate and is applicable to other starches and cereal products, the method appears sound and reliable.

The most important of the non-hydrolytic methods is that of Rask (ANALYST, 1927, **52**, 290), which presents various practical difficulties. These are overcome, even with sharps and bran, by the following procedure: One grm. of the material and 1 grm. of acid-washed sand are mixed in a centrifuge tube, stirred for about one minute with washed ether, and centrifuged, the liquid being then poured off. After two repetitions of this washing, the residue is mixed with 2·5 c.c. of water and 0·25 c.c. of *N* sodium hydroxide. After about 15 minutes, 5 c.c. of pure methyl alcohol are mixed in and then 5 c.c. of dilute methyl alcohol (5 alcohol: 2·5 water). The mixture is centrifuged, the layer of alcohol removed, and the residue washed twice with 10 c.c. of the dilute methyl alcohol, and finally three times with water. The mass is next stirred to a thick paste with a few c.c. of water, all lumps being broken down. A total of 20 c.c. of water is added to effect transference to a 100 c.c. flask, 20 c.c. of concentrated hydrochloric acid being then added and the volume made up with Rask's acid (21 grms. of HCl per 100 c.c.). The latter is used to rinse the centrifuge tube. The contents of the flask are filtered with the aid of suction through a Gooch crucible, charged with asbestos and with a layer of acid-washed sand, the filtrate being collected in a small dry flask. Of the filtrate, 50 c.c. are transferred by a calibrated pipette to a 200 c.c. beaker containing 110–115 c.c. of 96 per cent. alcohol, this step being completed within 35 minutes of the initial contact of the acid with the starch, so that appreciable hydrolysis of the starch may be avoided. Immediately after the 50 c.c. pipette has drained completely, but not until then, the mixture is stirred continuously for about 1 minute, or until the precipitate has become flocculent. When the precipitate has partly settled, the whole is centrifuged for 10 minutes, the liquid being then removed and the residue washed three or four times with 70 per cent. (vol.) alcohol and twice with 96 per cent. alcohol, the starch being thoroughly mixed with the alcohol before centrifuging. The final residue is transferred to a tared Gooch crucible with 96

per cent. alcohol and washed with ether, the crucible being placed for 10–15 minutes in an oven at about 40° C., and then dried at 130° C. to constant weight. With sharps and bran, 2–4 grms. must be used, the quantities of the methyl alcohol and sodium hydroxide mixture being increased in proportion. Volume allowances may be made when using wheat, bran or sharps, or, alternatively, the crude fibre may be retained on a small pad of glass wool before making the volume up to 100 c.c.

The malt diastase, barley diastase, and modified Rask methods have been applied to: (1) *Commercial starches*: Malt diastase gives slightly higher results than barley diastase, but the Rask method gives the highest starch percentages, these, when added to those for moisture and other components, giving 98·85 and 99·60 for the two starches examined. (2) *Flours :* The malt and barley diastase results differ but little, and are appreciably higher than the Rask results; it is found that the residue of the flour not dispersed by hydrochloric acid contains substances giving reducing sugars on treatment with diastase. (3) *Wheat Offals :*—The malt and barley diastase methods give fairly concordant figures, but the Rask results are low in all cases, indicating that diastase hydrolyses substances which are not strictly starch. This is supported by the observation that fibre separated by the method recommended by the Board of Agriculture and Fisheries (Fertilisers and Feeding Stuffs Regulations, 1928), and hence free from starch, gave about 7 per cent. of reducing sugars, calculated as maltose, when treated with barley diastase. (4) *Whole wheats :*—In all cases malt diastase gives rather higher results than barley diastase, the Rask results being parallel to neither of the other two.

From these results, the authors conclude that, for cereal chemists, the modified Rask method described above is the most generally useful. T. H. P.

Detection of Sorbitol in the Analysis of Jams. C. F. Muttelet. (*Ann. Falsificat.*, 1930, **23**, 602–605.)—Twenty grms. of fruit juice or 75 grms. of jam are dissolved in 4 to 5 parts of warm water, and a little charcoal added, and after 5 minutes' boiling the solution is filtered. The colourless filtrate is sterilised for 15 to 20 minutes at 115–120° C., and, after addition of bakers' yeast, is kept at 25–30° C. for a few days until fermentation is as complete as possible. A pinch of charcoal is added, the liquid filtered, and the filtrate concentrated *in vacuo* to a few c.c., and 1 to 2 c.c. of 50 per cent. sulphuric acid and 4 to 5 drops of freshly distilled benzaldehyde added. The corked flask is shaken for 10 to 15 minutes, and, after 12 hours' contact, a precipitate is formed corresponding to the amount of sorbitol present. To facilitate filtration, 100 c.c. of cold water are added, little by little, and after a few hours the precipitate is washed with warm water and a little alcohol, dried *in vacuo*, and weighed. The weight is about twice that of the sorbitol present. If desired, further purification may then be carried out. The use that may be made of the test may be judged from the following figures: Cherry juice contained 0·29 grm. per cent. of sorbitol, but none was present in red gooseberry or strawberry juice. The proportion found in home-made gooseberry jelly was nil, in cherry jam 0·125 per cent., and in strawberry jam, nil: but commercial

gooseberry jelly "pure fruit" contained 0·135 grm.; cherry jam "fantaisie," 0·025 grm.; and strawberry jam "pure sugar and fruit," 0·075 grm. per cent. The commercial gooseberry jelly was, in fact, gooseberry and apple (confirmed by the detection of malic acid); the cherry jam consisted of portions of cherry in sugar jellified with industrial pectin, and the strawberry jam contained strawberries in a syrup made of apple juice. D. G. H.

Notes on the Histology of the Almond. V. A. Pease. (*J. Agric. Res.*, 1930, **41**, 789–800.)—Four varieties of Californian almonds and one variety each from Etna, Marcona, Valencia, and Alicante were comparatively examined from a histological point of view, and the differences found indicate the possibility of developing an easily workable method for distinguishing the soft shelled Californian and hard-shelled European almonds when in the shelled condition. The cells of the outer epidermis of the testa or surface of the seed coat differ, in that those of the soft-shelled almonds are only slightly lignified compared to the others, and are to be regarded as poorly developed stone cells. Further, the stone cells of hard-shelled varieties are more elongated, the ratio of length to width being 2 to 1 against 5 to 4 in the soft-shelled almonds. D. G. H.

Nature of the Highly Unsaturated Fatty Acids Stored in the Lard from Pigs Fed on Menhaden Oil. J. B. Brown. (*J. Biol. Chem.*, 1931, **90**, 133–139.)—Reports by Brown and Deck (*J. Amer. Chem. Soc.*, 1930, **52**, 1135) and Brown (*J. Biol. Chem.*, 1928, **80**, 455) have shown that when fish oil was given to white rats, equilibrium between the diet and the deposited fat resulted in from 4 to 6 weeks, and that with a series of diets containing from 5 to 30 per cent. of menhaden oil the amount of highly unsaturated acids in the deposited fat was roughly proportional to their content in the diet. Relatively more of these acids, however, were found in the fat from animals on the diets of lower oil content. Analysis of the polybromides of the fatty acids from the body fats resulted in each case in higher bromine content than the bromides from the original fish oil acids, suggesting that the deposited acids were more unsaturated than those from the original oil. It was decided to feed a larger species of animals on a fish oil diet, with the hope of being able to isolate enough of the deposited unsaturated acids to study their properties and ascertain whether they had undergone change during assimilation. Pigs were chosen as experimental animals because they will readily eat food containing large amounts of the oil, and, further, the yield of lard is sufficient for the preparation of the highly unsaturated acids. The pigs fed on fish oil were decidedly more nervous during killing than the controls, and their carcases were yellowish in colour. The fishy odour was scarcely noticeable in the fresh carcase, but, on cooking, it had penetrated to all parts; even the innermost parts of the tongues were highly flavoured. When the pigs were given a diet containing about 14 per cent. of menhaden oil, the lipids and fatty acids of the livers were decidedly more unsaturated than those of the controls, indicating a mobilisation of highly unsaturated acids. Under these dietary conditions there was a storage of 2·7 per cent. of highly unsaturated acids in the lard. The highly

unsaturated fatty acids deposited were of about the same molecular weight and of lower iodine value than the mixture of acids isolated in a similar manner from the original mehaden oil, and, therefore, were less unsaturated. The explanation is given that the pig burns the more highly unsaturated acids from the oil, and deposits the remainder. With rats, the deposited acids were more unsaturated than those from the oil. The author believes that the metabolisms of the pig and the rat are sufficiently different to explain the apparent contradiction of results.

P. H. P.

Oxidation of Officinal Castor Oil by Potassium Permanganate. Study of Triazelain. G. Schuster. (*J. Pharm. Chim.*, 1931, **123**, 5–12.)—Castor oil, having a saponification value of 183 and an iodine value of 83, was oxidised with permanganate in acetone solution by the method of Hilditch (*J. Chem. Soc.*, **1927**, 3106; *cf.* ANALYST, 1929, **54**, 75), and 63·58 per cent. of crude triazelain was obtained, but neither stearic nor dihydroxystearic acids were found on saponification of this product; and when 3 per cent. of stearic acid was added to the castor oil the same amount was recovered after oxidation. It is concluded that no glycerides of saturated acids were present in the castor oil. Triazelain was synthesised by heating acid sodium azelaite and glycerin epichlorhydrin in a closed tube at 135–140° C. for 10 hours, after which the mass is taken up with hot water, the excess of epichlorhydrin removed, and the triazelain precipitated with hydrochloric acid. Triazelain is a dark yellow, oily, fluorescent liquid, insoluble in water, petroleum spirit or benzene, but very soluble in ether, strong alcohol and alkalis. It should be stored *in vacuo*. It readily saponifies, and is hydrolysed by 0·1 *N* hydrochloric acid. The sodium salt forms fine needle-shaped crystals. A colourless precipitate is formed with silver nitrate and a neutral solution of sodium triazelain, and with barium chloride, bismuth nitrate, cadmium sulphate and strontium nitrate, buff precipitates are formed. With magnesium chloride a buff precipitate of the triazelainate is formed, whilst the magnesium salt of azelaic acid under the same conditions is soluble. This allows of purification of triazelain by precipitating it as its magnesium salt.

D. G. H.

Some Oleaginous Forest Seeds of Angola. C. de M. Geraldes, A. d'Almeida and C. Duarte. (*Bull. Mat. Grasses*, 1930, **14**, 332–342.)—The seeds examined were obtained from North West Angola, and in every instance the oils were extracted with ether. *Allanblackia floribunda.*—It is considered that a variety particularly rich in oil might be developed by selection. The seeds are of a darker reddish brown than those of *Allanblackia sacleuxii*, and both trees attain a height of some 25 metres. The fat from the former species is the more important as a source of stearine. *Irvingia robur* has fruits consisting of 53·4 per cent. of epicarp and mesocarp and 46·6 per cent. of stone, and the stone is made up of 93·25 per cent. of endocarp and 6·75 per cent. of seed, which contains 7·2 per cent. of moisture, and 64·85 per cent. of fat. The seeds are not, therefore, of economical importance. *Balanites mayumbens* is a new type of *Balanites*, and has a larger proportion of seed to endocarp (48·2 to 51·8 per cent.) than other species, and its

seeds are larger—an important point, in view of the difficulty of decorticating. The oil has the same general characteristics as the oils of other species of *Balanites*. The oil of *Strimbosia Scheffleri* is of a reddish yellow brown colour and of a disagreeable taste and smell, although this may be due to the high acidity of the examples examined. The oil is consumed in small quantity by the natives, but in larger proportions it produces vomiting. The seeds of *Mimusops Ebolowensis* yield kernels with 4·75 per cent. of fat, but a very hard thick episperm is present, and the seeds are economically unimportant.

	Allanblackia floribunda, sacleuxii Nua.		*Balanites mayumbens.*	*Strimbosia Scheffleri.*
Common Name.	Lalanjo.	M'bunze.	Buzupundi.	M'senha.
Seed.				
Shell, per cent. ..	14·82	15·57	9·37	37·6
Kernel	85·18	84·43	90·63	62·4
Kernel.				
Moisture, per cent. ..	4·11	2·98	10·10	13·70
Fat, per cent. ..	68·53	72·09	39·06	15·58
Fat.				
M.pt., °C.	40·7	41·8–42·8		
Solidification point, °C.	39·5–40·5	41·0–42·0		
Sp.gr. at 15° C. ..	0·9187	0·9194	0·9171	0·9353
$n_D^{50°}$	1·4529	1·4551	1·4602	1·4716 (25°)
Saponification value ..	195·0	207·85	204·61	216·2
Iodine value ..	33·3	29·5	101·0	83·6
Acid value	7·5	35·3	71·12	39·1
M.pt. of fatty acids, °C.	—	61–63	—	—

D. G. H.

Evaluation of Pyrethrum Flowers. J. T. Martin and F. Tattersfield. (*J. Agric. Sci.*, 1931, **21**, 115–135.)—For pyrethrum flowers rich in pyrethrins the method of determination given by Tattersfield and Hobson (ANALYST, 1929, **54**, 351) yields low results, and is now modified in various ways. With samples containing below 0·7, 0·7–1·5, and above 1·5 per cent. of total pyrethrins, 10, 5, and 2·5 grms. are taken for analysis. These are extracted with petroleum spirit, and, after the bulk of the solvent has been evaporated in a current of carbon dioxide and the rest in a vacuum desiccator, the residue is extracted with four quantities of 2·5 c.c. each of gently warmed purified methyl alcohol, each of which is cooled and filtered through cotton wool into a 100 c.c. Kjeldahl flask. After a final washing with 2·5 c.c. of cold methyl alcohol, a few drops of methyl alcoholic phenolphthalein are added, and then, dropwise, *N* methyl alcoholic potassium hydroxide, until the liquid is just alkaline. An excess of 5 c.c. of the alkali is then added and the mixture heated in a reflux apparatus for 8 hours, the methyl alcohol being expelled in a partial vacuum at a temperature not exceeding 25° C., and the residue dissolved in water. The volatile acid is next distilled off in steam, the

volume in the distillation flask being kept below 30 c.c. Two lots of 50 c.c. are distilled off, and the acids in the first of these extracted with two 50 c.c. quantities of petroleum spirit, each extract being washed with 20 c.c. of water. The two extracts are combined, evaporated with 20 c.c. of water on a water-bath, and the residue titrated while warm with 0·02 *N* sodium hydroxide, the sides of the flask being washed down with a little neutral methyl alcohol towards the end of the titration; 1 c.c. of 0·02 *N* alkali represents 3·36 mgrms. of monocarboxylic acid or 6·6 mgrms. of pyrethrin I. The second 50 c.c. of distillate may be extracted with petroleum spirit, but should not show more than a trace of titratable acid. The hot aqueous residue in the distillation flask is treated with 0·2 grm. of calcium sulphate and filtered the next day through cotton wool, washed three or four times with water and extracted exhaustively with sodium-treated ether in the apparatus previously described (*loc. cit.*). In a rapid extractor 20 hours appears to be the minimum time necessary for complete extraction of the dicarboxylic acid with samples of high pyrethrin content. After addition of 20 c.c. of water the ether is evaporated and the aqueous layer heated to boiling, cooled and filtered through cotton wool, the filtrate being heated to boiling and titrated with 0·02 *N* sodium hydroxide; 1 c.c. of the alkali corresponds with 1·98 mgrm. of dicarboxylic acid or 3·74 mgrms. of pyrethrin II. The method requires considerable care, the determination of pyrethrin II being attended with various technical difficulties.

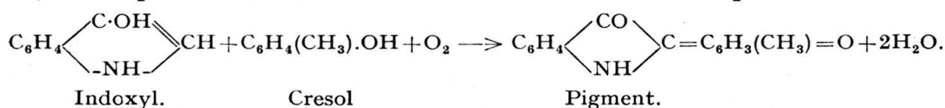
A short method for determining the total pyrethrins is given, two procedures being described, the first for use with 0·5 grm. of the powdered material, and the second with a single flower head (about 0·1 grm.). This method, which gives results in general concordance with both the acid method and the Gnadinger and Corl method (ANALYST, 1929, **54**, 754), depends on partial reduction of standard alkaline potassium ferricyanide solution by means of the ketone group of the pyrethrolone fraction of the pyrethrin molecule. The ferricyanide present before and after the reaction is determined by liberating its iodine equivalent and titrating with thiosulphate. Graphs are given showing the relationship between the amount of ferricyanide reduced, expressed as c.c. of 0·005 *N* thiosulphate, and the number of mgrms. of pyrethrins I and II in an aliquot portion of the final pyrethrin extract.

Good agreement is obtained between the analytical data and the results of insecticidal tests on *Aphis rumicis* T. H. P.

Biochemical.

Geographical Location and Iodine Content of the Thyroid Gland. F. Fenger, R. H. Andrew and J. J. Vollersten. (*J. Amer. Chem. Soc.*, 1931, **53**, 237–239.)—The yearly average iodine content for hog glands from North Dakota (latitude 47° N., winters severe) is 0·32 per cent., whereas that for glands from Texas (33° N., winters mild) is 0·60 per cent., calculated on the desiccated fat-free basis. The seasonal variation is the more pronounced in the former case. These differences are attributed to geographical differences. T. H. P.

The Urocarmine Reaction. W. R. Fearon and A. C. Thompson. (*Biochem. J.*, **1930, 24,** 1371–1378.)—A specimen from some miscellaneous urines was found, on treatment with concentrated hydrochloric acid and an oxidising agent, such as hydrogen peroxide or potassium chlorate, to give a carmine colour, which investigation showed arose from a condensation between indoxyl and *o*- or *m*-cresol present in the urine, in accordance with the equation:



Further investigation with various phenols of biological interest suggested that the condensation takes place between the indoxyl and the phenol in the unsubstituted *p*-position of the latter to form the leuco-base; the pigment was not obtained with any of the *p*-substituted phenol compounds examined. In order to distinguish them, therefore from other red urinary pigments, such as indirubin, urorosein and the scatole-reds, the term *urocarmine* has been applied to the class of indogenide pigments obtained from the condensation of indoxyl with various phenols unsubstituted in the *para*-position. The reaction might be of use in determining the presence or absence of *p*-substitution.

Method of demonstration of the urocarmine test.—This is a modification of the indigo-blue test made under conditions less favourable for the production of the blue dye; 2 c.c. of urine are treated with two drops of 0·1 per cent. potassium chlorate solution or of 3 per cent. hydrogen peroxide, and then 10 c.c. of colourless concentrated hydrochloric acid are added. The mixture is well shaken, left to stand for a few minutes, and extracted first with chloroform and then with amyl alcohol. Under these conditions most normal urines give a variable indigo-blue reaction, the pigment dissolving in the chloroform, but some specimens will be found to display a reddish colour not removed by extraction with chloroform, but very soluble in amyl alcohol. On the addition of resorcinol or *o*-cresol, followed by acidification, most, if not all, normal urines give a urocarmine reaction, and this may be made the basis of a simple colorimetric method for the determination of indoxyl. The preparation and isolation of *o*-cresol urocarmine are described. The urocarmine reaction accounts for many of the pigments obtained from urine which are insoluble in chloroform. The classification of the urorubine reactions of urine can now be simplified.

Classification of the red indogenide pigments.

(A) Pigments soluble in chloroform.
  Indirubine or indigo-red.

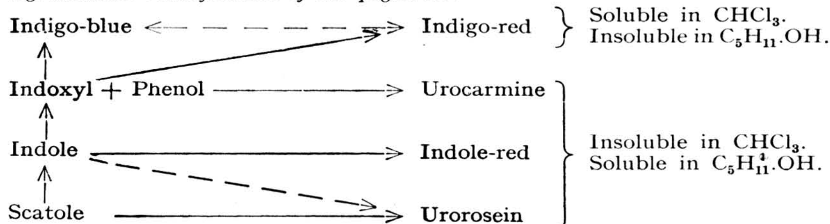
(B) Pigments insoluble in chloroform.
  1. *Urocarmines.* Simple condensation products of indoxyl and urinary phenols unsubstituted in the *para*-position. Both chromogen and pigment are soluble in amyl alcohol. Chromogen precursors can be resolved by steam distillation into volatile and non-volatile components.
    (*a*) *Phenol indogenide.*
    (*b*) *Cresol indogenides.*

  The list might be extended to include the indogenides of the rarer urinary phenols, catechol and resorcinol, which are not volatile in steam.

2. *Indole reds*. Produced by the autoxidation of indole. Only likely to be formed when indole occurs free in urine, a condition so rare as to be improbable.
   (*a*) *Indole red* [Oddo (*Gazz. Chim. Ital.*, 1916, **46**, 323); Baudisch and Hoschek (*Ber.*, 1916, **49**, 2579)].
   (*b*) *Urorubin* [Weiss (*Klin. Wochenschr.*, 1930, **9**, 248)].
3. *Scatole-reds*, or *uroroseins*. [Porcher and Hervieux (*J. Phys. Path. Gen.*, 1908, **7**, 815)]. Derived directly or indirectly from the biochemical oxidation of scatole or of tryptophan. Sometimes included among the indole-reds. Chromogen precursors cannot be resolved by steam distillation.
   (*a*) *Indolepropionic acid* [Stokvis (*Jahrb. Thierchem.*, 1901, **31**, 444)].
   (*b*) *Indoleacetic acid*. Believed by Herter (*J. Biol. Chem.*, 1908, **4**, 253) to be the chromogen of the original urorosein of Nencki and Sieber (*J. prakt. Chem.*, 1882, **26**, 333).
   (*c*) *Indolealdehyde*. Believed by Ellinger and Flamand (*Z. physiol. Chem.*, 1909, **62**, 276) to be the chief chromogen of the scatole-reds.
   (*d*) *Indolecarboxylic acid*. [Maillard (*Dictionnaire de Physiologie*, 1913, Richet, Paris).]

In alcoholic solution the scatole-reds show well-defined absorption spectra.

Diagrammatic classification of the pigments.



Solutions of indole do not give a urocarmine reaction with the appropriate phenols unless the mixture is strongly oxidised (*e.g.* with potassium chlorate), when colours are obtained identical with the corresponding indoxyl colours; this is probably due to the oxidation of indole to indoxyl. Hence, with the use of 3 per cent. hydrogen peroxide and 1 per cent. potassium chlorate as oxidising agents in the cold, it is possible to distinguish between indole and indoxyl, since the former only gives the urocarmine reaction with the chlorate, whereas the latter gives a urocarmine with both oxidising agents. When positive, the urocarmine reaction in urine indicates the presence in the urine of indoxyl and phenols unsubstituted in the *para*-position, and hence constitutes a test for phenoluria. P. H. P.

Fastness of Dyes to Perspiration. C. C. N. Vass. (*J. Soc. Dyers and Col.*, 1931, **47**, 9–10.)—Reports of the investigation initiated in June, 1928, by the Fastness to Perspiration Sub-Committee of the Fastness Committee of the Society of Dyers and Colourists, under the direction of Prof. B. A. McSwiney, have been published in the *J. Soc. Dyers and Col.*, 1929, **45**, 217; 1930, **46**, 190. Perspiration was collected from a wide range of normal, coloured, obese, and rheumatic male and female subjects, and, with one exception, freshly shed samples were acid, becoming alkaline on standing. The urea nitrogen was always greater than the ammonia nitrogen, but diminished on standing with total disintegration of the urea, and the salt concentration varied from 2·65 grms. per 1000 c.c. to 5·01 grms.

for normal male subjects. The average concentrations of the constituents deduced for each type, which were all very similar, conformed very closely to those of individual analyses. In every case the reducing power of freshly-shed normal female perspiration was greater than that of male, particularly so in the case of stout females. The changes observed on standing are shown to be due to the action of bacteria normally present on the skin. The data established concerning the reactions and constituents of perspiration are being used to formulate perspiration-test liquors. D. G. H.

Application of the Seed of *Soya hispida* Deprived of Uricase. Qualitative and Quantitative Analysis. R. Fosse, A. Brunel, P. de Graeve, P. E. Thomas and J. Sarazin. (*Compt. rend.*, 1930, **191**, 1388–1390.)—The authors' method for the selective destruction by heat of uricase in the presence of allantoinase and urease (*id.*, 1930, **191**, 1153) is applied to the detection of allantoin, a solution containing 10 mgrms. per litre of which is warmed at 40° C. for 30 minutes with 1 per cent. of active uricase-free soya and chloroform. The mixture is filtered, the filtrate adjusted to 0·1 *N* acidity by addition of *N* hydrochloric acid, and heated at 100° C. for 1 minute. Addition of 4 drops per c.c. of 1 per cent. phenylhydrazine hydrochloride to the warm solution followed, after cooling, by 2 drops per c.c. of 5 per cent. potassium ferricyanide solution and finally by 2·5 c.c. per c.c. of concentrated hydrochloric acid, produces a red coloration. With mammalian blood the serum is allowed to ferment overnight at 40° C. with the enzyme, and the proteins coagulated with 20 per cent. of solid trichloroacetic acid. The method, which depends on the conversion of allantoin into allantoic acid, which is then decomposed by the mineral acid into glyoxylic acid and urea, may be used in the presence of uric acid (cf. *id.*, 1929, **188**, 1418) if the uricase (which produces allantoic acid from uric acid) is destroyed. The maximum errors obtained were $\pm 0{\cdot}9$ per cent. In the case of dog's urine, daily determinations of the total nitrogen (micro-Kjeldahl) and of the urea (xanthydrol) showed that whilst the allantoin content varied between 0·6 and 3·3 grms. per litre, the ratios of allantoin nitrogen to 100 parts of total nitrogen, and of allantoin to 100 parts of urea, were constant (1 to 1·2). The production of allantoic acid by untreated soya from potassium urate is completely inhibited by 10^{-5} parts of potassium cyanide. Allantoin in uric acid should, however, be determined in the presence of 0·6 to 0·8 grm. per litre of cyanide if the untreated soya seed is used, since the limiting inhibiting quantity of cyanide is raised in the presence of allantoin. Below this quantity a portion of the uric acid is fermented, and above it the activity of the allantoinase is inhibited. J. G.

Method for Determination of Enzyme Yield in Fungus Cultures, Z. I. Kertesz. (*J. Biol. Chem.*, 1931, **90**, 15–23.)—Fernbach (*Ann. Inst. Pasteur*, 1890, **4**, **1**, 641) proposed a method and a unit for the determination of sucrase. At that time the method was regarded as of great importance, but later work showed it to have serious defects. The essential mistake was that the enzyme was not determined in the mould directly, but in a solution made up from the

killed cells, and this result was set down as the enzyme content of the mould. The great importance of Fernbach's idea is generally conceded, but his method is no longer used for the determination of the enzyme content of a plant or of an enzyme preparation. A new method is now presented by the author for the determination of the enzyme yield of mould cultures and for obtaining comparable enzyme determinations on solid and liquid materials. As an example, the method is applied to the sucrase of *Penicillium glaucum*, and data are presented to show the significance and suitability of the method. The total enzyme content of the mycelium of a mould culture may be expressed by the formula

$$E_1 = \frac{k \times \text{grms. of sucrose}}{\text{dry matter}} \times (\text{total dry matter yield of the culture in grms.})$$

in which k is the monomolecular reaction constant, sucrose is the total sucrose content of the reaction mixture in grms., and dry matter the amount of dry mycelium in grms. which supplied the enzyme used. The total sucrase content of the medium can be expressed in the same way, but in this case the calculation is made on the basis of volume rather than weights.

$$E_2 = \frac{k \times \text{grms. of sucrose}}{\text{c.c. of medium used}} \times (\text{volume of entire culture medium in c.c.}).$$

By the addition of these two values ($E_1 + E_2$) a number is obtained which indicates the sucrase, or other enzyme, yield of the whole culture. In duplicate cultures growing on identical media, on the 5th day the E_1 is practically the same, in spite of the fact that the enzyme activity (If_1) and dry matter yield vary greatly. With complete salt nourishment the E_1 increases as the sucrose content of the medium is increased. In the absence of one important nutrient element (K,P,Mg), and increasing sucrose supply, the value of E_1 is roughly constant. In *Penicillium glaucum* cultures growing normally, the value of $E_1 + E_2$ reaches a maximum in the first few days; afterwards it decreases rapidly. With the use of the E values it is possible to study the sucrase yield of mould cultures, especially the study of the distribution of the enzyme between mycelium and medium, since the values obtained are directly comparable. The proposed method is applicable to the determination of other enzymes in fungal or bacterial cultures, since the same principles apply to the determinations of other enzymes. P. H. P.

Determination of Peroxydase Activity. J. D. Guthrie. (*J. Amer. Chem. Soc.*, 1931, **53**, 242–244.)—A mixture of α-naphthol and *p*-phenylenediamine is used for the determination of oxydase activity, owing to its oxidation to an indophenol by atmospheric oxygen in presence of the enzyme, but in nearly neutral media is too sensitive for peroxydase. In more acid solutions, in which, moreover, catalase is inactive, the reaction is, however, sufficiently slow to be followed quantitatively, and the procedure involved has now been standardised so as to allow of the comparison of determinations made at different times. The substrate is made by preparing a citrate buffer of *p*H 4·5 by dissolving 21 grms. of crystallised citric acid in 170 c.c. of *N* sodium hydroxide solution and diluting to one litre.

To 200 c.c. of this solution are added 200 c.c. of water, 1 grm. of *p*-phenylenediamine hydrochloride, and 20 c.c. of a 4 per cent. solution of α-naphthol in 50 per cent. alcohol, the liquid being then filtered. Of this freshly-prepared substrate, 25 c.c. portions are placed in unlipped centrifuge tubes of about 80 c.c. capacity, these being left for a time in a water-bath at 25° C. to acquire this temperature, and then treated with 0·5–2·0 c.c. of the juices or extracts containing the enzyme. The reaction is started by adding 5 c.c. of 0·05 *N* hydrogen peroxide solution and stopped, after the lapse of 10 minutes, by adding 5 c.c. of 0·1 per cent. aqueous potassium cyanide solution. To each tube 25 c.c. of toluene are added, the well-corked tubes being shaken and centrifuged. The clean toluene layers containing the indophenol are compared colorimetrically with the standard. A blank test on the reagents is advisable.

The standard is prepared by adding 100 c.c. of 2 *N* hydrogen peroxide and 2 c.c. of 10 per cent. aqueous ferric chloride ($FeCl_3$, $6H_2O$) solution to 800 c.c. of the substrate, the indophenol being filtered off the next day and recrystallised from a 1:1-mixture of absolute alcohol and toluene; 0·05 grm. of this preparation is dissolved in 50 c.c. of the warm mixed solvent, toluene being added to make the total volume one litre. This solution keeps well. A solution of 2 grms. of iodine in a litre of chloroform is also satisfactory as a standard. T. H. P.

Fading of Tropaeolin 00 in the Titration of Organic Acids in Urine. K. L. McCluskey. (*J. Biol. Chem.*, 1931, **90**, 197–201.)—In a study of urine acidity in tuberculosis the method of Van Slyke and Palmer (*J. Biol. Chem.*, 1920, **41**, 567; ANALYST, 1920, **45**, 229) was used for the determination of the organic acids. This method is based on the fact that at *p*H 8 the organic acids in the urine are present as salts, and that the addition of nearly a full molecule of hydrochloric acid for each molecule of the salt of the weak acid is necessary to free the weak acid. This change is practically complete at *p*H 2·7, and the indicator which has been found to be satisfactory, with few exceptions, is tropaeolin 00. Occasionally fading of the indicator occurs, especially near the end-point (2·7). The ingestion of drugs by the subjects has been investigated, but has not been found to be the cause of the fading. It became imperative to find either a more suitable indicator, or a method of removing the interfering substance. As the result of observations a method was found by which the interfering substance could be removed by bubbling air for half an hour through the urine, to which concentrated hydrochloric acid had been added in the proportion of 0·5 c.c. to 100 c.c. of urine. This brings the *p*H of most urine to the neighbourhood of 2·7. It is shown that the aeration of urine in the presence of hydrochloric acid (*a*) will remove an easily oxidisable substance found to react with tropaeolin 00; (*b*) will remove carbonates, a necessity when present in quantities greater than 0·5 per cent.; (*c*) may give values on an average 5 per cent. lower than does untreated urine. This difference is not due to loss of volatile acids, to incomplete removal of the carbonates, to changes in the uric acid, creatinine, and creatine, or to the salt effect upon the indicator, but may be due to pigment content. The urinary

substance found to react with tropaeolin 00 is an easily oxidisable substance, and may be an unoxidised sulphur compound arising from the destruction of tissue protein, and is probably present in other diseases besides tuberculosis. Upon repeated examinations this substance has been found to occur at intervals in 30 to 40 per cent. of the patients in very advanced phthisis. P. H. P.

Sterol Content and Antirachitic Activatibility of Mould Mycelia. L. M. Pruess, W. H. Peterson, H. Steenbock and E. B. Fred. (*J. Biol. Chem.*, 1931, **90**, 369–384.)—A brief review of the literature is given which shows that very little is known of the number and kind of sterols found in moulds, and the work that has been done on their identification is more or less conflicting. A study is reported of a large number of moulds which were tested with respect to (1) their ability to grow on a synthetic culture medium, and (2) their antirachitic activatibility. In a preliminary survey, 55 moulds were used to inoculate a synthetic, inorganic medium containing 4 per cent. of glucose as the source of carbon. Of these moulds, twenty-three showed good growth in flasks. The yields of dry pad varied from 7·3 to 35·0 per cent. of the glucose consumed. Eleven of the twenty-three moulds, representing the principal species, were grown in mass cultures in large tin pans. The weight of dry pad ranged from 9·5 to 25·6 per cent. of the glucose utilised. Different strains of the same species also differed in their utilisation of glucose. Increasing the glucose content of the medium to 10 or 20 per cent., in most cases, more than doubled the yield of dry pad. When the inorganic medium was supplemented with an aqueous extract of malt sprouts or fresh yeast, the mycelial growth of one of the strains studied, *Aspergillus oryzae*, Culture 2, was increased from 20 to 50 per cent. Increasing the period of incubation of this strain from 10 to 50 days caused a 56 per cent. decrease in the weight of pad. The autoclaved, dried, and finely-ground pads of 12 of the 23 moulds showing good growth were irradiated with ultra-violet light and given to rachitic rats to test their antirachitic potency. Five kinds of mushrooms, gathered in the open, were similarly tested for their antirachitic activatibility. Eight of the moulds and three of the mushrooms brought about distinct healing of rickets, even when given at the dosage of 10 mgrms. of irradiated material per rat over a period of 7 days. The total alcohol-soluble sterol in eleven moulds and four mushrooms (determined by the gravimetric digitonide method) varied from about 0·1 to 1·0 per cent. of the dry weight of the fungus material. The amount of sterol left unextracted by the alcohol ranged from 0·01 to 0·40 per cent. of the dry pad. In most cases, 90 per cent. or more of the alcohol-soluble sterol was present in the free state. The sterol contents of the moulds varied with the species, and also with different strains of the same species. Increase in the glucose content of the medium caused a decrease in the percentage of sterol. Supplementing the inorganic medium with organic nutrients (aqueous extract of malt rootlets or fresh yeast) produced no appreciable change in the sterol content. Lengthening the period of incubation increased the percentage of sterol; the weight of pad, however, decreased so that the quantity of sterol per unit of apparatus remained about the same. P. H. P.

Study of the Antimony Trichloride Colour Reaction for Vitamin *A*. E. R. Norris and A. E. Church. (*J. Biol. Chem.*, 1930, **89**, 589.)—Several workers have shown that there is a falling off in weight-gain in rats fed for 3 or 4 weeks on a diet containing cod-liver oil, and that this falling off is not arrested by increasing the amount of oil. It is here demonstrated that this phenomenon is due to the vitamin *A* being destroyed by the oil in which it has been dissolved and stored during the course of the feeding experiment, rather than to the presence of some harmful physiologically active constituent of the diet, such as *iso*-amylamine or choline. A test was carried out on the unsaponifiable, cholesterol-free fraction of cod-liver oil, to ascertain the effect on it of the antimony trichloride colour reaction. Portions of the vitamin fraction were dissolved in chloroform, olive oil, arachis oil and in coconut oil, colour readings being taken before and after 6 weeks' storage in the dark and cold and plotted against concentration. A study of the dilution curves shows that the chromogenic substance was destroyed in the arachis oil, destroyed to the extent of 30 per cent. in the olive oil, and not destroyed in the coconut oil or in the chloroform. Some samples of coconut oil, however, have a considerable destructive action. The destructive action of olive oil can be partly, and of arachis oil completely, overcome by adding 0·002 to 0·05 per cent. of hydroquinone. The lack of weight-gain referred to can be stopped and weight-gain resumed by adding to the vitamin *A* diet the vitamin *B* complex of certain yeasts. R. F. I.

Study of the Effect of Nitrous Acid upon Components of the Vitamin *B* Complex. H. C. Sherman and M. L. Whitsitt. (*J. Biol. Chem.*, 1931, **90**, 153–160.)—Experiments are reported which were made with the purpose of throwing further light upon the differentiation of vitamins $B(B_1)$ and $G(B_2)$ by means of strictly parallel measurements of the effects of nitrous acid upon these two vitamin values or potencies in the same solution. The "protein-free milk" preparation of Osborne and Mendel, containing both of these vitamins, was chosen for the work. The investigation extends that of previous workers, first, by the use of different nitrous acid treatments (including a more drastic form), and second, by the strictly parallel study of the two vitamin potencies by rat growth methods in the same material before and after treatment. The authors have sought to interpret the experimental data in the light of the present evidence that more than two components of the vitamin *B* complex may be involved. A preliminary experiment indicated that neither the vitamin *B* nor vitamin *G* concentration of the protein-free milk solution was measurably diminished by standing 14 hours at room temperature acidulated with hydrochloric acid (1:1 concentration) as necessary in the more drastic nitrous acid treatment. The results show that treatment by the aspiration method had little if any influence upon vitamin $B(B_1)$, whereas the drastic treatment with nitrous acid, generated very abundantly directly in the vitamin solution, resulted in a large diminution of the vitamin $B(B_1)$ potency, as shown both by the weight curves of the experimental animals and the development of polyneuritic symptoms. Less drastic direct treatment yielded an intermediate result. It is suggested that vitamin *B* may be a nitrogenous base, but of

such structure as to be more resistant to nitrous acid than are the typical primary amines. There was no destruction of vitamin $G(B_2)$ under treatment by the aspiration method; with the drastic method, subsequent feeding tests indicated a partial destruction of vitamin G when the data were taken for an 8-week, but not when taken for a 4-week, experimental feeding period. It is probable that vitamin $G(G_1, B_2)$ is itself stable toward nitrous acid, but that certain indications of loss of vitamin G potency show more or less destruction of one of the newer and not yet clearly defined factors, which also are now being found to be essential to the growth of rats. Whatever the component of the vitamin G complex which is affected by the nitrous acid treatment, there are indications that the reaction involved may be one of oxidation rather than deaminisation in this case. From the results it appears that vitamin B behaves *in vitro* more like a nitrogenous base, and vitamin G more like a neutral organic substance. P. H. P.

Colour Reaction of Japanese Acid Clay with Carotene. K. Kobayashi, K. Yamamoto and J. Abe. (*Chem. News*, 1931, **142**, 66.)—Japanese acid clays dried for two hours at 150° acquire an intense activity in the colour test for carotene in a medium of benzene; with alcohol or ether, the results were unsatisfactory. Japanese acid clay gives the same vivid bluish-green colour with carotene, liver oil, and vitamin A as is produced by phosphoric acid and the anhydrous chlorides of aluminium and zinc. (*Cf.* ANALYST, 1927, **52**, 553; 1929, **54**, 562.) R. F. I.

Toxicological and Forensic.

Dangerous Properties of Ethylene Chlorhydrin. J. D. Pratt. (*Nature*, 1930, **126**, 995.)—Attention is drawn to fatal cases (*Zentr. Gewerbehygiene*, 1927, **4**, 712; *Ann .Rept. of Chief Inspector of Factories and Workshops*, 1930, 95) resulting from inhalation of vapours of ethylene chlorhydrin, which act as a metabolic poison having a specially severe effect on the nervous system and producing muscular weakness, inertness, refusal of food, sleepiness, and finally death by paralysis of respiration. These toxic effects have apparently hitherto been unsuspected (*cf.* Denny, *J. Ind. Eng. Chem.*, 1928, **20**, 578). J. G.

Detection of Sperma in Forensic Cases. J. Peltzer. (*Chem. Ztg.*, 1931, **55**, 70.)—The following simple and rapid method gives trustworthy results: The suspected spots on the clothing are dabbed in various places with 3 per cent. hydrogen peroxide solution by means of a glass rod. The presence of sperma gives rise to a copious froth, which is removed by placing a microscope slide on it. Secretion which has penetrated the fabric may be recovered by pressing the treated spots with tweezers and scratching the expressed froth with a platinum loop, from which it is transferred to the slide. Some of the preparations are then treated with a platinum loopful of 2 per cent. aqueous eosin solution. Others are fixed by a short exposure to a flame and then covered with iodine in potassium iodide solution; the presence of sperma is indicated by the formation of long, pointed, chocolate-brown crystals, which disappear after a few minutes, but

reappear on addition of fresh iodine in iodide solution. If no crystals form, microscopic examination of the stained and unstained preparations will fail to reveal spermatozoa. T. H. P.

Bacteriological.

New Coli Test. A. Van Raalte. (*Chem. Weekblad*, 1930, **27**, 663.)—In examining milk, 1 c.c. is added to 9 c.c. of a medium containing 10 grms. each of peptone and of sodium chloride and 250 mgrms. of sodium carbonate per litre. Successive dilutions are then made from 1 c.c. of mixture and 9 c.c. of medium so as to give a range containing 1 part of milk in 10, 100, etc., to 100,000. These are tested for indole after 24 hours at 37° C. No reaction should be obtained for a dilution of 1 in 10,000 of ordinary trade milk, or 1 in 100 of "model" or pasteurised milk. Carelessly prepared milk may give a positive reaction in dilutions of 1 in 100,000. The 1 in 10 dilution usually gives negative results owing to coagulation.

J. G.

The Aspergilli and their Relation to Decay in Apples. G. A. Huber. (*J. Agric. Res.*, 1930, **41**, 801–817.)—The Jonathan apples, the fungus flora of which was to be examined, were wrapped in sterile wraps immediately on picking, sorted, packed, shipped, and kept in cold store until they were washed in the culture room with stiff stencil brushes for 5 minutes, in a sterile chamber containing 100 c.c. of sterile water. Plates were then made in triplicate with 0·125, 0·25, 0·5, and 1 c.c. from the thoroughly shaken wash waters, potato agar containing 2 per cent. dextrose being used as medium, and 1 drop of 25 per cent. lactic acid being added to each tube of medium before pouring, to inhibit bacterial growth. Between 1000 and 271,000 fungus colonies were yielded by each apple, representing altogether 11 forms of *Aspergillus* isolated from the surface of normal apples. Seven of these forms caused decay when inoculated into normal apples under storage conditions at temperatures of 18° to 22° C., but none of them caused decay at cold storage conditions (0°C.). The forms of decay varied from firm, moist rots to dry, leathery rots, whilst *Aspergillus niger* caused a very soft watery rot. D. G. H.

Organic Analysis

Influence of Acid Chlorides and of Pyrrole on the Colour Test for Reactive Organo-metallic Compounds. H. Gilman and L. L. Heck. (*J. Amer. Chem. Soc.*, 1930, **52**, 4949–4954.)—It has been found that some acid chlorides interfere, by giving disturbing colours, with the sensitive colour test for reactive organo-metallic compounds, as, for example, Grignard reagents, described by Gilman and his collaborators (*e.g. J. Amer. Chem. Soc.*, 1925, **47**, 2002; *id.*, 1930, **52**, 1604), which consists in adding a small volume of the organo-metallic mixture to be tested to Michler's ketone in benzene, hydrolysing with water, and then developing the colour with a glacial acetic acid solution of iodine. Such interference is not general, but has been noted with benzoyl chloride and bromide, phosgene, oxalyl chloride, thionyl chloride and phosphorus pentachloride. Certain amines also interfere; in particular, pyrrole. S. G. C.

Gravimetric Determination of Formaldehyde and Urotropine. M. V. Ionescu and C. Bodea. (*Bull. Soc. Chim.*, 1930, IV, **47**, 1408–1419.)—In absence of other aldehydes, formaldehyde may be determined by means of its reaction with dimethyldihydroresorcinol (methone) (ANALYST, 1928, **53**, 507). The cold, aqueous, neutral solution of not more than 0·3 grm. of formaldehyde is treated with excess of the clear methone solution (0·5–1 per cent.), the liquid being either left for 6 hours at the ordinary temperature, with occasional stirring, or boiled for 10 minutes, then allowed to cool, and allowed to stand for 30 minutes. The crystalline precipitate formed ($C_{17}H_{24}O_4$) is collected in a Gooch crucible, well washed with cold water and dried at 110–115° C. Multiplication of the weight of the precipitate by 0·10274 gives the amount of formaldehyde.

Urotropine may be determined similarly, the precipitation being carried out in the boiling solution, which is left to cool before filtration. The weight of the precipitate is converted to that of the urotropine by multiplying by 0·07993. The difference between the velocities of reaction of formaldehyde and urotropine with the methone is not sufficiently great to allow of the determination of both compounds when present together. T. H. P.

Oil of Amber (*Oleum Succini*). T. T. Cocking. (*Perf. and Ess. Oil Record*, 1930, **21**, 477–478.)—Genuine oil of amber, which is obtained by destructive distillation of genuine amber, is usually substituted in this country by "Oil of Amber" (*Oleum Succini Rect.*), obtained similarly from other resins. The physical properties of 3 samples of the latter of different origins are tabulated, and the resulting variations obtained indicate that the limits of the B.P. Codex are too narrow. The following more complete characters are suggested:—Sp. gr. 0·850 to 0·875, $[\alpha]$ $-12°$ to $+12°$, n (20° C.) 1·465 to 1·482, solubility in 90 per cent. alcohol 1 in 5 to 6 volumes. Corresponding values and other characteristics are also tabulated for genuine oil prepared by the author (by distillation below 300° C., separation of the acid layer and redistillation in a vacuum), and by Messrs. Schimmel (1903), and for commercial oil prepared by the author from colophony. The author's values for the genuine oil are: Sp. gr. 0·935; $[\alpha]+20°$; n_D^{20}, 1·5155; acid value, 13·0; ester value, 2·0; saponification value, 15·0; boiling below 150° C. 0, at 150 to 200° C. 15 per cent.; 200 to 250° C., 15 per cent.; 250 to 300° C., 43 per cent. The lower fractions of the oil from colophony had a terebenthic odour, but the higher fractions had the true odour of *Oleum Succini Rect.* The genuine oil was golden-yellow, but darkened on storage. J. G.

Anti-oxidants and the Autoxidation of Fats. H. A. Mattill. (*J. Biol. Chem.*, 1931, **90**, 141–151.)—The control of autoxidation reactions, by means of anti-oxidants and pro-oxidants (promoters), is increasingly useful in industry. To secure information on the chemical nature of the anti-oxygenic substances that are found in natural oils and that prevent the autoxidative destruction of fat-soluble vitamins, a series of hydroxy aromatic compounds was tested for their capacity, when used in a quantity of 0·02 per cent. of the fat mixtures, to prolong the thermal oxidation induction period of a standard mixture of lard and cod-liver

oil. The observations indicate that the anti-oxygenic capacity of phenols resides in two hydroxyl groups in the ortho- or para-configuration; when the groups are in the meta position the compound is inactive. The hydroxyls are ineffective unless attached directly to the ring; the fully hydroxylated inositol is inactive. In the naphthols one hydroxyl group is sufficient, and, in keeping with its accepted behaviour, α-naphthol has the character of an ortho compound, and is much more effective (more than 10 times), as an anti-oxidant, than β-naphthol. Quinone is effective, and β-naphthoquinone is even more so, but the α form of the latter is entirely inactive. The relation of these facts to the more recent theories of the electronic structure of the benzene ring and autoxidation is briefly discussed, and it is suggested that in the preparation and manipulation of easily autoxidisable substances, the presence of traces of anti-oxidant will prevent undesirable oxidative changes. A number of sterols of animal origin and sitosterol from wheat, maize and lettuce were all inactive. This was to be expected, since there is only one hydroxyl, although the presence of some other sufficiently positive group might serve in its place. The existence of pro- and anti-oxygenic substances among the non-saponifiable constituents of natural fats and oils suggests that some of these may be concerned with the physiological action of the fat-soluble vitamins, and methods for their segregation from the sterols are under investigation.

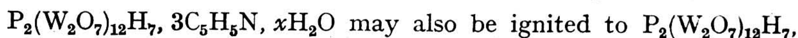
P. H. P.

Identification of Phenols. C. F. Koelsch. (*J. Amer. Chem. Soc.*, **1931**; **53**, **304–305.**)—Good yields of the sodium salts of aryloxyacetic acids are obtained by treating phenols, dissolved in aqueous sodium hydroxide, with chloroacetic acid. The acids themselves are crystalline solids, easily purified by crystallisation, and sufficient is obtained from 1 grm. of a phenol to allow of the determination of the equivalent and melting point. A mixture of 1 grm. of the phenol and 3.5 c.c. of 33 per cent. sodium hydroxide solution is treated with 2·5 c.c. of 50 per cent. chloroacetic acid solution, a little water being added when necessary to dissolve the sodium salt of the phenol. The test-tube is stoppered loosely and heated for one hour in a gently-boiling water-bath. The solution is then cooled, diluted, acidified to Congo red with a mineral acid, and extracted once with ether, the ethereal extract being washed once with a little water and the aryloxyacetic acid removed by washing with dilute sodium carbonate solution. Acidification of this extract gives the free acid, which is recrystallised from water. The uncorrected melting points of the acids thus obtained from a number of phenols are as follows:—Phenol, 98–99° C.; *o*-, *m*-, and *p*-cresols, 151–152° C., 102–103° C., and 134–136° C., respectively; *o*-, *m*-, and *p*-chlorophenols, 143–145° C., 108–110° C., and 155–156·5° C.; *o*-, *m*-, and *p*-bromophenols, 141–143° C., 107–108·5° C., and 157° C.; *o*-, *m*-, and *p*-iodophenols, 134–135° C., 114–115·5° C., and 154–156° C.; *o*-, *m*-, and *p*-methoxyphenols, 116–116·5° C., 111–113° C., and 110–112° C.; thymol, 148–149° C.; carvacrol, 150–151° C.; α-naphthol, 191–192° C.; and β-naphthol, 153–154·5° C. Certain of these results differ somewhat from those recorded in the literature, and in other cases no previous determinations are recorded.

T. H. P.

Detection of β-Naphthol. G. De Haas. (*Pharm. Weekblad,* **1931, 68,** 29–32.)—A modification of Autenrieth's test for thymol ("*Auffindung der Gifte,*" p. 55) is described, in which 1 c.c. of a dilute aqueous solution of β-naphthol containing a little alcohol is mixed with 5 c.c. of glacial acetic acid, and a lower layer of 5 c.c. of concentrated sulphuric acid added. A yellow-green colour is produced as a ring at the liquid-junction, and, on shaking, spreads throughout the mixture as a fluorescence. Thymol, cresols, phenol and guaiacol give violet, brown, violet and red colours, respectively, whilst α-naphthol gives a ring of indefinite shade and no fluorescence. The test has a maximum sensitiveness of 1 in 100,000 (Millon's reagent and bromine 1 in 10,000, ferric chloride 1 in 1,000), and is due to a sulphonation product of β-naphthol which is not extractable by ether, chloroform or petroleum spirit. J. G.

Detection and Determination of Pyridine. S. B. Tallantyre. (*J. Soc. Chem. Ind.,* 1930, **49**, 466-468T.)—"Pyridine bases" from tar distillates are usually assumed to include pyridine, picolines, lutidines and collidines (b.pt. 90° to 160° C.), and are completely soluble in water, whilst "heavy bases" are immiscible with water (b.pt. 160 to 250° C.), and include lepidines, quinolines, etc. *Distillation.*—For the separation of the former by distillation, especially in the presence of ammonia, the *p*H value should be adjusted to about 10 by cautious addition of sodium hydroxide solution till a very faint pink is obtained with phenolphthalein. Ladd's method (ANALYST, 1919, **44**, 299) is recommended for titration of the distillate, and the factor 0·75 converts the bases, calculated as pyridine, into "pyridine bases." *Extraction.*—About 80 grms. of sodium chloride are dissolved in 250 c.c. of (*e.g.* tar- or gas-) liquor, and the solution extracted with 150, 100 and 100 c.c. portions of benzene, the combined extracts being washed with concentrated salt solution and dried over sodium sulphate. The bases are then extracted in 25 c.c. of 0·5 *N* sulphuric acid, followed by two 15 c.c. portions of water, and the combined extracts titrated with 0·5 *N* sodium hydroxide solution (*cf.* Ladd, *supra*). *Precipitation.*—Mercuric chloride (5 per cent.) has a sensitiveness of 1 in 1,000, and iodine (Harvey and Sparks, *id.*, 1918, **43**, 146) 1 in 200,000, though the latter is recommended only when the solution is quite clear and when a gravimetric result is not required. Phosphotungstic acid (5 per cent.) should be used in slight excess in the presence of about 1 per cent. of mineral acids and in the absence of ammonia and of large quantities of salts. It then serves as a nephelometric method having a sensitiveness of 1 in 50,000. The precipitate,


$P_2(W_2O_7)_{12}H_7, 3C_5H_5N, xH_2O$ may also be ignited to $P_2(W_2O_7)_{12}H_7$,

whence the factor 0·041 gives the amount of pyridine. Silicotungstic acid (5 per cent.) is less sensitive to pyridine bases (1 in 8,000), and more sensitive to heavy bases (1 in 50,000), and is affected less by ammonia. It is used in a faintly acid medium, and the factor 0·12 is used for conversion of the weight of residue after ignition (SiO_2,$12WO_3$). Spacu's pyridine test for copper (ANALYST, 1925, **50**, 580 *et seq.*) may also be used, 25 c.c. of a 0·02 per cent. solution of pyridine being mixed with 2·5 c.c. of 5 per cent. potassium thiocyanate solution, 5 drops of

5 per cent. copper sulphate solution and 5 c.c. of chloroform, when the chloroform is coloured green. Analogues of pyridine do not react, but aniline and piperidine give similar compounds. A specific test for pyridine in aqueous solution, in the presence of ammonia, quinoline, nicotine or pyrrole, is the yellow colour, turning to a brown precipitate, produced on shaking 50 c.c. of sample (1 of pyridine in 350,000) with 1 drop of aniline and 1 c.c. of a fresh mixture of 3 volumes of bromine water and 1 of 5 per cent. potassium cyanide solution. The colour may be matched against that produced from a standard, and the test has been applied to ammonium sulphate and methylated spirits. In the latter case 5 c.c. are acidified with sulphuric acid, the alcohol removed on the water-bath, the residue extracted with 25 c.c. of water, and the filtrate neutralised with sodium hydroxide and tested. J. G.

Determinations of Piperidine in a Mixture of Pyridine and Higher Homologues. A. Travers and Franquin. (*Compt. rend.*, 1930, **191**, 1340–1343.)—The neutralisation-curves of these bases were obtained by addition of various quantities of each base to 25 c.c. of 0·01 or 0·02 *N* sulphuric acid, and determination of the corresponding *p*H values by means of the quinhydrone or hydrogen electrode. On account of the volatility of pyridine and α-picoline, measurements were made at 0° C. against a saturated calomel electrode at 15° C. It is then calculated that, assuming the *p*H of the sulphuric acid to be the same at 0° C. as at 15° C., the *p*H of the mixture at the various stages of neutralisation is given by $(E-260)/54{\cdot}1$, where E is the corresponding measured potential-difference in millivolts. The ionisation constants derived from the curves are, pyridine $0{\cdot}42\times10^{-9}$(0° C.), α-picoline $1{\cdot}7\times10^{-8}$(0° C.), αα′-lutidine $3{\cdot}3\times10^{-7}$(15° C.), and piperidine $1{\cdot}10\times10^{-3}$(15° C.). The αα′-lutidine and α-picoline, and particularly piperidine, give sharp end-points, and piperidine may thus be titrated in admixture with the other bases after distillation with barium hydroxide to destroy any piperidine bicarbonate. A curve is also shown for 10 c.c. of 0·02 *N* piperidine mixed with 5 c.c. of each of the other bases in 0·02 *N* solution in each case.

J. G.

Inorganic Analysis.

Rapid Gravimetric Determination of certain Elements. J. Dick. (*Z. anal. Chem.*, 1930, **82**, 401–415.)—The procedure, consisting in washing a precipitate with alcohol, then ether, and weighing it after drying *in vacuo* (ANALYST, 1927, **52**, 494, 660; 1928, **53**, 508, 509; 1929, **54**, 618), has been extended to zinc, manganese, cobalt, and cadmium ammonium phosphates, elementary bismuth, selenium, and tellurium, and cuprous thiocyanate. W. R. S.

Interference of Alkaline Earths in the Determination of Lead. J. Majdel. (*Z. anal. Chem.*, 1931, **83**, 36–45.)—The influence of the sulphates of barium, strontium, and calcium on the solution process of lead sulphate in ammonium acetate (after the familiar evaporation of the solution to fumes of sulphuric acid) was submitted to an exhaustive study. It was confirmed that barium strongly interferes, the precipitated $(Pb,Ba)SO_4$ being insoluble in ammonium acetate.

The following losses (in per cent. of lead taken) were observed: Pb:Ba as 10:1, 5·5; 1:1, 46·5; 1:2, 80·5; with 1:10, all the lead remains insoluble. Strontium markedly interferes, but the error is positive, as $(Pb,Sr)SO_4$ is soluble in ammonium acetate. Small amounts of calcium are harmless, whilst, with increasing quantities ($Pb:Ca < 1:2$), a positive error in the lead result is obtained. For the accurate separation of lead from the alkaline earths, it is necessary to convert the lead into sulphide. W. R. S.

Determination of Small Amounts of Zinc in the Presence of Lead Salts. M. E. Stas. (*Pharm. Weekblad,* 1931, **68**, 93–97.)—In the author's version of Berg's method (ANALYST, 1927, **52**, 494), 45 c.c. of test solution, 5 c.c. of 10 per cent. acetic acid and 2 grms. of sodium acetate are treated at 60° C. with 3 c.c. (or sufficient excess to produce a canary-yellow colour) of a fresh alcoholic 2 per cent. solution of *o*-hydroxyquinoline. The mixture is heated to boiling, filtered after 24 hours on a 7 cm. paper, and the precipitate washed with 40 c.c. of water. The filter is then placed in the neck of an Erlenmeyer flask, and the precipitate washed through with 2 *N* hydrochloric acid followed by water, and titrated with 0·05 *N* potassium bromate solution according to the author's method (*Pharm. Weekblad,* 1930, **67**, 1245, and Berg, *loc. cit.*), when 1 c.c. = 0·408 mgrm. Zn. Under these conditions 100 mgrms. or less of lead do not react (*cf.* Marsson and Haase, ANALYST, 1929, **54**, 494), and the maximum recorded error for 0·1 to 2·5 mgrms. of zinc with 10 to 100 mgrms. of lead is +0·04 mgrm. J. G.

Detection and Determination of Nickel in Presence of much Cobalt. F. Feigl and H. J. Kapulitzas. (*Z. anal. Chem.,* 1930, **82**, 417–425.)—The limitations of the dimethylglyoxime reaction, as applied to traces of nickel, are discussed. A new method is described, capable of detecting and determining the trace of nickel invariably present in cobalt salts guaranteed nickel-free. The salt (15 to 25 grms.) is dissolved in a minimum of water, and the solution treated with a saturated one of potassium cyanide until the precipitate has re-dissolved. The cobaltocyanide is oxidised with 3 per cent. hydrogen peroxide, and the solution warmed; if not clear yellow, more peroxide is required. The excess is destroyed by evaporation to one-quarter bulk. A slight precipitate, insoluble in excess of cyanide, is filtered off. The filtrate (200 to 300 c.c.) is treated with solid dimethylglyoxime, warmed to about 60° C., and 40 per cent. formaldehyde added until the liquid smells of it: $K_2Ni(CN)_4 + 2HCOH = Ni(CN)_2 + 2CN.CH_2.OK$. The nickel cyanide reacts with the solid reagent, the cobalticyanide remains unaffected. After standing $1\frac{1}{2}$ hours, the precipitate is collected, washed, dissolved in dilute hydrochloric acid, the solution filtered, and the nickel precipitated as usual with one per cent. alcoholic dimethylglyoxime. The method is applicable to cobalt salts containing much iron. Cobalt salts absolutely free from nickel may be prepared by the above procedure; the filtrate from the nickel precipitate, containing cobalticyanide, is evaporated to dryness on a sand-bath, and the residue stirred and heated till charred. It is made into a paste with water and

strong hydrochloric acid, and heated some hours on the water-bath. The liquid is diluted and filtered, and the filtrate reserved. The residue is dried and ignited, mixed with hydrochloric acid, then water, the liquid filtered and added to the first filtrate. From the solution the cobalt is recovered by precipitation with alkali.

W. R. S.

Determination of Metallic Iron in Ores. W. Ackermann. (*Chem. Ztg.*, 1931, **55**, 30.)—A process has been proposed (Wilner-Merck, *Z. anal. Chem.*, 1902, **41** 710; Treadwell, *Lehrbuch*, p. 527) for the determination of metallic iron when in admixture with iron oxides, in which the mixture is treated with mercuric chloride solution, when, it is claimed, the metallic iron reacts, giving ferrous chloride which can be titrated, and the non-metallic portion is unattacked. The present author has tested the applicability of this process to the determination of metallic iron when mixed with various iron compounds with which it is likely to be associated in analytical samples of metallurgical products. Satisfactory results were obtained for metallic iron in synthetic mixtures with ferrous or ferric oxides, red iron ore and magnetite. With certain mixtures, however, *e.g.* containing metallic iron and brown iron ore, low results were obtained, whilst, on the other hand, mixtures containing cementite, ferrophosphorus or iron sulphide gave excessively, and iron pyrites slightly, high results for the metallic iron content. S. G. C.

Determination of Carbon in High Sulphur Steels by Direct Combustion. H. A. Bright and G. E. F. Lundell. (*Bureau of Standards J. Research*, **1930**, **5**, 943–949.)—The oxides of sulphur, which are formed in the determination of carbon by direct combustion in oxygen, cause high results if they are not removed from the gas stream, and special attention is necessary to secure the complete preferential absorption of these oxides when the sulphur content of steel is greater than 0·10 per cent. These oxides of sulphur have been shown to consist of sulphur trioxide with more or less sulphur dioxide. The efficiency of the absorbents for these oxides commonly used in the analysis of ordinary steels, *e.g.*, granulated zinc, chromic acid in water or concentrated or dilute sulphuric acid, a column of "ironised" asbestos in the exit end of the combustion tube, or substances added to the sample, has been found insufficient for high sulphur steels, particularly in continuous routine work. Lead dioxide heated at 280° C. is fairly good, but it has certain disadvantages in that it requires an additional furnace, and it must be heated at 250° C. until a uniform blank is obtained; moreover, it must be kept out of contact with carbon dioxide of the air when not in use. Tests have been made of a method of absorption due to H. E. Slocum, which consists of a train in which the gases from the combustion tube are passed first over platinised silica gel heated to 440° C., which acts as a catalyst for oxidising sulphur dioxide, and then through a tower containing closely packed ironised asbestos for removing sulphur trioxide. This method is satisfactory, provided that there is sufficient contact surface of platinised silica gel, although no data are available at present as to how long the catalyst will function satisfactorily. The method of absorption of sulphur oxides advocated in the paper employs chromic acid in conjunction

with asbestos as follows:—The exit gases from the combustion tube are first passed through a special absorption tube (of which a diagram is given) containing about 8 to 10 ml. of a 50 per cent. aqueous solution of chromic acid in the right arm and a 9 to 10 cm. column of closely packed asbestos, plain or ironised, in the left arm. All of the sulphur dioxide is removed by the chromic acid. Some, but not all, of the sulphur trioxide is condensed during the passage through the asbestos and the solution. The first tube is followed by another of identical design, which contains sulphuric acid (97 per cent.) in the right arm, and asbestos in the left arm. Thereafter the gases pass through "anhydrone" (anhydrous magnesium perchlorate) to complete the drying and also to condense sulphur trioxide mist which may have escaped absorption in the first two tubes. The carbon dioxide is absorbed in "ascarite" (with anhydrone) contained in a Fleming tube. The paper contains many details of interest to steel chemists. S. G. C.

Detection of Cobalt as Caesium Cobaltinitrite. H. Yagoda and H. M. Partridge. (*J. Amer. Chem. Soc.*, 1930, **52**, 4857–4858).—The solubility in water of caesium sodium cobaltinitrite, $Cs_2NaCo(NO_2)_6$ (0·05 mgrm. per c.c. at 17° C., Rosenbladt, *Ber.*, 1886, **19**, 2531), is lower than that of potassium cobaltinitrite, and serves as a more delicate test for cobalt than the latter salt. The mixture of cobalt and nickel sulphides, from the usual procedure, is dissolved in *aqua regia* and evaporated just to dryness. The residue is dissolved in 1 or 2 c.c. of 6*M* acetic acid. To this solution 2 c.c. of 6*M* sodium nitrite and 0·5 c.c. of 0·5*M* caesium nitrate are added. Precipitation of the yellow caesium sodium cobaltinitrite was found to be instantaneous when more than 0·5 mgrm. per c.c. of cobalt was present, but it required 2 minutes to reveal 0·05 mgrm. per c.c. The sensitiveness of the test may be increased by substituting potassium nitrite for sodium nitrite in the method, when, it is claimed, a solution containing 0·01 mgrm. of cobalt per c.c. will yield a yellow precipitate (probably $Cs_2KCo(NO_2)_6$ in about 3 minutes. Considerable quantities of iron, manganese, or nickel do not interfere. S. G. C.

Determination of Magnesium with 8-Hydroxyquinoline—Gravimetrically, Volumetrically and Colorimetrically. A. W. Hough and J. B. Ficklen. (*J. Amer. Chem. Soc.*, 1930, **52**, 4752–4755.)—The scope of this paper is the application of the already established 8-hydroxyquinoline method to the rapid determination of magnesium in dilute solutions, particularly boiler-feed waters. The solution (50–100 c.c.) is made ammoniacal with 20 c.c. of "ammonia reagent" (not specified), heated to 70° C., and 100 c.c. or more of a solution of 8-hydroxyquinoline (0·05 per cent.) added, the necessary excess of which is shown by the yellow colour of the filtrate. The precipitate is washed, after filtration, with a dilute solution of ammonia, ignited, and weighed as magnesium oxide. Good results were obtained over the range 1–10 mgrms. of magnesium. In the volumetric method, the filter carrying the precipitate is digested with hot *N* sulphuric acid (100 c.c.), and this is titrated (apparently in presence of the filter paper) with potassium permanganate (4·17 grms. per litre) until the pink colour persists for

2 minutes. Fairly good results were obtained with amounts of magnesium within the range 0·1–3·5 mgrms., beyond which the end-point of the titration became obscure; 1 c.c. of the permanganate solution is equivalent to 0·0001 mgrm. of magnesium (on what this is based is not stated). In the colorimetric method, use is made of the yellow colour of the uncombined 8-hydroxyquinoline remaining in the solution after filtration of the magnesium salt. The depth of colour, which varies in the opposite direction to the amount of magnesium in the sample, is compared in a "100 c.c. colorimeter," the 8-hydroxyquinoline reagent being used as the standard; 1 c.c.=0·0000416 grm. Mg. Fairly good results were obtained over the range 0·5–5·0 mgrms. S. G. C.

Quantitative Precipitation of Sulphides in Buffered Solutions. I. Cobalt Sulphide. M. E. Haring and M. Leatherman. (*J. Amer. Chem. Soc.*, 1930, **52**, 5135–5141.)—The paper contains the results of a study of the precipitation of cobalt sulphide from pure solutions of cobalt chloride over a range of *p*H values 6·15 – 3·10, adjusted by additions of ammonium acetate and acetic acid, and measured by a hydrogen electrode before the admission of hydrogen sulphide. The solution contained in an Erlenmeyer flask was heated to boiling, and hydrogen sulphide was passed through the flask, but not through the solution, for about 5 minutes, after which the exit was closed and the solution allowed to cool under the pressure of the Kipp's apparatus (45 minutes to 1 hour, overnight for low *p*H values). After filtration, the precipitate was not washed and the cobalt was determined by roasting the precipitate and reducing it in hydrogen at 1000° C.; a reduction temperature of 800° C. was found insufficient to prevent the cobalt being pyrophoric. At the higher *p*H values precipitation was very rapid, and the precipitate was flocculent and bulky; the speed of precipitation diminished with diminishing *p*H and the precipitate was compact. Precipitation was complete within 0·5 per cent. down to *p*H 3·6, but thereafter low results were obtained. The optimum *p*H value for the precipitation is stated to be 3·93, when the precipitate is compact and granular.

About the same quantities of cobalt (0·2 grm.) as chloride in the same volumes of solution (90 c.c.) were used throughout the work. From a few experiments, the numerical results of which are not communicated, it is stated that large quantities of ammonium salts and a low concentration of cobalt ion appear to diminish somewhat the precision of the method.

II. Nickel Sulphide. M. E. Haring and B. B. Westfall. (*Id.*, 5141–5145.)—A similar study was made of the precipitation of nickel sulphide over the *p*H range 6·81 – 3·30. The solutions (90 c.c.) containing 0·2 grm. of nickel (as nickel ammonium sulphate), and the requisite ammonium acetate and acetic acid were heated to 90° C., before saturation with hydrogen sulphide, and, just before the end of the precipitation, the temperature was raised to 60° C.; this modification helped to reduce the adsorption of nickel sulphide by the glass. The precipitate was filtered off on a platinum Gooch crucible, and the nickel weighed as nickel oxide after roasting at 1000° C.; reduction in hydrogen, even at 1000° C., was

not practicable, because of the pyrophoric nature of reduced nickel. The precipitation of nickel sulphide was found to be quantitative down to *p*H 4, and 4·4 is stated to be the optimum *p*H value for the precipitation, *i.e.* the lowest value consistent with complete precipitation and a reasonable time for it (about 1 hour). S. G. C.

Detection of Chlorate in Perchlorate. T. P. Raikowa-Kowatschewa. (*Z. anal. Chem.*, 1930, **82**, 415–417.)—The perchlorate solution (1 to 3 c.c.), or 1 grm. of the finely-powdered salt, is shaken with 5 c.c. of fresh hydrogen sulphide water, and left for a short time. If chlorate is present, an opalescence appears after about 15 seconds, and a white opaque solution results after 3 to 4 minutes. Chlorate-free perchlorate yields a perfectly clear solution. Nitrate dissolves to a clear solution which becomes opalescent after about 10 minutes, but not opaque on longer standing. W. R. S.

Direct Nesslerisation of Ammonia in Sea Water. H. Wattenberg, (*Conseil Perm. Internat. Explor. Mer. Rapp. Reunion*, **53**, 108; *Pharm. J.*, 1931. **126**, 11).—Ammonia in sea-water may be determined by direct addition of Nessler's reagent to the sample, provided that precipitation of the calcium and magnesium is prevented by previous addition of Rochelle salt. Five c.c. of a 30 per cent. solution of this tartrate are added to 100 c.c. of the sample, the mixture is added to 10 c.c. of 20 per cent. sodium hydroxide, the 2 c.c. of Nessler's reagent then added and the colour compared with that given by standards after standing for 15 to 45 minutes. R. F. I.

Microchemical.

Micro-chemical "Spot" Tests for some of the Heavy Metals, using Dithizon (Diphenyl-thiocarbazone). H. Fischer. (*Mikrochem.*, 1930, **8**, 319–329.)—A dilute solution of dithizon in carbon tetrachloride or carbon disulphide (1–2 mgrms. per 100 c.c.), when shaken with a dilute, nearly neutral, solution of many of the mono- or di-valent heavy metals, changes in colour. Details of the tests are given for copper, lead, silver, zinc, and cobalt, and the smallest amount recognisable in the presence of various proportions of other metals is given in each case. The tests may be carried out on a porcelain "spot" plate, in micro-test tubes, or by means of filter paper impregnated with the solution of the reagent.

Copper.—The test for copper, in which the green colour of the reagent is changed to brown, is carried out either in neutral solution, when in a drop of 0·05 c.c. the smallest amount recognisable is 0·03γ of copper, or in the presence of 2 per cent. ammonia, when 0·02γ of copper can be detected, or in the presence of 2 per cent. ammonia and 2·5 per cent. ammonium chloride, when 0·03γ of copper can be detected. The copper is recognisable in the presence of more than 30,000 times the quantity of lead, zinc, cadmium or nickel. The presence of 10 per cent. of acetic acid makes the test about 500 times less sensitive.

Lead.—The test for lead is best carried out in the presence of potassium cyanide, when none of the other heavy metals react with dithizon. For lead the colour change is from green to red. The smallest amount recognisable in a drop of 0·05 c.c. is 0·1–0·2γ of lead, according to the other ions present. The test can be carried out in the presence of silver, copper, nickel, zinc, cadmium or antimony in more than 10,000 times the concentration. Ammonium chloride should be added when zinc or cadmium is present.

Silver gives a characteristic violet precipitate. The test is best carried out in dilute sodium hydroxide solution; in 4 per cent. sodium hydroxide the amount detectable is 0·3γ of silver. A little Rochelle salt should be added to prevent hydroxide precipitation.

Zinc colours the reagent purple red; the test may be carried out in 10 per cent. acetic acid solution, when 0·9γ of zinc may be detected, or in the presence of 10 per cent. acetic acid and 5 per cent. ammonium acetate, when 0·05γ of zinc can be detected. The test is not successful in the presence of silver, mercury, cobalt or much copper, though nickel and small amounts of copper may be present.

Cobalt.—The test for cobalt is carried out in 2 per cent. ammonia solution, when 0·04γ of cobalt is detectable, but in the presence of zinc a solution of dithizon in sodium hydroxide is used. With zinc alone there is a blue-violet colour, turning to grey in a few minutes, but in the presence of cobalt the colour retains its intensity for some hours, so that less than 0·1 per cent. of cobalt in zinc can be detected in this way. J. W. B.

Tests for Zirconium. F. Pavelka. (*Mikrochem.*, 1930, 8, 345–351.)—*Carminic Acid Test.*—The yellow acid solution of carminic acid gives a permanganate-coloured compound with zirconium ions. The test solution should be acid (4–5 drops of 2 *N* hydrochloric acid per c.c.), and a dilute carminic acid solution is added; the colour change is visible after a few minutes on the water-bath. The smallest amount recognisable is 10γ of zirconium in a dilution of 1:100,000. The colour for 20γ is approximately that of *N*/1500 potassium permanganate. In the presence of thorium, cerium and aluminium the solution should contain 20 per cent. by volume of concentrated hydrochloric acid. Titanium interferes with the test, and also sulphates, phosphates and fluorides.

Gallocyanin (*dimethyl-amino-hydroxy-oxazon-carboxylic acid*) *Test.*—Zirconium changes to blue the red coloured solution of gallocyanin in acid. The test is carried out as with carminic acid, and 2γ of zirconium can be detected in 1:500,000 dilution. In the presence of aluminium, thorium, beryllium or cerium 10 per cent. of hydrochloric acid should be present. Titanium interferes. When the gallocyanin complex is precipitated with sodium arsenate solution (4 per cent.) the precipitate formed is distinctly blue, and can be concentrated by filtering through an Emich filter stick with an asbestos filtering surface, and, on comparing the colour with a blank, 2–3γ of zirconium can be recognised by giving a distinct blue colour. The gallocyanin compound can also be precipitated with *m*-nitrophenyl-arsenic acid, when 5–10γ of zirconium can be detected in the presence of

500 times the amount of beryllium and thorium, but titanium interferes. By filtration, as before, as little as 1γ can be detected by comparing the colour of the asbestos filtering mass with a blank. J. W. B.

Physical Methods, Apparatus, etc.

Electric Heater for Pregl's Micro Combustion. B. Flaschenträger. (*Mikrochem.*, 1931, **9**, 15–19.)—An improved and simplified electric heater for the micro-combustion is made up of three parts, the large heater for maintaining the oxidising portion of the tube at a red heat (which uses about 800 watts), a small movable heater for burning the substance (using about 300 watts), and a low-temperature heater for heating the portion of the tube containing the lead peroxide (using about 100 watts). The low-temperature heater may be removed for the combustion of nitrogen, sulphur or halogens. Platinum foil, which is cheaper and lasts longer, is used in the heaters, instead of platinum spirals. The apparatus is obtainable from Heraeus. The advantage of electric heating over gas heating for the micro combustion is that constancy in temperature and pressure of the combustion space, which are important on the small scale, are more easily obtainable. J. W. B.

Nature of the Dust in the Air of Cotton Card Rooms. The British Cotton Industry Research Association. (*J. Textile Inst.*, 1931, **21**, 595–604T.)—The paper is an abridgment of the Report made in April, 1928, by the British Cotton Industry Research Association to the Federation of Master Cotton Spinners' Associations, and is based mainly on investigations by T. B. Bright, E. Rhodes, and F. Summers. The dust produced during the carding of Indian, American and Egyptian cottons in 17 card rooms, covering as wide a range of practical conditions as possible, was investigated and was found to be mainly made up of very minute particles with an admixture of very large particles. About 1 per cent. of the total dust might consist of fungus spores, especially those of the *Aspergillus niger* group. The living organisms were collected by aspirating 50 litres of air through a plug of anhydrous sodium sulphate contained in a glass tube of internal diameter ¾ in. and length 8 in., and which was placed above a slight constriction about 2 in. from one end, with a plug of sterilised bacteriological cotton wool above. Two 10-litre aspirators were used alternately. The sodium sulphate was dissolved in 1 litre of normal saline, and 1 c.c. of solution transferred to agar which, after cooling, was incubated. Cultures were also made at dilutions of 1/10 and 1/100. Beer-wort agar at 25° C. was found the most suitable medium. The ratio of organisms of all kinds to total dust did not vary greatly from test to test, but the spores of *Aspergillus niger* rarely formed less than 50 per cent. of the total spores, and at times exceeded 90 per cent. The dust was collected for chemical analysis by passing the air through a scrubber consisting of a pair of 2-litre aspirator bottles with a large filter flask as a trap between the second and the vacuum pump. The bubble stream was very fine, this being ensured by causing the air to pass through the pores of a Gooch crucible fitted into the neck

of the second aspirator. After collection, the water from the apparatus was gently boiled, 1 per cent. of formalin added, and the dust collected on a tared filter paper and dried and weighed (the part soluble in water was neglected). After ashing and weighing, the silica was fixed with hydrochloric acid and determined. About 90 per cent. of the dust consisted of organic matter (cotton hair fragments, seed coat particles and fungus spores) and approximately 60 per cent. of the inorganic matter was silica. The kind of cotton or the method of mixing does not very much affect the character of the dust, but the quantity of particles and proportions of the different kinds of particles vary; *e.g.* Egyptian Uppers gave rise to more black mildew spores than the Texas sample. D. G. H.

Reviews.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By A. F. HOLLEMANN, Ph.D., LL.D., D.Sc., F.R.S.E. Seventh English Edition. Pp. xx+594. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Limited. 1930. Price 17s. 6d. net.

To those who welcomed the first English edition of Hollemann in 1902 it will be no surprise to find that seven English editions have been called for in less than thirty years. It is generally taught that Wöhler's synthesis of urea in 1828 broke down the distinction between inorganic and organic chemistry; one thing it did not do, break down the division between the ways in which the two branches of the science were taught. The ideas and methods of physical chemistry were soon utilised by the inorganic man; the organic chemist may have realised their importance, but hardly introduced them into his teaching. In these days of "indeterminancy" it is unwise to insist too strongly on cause and effect; it may be remarked, however, that the realisation of the industrial synthesis of the simpler "organic" compounds, such as methyl alcohol, urea and acetic acid, seems to be due to a combination of physical chemistry and engineering. The first edition of Hollemann departed from the traditional method of teaching organic chemistry, and in the present edition it will be noted how physical ideas are continually introduced. Thus, the reproduction of a few fractional-distillation curves on p. 22 warns the reader immediately as to the limits set to separation by distillation, and renders subsequent reference to "hydrates" of some of the lower alcohols unnecessary.

The book is divided into three main portions: An Introduction (pp. 1–32), First Part, The Aliphatic Compounds (pp. 33–348), and Second Part, Cyclic Compounds (pp. 349–560). The short introduction deals with the history of organic chemistry and successively with qualitative and quantitative analysis

and the determination of molecular weight. Half a page (p. 17) is devoted to "the element carbon." This is a liberal allowance, as organic text-books go, but one sometimes feels that it would not be illogical if a Text-book of Organic Chemistry began with a short account of the properties of the element carbon, both physical and chemical. Even the diamond and graphite lattices and the water-gas equation might be included, let alone a list of the elements with which carbon can enter into direct combination. The remainder of the introduction is concerned with laboratory methods, *e.g.* distillation, separation of solids and liquids, the polarimeter, etc.

On turning to the First Part, we meet first the alkanes, C_nH_{2n+2}, as Professor Hollemann systematically calls the paraffins. These are dismissed somewhat briefly, but serve as a convenient peg on which to hang an account of isomerism and structure. In dealing with the alkanols (alcohols, $C_nH_{2n+1}OH$) it is possible to introduce the subject of optical activity (pp. 57–61), and in much the same way strength of bases (p. 74), velocity of formation of tetra-alkylammonium iodides (p. 77), melting-points of homologues (pp. 94 and 178), viscosity and fluidity (p. 97), surface-tension of soap solutions (p. 100), electrolytic dissociation and strength of acids (pp. 102, 191), ester equilibrium (pp. 107–111), molecular refraction (p. 154), formation of lactones (p. 207), thermal analysis (p. 372), etc., are dealt with as occasion offers.

For the rest, the First Part is a clear and concise account of the chemistry of the fatty series, stereochemistry and tautomerism being dealt with as occasion arises. Special attention may be drawn to the sections (pp. 231–281) dealing with the carbohydrates. They occupy about one-eleventh of the whole book, and for this, justification is to be found in the interest taken in the subject and the way in which the author has treated it. The proteins receive about 12 pages and the uric acid group about 8 pages, so that those parts of chemistry dealing with life receive fair treatment. Attention may be drawn to the special articles devoted to "Cyanogen Derivatives" and "Derivatives of Carbonic Acid"; they are to be recommended.

The aromatic series is treated on very sound lines, though more space for the Vegetable Dyestuffs and Tannins would have been welcome. The Hydrocyclic (hydro-aromatic) Compounds are allotted 20 pages, and included in this small space are accounts of the *cis-trans* isomerism associated with this series, and of the more important terpenes and camphor.

The space given to Heterocyclic Compounds is only 38 pages, and this has to suffice for pyridine, furan, pyrrole, thiophene, pyrazole, quinoline, *iso*-quinoline, indol (including indigo) and their derivatives, as well as for the alkaloids. It is not enough, and when a new edition is called for, it is to be hoped that the heterocyclic compounds will get rather more space.

The book is well-written and full of information, the printing and general appearance are good, and the index is adequate. Misprints are very rare. As a general text-book of organic chemistry the work may be very heartily recommended.

J. T. HEWITT.

THE MANUFACTURE OF ARTIFICIAL SILK (RAYON). Second edition. By E. WHEELER, M.B.E., A.C.G.I., F.I.C. (Monographs on Applied Chemistry, Vol. I.) Pp. xi+177. London: Chapman & Hall. Price 12s. 6d.

This book is one of a series of monographs on applied chemistry, and in attempting to assess its value it is, perhaps, worth while to examine the aim behind the series. Dr. Howard Tripp, whose task it is to act as editor for the series, clearly indicates in the preface his ideal, for he says that in looking on "scientific discoveries and their application to human welfare" it becomes necessary to attempt an evaluation of their real worth. He suggests, and with justice, that our scientific journals are "being swamped by a mass of second- and third-rate material that is thought to be worth publishing, but which posterity will decree would have been better left in manuscript form," and he has designed this series of monographs with a view to suppressing the chaff and presenting the germ in an accurate, assimilable and attractive form. As a sample of the series, Mr. Wheeler's book has, beyond doubt, fulfilled this aspiration, and justification of this is afforded by that delight of all authors—a second edition.

The present volume has not departed to any appreciable extent from the first volume except, of course, that it has been brought up to date in a very thorough manner. As is indicated in the sub-title, special reference is made to viscose silk, 50 pages being devoted entirely to the manufacturing details of the process. At the same time, the three other processes which are used commercially to-day are not by any means neglected, and, in all of these, the steps in the processes of manufacture are very concisely and clearly described. References are also made to practically all the attempts which have been made to produce artificial silks from other materials, as well as to the latest work of Lilienfeld on esters of cellulose.

Two chapters are devoted to the properties of artificial silk, one of which deals with the intricate business of dyeing. In dealing with this aspect of artificial silk, the author retains his aloofness from theoretical discussion, which characterises the whole book, although just once, on p. 129, he alludes to the theoretical work of Ellis on the effect of different acid groups in the dyestuff on the affinity of the dye for cellulose acetate.

From the analyst's point of view, the appendix will prove attractive, since the author describes suitable methods for controlling the manufacture of viscose, for testing the physical properties of the silk, and for the identification of the different varieties.

The book must be looked on as an excellent survey of the manufacture of rayon, with a sufficiency of recipe to enable a chemist to perceive the general lines on which the industry works. The English is fluent yet concise, and the printing, including a number of interesting photomicrographs and pictures of plant, well done. It is not, however, a book to stimulate the imagination. R. H. MARRIOTT.

CHEMICAL ANALYSIS OF SPECIAL STEELS. Fourth Edition. By C. H. JOHNSON. Pp. 721 and index. New York: Wiley. London: Chapman & Hall. Price 37s. 6d.

This book—"Johnson"—is well known in all laboratories that deal with

metallurgical materials, and the previous edition has been expanded to include 18 appendices, amounting to 176 additional pages with 28 new illustrations. The book is presented on good paper and in clear readable type, while the appendices, which include new data and modern methods of analyses, are printed in smaller type. This is meant to be a comprehensive text-book, but it is doubtful whether this method of presentation of a new edition will be a popular one, as the information given is very scattered; yet a complete resetting of the third edition "would probably never have been done."

The author is clearly an enthusiast and realises *ab initio* that modern conditions demand a specialised knowledge in the realm of alloy steels, and he provides for most of the materials that are likely to find their way into the modern steel works' laboratory. Much useful practical information is given, while it is claimed that "all methods are developed in extreme detail purposely for the benefit of the novice." This is true, as the book contains methods that are repeated "in extreme detail" with monotonous repetition throughout, while, since the author has attempted to bring the methods of analyses up to date, it seems unfortunate that the old stereotyped methods are still quoted in such minute detail, and that important developments even in steel analysis, that have taken place during the past ten years have been completely ignored.

It has been proved by Clarke (ANALYST, 1927, **52**, 466) that in the determination of vanadium in a tungsten steel the tungstic acid retains notable amounts of the element, but in the method described on p. 7 the author does not recover this occluded vanadium, and the excellent method of a direct precipitation of the metal as the ferrocyanide (Evans and Clarke, ANALYST, 1928, **53**, 475), which obviates the necessity of separating tungsten, has been overlooked. In the determination of phosphorus as ammonium phosphomolybdate (pp. 310, 522, etc.) the interference of chromium, arsenic, silicon, etc., has not been considered, and in the determination of sulphur in alloy steels the author is in the happy position of being able to dissolve the materials in *concentrated* nitric acid (pp. 335–7), and does not consider high chromium steels of the well-known stainless variety, which are not decomposed by either nitric acid or *aqua regia*. In this country the direct "bismuthate" method for manganese in steels containing less than 2 per cent. of chromium is deservedly popular, in preference to the use of peroxide of lead, as on p. 601.

It is stated on p. 56 that "there is much demand for the determination of chromium in steels with less than 0·10 per cent. Cr," and that "all plain carbon steels without exception contain from 0·01–0·1 per cent. of nickel and chromium" (p. 604), yet the author does not appear to be aware of the well-known method of Evans (ANALYST, 1921, **46**, 38), which is used in modern laboratories for the accurate determination of traces of chromium in steels. The book, in fact, is sadly lacking in suitable colorimetric methods for such elements as nickel, copper and cobalt in steel,* bismuth in lead alloys, etc., where large weights of sample are employed by the old methods of analysis (pp. 209, 605, 688). There are better

* *Cf.* ANALYST, 1930, **55**, 318.

methods for the determination of lead in copper alloys than the unsatisfactory separation and weighing as the sulphate (p. 662), while the separation of copper in these alloys as sulphide (p. 663) is an old procedure that has been generally replaced by the cleaner and more accurate electrolytic separation, as described by Etheridge (ANALYST, 1924, **49**, 371). Methyl orange is not sufficiently sensitive as an indicator for very dilute solutions in acidimetry titrations, as described, for example, on p. 653.

A good feature of the book is that the results of test analyses, together with representative analyses of many materials, are given, and many useful references to original papers—mostly American—are quoted. Chemists will welcome the chapter on such matters as the testing of lubricating oils (Chap. XIX) and on metallurgical practice, such as the microscopic examination of steel (Appendix XVI), heat treatment and "spheroidising" (Appendix XVIII).

The English is poor in parts, and the constant reiteration of the words "proven" and "gotten" will irritate English readers. The author has a curious nomenclature of his own, coining expressions, for example, such as "adding a slight excess of *ammonium*" (pp. 48, 52, 111, etc.), "*ammonia* salts" (p. 411), "fill the tube with *the H*" (p. 184), "H Fl" (p. 193), "8 per cent. Ti ferro" (p. 64). These are not to be recommended, while instructions to "dissolve 200 mgs. of steel" (p. 16, etc.), "170 mgs. of potassium dichromate" (p. 18), etc., will appear rather confusing to the novice. Several errors in printing may be noted, *e.g.* "*anealing*" (p. 423), $KCLO_3$ (p. 592, etc.), *HNO* for HNO_3 (p. 596), Cr_2O_2 for Cr_2O_3 (p. 623), a saturated solution of $BaSO_4$ for $BaCl_2$ (p. 177); the number of a page is omitted in a reference at bottom of p. 377.

Many of the methods described are excellent, however, and have been tested for accuracy, and the book is, in effect, an encyclopaedia of knowledge to the metallurgical chemist. B. JONES.

I SOFFIONI E I LAGONI DELLA TOSCANA E LA INDUSTRIA BORACIFERA. By RAFFAELO NASINI. Pp. xi+658. Rome. 1930.

The publication of this sumptuous volume, which is the work of Senator Nasini and various collaborators, has been rendered possible by the generosity of Prince Piero Ginori Conti, to whom the industrial utilisation of the heat furnished by the soffioni of Tuscany is so largely due. The introductory chapter consists of a lecture delivered in 1923 by Nasini, whose acquaintance with Lardarello began as long ago as 1877. A very complete account is next given of early references to the soffioni and lagoons (corrupted from the Latin *lacunae*). These were known to contain sulphur, alum, salt and vitriol, and the mineral wealth of the district in which they occurred was recognised, long prior to the discovery of their content of boric acid, known as Homberg sedative salt, in 1777 by Hoefer, who then held the position of druggist to the Grand Duke of Tuscany. Hoefer detected the acid by the green colour it imparted to a spirit flame.

During the early years of the nineteenth century considerable progress was made in the methods of extraction, the development of a flourishing industry being

due mainly to the exertions of Count Francesco De Lardarel (1789–1858). Notable improvements were effected by the introduction of so-called Adrian boilers for concentrating the clarified lagoon waters and by that of artificial soffioni and artesian borings, suggested in 1840 by Professor Gazzeri. In 1912, the whole of the factories came into the possession of Count Florestano De Larderel and Prince Ginori Conti, who founded the powerful "Società Boracifera di Lardarello." Since that time great strides have been made in various directions, notably by the installation of an enormous plant for the liquefaction of the carbon dioxide issuing in vast quantities with the steam, the recovery of argon and helium, and the improved utilisation of the steam, of which more than 60,000 kilos per hour is available.

The bulk of the work, occupying 500 pages, consists mostly of an account of the large amount of scientific work carried out during the past twenty-five years by Nasini and his co-workers on boric acid and other boron compounds, and on subjects suggested by a study of the soffioni and lagoons.

The printing and form of the volume are irreproachable, the numerous illustrations are well reproduced, and the matter included is of great practical and historical interest. The book is not on sale. T. H. Pope.

Anleitung zur Organischen Qualitativen Analyse. By H. Staudinger. 2nd Edition. Pp. xv+144. Berlin: J. Springer. Price M. 6.60.

This practical little text-book, which deals with the qualitative analysis of organic compounds and mixtures in a systematic manner having some analogy with the systems of inorganic analysis, has deservedly reached its second edition within the space of six years.

The introductory section, which forms the theoretical basis of the work, has been considerably enlarged, although still following the original classification into main groups in accordance with volatility, melting point and solubility, and the separation of these groups into subsidiary groups. The analytical scheme for the separation of mixtures is also given in the form of tables, which are the work of Dr. W. Frost.

In the special sections, on the separation of organic compounds, as classified into chemical groups, the various sub-divisions are also based on physical properties, and there are copious tables of the recorded data for the identification of individual substances (*e.g.* melting points of mixtures).

The actual methods of determining physical constants and molecular weights are not described, as the book is intended to supplement, not to replace, the ordinary text-books on practical organic chemistry.

As a laboratory guide it can be warmly recommended, not only to students, but also to analysts whose work involves the examination of mixtures of unknown organic substances. Editor.