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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 on Wednesday, November 1st, in the Chemical Society's Rooms, Burlington House. The President, Mr. P. A. Ellis Richards, F.I.C., was in the chair.

Certificates were read for the first time in favour of: Messrs. Henry Aldous Bromley; Walter Horace Clulow; William Plenderleith Lewellen Hope; Robert Faraday Innes, F.I.C.; Osman Jones, F.I.C.; Alan West Stewart, D.Sc. (Brux.), A.I.C.; and William Heaton Thorns.

Certificates were read for the second time in favour of: Messrs. George Scott Robertson, D.Sc. (Dun.), F.I.C.; Frederick John Martin, M.A. (Cantab), A.I.C.; and Frederick Stanley Shadbolt, A.I.C.

The following were elected Members of the Society: Messrs. Archibald Steele Whamond and Thomas John Ward.

The following papers were read: "The Colorimetric Estimation of Pyrogallol, Gallotannin and Gallic Acid," by C. Ainsworth Mitchell, M.A., F.I.C.; "The Estimation of Narcotine and Papaverine in Opium," by H. E. Annett, D.Sc., F.I.C., and M. N. Bose, M.A.; "The Estimation of Codeine," by H. E. Annett, D.Sc., F.I.C., and R. R. Sanghi; "The Estimation of Morphine," by J. R. Nicholls, B.Sc., F.I.C.; and "Further Notes on the Estimation of Potassium by Perchlorate and Cobaltinitrite Methods," by R. L. Morris, F.I.C.

The Action of Natural Waters on Lead.

By JOHN C. THRESH, M.D., D.Sc., F.I.C.

(*Concluded from p.* 468.)

Part II. The Action of Moorland Waters on Lead.

The results obtained by experiments made with solutions of single salts in distilled water demonstrated that the presence or variation in quantity of any one of these could not explain the results obtained from different waters, but that the silicates, carbonates, sulphates and salts of some organic acids, together with this organic acid and free carbonic acid, were the constituents which by their varying quantity might cause the differences observed.

Characteristics of Moorland Waters. In moorland waters containing only a few mgrms. of solid matter in solution in 100 c.c. the carbonates present would have no appreciable effect in preventing the oxidation of lead, but a very insoluble lead carbonate might be formed, and, in the absence of appreciable quantities of carbonic or citric (?) acid, practically no lead might remain in solution. An alkaline silicate, on the other hand, would markedly retard or prevent the solution of the lead, and form on the metal an even more difficultly soluble lead compound. Acids like citric, and their salts, however, dissolve a small quantity of the lead, but the salts not so much as would an equivalent quantity of free acid. The only action of sulphates seems to be a coagulative one, the calcium and magnesium salts being more active than sodium sulphate, in precipitating the lead compounds formed when the water has become alkaline from solution of lead oxide.

The organic acids which are recorded as having been found in infusions of bilberry, of heather and of bog-moss, are citric, malic, quinic, acetic, and benzoic; infusions of these plants act on lead as does citric acid. Quinic acid has a somewhat similar effect to citric, but apparently acetic, malic and benzoic acids, unless in a free state, have no special action.

In the experiments to be recorded the organic matter in the imitation waters made was in all cases citric acid, and this not in excess of what might be found in the water imitated. Before this investigation had been commenced all attempts to make an imitation of a natural moorland water, which should have the same electric conductivity, hydrogen ion concentration, and action on lead, were utter failures, and the chief object of the investigation was to enable me to make reasonably accurate imitations. This has been fairly well accomplished, as the following results show.

In the final Table (p. 504) will be found a record of over 40 moorland waters from various parts of the kingdom arranged in order of the extent with which the waters oxidised the lead foil inserted therein in 24 hours, the waters giving up the minimum quantity of oxygen being placed first. It will be noted that the physical and chemical examinations do not permit of any opinion being expressed

upon the action of the waters on lead, but it seems quite probable that, if the organic acid and silica were also determined, the extent of this action could be predicted. The most surprising result of the examination of these waters was the large proportion which had no apparent action, beyond a slight dulling of the surface of the lead foil. That the largest proportion gave up less than 50 per cent. of the dissolved oxygen in the 24 hours, may be due to the fact that most of the samples came from Derbyshire, but it is worthy of mention that not a single sample giving up more than 50 per cent. of the oxygen came from that county. This suggests that the geological characteristics of the gathering ground, or the nature of the plants growing thereon, or both, have a marked influence on the character of the water collected.

NATURAL WATERS AND THEIR IMITATIONS.—The Table on p. 502 gives examples of the characteristics of five waters imitated.

The first 25 samples gave up less than 25 per cent. of their dissolved oxygen, and all came from the moors around Glossop in North Derbyshire, with the exception of No. 11, which was from Lake Wyrney, as supplying Liverpool.

In the case of the imitations of waters No. 1 and No. 11 small differences in the amounts of citric acid and of silica markedly affected the action on lead.

The next eight waters yielded over 25 per cent., but less than 50 per cent. of their dissolved oxygen to the lead foil immersed therein. Five came from the Derbyshire moors, No. 30 from Lancashire, No. 27 from Durham, and No. 23 from South Wales. No. 32 was fairly closely imitated, as shown in the table; no doubt a slight increase in the silicate would have given a nearer approach, but the electric conductivity would then have been too high.

Waters Nos. 34 to 42 inclusive gave up more than 50 per cent. of their dissolved oxygen to the lead foil, and it is noteworthy that not a single one of these came from Derbyshire, that only one contained more than a trace of silica, and that only one contained any free acid other than carbonic. No. 35 was from a Wakefield reservoir, Nos. 34, 37, 39, and 41 came from Dartmoor, 36 from Wales, 40 from Cumberland, 42 from Loch Katrine, and 38 from Durham. The imitations of two of these (Nos. 36 and 42) are recorded above.

No nearer approach could be made to the Welsh lake water (No. 36). Apparently the organic colouring matter had some effect, increasing the electric conductivity and retarding oxidation. This water was much more highly coloured than any other sample of water examined.

Loch Katrine water (No. 42) is typical of the waters which oxidise lead freely, and it is significant that such waters do not necessarily have a prolonged action on lead pipe. The two waters examined which acted most vigorously on lead were No. 40 (Cumberland lake supply) and this No. 42 (Loch Katrine). Samples were examined which had stood all night in domestic supply pipes, one from a house over 20 years old, and another from a house only recently erected, yet both were practically free from lead. Experiments now being made indicate that meaning is due to some colloid derived from heather, bilberry, or possibly from bog-moss, and more cannot be said at present.

NATURAL WATERS AND THEIR IMITATIONS.

	No. 1 Hurst Reservoir Water		No. 11 Lake Wyrney Water		No. 32 Turnshaw Reservoir Water		No. 36 Welsh Lake Water		No. 42 Loch Katrine Water	
	Natural	Imitation	Natural	Imitation	Natural	Imitation	Natural	Imitation	Natural	Imitation
	—	—	—	—	—	—	Deep yellow-brown	—	—	—
Value of P_H	4	4	6·75	7	8	7	6	6	6·5	6·5
Free carbon dioxide	0·15	0·2	0·55	0·5	0·6	0·7	0·5	0·5	0·25	0·3
Acidity after boiling, c.c. $N/22$ Acid	0·55	0·5	nil	nil	—	—	—	—	0	0
Carbon dioxide as bicarbonate	—	—	1·7	1·7	0·7	0·7	0·4	0·4	0·35	0·4
Sulphates (SO_4)	4·0	4·0	1·9	2·0	3·0	3·0	0·6	0·6	0·6	0·6
Chlorides (Cl)	1·1	1·1	1·1	1·1	1·2	1·2	0·9	0·9	0·5	0·5
Silicates (SiO_2)	1·0	0·9	0·16	0·16	0·45	0·35	0·25	0·2	0·01	0
Organic Acid (as citric, mgrms.)	(?)	1·0	(?)	0·5	(?)	0·3	(?)	0·2	(?)	0·4
Hardness	4°	4°	3°	3°	5°	5°	1·5°	1·5°	1°	1°
Electric Conductivity	107°	107°	97°	98°	103°	104°	62°	54°	40°	40°
Oxygen in 100 c.c.	1·170	1·115	1·133	0·967	1·060	1·140	1·103	1·08	1·079	1·080
Oxygen used	0·09	0·105	0·175	0·205	0·42	0·54	0·645	0·525	1·01	0·98
Lead oxidised	1·15	1·35	2·25	2·6	5·4	7·0	8·35	6·8	13·0	12·7
Appearance after 24 hours' contact with lead	C & B	C & B	C & B	C & B	C & B	C & B	Dull	Dull	Turbid but cleared well	Turbid but cleared well
Deposit	None	None	None	None	None	None	White	White	Flaky, fawn colour	White
Lead in solution	0·85	0·88	0·07	0·05	0·03	0·05	0·365	0·38	3·0	3·3
Lead in suspension	None	None	None	None	None	—	0·96	1·62	7·7	8·15

NOTE.—C & B = clear and bright.

In the Loch Katrine water there is very little silica, but an appreciable amount of organic matter, containing a salt of an organic acid, apparently citric acid. In imitating this water it was not necessary to use any silica.

So far no water has been met with which could not be very closely imitated.

USE OF SILICA IN PRACTICE.—The silicate may prove to be even more important than is here indicated, since it not only tends to prevent the oxidation of lead, but also of iron and aluminium. It was suggested to a water authority deriving water from moorlands, that the action of the water on lead could be prevented by the use of a sodium silicate. This water acted not only on lead, but also upon iron. The water was continuously turbid, as delivered to the consumers, and great expense was incurred in flushing and scraping the mains. The water, after treatment with silicate, ceased to act on lead, and in a few days the water delivered in the town became free from colour and was described as "brilliant." When the mains were flushed, to the surprise of the men, there was no iron oxide to wash away. The effect could only be described as marvellous. If it continues, further details will be published.

Sodium silicate is very cheap, and being in liquid form, is easily diluted and the dose regulated. Its great advantage is that it decreases the oxidation of the lead and forms a very insoluble coating on the metal, whereas carbonates have very little effect upon the oxidation, produce a more easily dissolved deposit, and frequently some of this is suspended in the water and carried forward when the velocity of the current is increased. Lime, in the absence of a silicate in the water, has apparently very little effect.

OTHER WATERS.—A few words may be said about certain other waters recently examined, because they were used for domestic purposes and were suspected of causing plumbism. The amounts, in some cases, were too small for any extended examination. No. 44 was interesting because the lead was traced to the friction of the pump piston on the lead pump barrel. The water itself did not dissolve any lead. It is doubtful, also, whether No. 43 was dangerous. In Nos. 45, 46 and 47 the free carbonic acid was responsible for the action, but in Nos. 48*a* and *b* there was a non-volatile acid present. They came from the same well, which supplied a workman's cottage on a sewage farm. No. 48*a* was the first sample examined, 48*b* a sample sent after the well had been emptied once or twice and cleansed. It is the only water examined in which the acid present seemed to be "inorganic." It was loaded with nitrates, and, when evaporated, gave off red fumes before becoming dry.

There are three gentlemen to whom I should like to express my indebtedness—Dr. Milligan, Medical Officer of Health, Glossop; Mr. Page, Chief Chemist at the Rothamsted Experimental Station; and my assistant, Mr. Martin, A.I.C., as each has rendered me great assistance.

ACTION OF MOORLAND WATERS ON LEAD.

Arranged in order of amount of Lead oxidised in 24 hours.

No.	Nature of source	Approx. value of P_H	Electric Conductivity at 20° C.	Volatile acid as CO_2	Non-volatile acid as N/22 acid	Alkalinity as N/22 carbonate	SO_4	SiO_2	Hardness	Oxygen taken up Per Cent.	Equivalent to amount of lead oxidised	Lead in poured-off liquid	Turbidity or Deposit
1	S	4·5	107	0·15	0·55	0·0	3·0	1·0	4·0	8	1·15	0·85	Nil
2	S	6·5	92	0·15	0·0	0·3	3·4	—	3·5	10	1·45	0·55	Nil
3	S	7	65	0·05	0·0	0·1	2·0	—	2°	10	1·4	0·10	Nil
4	R	5	72	0·1	0·0	0·15	2·3	—	2·5	10	1·6	0·13	Nil
5	R	7	80	0·1	0·0	0·15	3·2	—	2·5	10	1·6	0·10	Nil
6	S	5·5	90	0·3	0·0	0·05	2	—	3	10	1·3	0·76	Nil
7	S	6	89	0·55	0·0	0·25	2·6	—	3·5	11	1·6	0·60	Nil
8	R	4	109	0·45	0·2	0·0	2·7	—	3·5	14	2·05	0·60	Nil
9	R	5	98	0·45	0·1	0·0	3·0	—	3	14	1·4	0·40	Nil
10	R	7	80	0·1	0·0	0·15	2·0	—	2·5	15	1·4	0·10	Nil
11	L	6·8	97	0·55	0·0	0·85	1·9	0·16	3·5	15	2·25	0·07	Nil
12	R	4·5	95	0·4	0·1	0·0	4	—	2·8	16	2·25	0·34	Nil
13	S	5	102	0·3	0·3	0·0	2	—	3	16	2·45	0·66	Nil
14	S	7	105	0·15	0·0	0·25	4	—	3·5	17	2·5	0·22	Nil
15	R	6	92	0·40	0·0	0·3	2·9	—	3	17	2·5	0·62	Nil
16	R	6	95	0·55	0·0	0·25	3·7	—	3·5	17	2·45	0·87	Trace
17	R	4	106	0·3	0·4	0·0	3·2	—	3	17	2·5	0·68	Trace
18	R	7	110	0·5	0·0	1·7	—	0·3	4½	19	2·65	0·27	Nil
19	R	7	151	0·1	0·0	0·5	3	—	5½	20	2·4	0·05	Nil
20	R	6	106	0·6	0·0	0·2	3·4	—	3·5	20	2·85	0·93	Trace
21	S	6·5	95	0·15	0·0	0·3	3·1	—	3·5	21	3·15	0·05	Nil
22	R	7·5	109	0·15	0·0	0·55	3	—	4	22	3·3	0·03	Nil
23	R	6	147	0·3	0·0	0·05	4	—	5	22	3·6	0·125	Nil
24	R	6	200	0·15	0·0	0·55	4 ?	—	—	24	3 6	0·18	Nil
25	R	5	100	0·5	0·0	0·05	3	—	3	24	3·5	0·82	Trace
26	R	4	106	0·2	0·5	0·0	3·2	—	3	27	4·0	0·62	Nil
27	R	7	86	0·2	0·0	0·75	—	0·6	3·5	27	3·5	0·05	Nil
28	R	7	110	0·3	0·0	0·15	3	—	3	28	4·15	0·07	Nil
29	S	7	—	0·1	0·0	0·2	3	—	3	29	4·1	0·04	Nil
30	R	6·5	138	0·5	0·0	0·5	—	—	3·5	31	4·5	0·145	Nil
31	R	5	180	0·3	0·0	0·15	4·0	—	6·5	39	5·7	0·025	Nil
32	R	8	—	0·6	0·0	0·35	3	0·45	5	40	5·4	0·04	Nil
33	S	4·5	90	4·9	0·0	0·55	—	—	—	46	5·5	0·26	Nil
34	R	8	—	0·2	0·0	0·8	2	—	3	50	6·5	0·2	Trace
35	R	4	—	0·2	1·5	0·0	2	—	3	54	7·2	1·55	Nil
36	L	6	62	0·5	0·0	0·2	0·6	0·2	1·5	58	8·35	0·36	Trace
37	S	7·5	—	0·2	0·0	0·15	0·8	—	0·5	60	7·75	0·125	Trace
38	S	6	70	0·4	0·0	0·25	0·8	0·4	1·5	61	7·9	1·45	Much
39	S	7	—	0·2	0·0	0·45	—	—	—	71	8·65	0·8	Much
40	L	7	—	0·1	0·0	0·3	0·1	—	1·5	73	9·4	4·45	Nil
41	R	6	38	0·25	0·0	0·3	1	0·04	0·5	80	9·9	2·2	Marked
42	L	6·25	41	0·2	0·0	0·15	0·6	0·01	0·5	90	13·0	3·0	Marked
						Rain Water from Underground Tanks.							
43	—	—	105	0·8	0·0	1·8	2	—	5	28	3·5	0·06	Nil
44	—	—	—	0·1	0·0	0·5	—	—	6°	40	5·15	0·0	Nil
45	—	5	—	2·3	0·0	0·0	—	—	16°	—	—	0·46	Nil
						Well Waters Suspected of Causing Plumbism.							
46	—	5	—	7·2	0·0	0·4	8·1	—	15	44	5·15	2·05	Nil
47	—	6	—	2·1	0·1	0·0	5·5	—	7	—	—	0·60	
48*a*	—	3·5	988	3·1	4·6	0·0	20	—	28	20	2·6	2·8	Nil
48*b*	—	4·5	—	2·4	2·4	0·0	20	—	28	11	1·3	0·9	Nil

NOTE.—S represents surface water; R reservoir water; and L lake water.

Discussion.

Mr. Raymond Ross said that he was extremely interested in the author's paper, more especially as it dealt with moorland waters, and referred to two reservoirs in his (the speaker's) district, the water from one of which did not act, and never had acted, on lead, whereas the other (although only a mile distant) acted strongly on lead at all times of the year. He doubted whether this was caused by smoke carried by the wind, which he was much interested to hear could have this effect on the water. He would like to know if the author could give an explanation of the difference between these two waters. At one time the water had been treated with chalk, but this very soon blocked up the sand filters, and the treatment was discarded as ineffective. The water had then been treated with aluminium sulphate and lime (leaving the water just acid), followed by filtration through mechanical filters and the addition of clear lime water controlled by means of Venturi meters, and no lead had been found in water treated by this method. It had been found that if too much lime were added before filtration (so that the water had an alkaline reaction) dirt was extracted from the filters. They had never had lead poisoning in the district since this method of filtration had been employed.

Mr. E. M. Hawkins said that he had found in practice that rain water stored in tanks, made merely by digging 20ft. down into clay cementing, never acted on lead, and he enquired whether that was due to silicate in the water.

Mr. R. L. Collett asked whether Dr. Thresh had experimented with different kinds of lead, or lead which had been soldered; or whether the presence of air had an influence on the action of water on lead.

Dr. A. F. Joseph instanced the case of a farmer (being treated medically for rheumatism) who was really suffering from lead poisoning, the water on his farm (when analysed) being found to contain 15 grains of lead per gallon.

Dr. Thresh, in replying to Mr. Raymond Ross, said that the difference was due to the amount of silicate in the water; he had found the same thing in water from certain parts of Yorkshire. As regards Mr. Hawkins' question, tank water would contain a fair amount of carbonate of lime; few well waters were free from carbonates. With reference to Mr. Collett's enquiries, he had used assay lead foil in most of his experiments, but had carried out some with pure lead sheet of 99·99 per cent. purity, from Newcastle.

As regards lead poisoning, there were probably numbers of cases not recognised. In certain experiments he had taken samples of water where the pressure was 100-ft. and from the same main where the pressure was 600-ft., and in order to get comparable results he had had the main tapped in the morning, at noon, and again at night. In the morning the sample might contain a distinct amount of lead, at noon nothing, and at night only a very small trace. When the pressure was highest he had found the most lead present. Morning samples alone gave concordant results.

Errata in Part I.—Page 459 last par. The signs + and − should be transposed.
Page 463, 9th line from bottom. For "and in the process" read "it."
Page 468, 5th line from end. For "and" read "in."

The Estimation of Morphine.

By JOHN RALPH NICHOLLS, B.Sc., F.I.C.

(*Read at the Meeting, November* 1, 1922.)

The various pharmacopœial methods for the estimation of morphine in its preparations depend upon the precipitation of the alkaloid by ammonia and the use of a correction for the quantity remaining in solution. It is obvious that these methods cannot be employed when the morphine content is small or when little material is available, since the solubility correction is comparatively large. Hence, it seemed desirable to have a general method which could be employed in all cases, and an extraction method appeared preferable.

Extraction of Morphine.—Of the many solvents which have been suggested for the extraction of morphine from ammoniacal solutions, one of the most useful is a mixture of chloroform and alcohol. The alcohol distributes itself between the upper aqueous layer and the lower chloroform layer, and serves the double purpose of retarding or preventing the crystallisation of the base from the upper layer and of increasing its solubility in the lower. In addition, separation is rapid, and the lower layer can easily be evaporated on the steam bath for the recovery of the morphine. Puckner (*J. Amer. Chem. Soc.*, 1901, **23**, 470) employed a mixture of four parts of chloroform to one of alcohol, but found that not all the morphine was removed in five extractions. Eaton (*Bur. Chem. U.S. Dept. Agric. Bull.*, **137**, p. 188) used 50 c.c. of morphine solution with 20 c.c. of alcohol and 30 c.c. of chloroform for the first shaking, and a mixture of four parts of chloroform to one of alcohol for several subsequent extractions. Fuller (*Chemistry and Analysis of Drugs and Medicines*, 1920) recommends many extractions with a mixture of two parts of chloroform to one of alcohol. Morphine is readily soluble in such a mixture, but since, during extraction from aqueous solution, part of the alcohol passes into the upper layer, the first actual extracting liquid may not dissolve much morphine. A second shaking with a similar mixture may extract much more of the base, since a less proportion of alcohol passes to the upper layer, the lower layer being richer in alcohol than the first extracting liquid.

In a number of cases where such a mixture was employed it was found that the number of extractions required to remove all the morphine varied considerably (from three to ten or more), depending upon the quantity of morphine present and the volume ratio of morphine solution to extracting solvent. Experiments were therefore carried out in order to find the most suitable conditions for the rapid extraction of the whole of the morphine.

Conditions for Quantitative Extraction.—Since the base is more soluble in alcoholic solutions than in water, it appeared desirable to add the alcohol to the morphine solution before freeing the base with ammonia. The first experiments, therefore, consisted in one extraction with chloroform of an ammoniacal alcoholic solution of morphine. After trial, it was decided to fix the ratio of chloroform to

morphine solution at approximately one to two by volume. Experiments on the distribution of the three liquids—water, alcohol and chloroform—had shown that such a ratio would give, in the lower layer, the greatest proportion of alcohol and the least proportion of water, consistent with economy of chloroform. The following table shows the rapid increase in the amount of morphine extracted with increasing alcoholic strength. In each case 20 c.c. of a solution of morphine hydrochloride (containing 0·076 grm. of anhydrous morphine) were treated with 1 c.c. of 4 *N* ammonia solution and extracted once with 10 c.c. of chloroform, 1 c.c. of the latter being used to wash the outlet of the separator.

Approx. per cent. of alcohol by vol.	0	12½	25	37½	50
Morphine extract, Grm.	0·001	0·015	0·0375	0·058	0·0655
Morphine estimated by titration, Grm.	—	0·014	0·037	0·055	0·063
Approx. per cent. removed by one extraction	1	18	49	72	83

When the alcohol was increased much above 50 per cent. an appreciable amount of ammonium chloride was removed, and, on evaporation, inter-reaction occurred, with the formation of morphine hydrochloride, so that the titration of the extract was valueless. With solutions containing up to 50 per cent. of alcohol no ammonium salt was extracted, but it was found that the weight of morphine residue always exceeded the titration value, due to alcohol which was persistently retained by the base, even after drying to constant weight.

With a given ratio of chloroform to alcoholic morphine solution the distribution of the base between the two layers depends solely on the proportion of alcohol present. The best conditions for extraction will therefore be obtained from a consideration of the distribution factors for different strengths of alcohol.

As a result of numerous experiments it was found that satisfactory extractions could be made from approximately 50 per cent. alcoholic solutions. During the first shaking the chloroform takes up about half its volume of alcohol, so that, after separation, the two layers are approximately equal in volume. The lower layer abstracts about 85 per cent. of the morphine. Subsequent extractions are made after addition of alcohol to bring the percentage up to 50, and each such extraction removes about 85 per cent. of the remaining morphine. The actual amounts removed by one extraction from solutions containing up to 0·2 grm. of morphine varied between 80 and 88 per cent., the variations being probably due to the facts that the solutions were made up with 95 per cent. alcohol, and may have varied in strength from 45 to 55 per cent. of alcohol by volume, and that the chloroform was measured from a cylinder.

The following table shows the amounts of alkaloid successively removed by such a method:

	Grm.
Anhydrous morphine in solution	0·092
,, ,, 1st extract (by titration)	0·080
,, ,, 2nd ,, (,,)	0·010
,, ,, 3rd ,, (colorimetrically)	0·0012
,, ,, 4th ,, (,,)	0·0002
,, ,, remaining in solution (colorimetrically)	0·0001

To ascertain if even larger quantities than 0·2 grm. could be extracted, 1 grm. of morphine crystals (=0·940 grm. of anhydrous morphine) was dissolved in 20 c.c. of warm dilute sulphuric acid (cold acid would not dissolve this quantity), and, after the addition of 20 c.c. of alcohol and 0·5 c.c. of conc. ammonia solution, was shaken with 20 c.c. of chloroform. The resulting lower layer of about 30 c.c. (slightly warm in this case owing to the acid solution being warm) extracted 0·800 grm. of anhydrous morphine, as estimated by titration. Williams (*Amer. J. Pharm.*, 1914, **86**, 308) has shown that the solubility of recently-liberated morphine in a mixture of two parts of chloroform to one of alcohol is 1 in 76, whereas, in this case, the solubility appeared to be about 1 in 38. To see if this was due to the small increase in temperature or to a condition of supersaturation, the following experiment was made:—Morphine crystals (0·51 grm.) were dissolved in 15 c.c. of dilute acid, and 15 c.c. of alcohol, 1 c.c. of ammonia solution, and 15 c.c. of chloroform added. The mixture was vigorously shaken, at frequent intervals, during two hours, and allowed to stand overnight. There was no apparent separation of morphine. The lower layer was filtered, and 10 c.c., on evaporation, yielded 0·19 grm. of anhydrous morphine (estimated colorimetrically), a result showing an apparent solubility of 1 part in 53. The remainder of the filtered lower layer was seeded with a small morphine crystal and well shaken during six hours (when it was apparent that some morphine had separated), and then left overnight. After filtration, 5 c.c. were evaporated, yielding 0·058 grm. of anhydrous morphine, a result showing a solubility of 1 part in 86. Hence, the extraction of large quantities of morphine is assisted by supersaturation.

Morphine Preparations.—The above-described method of extraction was next applied to preparations of morphine. A suitably prepared aqueous solution was made alkaline with sodium, potassium or calcium hydroxide, and extracted successively with ether and chloroform, the extracts being washed once with the fixed alkali, and the washings added to the main bulk. By this means nearly all other alkaloids were removed without loss of morphine. An equal volume of alcohol and excess of ammonium sulphate (if ammonium chloride is used the extract may contain traces of chlorides) were added, and the morphine extracted as before. It was found that, in addition to morphine, a certain amount of colouring matter was frequently removed, and when the original preparation contained opium, narceine was also extracted. Nothing that was removed, however, interfered with the estimation of morphine either by titration, or colorimetrically, or polarimetrically, except in one or two instances where much colouring matter was extracted. In these cases the evaporated extracts were cleaned by solution in lime water or dilute sulphuric acid, filtration, extraction with chloroform and re-extraction of the morphine, as before. In one case the morphine was precipitated from acid solution by iodine, and the precipitate filtered, washed, treated with sodium thiosulphate, and the morphine re-extracted. A tincture of opium was assayed by the B.P. method, and gave 1·17 grms. of anhydrous morphine per 100 c.c. Ten c.c. of the filtered lime-water solution prepared for that estimation were extracted, as described above, and in a considerably shorter time gave an identical result by titration.

With certain preparations much time was saved by extracting all the alkaloids together from ammoniacal 50 per cent. alcoholic solution by means of chloroform, and subsequently separating the morphine.

General Extraction Method.—The general method for extraction of morphine can therefore be described as follows:—To one volume of morphine solution (from which if necessary other alkaloids have been removed by means of ether or chloroform from the solution made alkaline with sodium, potassium, or calcium hydroxide), add one volume of alcohol, make the liquid ammoniacal and shake it with one volume of chloroform. After running off the separated lower layer, add half a volume of alcohol and shake with one volume of chloroform. Separate and repeat the process for a third extraction; if the quantity of morphine exceeds 0·1 grm., a fourth extraction should be made. Evaporate the combined extracts on the steam bath, dissolve the residue in standard acid, make up to definite volume, and estimate the morphine as described below.

ESTIMATION OF MORPHINE.—1. *Titration.* A large aliquot portion of the filtered liquid is titrated with standard alkali, with methyl red as indicator (slightly low results are given with methyl orange or cochineal), and the corrected difference figure calculated to morphine.

2. *Colorimetric Estimation.* The method used is that of Georges (ANALYST, **1906, 31,** 265). A portion of the acid solution is diluted so that it contains not more than 4 mgrms. of morphine per 10 c.c. One drop each of *N* sulphuric acid and saturated potassium iodate solution is added for every 1 c.c. of solution taken, and after 5 minutes, 1 drop of concentrated ammonia solution for every 1 c.c. of solution is added, and the colour compared, after 2 minutes, with a series of standards made up at the same time. The limiting dilution is about 1 in 30,000.

3. *Polarimetric Estimation.* Part of the filtered acid solution is read polarimetrically. By the use of white light with a saccharometer, the rotation of anhydrous morphine in dilute sulphuric acid at 20° C. was found to be $[\alpha]_J = -140°$, and was independent of variation in the quantity of excess acid.

With quantities of morphine greater than 10 mgrms. the titration figure (with *N*/50 solutions) is by far the most accurate. The colorimetric estimation is very useful for small quantities of morphine and as a check on the titration, but it is hardly possible to avoid an error as great as ± 2 per cent. of the actual morphine. The polarimetric reading is usually so small that the experimental error is considerably greater. It forms, however, a rapid check on the titration figure when a moderate amount of morphine is present.

The above-described general method can be employed for the estimation of heroin and similar derivatives of morphine. The base is extracted by ether or chloroform, hydrolysed with weak potassium hydroxide solution to morphine, and the latter extracted and estimated.

SUMMARY.—(1) When two volumes of an ammoniacal 50 per cent. alcoholic solution of morphine are shaken with one volume of chloroform about 85 per cent. of the total morphine passes into the lower layer.

(2) By making the ratio of water, alcohol and chloroform approximately

the same in each extraction all the morphine can be removed in three or four extractions.

(3) The morphine in the extract is estimated either by titration or colorimetrically or polarimetrically.

The author desires to express his thanks to Sir Robert Robertson, Government Chemist, for permission to publish this work.

GOVERNMENT LABORATORY, LONDON.

Notes.

The Editor desires 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.

TWO UNCOMMON ANIMAL FATS.

THE author recently had the opportunity of personally obtaining samples of the fat of the Ceylon bear and of the cabaragoya. Lewkowitsch does not give an analysis of either of these fats, and there are few records of the examination of the fat of any reptile.

The Ceylon bear is *Melursus ursinus*; it has black shaggy fur, and weighs up to 200 pounds. Its food consists of the larvæ of ants, grubs and beetles of all kinds, and it is very fond of honey; in the dry season it feeds largely on jungle fruits. The fat was obtained from two bears, one a medium-sized female, and the other a large male. It was separated from the tissue by boiling with water, and was filtered and dried at 105° C. It was brown in colour, and, on standing, deposited about 30 per cent. of stearine.

The cabaragoya, *Hydrosaurus salvator* (Laur.) is a large species of iguana; the specimen from which the fat was obtained was between 5 and 6 feet long. It lives in marshy districts, and feeds on small insects, and on crabs which infest the rice fields; it is often the only scavenger of a native village. Emerson Tennent states that the Singhalese believe that the fat, externally applied, is a cure for cutaneous disorders, but that taken inwardly it is poisonous. No poisonous effect, however, was observed in the case of a frog which was given a dose by the mouth. The fresh fat was boiled with salt water, washed with hot water, filtered and dried at 105° C. On cooling to 30° C. it set to a yellow solid fat.

Analysis of these fats gave the following results:

	Specific gravity at 15·5	Butyro-refractometer reading at 40°C.	Acid value	Saponification value	Iodine value (Wijs)	Unsaponifiable matter Per Cent.
Bear 1	0·9146	48·2	2·31	196·7	56·7	0·69
Bear 2	—	46·2	—	197·2	60·7	—
Cabaragoya	0·9142	·49·7	2 19	196·0	63·4	0·84

MIXED FATTY ACIDS.

	Solidifying point	Butyro-refractometer reading at 40° C.	Neutralisation value	Iodine value (Wijs)
Bear 1	37·7° C.	35·8	207·4	55·4
Cabaragoya	38·0° C.	40·7	207·9	60·1

The cabaragoya being a reptile and therefore cold-blooded, the fat might have been expected to resemble the fish oils rather than the animal fats. An examination of the figures, however, shows that this is not the case.

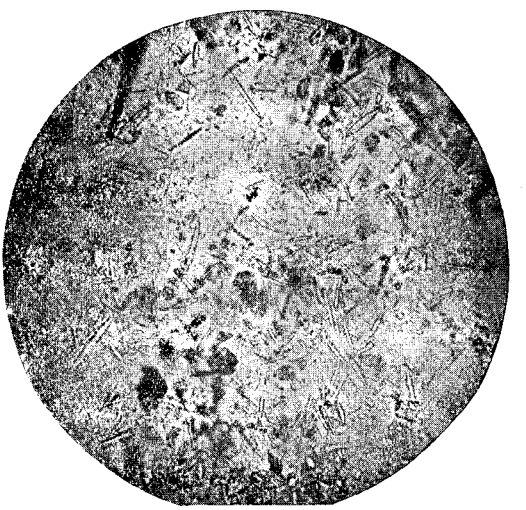
WILLIAM NORMAN RAE.

GOVERNMENT ANALYST'S LABORATORY,
COLOMBO, CEYLON.

AN ADULTERANT OF LIQUORICE PASTE.

THE manufacture of liquorice paste is an important Sicilian industry, and in Catania and Messina there are a number of factories engaged in its production.

From time to time various forms of adulteration have been noted, and recently, perhaps, the most frequently practised has been the addition of extract of *Carlina gummifera*, a variety of the *Carlina acaulis* found in considerable quantities in Sicily, and known in the dialect as *Masticogna*.



This root contains no starch, but is rich in inulin, and gives some 25 to 30 per cent. of an extract which, when concentrated, resembles liquorice paste in consistence and appearance.

An extract of this sort made in the laboratory was found to contain, after hydrolysis, as much as 60 per cent. of reducing sugars; hence, since in normal Sicilian liquorice paste the total quantity of sugars is generally from 8 to 12 per cent., an admixture of masticogna extract gives a product in which the percentage of sugar will be unduly high, while the starch and glycyrrhizin will be notably diminished.

Similar effects are produced by other vegetable extracts which have been used for the purposes of adulteration, but the presence of even moderate amounts of masticogna can be recognised by the microscopical examination of the insoluble residue.

The masticogna root contains a considerable quantity of calcium oxalate in crystals of very small dimensions and of a characteristic form, quite different from anything found in liquorice, and this permits of their ready identification.

The accompanying photomicrograph shows the appearance of these crystals, magnified 300 diameters, and their detection in the residue of a sample of liquorice paste is a clear indication of adulteration with masticogna extract.

It is hoped to give, at a later date, the results of a more complete examination of this substance.

ALEX. H. BENNETT.

MESSINA, SICILY.

Notes from the Reports of Public Analysts.

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

CITY OF BIRMINGHAM.

PUBLIC ANALYST'S REPORT FOR THE THIRD QUARTER, 1922.

DURING the third quarter of the year 1282 samples were submitted for analysis, of which 1113 were taken under the Sale of Food and Drugs Acts, 1101 being bought informally; of these 40 were adulterated. Twelve samples were bought formally, and 6 of these were adulterated.

MILK.—Of the 607 samples analysed 19 were adulterated. The average composition of all the samples was: Fat, 3·66; and solids-not-fat, 8·82 per cent. One sample taken from a serving can contained 2·6 per cent. of fat and 45 grains of boric acid per gallon. The vendor was fined £5 under the Food and Drugs Acts, and £10 under the Sale of Milk and Cream Regulations.

For 10 years the milk in Birmingham has been practically free from preservatives, but in the last 12 months they have been found in several cases.

BAKING POWDER.—Five of the 8 informal samples were tartrate powders, and two contained acid calcium phosphate. One of these was practically free from calcium sulphate, but the other contained about 13 per cent. of that salt, whereas not more than 10 per cent. is permissible. The vendor was cautioned.

EGG SUBSTITUTE POWDER.—Three of the 7 informal samples had been prepared with tartaric acid and were correctly labelled, whilst two, prepared by the maker of the adulterated baking powder were made from acid calcium phosphate which contained about 14 and 16 per cent. of calcium sulphate respectively. The labels stated: "Not made from eggs, but is a complete substitute, giving the same lightness, richness and appearance to cakes, etc." As eggs contain about 11 per cent. of fat and about 2 per cent. of nitrogen, and as these samples contained less than 0·5 per cent. of fat and 0·6 and 0·8 per cent. of nitrogen respectively, these labels were false, and the makers were cautioned for them, as well as for the adulteration. Another sample containing 0·2 per cent. of fat and 0·6 per cent. of nitrogen was marked: "A complete substitute for eggs, to which it imparts lightness and richness." In this case, also, the maker was cautioned for use of a false label.

CAKE.—Nine of the 10 informal samples of cake contained from 0 to 5 grains of boric acid per lb., and were passed as genuine. Of 24 informal samples of sponge cake, etc., four were adulterated, containing respectively, 21, 33, 25, and 26 grains of boric acid per lb. These results show the great improvement effected in the composition of sponge cakes by the circular sent out by the Public Health Committee.

SAUSAGES.—One of 13 informal samples was free from boric acid, and the other 12 contained from 10 to 54 grains per lb. Taking as the limit 0·25 per cent. (17·5 grains per lb.), as recommended in a report to the Local Government Board in 1908, eight samples containing from 22 to 54 grains of boric acid per lb. were condemned. In no case was any notification of the presence of a preservative in the sausages made to the purchaser. One informal sample of *preserved pork*

sausage contained 27 grains of boric acid per lb., and was passed as genuine. This sample was labelled "These sausages contain a small percentage of boron preservative." The 14 samples of sausages contained from 55 to 74 per cent. of meat. Two of 4 informal samples of *polony* contained excess of boric acid (22 and 24 grains). Three of the samples contained from 12 to 16 per cent. of proteins and 16 to 35 per cent. of fat.

SAGO.—Two informal samples were not sago, but tapioca.

J. F. LIVERSEEGE.

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.

CREAM CONTAINING FORMALDEHYDE.

ON July 26, 1922, Frederick Pavey was summoned before the Kingston Borough Bench for selling cream containing an unauthorised preservative, formaldehyde, and G. Belding & Co., Holloway, were summoned for aiding and abetting him.

The Public Analyst's certificate stated that two samples of cream submitted to him contained 0·01 per cent. of formaldehyde.

Evidence was given by the assistant to the County Inspector that after the purchase of the cream the wife of the first defendant had stated that a little preservative had been added to the cream, and that it should have been labelled. He had also interviewed Mrs. Belding, who had stated that formaldehyde was made from a secret known to her son, and was sold to purchasers by request; it was purchasers' fault if they sold it when they ought not to do so.

The County Inspector said that two days later he had purchased a sample of preserved cream from Mrs. Pavey, who told him that she did not think that it was preserved with boric acid, although the label stated that boric acid was present.

The defendant, Pavey, said that he did not know that the solution he purchased from the Beldings was formaldehyde, or that it was injurious to health. He was told that it was a sterilising fluid, and that it was quite harmless.

The magistrates inflicted penalties of £2 for selling adulterated cream and £2 for failing to label the cream, in each case with costs.

The summons against the Beldings was dismissed on the submission of counsel that there was no evidence before the Court connecting those defendants with the sale of that cream.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

FOOD INVESTIGATION BOARD.

THE BACTERIOLOGY OF CANNED MEAT AND FISH.*

THE investigation was made with the following objects:—(*a*) To study how far canned foods contain living bacteria or their toxic products. (*b*) To ascertain to what extent canned foods passed for consumption are free from bacteria, and, if

* *Special Report No.* 11. By W. G. Savage, M.D., R. F. Hunwicke, B.Sc., A.I.C., and R. R. Calder, B.Sc. 72 pp. H.M. Stationery Office. 1922. Price 2s. 6d. net.

not sterile, the importance and significance of the bacteria present. (*c*) To study the bacteria associated with the spoilage of canned goods, with a view to diminishing wastage from such causes.

The present report is based on the examination of 344 samples of canned meat and fish from various sources.

METHODS OF EXAMINATION AND RECORDING.—In every case the physical condition of the can was recorded. The outside of the cleaned cans was sterilised by moistening them with methylated spirit and setting this alight, and special precautions were taken to avoid outside contamination.

The primary culture media used were egg-meat broth, incubated anaerobically for anaerobes, nutrient broth, nutrient agar on plates, etc. A general reaction of $P_H = 7 \cdot 2$ was found suitable. The palladium-hydrogen jars recommended by Fildes (*Med. Research Committee Special Report* No. 12) were mainly used for anærobic cultivations. Full details of the composition of all the media used are given.

CULTURAL TESTS AND CLASSIFICATION.—Among the characteristics regarded as of special importance in the investigation were the powers of resistance, ability to decompose proteins (growth on blood serum for liquefaction and ability to peptonise milk), and ability to decompose carbohydrates with the production of gas. It was found that in practice the presence of indol as a product of growth was no indication of the power of the organism to decompose proteins. The ability to liquefy gelatin was only of value as a differentiation test. The production of hydrogen sulphide did not indicate that the organisms producing the gas were of greater significance from the point of view of the production of unsoundness than others not producing it.

SIGNIFICANCE OF THE ORGANISMS ISOLATED.—The tabulated results show that sound samples of canned goods are comparatively non-sterile, this being almost entirely due to the presence of sporing aerobic bacilli, thermophilic sporing bacilli, and micrococci. In almost every case they must be regarded as survivors of bacteria originally present, and not as additions through leaks.

These surviving bacteria do not in any way injure the foods in which they are present, because of their inability to multiply and cause decomposition under the existing conditions. The sporing types are probably present only as spores. No bacilli possessing any virulence or toxicity to man were isolated, and the presence of sporing bacilli does not throw suspicion upon the wholesomeness of the samples.

The importance of these findings is (*a*) that they show that sterility is not in itself a reliable test of soundness, and (*b*) that unsoundness is not solely, or even usually, due to outside contamination, but that the conditions within the can have become changed (*e.g.* by access of sterile air) in such a way as to enable bacteria *already present* to multiply and decompose the food.

RELATIONSHIP OF DIFFERENT TYPES OF BACTERIA TO UNSOUNDNESS IN THE FOOD.—Whilst yeasts are of great importance as a cause of unsoundness in substances containing sugars, such as canned milk and fruit, they are of no importance in meat and marine products.

Moulds are chiefly of interest as evidence of the access of air, and, when present, can make the food unsound.

The obligate anaerobic bacilli, when found, were nearly always associated with conditions of decomposition, but they may be present in very small numbers without decomposition changes. All the strains isolated were definitely proteolytic. The sporing aerobic bacilli were widely distributed in all varieties of meat and marine products, good and bad alike. The majority of those isolated had proteolytic properties, and must be regarded as potential causes of decomposition.

Given leaks in the tin, so that they can obtain a supply of oxygen, they may multiply and decompose the food. An observation not previously recorded is that a considerable proportion of these aerobic sporing organisms can multiply under stringent anaerobic conditions. They cannot grow with sufficient freedom, however, to produce proteolytic enzymes, and therefore cannot decompose proteins.

The thermophilic bacteria were found to be widely prevalent in these canned products; but, as nearly all of them are non-proteolytic and unable to decompose these foods, they cannot be considered as likely causes of spoilage.

Non-sporing bacilli were found in many samples, their significance depending upon their biological properties. Those capable of fermenting carbohydrates with gas production are actual or potential causes of gas-development within the cans, but they do not cause any material decomposition change unless, in addition, they possess proteolytic properties. The strains (such as *B. proteus*) which possess both properties, are important causes of decomposition. The non-sporing bacilli, which are neither proteolytic nor fermentative, are of no significance as causes of unsoundness.

Micrococci were present in 23 per cent. of the samples, including 16 per cent. of sound cans. The results obtained indicate that they cannot be regarded as a cause of spoilage, and that, at most, they may assist more proteolytic types.

CONDITIONS UNDER WHICH CANS BECOME UNSOUND.—We have to regard canned meat and fish products as, at the best, only partly sterilised. The food is sound rather on account of its being free from oxygen than because it is sterile. Whether the food becomes unsound depends on many factors, including (1) the extent of bacterial contamination, (2) the type of bacteria present, (3) the efficiency of the "processing" of the cans, (4) access of air to the contents, and (5) the temperature environment.

In the past, minute leaks in cans, through rust, etc., have been regarded as important because they admitted outside bacteria to invade the food. The present results indicate that greater significance is to be attached to leaks as a means of supplying oxygen to bacteria already in the food than as paths of infection.

Manufacturers who wish to ensure the absence, or, at least, a minimum of spoilage, must be encouraged to obtain their food products as fresh as practicable, to can them as speedily as possible under conditions of great cleanliness, to treat their products so as to ensure the presence of a vacuum, to employ the right "processing" temperatures, and, by the use of tin plate of good quality and efficient methods of closing the cans, to avoid causes of leakage and maintain the vacuum obtained.

The report concludes with a summary of previous investigations upon the bacteriology of canned meat and fish, since 1894, and a bibliography containing 28 references.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Estimation of the Acidity of Flour. Arpin and M. T. Pecaud. (*Ann. Chim. anal.*, 1922, **4**, 262–266.)—Acidity alone is not a reliable criterion of the soundness of flour, because this factor varies with the quality and percentage extraction of the wheat and with the time of storage. Flour recently milled from good wheat shows 0·03 to 0·04 per cent. of acid as H_2SO_4, but, after storage, the figure may rise to 0·05 per cent. and, in the case of old flours, it may even be 0·125 per cent. and the flour still be quite capable of making sound bread, although inferior to that from a flour of normal acidity. To judge of the quality of flour the acidity should be considered in conjunction with the diminution in fat content and the increase in soluble nitrogen, and with the gluten content. The acidity is best estimated by extracting the flour for a day with 90 per cent. alcohol, decanting the alcohol and titrating with 0·02 *N* alcoholic potassium hydroxide solution, with the use of 5 drops of a 10 per cent. tincture of turmeric as indicator. Phenolphthalein does not give a satisfactory end-point in alcoholic solutions, and when water is used for the extraction of the flour the acidity is found to increase indefinitely with the time of maceration. H. E. C.

Characteristics of Wheat Starch. T. E. Wallis. (*Pharm. J.*, 1922, **109**, 82.)—The larger grains of wheat starch vary in diameter from 15 to 45 microns, whilst those of barley starch do not exceed 40 microns, and this difference may serve to identify wheat starch in admixture with barley starch. By mixing weighed amounts of lycopodium spores and wheat starch prepared in the laboratory, and making microscopic counts of the mixture suspended in olive oil (ANALYST, 1919, **44**, 321; *Pharm. J.*, 1921, **108**, 48) the author has estimated the number of grains of 40 microns and over to be 392 in 1 mgrm. of the dry starch, and the proportion of these to the total number of starch grains present was approximately 1 in 5500. Examination in a similar manner of commercial wheat starches gave 622 and 569 as the number of grains not less than 40 microns per mgrm. of starch. The number of larger grains present is readily increased by suspending the starch in water and decanting the liquid several times at intervals of an hour. In the quantitative analysis of mixed flours it is necessary for the analyst to prepare his own specimens of pure starches by a standardised process, and to treat the mixture under examination by the same process in order to obtain comparable results. Increased accuracy may be obtained by mixing similar pure starches in the proportions found, and correcting the first result by using as a standard the number of large grains found in starch prepared from the mixture of known composition. The author has not determined whether the proportion of large grains present is the same in different varieties of wheat. T. J. W.

Depolymerisation Product of Potato Starch. A. Pictet and R. Jahn. (*Helv. Chim. Acta*, 1922, **5**, 640–644.)—When potato starch is heated with 10 parts of glycerin to 190° C., a clear solution is obtained; the liquid, on being kept for about 45 minutes at 200°–210° C., ceases to produce any coloration with iodine solution. If, then, most of the glycerin is eliminated by distillation *in vacuo* (2 to 4 mm.), care being taken not to raise the temperature further, a pale yellow, vitreous, transparent mass remains. This is dissolved in water, and the solution is filtered to remove a very slight brown precipitate, concentrated to a syrup on the water-bath, and triturated with alcohol to remove the last of the glycerin. The resulting white, amorphous powder is purified by repeated solution in water, followed by precipitation with alcohol. The yield reaches 90 per cent. of the starch taken. Analysis and cryoscopic determination establish the formula $(C_6H_{10}O_5)_3$, but the compound is not identical with triamylose or isotriamylose; it has been given the provisional name *trihexosane*. It is easily soluble in water and in pyridine, and is soluble in warm dilute acetic acid, from which it deposits, on cooling, as an amorphous powder. It decomposes at 230° to 232° C., without fusion; $[\alpha]_D = +162{\cdot}2°$. It does not reduce Fehling's solution; heated with dilute sulphuric acid, it is converted into dextrose. A nono-acetate has been prepared.

W. R. S.

Foods for Diabetics. E. M. Bailey. (*Connecticut Agric. Exper. Stat.*, 1922, *Bull.* **236**, 235–247.)—Fifty-one samples of foods, either specially manufactured for diabetic patients or used by them, were analysed, including soya bean bread, prepared in the laboratory and dried dahlia tubers. The following results are typical of those obtained:

	Moisture Per Cent.	Ash Per Cent.	Nitrogen Per Cent.	Protein N×6·25 Per Cent.	Protein N×5·70 Per Cent.	Fibre Per Cent.	N-free Extract Starch Per Cent.	N-free Extract Sugar as Dextrose Per Cent.	N-free Extract Other N-free Extract Per Cent.	Ether Extract Per Cent.
1. Gluten bread	35·29	1·65	6·52	—	26·16	0·30	22·78	1·01	6·84	5·97
2. Starchless breakfast food	10·39	2·06	0·32	2·00	—	4·16	64·13	6·72	10·33	0·21
3. Cassava cakes	10·42	2·16	0·28	1·75	—	4·83	66·77	2·76	11·08	0·23
4. Soya bean bread	37·70	5·88	5·38	21·75	—	0·88	3·70	2·52	9·53	18·04
5. Croustils, glutenised	7·88	1·50	4·84	30·25	—	0·46	44·55	5·36	3·29	6·71
6. Allison flour (cotton seed)	6·65	6·20	8·07	50·44	—	4·83	0·56	8·25	15·18	7·89
7. Bread of gluten	10·11	2·71	10·78	—	61·45	0·51	9·96	1·24	8·04	5·98
8. Aleurone bread	7·00	2·81	12·07	—	68·80	0·21	6·51	0·15	8·23	6·19
9. Special diabetic bread	7·01	2·91	10·48	—	59·74	0·57	16·12	1·52	5·38	6·75
10. Washed bran	9·13	—	1·79	11·19	—	—	4·59		—	7·39
11. Bran muffins	28·41	—	1·33	8·33	—	—	4·76		—	6·11
12. Bran muffins (edible portion)	41·51	6·50	1·00	6·26	—	6·72	1·54	4·83	27·03	5·61
13. Cellu biscuit	29·31	—	0·48	3·00	—	—	4·76		—	11·81
14. Passover bread	7·04	0·60	2·38	14·88	—	0·38	70·46	—	6·64	0·37
15. Dahlia tubers, dried	2·13	7·97	3·12	19·50	—	8·55	60·50			1·35

The samples bracketed together were made by the same firm. Three samples of gluten bread, typified by No. 1, were remarkably uniform in composition, and showed a substantial reduction in carbohydrates as compared with ordinary wheat bread. The success of this, or any other bread for diabetics, will entirely depend on the patient's carbohydrate tolerance. Cassava breakfast food and cakes (Nos. 2 and 3) contained about 70 per cent. of available carbohydrate, over 90 per cent. of which was starch with the microscopic characteristics of cassava starch. To label these products "starchless" is utterly deceptive. The experimental soya bean bread was palatable, and showed a low content of available carbohydrate. Assuming the glucose yield of soya bean protein in metabolism to be equal to that of wheat protein, it would require about 2 parts of this bread to yield the same amount of glucose in metabolism as 1 part of ordinary wheat bread. The glutenised "Croustils" (No. 5) are advertised as being recommended or prescribed for diabetic patients, but the analysis showed that this product contained more than 50 per cent. of starch and reducing sugars. It would appear from the guarantees of aleurone, "essentiel" gluten, and special diabetic breads (Nos. 7, 8 and 9) that they are designed to represent 3 classes of carbohydrate tolerance, viz. 10, 20 and 30 per cent. In the main, the claims were justified by the analyses, except that aleurone bread contained 15 to 20 per cent. of carbohydrates, instead of 10 per cent. Samples 10 to 13 were prepared from washed bran or "cellu" flour as the basic constituent. The Cellu Products Company has published a number of recipes for making non-nutritive "foods" in which the "fatty" constituent is mineral oil. The saponification values of the ether extracts of various "cellu" products ranged from 3·2 to 10·5, and that of the bran products from 8·0 to 12·8. The ether extracts from bran muffins gave a saponification value of 90·1, whilst that from washed bran alone had a value of 152·7. It is obvious, therefore, that the ether extract should be practically disregarded in calculating the energy value of most of these products. Probably the nearest approximation to the true value can be obtained by including in the formula for calculating calories the nitrogen expressed as protein, carbohydrates represented by starch and soluble reducing sugars, and not more than 10 per cent. of the "fat," except in the case of bran muffins, where 60 per cent. might be included. Calculated in this way, the energy values ranged from 50 to 100 cals. per 100 grms. Inclusion of all the nitrogen-free extract in the calculation, in the conventional way, increased these values by 100 to 150 calories. The Passover cake (No. 14) was said to be made from a gluten flour, but contained as much starch as ordinary wheat bread.

A further distribution of the nitrogen-free extract of dahlia tubers (No. 15) gave the following results:

	Per Cent.
Soluble in hot water before hydrolysis, as lævulose	1·68
,, ,, ,, after hydrolysis, as inulin	49·18
Direct acid hydrolysis of water-insoluble residue, as dextrose ..	4·92
Total nitrogen-free extract	60·50
Undetermined nitrogen-free extract	4·72

Thus inulin constitutes about 80 per cent. of the total nitrogen-free extract. Human fæcal extracts contain an enzyme which attacks inulin, with the formation of reducing sugars, and the acidity of the gastric juice is sufficient to hydrolyse it. The apparent utilisation and tolerance of inulin in the body had led to its use, to some extent, in the diet of diabetics, either as an addition to wheat gluten or as a vegetable. Later observations, however, have shown that inulin has little, if any, nutritive value, and that no material amount of lævulose is derived from it. Whatever small proportion of lævulose may be produced by the action of the gastric juice upon inulin will behave in diabetic metabolism in the same way as lævulose from any other source.

Cryoscopy of Milk. E. M. Bailey. (*Connecticut Agric. Exper. Stat.*, 1922, *Bull.* **236,** 251–271.)—The results obtained with 216 samples of genuine milk from (*a*) normal individual cows, (*b*) normal herds, (*c*) healthy cows under abnormal conditions, and (*d*) cows which are diseased or otherwise physically abnormal, were classified, and the following conclusions were drawn:—(1) There is an appreciable, and may be a conspicuous difference in freezing-point depression between morning and evening milk. (2) The minimum depression of −0·530° C., and maximum of −0·566° C. for milk from normal individual cows, and the minimum of −0·530° C. and maximum of −0·562° C. for milk from normal herds is reasonably substantiated by the experience of all the collaborators. (3) Moderate exercise or moderately delayed milking is not reflected in the freezing-point depressions of the milk, whilst long-delayed milkings (9½ to 10½ hours) may or may not be followed by depressions varying from the normal. Severe exercise, strain or fatigue, are followed by materially increased depressions. (4) The milk from tuberculous cows, or those otherwise in poor or abnormal physical condition, has generally fallen within the limits for normal milk. The few exceptions noted have been in the direction of increased depressions.

Casein and Calcium Caseinate. E. M. Bailey. (*Connecticut Agric. Exper. Stat.*, 1922, *Bull.* **236,** 233–234.)—Dietetic casein, for use in the feeding of infants and under-nourished persons, and of diabetic patients, should contain not less than 15 per cent. of nitrogen on the moisture-free basis. Calcium caseinate is also used medicinally in certain disorders. Six samples of pure casein preparations and five of calcium caseinate, including three commercial preparations and one made in the laboratory, gave the following results on analysis:

	Casein.					
	1	2	3	4	5	6
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Moisture	7·89	7·75	8·86	6·40	9·68	6·23
Ash	0·55	0·61	0·52	0·38	0·60	1·30
Fat	0·80	0·40	0·23	1·00	0·50	0·75
Nitrogen	14·08	14·08	13·84	14·36	13·82	14·34
Casein ($N \times 6{\cdot}38$) ..	90·76	91·24	90·39	92·22	89·22	91·72
Lactose	None	None	None	None	None	None
Undetermined	0·93	1·40	2·09	0·62	1·06	0·24
Acidity—c.c. $N/10$ alkali per grm.	10·0	10·5	11·4	10·4	10·0	6·7

CALCIUM CASEINATE.

	Moisture Per Cent.	Nitrogen Per Cent.	Protein (N × 6·38) Per Cent.	Calcium oxide Per Cent.	Phosphoric anhydride Per Cent.	Fat Per Cent.	Moisture-free Nitrogen Per Cent.
No. 4 T.B.O. ..	9·75	13·68	87·28	1·65	1·95	0·43	15·16
Larosan	10·38	13·06	83·31	2·37	1·69	2·36	14·58
Larosan	9·87	13·12	83·71	2·16	1·65	2·57	14·56
Protolac	8·90	12·72	81·15	2·66	1·80	0·75	13·96
Casec	7·60	12·48	79·62	1·50	1·54	2·40	13·50

Determination of the P_H Value of Commercial Glucose as a Substitute for the "Candy" Test. O. A. Sjostrom. (*J. Ind. Eng. Chem.*, 1922, **14**, 941–943.)—When mixtures of commercial glucose, cane sugar and water are heated together, the amount of cane sugar inverted under given conditions depends on the acidity of the glucose; it is found that if more than 8·5 per cent. of invert sugar has been formed the product yields an unsatisfactory "candy." The P_H value of the glucose may be determined by diluting the sample to 22° Bé. and comparing 10 c.c. of this solution with standard citrate mixtures (prepared as described by Clark) after exactly 0·2 c.c. of a 0·02 per cent. alcoholic methyl red solution has been added to each. Tables are given showing that a P_H value of 4·1 to 5·2 corresponds with 8·5 per cent. of invert sugar on the dry substance. In case a product has a higher value than this, the invert sugar should be estimated by means of Fehling's solution before a batch is rejected. W. P. S.

New Oil Nuts from South America. (*Bull. Imp. Inst.*, 1922, **20**, 147–152.)—*Mamarron* (from Columbia): This is a species of *Attalea* closely related to the Corozo palm previously described (*Bull. Imp. Inst.*, 1917, **15**, 479) as *Scheelea* or *Attalea excelsa*, but now thought to be more nearly allied to *Scheelea insignis*. These nuts are larger than the former specimens, and usually contain one kernel, and have shells $\frac{3}{8}$in. thick. They yield fat of higher saponification and lower iodine value, but in general character much like cohune and palm kernel oil. Material is being obtained for a complete identification of the various Corozo palms of Columbia. In the case of the present sample the kernels yielded 69·9 per cent. of oil, which had the following characteristics: Sp. gr. 100°/15° C. 0·8679; melting point, 24·0°C.; melting point of fatty acids, 23·0° C.; acid value, 2·3; saponification value, 250·9; iodine value, 10·8; unsaponifiable matter, 0·4 per cent.; volatile acids: soluble, 8·6; insoluble, 10·8; and n_D^{40}, 1·449. The residual meal, which was free from alkaloids and cyanogenetic compounds, had the following percentage composition: Moisture, 12·6; crude proteins, 22·4; carbohydrates (by difference), 41·3; crude fibre, 11·7; and ash, 5·0; and a nutrient ratio of 1:2·5, with food units 115.

Conejo or Rabbits fruit, probably a new species of *Heisteria*, is also from Columbia. The nuts, made up of 34 per cent. of shell and 66 per cent. of kernel, were larger than those of the usual species of *Heisteria* and yielded 61·2 per cent. of a yellow viscous oil with the following characteristics: Sp. gr. at 15°/15° C.,

0·9940; melting point of fatty acids, below 10° C.; acid value, 4·2; saponification value, 187·8; iodine value, 140·0; unsaponifiable matter, 2·1 per cent.; volatile acids: soluble, 0·2; insoluble, nil; acetyl value, 128; and n_D^{40} 1·502. The oil polymerises after prolonged heating at 200° C., and suddenly decomposes at a temperature between 250° and 285° C. It is not a good drying oil, but might be suitable for rubber substitutes. The residual meal, though of high nutritive value, contains a trace of alkaloid. D. G. H.

Bone Fat and Neats' Foot Oil. H. Eckart. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1922, **44**, 1–29.)—Bone fat extracted by different methods had the following characteristics: Sp. gr. at 50°/30° C., 0·9009 to 0·9034; m. pt., 44° to 45° C.; solidification point, 32·6° to 33·8° C.; acid value, 0·3 to 0·6; saponification value, 189·6 to 195·2; Hehner value, 94·1 to 95·6; Reichert-Meissl value, 0·2 to 1·7; iodine value (Hanus), 49·1 to 51·6; acetyl value, 12·0 to 14·8. *Fatty acids*: M.pt., 42·5° to 44° C.; and mean molecular equivalent, 278·8 to 284·8. Marrow fat gave very similar results.

Samples of neats' foot oil had: Sp. gr. at 50°/50° C., 0·9026 to 0·9049; solidification pt., −2° to +4° C.; acid value, 0·1 to 6·3 (bleached oil); saponification value, 191·8 to 196·2; Hehner value, 93·3 to 96·6; Reichert-Meissl value, 0·4; iodine value, 57·4 to 72·3; acetyl value, 7·7 to 9·8. *Fatty acids*: Melting point, 29·5° to 41·2° C.; neutralisation value, 195 to 202; and mean molecular equivalent, 278 to 288. The average percentage composition of the two materials was as follows:

	Stearic Acid	Palmitic Acid	Oleic Acid	Glycerol	Unsaponifiable matter
Ox bone fat ..	19–21	20–21	53–59	5–10	About 0·5
Neats' foot oil ..	2–3	17–18	74·5–76·5	5–10	0·1–0·5

The unsaponifiable matter consisted of cholesterol.

Adulteration of Oil of Lemon with Terpenes. G. Ajon. (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 389–391.)—The methods used for estimating citral in oil of lemon give, not the citral alone, but all the carbonyl compounds present, calculated as citral; to this result the term "analytical citral" is applied by the author. Of these carbonyl compounds some (citral) react with sodium sulphite in dilute solution to form sulphonic compounds, whilst others (citronellal, methylheptenone) exhibit no such reaction. Oil of lemon adulterated by addition of terpenes and citral will contain more methylheptenone than the corresponding genuine oil, and the added citral will have also the functions of citronellal, so that treatment with sodium sulphite will establish distinct differences between the genuine and the adulterated oil. It is, indeed, found that he first distillates of an oil of lemon adulterated in this way how contents of analytical citral higher than tho e of the corresponding genuine product, and the last distillates, in which more particularly the citral and citronellal are collected, are greatly impoverished in citral by the action of the sulphite reagent. Numerical and graphical results are given in support of these conclusions. T. H. P.

Loss of Morphine on Storage of Powdered Opium. H. E. Annett and H. D. Singh. (*Pharm. J.*, 1922, **109**, 304–305.)—Indian opium which had been dried and powdered by exposure to the atmosphere at a temperature approximating 100° F. was assayed for morphine after storage for periods up to four years. The original morphine content of different samples ranged between 4·9 and 16·3 per cent., but the losses found were fairly constant for different samples stored during the same period. During a period of 4 years the losses varied from 2·5 to 3·2 per cent.; in 3 years from 1·0 to 2·4 per cent.; in 2 years from 1·4 to 2·4 per cent.; and in one year from 0·2 to 0·8 per cent., calculated on the original samples. Thus the original content of morphine had diminished in different samples by 12 to 50 per cent. The analyses were carried out by the method given in the *B. P.* 1914. Opium stored in a moist condition shows no diminution in morphine content, and the loss experienced in the dry state is attributed to the action of oxidising enzymes in the presence of air. T. J. W.

Loss of Morphine in Powdered Opium. C. E. Sage. (*Pharm. J.*, 1922, **109**, 353–354.)—Referring to a paper by Annett and Singh (*see* previous Abstract), the author states that he has frequently found a loss of morphine in dried extract of Turkey opium, compared with the same extract kept in the moist condition. Examination of samples of *Pulv. Ipecac. Co.*, made several months after their preparation, shows that they are usually below strength, which indicates loss of morphine on storage. In some cases shipments of Persian opium have been refused by the purchasers owing to deficiency of morphine, although the same samples gave satisfactory results immediately before and after shipment. Ammonia is liberated when opium is rubbed down with lime and water before analysis, and old samples appear to evolve a greater quantity of the gas than fresh samples. This behaviour indicates that, during storage, morphine and other substances may be decomposed into ammonium compounds. T. J. W.

Alkaloids contained in Extract of Belladonna. A. Goris and P. Costy. (*Bull. Soc. Pharmacol.*, 1922, **28**, 545; *J. Pharm. Chim.*, 1922, **26**, 266.) Belladonna leaves contain a large amount of hyoscyamine in proportion to atropine. The total alkaloidal content is practically the same in extracts made with alcohol and water, but in both cases a rise in temperature in the course of preparation affects the nature of the alkaloids. In the case of the alcoholic extract, the lower the temperature employed the greater the relative proportion of hyoscyamine in the product, until, with evaporation *in vacuo* in the cold, the resulting extract contains approximately the same proportion of hyoscyamine that is found in the original leaves. D. G. H.

Preparation and Racemisation of Hyoscyamine and its Sulphate. A. Goris and P. Costy. (*Bull. Soc. Pharmacol.*, 1922, **29**, 113; *J. Pharm. Chim.* 1922, **26**, 265–266.)—Hyoscyamine may be separated from atropine by taking advantage of their different solubilities in hot and cold benzene, and, similarly, cold absolute alcohol may be used to separate their sulphates. Isolated thus, the

rotatory power of hyoscyamine was found to increase with the diminution of the strength of the alcohol used as solvent. On studying the effect of heat on the racemisation of hyoscyamine it was found that at 100° C. in aqueous solution the sulphate was fairly stable if neutral glass was used, and the base changed little; but after the action of chloroform or water on hyoscyamine the temperature of 100° C. was sufficient to bring about complete isomerisation in course of time. At 106° C. the crystalline base begins to be transformed, and at 113° C. total racemisation takes place readily. D. G. H.

A Reaction of Veronal and Hypnotic Derivatives of Barbituric Acid and its Applications. R. Fabre. (*J. Pharm. Chim.*, 1922, **26**, 241–249.) The hydrogen atom of the –NH groups in veronal and its allies reacts with the mobile hydroxyl group of xanthydrol, in an acetic acid medium, to form dixanthylated derivatives, which can be separated and identified. Thus, if a solution of 1 grm. of veronal and 2 grms. of xanthydrol in acetic acid is boiled for a few seconds and cooled, a crystalline precipitate of a dixanthylated derivative is formed which can be purified by washing with boiling alcohol, and its melting point determined. This reaction is useful to supplement the somewhat inadequate tests given in the French Codex, since it is simple and rapid and is not given by other substances of similar therapeutic value, such as sulphonal. Since veronal and similar hypnotics figure increasingly in cases of poisoning, the reaction is also useful in toxicological investigations. The veronal has first to be isolated from the viscera, and a convenient method is as follows:—From 100 to 150 grms. of material are digested on a water bath for 3 hours with a mixture of 95 per cent. alcohol and 5 grms. of tartaric acid, cooled, filtered and concentrated by distillation. The residue is dissolved in 50 c.c. of distilled water, and after being made slightly alkaline, the solution is shaken up several times with ether to eliminate fatty matter. After acidification with dilute sulphuric acid the liquid is evaporated, and the residue taken up three times with ether, which dissolves the veronal. The residue from the extract obtained is purified by dissolving it in water, heating the solution for half an hour with animal charcoal, filtering and crystallising the filtrate. After several crystallisations the melting point can be determined. Identification by means of the xanthydrol reaction is carried out as follows:—A few cgrms. of veronal are dissolved in acetic acid so as to give an approximately 10 per cent. solution, and xanthydrol is added in the proportion of about twice the weight of veronal taken. The mixture is heated on a water bath for one minute, and left to cool. A crystalline precipitate forms which can be separated after 2 to 3 hours. After the crystals have been washed three times with a small quantity of boiling 95 per cent. alcohol and dried, their m.pt. can be determined. The search for these hypnotic compounds may also be made in the urine, since 60 to 65 per cent. of the veronal absorbed can be found in the urine excreted during the four following days. D. G. H.

Isolation, Assay and Properties of Colchicine. E. C. Davies and J. Grier. (*Pharm. J.*, 1922, **109**, 210–211.)—The isolation of colchicine is best

achieved by extracting powdered colchicum corms with methylated spirit, evaporating the alcohol and dissolving the residue in hot water, after which any oil present is removed by shaking the solution with petroleum spirit (ligroin), and the impure alkaloid is extracted with chloroform. The residue obtained on evaporation of the chloroform is dissolved in hot water, precipitated by phosphotungstic acid in the presence of 2 per cent. of sodium chloride and 0·5 per cent. of hydrochloric acid, and the granular precipitate is filtered off and washed free from salt with 0·1 per cent. hydrochloric acid, after which it is transferred to a separating funnel containing chloroform. Ammonia is then added in slight excess, and the chloroform extract and washings evaporated to dryness. The residue is dissolved in 50 per cent. alcohol, and the solution is evaporated on plates, the pure alkaloid being then obtained. It has a yellow colour, a melting point of 144° C., and is readily and completely soluble in water. Several methods of assaying colchicine were tested by the authors, the results obtained showing that 1 c.c. of 0·05 *N* Mayer's reagent is equivalent to 0·011 grm. of the alkaloid, and that precipitation with phosphotungstic acid in the presence of 2 per cent. of sodium chloride and 0·5 per cent. hydrochloric acid produces a compound containing four molecules of colchicine and one molecule of phosphotungstic acid. The alkaloid may be estimated colorimetrically by the addition of 0·1 *N* alkali, when a greenish tint is produced with solutions of greater concentration than 0·008 per cent. Conversely, colchicine may be used as an indicator with acid and alkaline solutions, the colour given by the acid being inappreciable, whilst the addition of alkali gives rise to a greenish tint. The pure alkaloid has a bitter taste and emits a hay-like odour when damped and gently heated. It is soluble in 22 parts of water, yielding a neutral solution with a lævorotatory action, is readily soluble in chloroform, methyl alcohol, 90 per cent. alcohol, and acetic acid, less soluble in ether, benzene, carbon tetrachloride and amyl alcohol, and is insoluble in petroleum spirit. It is completely extracted from acid solutions by shaking with chloroform, thus differing from berberine. In addition to the usual alkaloidal reactions, colchicine yields a crystalline double chloride with auric chloride, but no precipitate with platinic chloride. Bromine water gives a yellow precipitate soluble in ammonia solution to form an orange-coloured solution. No colour is produced by the addition of ferric chloride, but, on warming, the solution becomes brownish red. By mixing five drops of fuming nitric acid with the same volume of ferric chloride solution and an aqueous solution of colchicine, and heating the mixture to boiling point, a yellow solution, changing to olive green, is obtained which, when shaken with chloroform, imparts a ruby-red colour to the latter. Ether, containing sulphur dioxide, gives a canary-yellow precipitate, and this reaction may be used to detect sulphur dioxide in ether. No precipitate is formed with picric acid, but, on the addition of acid,* a resinous mass is produced. Nearly all of the salts of colchicine are very unstable, being decomposed by water; the tannate was the only stable compound examined. It is a greyish amorphous powder, soluble in excess of tannic acid solution and in hot water or dilute alcohol, but insoluble in cold water. T. J. W.

* Presumably a mineral acid.—EDITOR.

Sulphonated Derivatives of Naturally Occurring Sulphurised Hydrocarbons. C. Pepin and G. Reaubourg. (*J. Pharm. Chim.*, 1922, **26**, 258–261.)—The distillation of bituminous shales yields sulphurised oils of marked therapeutic value, and the disadvantages of insolubility and smell may be overcome by careful sulphonation and subsequent neutralisation with alkali, ammonia solution being generally used. A small proportion of sulphonated derivatives is sufficient to bring the mass into solution, and, since only the non-oxidised sulphur has any real therapeutic value, it is important to sulphonate as little as possible, and only traces of ammonium sulphate should be found in the product. Such sulphonated substances are sold under various names, such as *icthyol, sulphoicthyolate of ammonia*, etc. The non-oxidised sulphur can only be estimated indirectly by Thal's method of subtracting the sulphuric and sulphonic sulphur from the total sulphur. A good icthyol should satisfy the following conditions:—It should be of a brown-red colour, with a smell of mistletoe, and, on evaporation in the oven at 100° C., should give a residue of at least 50 per cent. of the original product. This residue should yield a negligible amount of ash. After precipitation with albumin and hydrochloric acid the addition of barium chloride should give only a slight opalescence (indicating absence of ammonium sulphate). The non-oxidised sulphur, calculated by Thal's method, should be less than 15 per cent. of the dry residue.

D. G. H.

Identification Tests for Neo-arsphenamine. L. Kofler and A. Perutz. (*Wiener. klin. Wochschr.*, 1921, **34**, 504–595; *Chem. Abstr.*, 1922, **16**, 2961–2962.)—Pure neo-arsphenamine gives the following reduction reactions:—Black precipitate with a silver nitrate solution on paper; dirty brown precipitate with Millon's reagent; light yellow precipitate with alcoholic mercuric chloride solution; and black precipitate with Nessler's reagent. Tincture of iodine gives a bright yellow precipitate, and Lugol's reagent (1 of iodine and 2 of potassium iodide in 20 of water) gives a yellow coloration; bromine water produces a reddish-brown precipitate, and ferric chloride solution a violet coloration. On treating a 10 per cent. solution of the drug with a little 3 per cent. hydrogen peroxide the yellow colour of the drug disappears, and, after a few seconds, a red coloration develops. When stronger solutions of hydrogen peroxide (perhydrol) are used the red coloration appears immediately. If the neo-arsphenamine solution is added to the hydrogen peroxide a yellowish-white precipitate, insoluble in excess of the solution of the drug, is obtained.

Bacteriological, Physiological, etc.

Sweetening Power of *p*-Hydroxy Phenylcarbamide Derivatives. C. Speckan. (*Ber. Pharm. Ges.*, 1922, **32**, 83–107; *Chem. Abstr.*, 1922, **16**, 2870–2871.)—In view of the fact that the ethoxy group of dulcin appeared to be the carrier of its sweet taste, experiments were made to determine the effect on the sweetening power of modifying this group by substituting halogen or various

radicles for hydrogen in the terminal CH_2 group. It was found that β-bromo-*p*-phenetylcarbamide or β-bromo-dulcin (m.pt., 162–164° C.) was still very sweet, and more readily soluble in hot water than dulcin. The lowering of the sweet taste in this case is to be attributed to the increase in the molecular weight by the substitution, since Sternberg (Fraenkel's *Arzneimittelsynthese*, 4th Ed.) has shown that halogen cannot depress the sweetening power of a compound. In preparing β-bromodulcin the tasteless by-product $C_2H_4(OC_6H_4NHCONH_2)_2$ was also obtained, and Sternberg's rule, that doubling of the substituted benzene nucleus inhibits the development of physiological properties, was again corroborated. Various attempts to substitute the halogen of bromodulcin by means of ammonia or aliphatic amines yielded only compounds of bitter taste. Experiments were also made to ascertain the effect of disregarding the influence of the ethoxy group and attempting to develop a similar sweetening effect through the union of corresponding groups with *p*-hydroxyphenylcarbamide. Most of the compounds prepared were without taste, but β-hydroxypropyl-*p*-oxyphenylcarbamide (m.pt. 176° C.) had a faintly sweet taste.

Isolation of Muscarine from Amanita Muscaria. H. King. (*J. Chem. Soc.*, 1922, **121**, 1743–1753.)—By extracting 25·5 kilos. of fresh specimens of the fly agaric (*Amanita muscaria*) the author has isolated pure muscarine chloride, and estimation of the physiological activity upon rabbit's intestine and the hearts of toads and frogs during the progress of the preparation showed that this weight of the fungus contained 0·4 grm. of muscarine. The method adopted was briefly as follows: The fresh fungi were immersed in alcohol for two weeks and the extract purified by evaporation, extraction with ether and precipitation with colloidal iron solution and basic lead acetate. The muscarine present in the aqueous extract was removed by successive precipitations with aqueous mercuric chloride, alcoholic mercuric chloride and phosphotungstic acid solutions, 80 per cent. of the base originally present being recovered. The combined precipitates contained choline and muscarine, with other substances, from which the muscarine was separated by fractional precipitation of choline hydrogen tartrate from 95 per cent. alcohol and subsequent fractional crystallisation of the aurichlorides. The gold salt of muscarine finally obtained was in the form of large glistening leaf-like crystals containing 38 per cent. of the metal, whilst the aurichloride of choline showed a gold content of 44 per cent. From the former value the molecular equivalent of muscarine chloride is calculated as 210, this being in agreement with the formula proposed by Nothnagel, viz. $(CH_3)\,NCl{\cdot}CH_2.CH(OH)_2HCl$. The physiological activity of the base obtained was such that 0·002 mgrm. was sufficient to arrest the action of the frog's heart in diastole. Similar reactions are shown by choline and muscarine with phosphotungstic acid, iodine in potassium iodide, and bromine water, but the bases may be distinguished by Mayer's reagent, which yields a crystalline precipitate with choline, but oily drops soluble in excess of the reagent with muscarine. The double salt, platinum choline chloride, forms prismatic or rhombic crystals, whilst the corresponding salt of

muscarine consists of cubes, octahedra or tetrahedra. With aqueous mercuric chloride solution a precipitate is given by choline only. Ergosterol, *l*-leucine, mannitol and fumaric acid were isolated and identified during the progress of this work, but trehalose was not detected. T. J. W.

Urease and Urea in Fungi. A. Goris and P. Costy. (*Comptes rend.*, 1922, **175**, 539–541.)—Urease occurs in all, or almost all, of the *Basidiomycetes* and *Ascomycetes*, and in nearly all the higher fungi, mostly in the hymenium, the proportion present varying widely with different species. When the enzyme is either lacking, or exists in only very small amount, urea is found in varying quantity in the thallophyte, following the vegetative stage. T. H. P.

Coloration of Potato Juice. H. Haehn. (*Zeitsch. Spiritusind.*, 1921, **44**, 253, 277, 286, 325, 330; *Chem. Abstr.*, 1922, **16**, 2875.)—The enzymic conversion of tyrosin into the dark product, melanin, appears to be a common occurrence in animal and vegetable tissues. The tyrosinase of potatoes is most active in media neutral to litmus; its action is inhibited by the addition of free acid or alkali, but not of potassium dihydrogen phosphate in sufficient quantity to make the liquid acid to litmus. The tyrosinase can be freed from activating salts by dialysis; it then becomes almost inactive towards tyrosin, but its activity is restored by adding the separated salts. Much greater activation is produced by the addition of a single salt of certain metals, notably calcium, strontium, barium, magnesium, zinc and cadmium. In general, the reaction on tyrosin produces a succession of colour changes, passing through pink, red, reddish-brown, violet, and dark blue, to black, these colorations probably being due to differences in the size of the melanin particle. If a solution containing red melanin is boiled it becomes black. It is suggested that the formation of melanin takes place in the following stages: Conversion of tyrosin into *p*-hydroxyphenylacetaldehyde by elimination of carbon dioxide, ammonia and hydrogen; introduction of a further hydroxyl group into the benzene nucleus; condensation of the previously liberated ammonia; and oxidation, to form dihydroxy-indigo or melanin. The organic component of tyrosinase thus probably contains several enzymes, including a phenolase, an amino-acidase, and an unknown condensing enzyme.

Fermentation of Pentoses by Moulds. W. H. Peterson, E. B. Fred and E. G. Schmidt. (*J. Biol. Chem.*, 1922, **54**, 19–34.)—The authors have cultivated 25 species of moulds at 28° C. in a synthetic medium containing equal volumes of a 4 or 8 per cent. solution of sugar and a mixture composed of molecular solutions of ammonium nitrate 250 c.c., monobasic potassium phosphate 100 c.c., magnesium sulphate 40 c.c., ferric chloride 2 c.c., and water 608 c.c. At intervals estimations were made of the sugar remaining in solution, the weight of carbon dioxide produced, and the weight of the mould culture after removal of the salts and drying at 100° C. No alcohol or volatile acid was formed by the cultures, but traces of a non-volatile acid were extracted from the medium by means of ether, the amount obtained being insufficient for identification. Rapid fermentation of the pentoses was produced by sixteen of the species examined, the most

active belonging to the *Aspergillus* and *Penicillium* groups. Among the species exhibiting slow fermentation were the *Mucors, Rhizopus nigricans* and *Cunninghamella*. It is suggested that this difference may be of value in the classification of the fungi. Very little difference was shown in the rates of fermentation of the two pentoses, and from 88 to 98 per cent. of the carbon contained in the sugar was recovered in the carbon dioxide and the mould substance produced. Cultures of *Aspergillus niger* produced a volatile substance which caused darkening of the sulphuric acid used for drying the evolved carbon dioxide, but this substance was not formed by *Penicillium glaucum*. T. J. W.

Bacterial Food Poisoning from Mutton. W. A. Young and G. D. Dawson. (*Lancet*, 1922, **203**, 608–609.)—In May of this year there was a limited outbreak of food poisoning in Manchester, in which 25 persons belonging to six separate households were affected. In each instance the illness was traced to mutton, or meat which had probably been in contact with the mutton, from the same retailer, but there was no evidence to show how the mutton first became infected. A bacillus of the Gaertner group was isolated from the remains of a leg of mutton, and from the tissues and secretions of a man who had died after eating some of the mutton. This bacillus had the general cultural characteristics of the inosite-fermenting food-poisoning bacteria, and was identified, by the method of "absorption of agglutinins," as a strain of *B. suipestifer* (or *aertrycke*) type mutton, the organism most commonly responsible for food poisoning in man.

Detection of Blood. P. N. van Eck. (*Pharm. Weekblad.*, 1922, **59**, 1098–1100.)—The well-known blue coloration given by blood with benzidine and hydrogen peroxide is not specific, since many other substances give a similar coloration with the reagent. If, however, blood is subjected to dry distillation, a tarry distillate is obtained which still gives the reaction strongly, whereas other organic substances examined (egg albumin, feathers, leather, hair) give a distillate which does not react in this way. Apparently the substance formed from the blood is a decomposition product, since the tarry distillate, when dissolved in glacial acetic acid, does not show the blood spectrum. The reaction is given by fæcal matter containing blood, but not by fæcal matter free from blood or by the organic substances normally present in fæces. When blood is burned in a stove the products of combustion give the reaction, whereas the distillates from anthracite, soft coal, wood or peat give a negative result. Of course, if the substance containing blood has been completely calcined, the residue does not give the benzidine reaction.

Comparison of the Benedict and Folin-Wu Methods for Blood Sugar Estimations. F. A. Csonka and G. C. Taggart. (*J. Biol. Chem.*, 1922, **54**, 1–3.)—Separate samples of blood were divided into two portions, one of which was precipitated by picric acid, as in the Benedict method (*J. Biol. Chem.*, 1918 **34**, 203), the other being treated with tungstic acid according to the method of Folin and Wu (ANALYST, 1920, **45**, 227). Each filtrate was then analysed by the two methods, a small volume of the Benedict picric-picrate solution being added

to the standard dextrose solution for the Folin-Wu estimation, when necessary. The results obtained by the latter method with both filtrates were in excellent agreement, but higher values were obtained with the Benedict method when the tungstate filtrate was used, and still higher values with the same method when the picric filtrate was used. The authors conclude that the discrepancies are due to the presence of a substance other than dextrose which is capable of reducing picric acid, but is without effect upon the Folin-Wu copper solution, and that more reliable results are given by the Folin-Wu method. T. J. W.

Hydrogen Ion Concentration of Human Saliva. H. E. Starr. (*J. Biol. Chem.*, 1922, **54**, 43–64.)—The saliva was collected beneath the surface of neutral petroleum oil, to avoid loss of carbon dioxide, and 1 c.c. was transferred to a test-tube containing 9 c.c. of freshly-boiled water and 1 c.c. of 0·01 per cent. brom-thymol blue solution covered with a layer of oil. After being mixed by means of a glass rod until the aqueous liquid was of uniform tint, the colour was compared with that of a series of standards prepared with 0·0667 M solutions of primary potassium phosphate and secondary sodium phosphate, successive standards differing by 0·1 P_H. An opal background was employed in order to overcome the opalescence of the saliva. The effect of dilution of saliva with from 5 to 15 volumes of water is to increase the P_H value by approximately 0·0275. Examination of over 600 specimens of normal healthy saliva showed 86 per cent. to have P_H values between the limits of 6·35 and 6·80, the mean value being 6·60. The effect of various physiological and pathological factors upon the P_H value of the saliva is shown by tables and curves. T. J. W.

Agricultural Analysis.

Estimation of Acids in Silage. W. Zielstorff and F. Benirschke. (*Chem. Zeit.*, 1922, **46**, 939.)—For the estimation of the acidity of silage a large sample should be taken to avoid errors due to moulds: One hundred grms. of the chopped silage are boiled with water for three hours under a reflux condenser, cooled, made up to 2 litres, and the liquid filtered. A cloth filter is more convenient than paper. For the estimation of the total acid, if the solution is not of too dark a colour, a part of it is simply diluted and titrated with 0·02 *N* sodium hydroxide solution, phenolphthalein being used as indicator; the solution to be titrated must be hot to eliminate the effect of carbon dioxide. Many silages, however, give a dark coloured filtrate which cannot be thus titrated; if animal charcoal is used as a decolorising agent the results are unsatisfactory. The best method is to boil 100 c.c. of the filtrate with kieselguhr for one minute under a reflux condenser, refilter through a pleated paper, and take an aliquot part for the titration. Other indicators tried proved unsatisfactory. For the estimation of the free volatile acids, 200 c.c. of the filtrate are subjected to steam distillation until a drop of the distillate tested with Congo-red is shown to be free from acidity. The amount it is necessary to collect depends upon the pressure of steam employed,

but may be about 200 c.c. No satisfactory method is given for the estimation of the combined volatile acids; they cannot be accurately estimated by steam-distillation after acidification with sulphuric or phosphoric acid, as some of the acid is apparently carried over with the steam, even after prolonged distillation and with the use of a dephlegmator. H. E. C.

Organic Analysis.

Estimation of Carbon and Hydrogen by means of the Sulphuric-Chromic Mixture. L. J. Simon and A. J. A. Guillaumin. (*Comptes rend.*, 1922, **175**, 525–527.)—In the case of compounds which are burnt completely by chromic acid, it is possible, by a simple modification of the process (ANALYST, 1922, 405), to estimate the hydrogen as well as the carbon. About 0·1 grm. of the substance is heated for four minutes at 100° C. with a known amount, in excess (1·5–2 grms.) of potassium bichromate, the volume of carbon dioxide formed being measured. The residue is made up to a definite volume and the residual bichromate determined in an aliquot part by treatment with ferrous sulphate and titration of the excess of the ferrous salt with permanganate solution. In calculating the results, two cases arise according as the compound contains excess of hydrogen or excess of oxygen over that corresponding with the type, $C_m(H_2O)_n$. With metallic salts it is necessary also to determine the proportion of the metal, or, more accurately, of its oxide. The method is applicable to di-acids with linear chains and to their methyl esters, to all derivatives of the sugar group not containing a methyl group united to carbon, to aromatic acids, and to phenols not substituted in the nucleus by methyl, ethyl, etc. T. H. P.

Estimation of Oxygen in Organic Compounds. H. ter Meulen. (*Chem. Weekblad.*, 1922, **19**, 191–192.)—The oxygen in an organic compound can be converted quantitatively into water by heating the substance in a current of hydrogen in the presence of nickel as catalyst. The compound is heated in a clear quartz tube, and the products of dry distillation first formed (carbon monoxide and dioxide, methane and water), are passed over nickel-asbestos heated to 350° C. If the catalyst has been recently prepared the whole of the oxygen will be converted into water, but if it has been used several times part of the carbon dioxide will not be reduced. In such cases, however, the carbon dioxide may be absorbed by means of soda-lime and the oxygen calculated from the increase in the weight. Direct estimation by this method of the oxygen in succinic acid, phenol, sucrose and ethyl alcohol gave results agreeing within 0·5 per cent. with the theoretical amounts.

New Accelerator for the Destruction of Organic Matter in the Kjeldahl Process. M. Sborowsky. (*Ann. chim. anal.*, 1922, **4**, 266–267.)—It is found that mercurous iodide has a remarkable effect in accelerating the destruction of the organic matter by sulphuric acid in the Kjeldahl process. In the presence of this iodide the oxidation proceeds several times as quickly as when mercury

alone is used, or from five to ten times the amount of carbohydrate matter can be dissolved in the same time. The subsequent procedure is the same as when mercury is used (decomposition of the mercury salt with hypophosphite, followed by distillation with excess of solution of sodium hydroxide). H. E. C.

Role of Hydrogen Ion Concentration in the Precipitation of Colloids. H. V. Tartar and Z. J. Gailey. (*J. Amer. Chem. Soc.*, 1922, **44**, 2212–2218.)—An experimental study was made of hydrogen ion concentration as a factor in the precipitation of suspensoids. , Suspensions of mastic and gamboge were coagulated by minimum additions of various acids and their ammonium and potassium salts, the liquid allowed to stand for 24 hours, and the hydrogen ion concentration in the clear solution determined electrometrically. The data secured prove that each solution is precipitated by acids at a definite hydrogen ion concentration, regardless of the concentration of the colloid, the negative ion being without effect. Widely varying amounts of the ammonium and potassium salts are required for coagulation, and the hydrogen ion concentration of the supernatant liquids varies considerably (*e.g.* $P_H = 4{\cdot}3$ to $8{\cdot}0$ for potassium salts with the mastic solution). The various salts coagulate the solutions at the same concentration if the hydrogen ion concentration is kept approximately constant by suitable addition of acid. Further work is in progress. W. R. S.

The Petrological Investigation of Brown-Coal. R. Potonié. (*Chem. Zeit.*, 1922, **46**, 810.)—Petrological investigation of brown coal disproves the hypothesis that coal has its origin in lignin. Traces of the lignified portions of plants are sometimes found in brown coals as in lignites, but such are accidental, and are not found in the mass of typical brown coals, which owe their origin to moorland weeds. In the formation of coal from the lignified portions the so-called lignin is changed into soluble humus, the cellulose being meanwhile unchanged; then, after further decomposition, the cellulose begins to turn into coal. Pure cellulose (a small proportion in the form of originally lignified elements) can be isolated by maceration from brown coal or lignite, and can be estimated by means of chlorozinc iodide solution or iodosulphuric acid. Pure cellulose has also been found in bituminous brown coal in which the lignifying substance has completely disappeared and coal formation from the cellulose has begun. Many intermediate products occur between lignites and natural fossil celluloses. H. E. C.

Coke Residue Test for Creosote Oils. C. S. Reeve and F. W. Yeager. (*J. Ind. Eng. Chem.*, 1922, **14**, 966–967.)—Concordant results cannot be obtained by coking the oils in glass bulbs according to the method prescribed by the *American Society Testing Materials*, Standard D–38–18, mainly owing to the difficulty of controlling the rate of distillation and to the quality of the glass; if the glass is not very hard it cannot be heated sufficiently to ensure complete coking. It is therefore recommended that the creosote oil be first subjected to retort distillation, and the residue boiling above 355° C., then heated in a platinum crucible under

the conditions given for estimating fixed carbon (*Amer. Soc. Testing Materials*, D-22-16). The procedure is simple, and the results are sufficiently accurate to offer comparable values. W. P. S.

New Reaction of Quinones. R. Pummerer. (*Chem. Zeit.*, 1922, **46**, 883–884.)—Quinones may be phenylated in the presence of aluminium chloride and azobenzene in a manner similar to that described by the author for benzene (*cf. J. Chem. Soc.*, 1922, **122**, i. 24); the presence of hydrogen chloride is unnecessary. The final reaction may be thus represented:—Three quinone + 2 benzene = 1 diphenylquinone + 2 hydroquinone; but is not a true case of the Friedel-Craft reaction. When benzene, or better, toluene, anethole, or phenol, is added to the quinone, there is produced a 2:5-diarylquinone which is in the form of a beautifully crystalline yellow or red stable substance, which gives no free iodine with hydrogen iodide, and forms, with sodium hydrosulphite and sodium hydroxide, a colourless vat-dye which is sensitive to air. Ditolylquinone is dimorphic, existing in a red and a yellow form; light turns it yellow, and heat turns it into the red variety. H. E. C.

Estimation of Anthraquinone. P. A. Nelson and C. E. Senseman. (*J. Ind. Eng. Chem.*, 1922, **14**, 956–957.)—The method proposed consists essentially in reducing the anthraquinone to the red compound known as oxanthranol by means of zinc dust in 5 per cent. sodium hydroxide solution; the red coloured solution is then filtered under reduced pressure, and the filtrate is titrated with permanganate solution. Half a grm. of the finely powdered sample is mixed thoroughly with 4 grms. of zinc dust, the dry mixture is transferred to a beaker, 100 c.c. of boiling 5 per cent. sodium hydroxide solution are added, and the mixture is kept at 95° C. for five minutes. The filter tube consists of a glass tube 3·5 cm. in diameter and 24 cm. long, and the lower end is drawn out to form a tube about 5 mm. in diameter. A perforated filter plate at the bottom of the filter tube supports a layer of asbestos, and a piece of brass gauze is placed over the asbestos and kept in place by indenting the wall of the tube. The stem of the tube is connected with a three-way tap, one arm of which reaches to the bottom of a receiver; the other arm of the tap is connected with a burette containing potassium permanganate solution. The tube is surrounded by an electrical heater and is provided with a stirrer. Boiled water is poured into the tube and drawn through into the receiver, and the air is then exhausted from the receiver as completely as possible. The mixture in the beaker is now transferred to the filter tube, in which it is stirred and kept at 95 C., and the liquid portion is then drawn through the filter into the receiver, care being taken that no air enters. Three or four additions of sodium hydroxide solution are made to the filter tube in order to reduce any remaining anthraquinone; the reduction is complete when no more red solution is formed after heating and stirring for about five minutes. The contents of the receiver are then titrated with the permanganate solution; this is admitted through the three-way tap, and after each addition, a small quantity of sodium hydroxide solution is admitted from the filter tube so as to wash out permanganate solution from the tube below

the tap. The permanganate solution is standardised against pure anthraquinone after this has been reduced under similar conditions. The presence of phenanthraquinone does not interfere with the estimation of anthraquinone. W. P. S.

Detection of Pyridine. F. Lehner. (*Chem. Zeit.*, 1922, **46**, 877.)—The test is based on the fact that pyridine, when mixed with aniline and cyanogen bromide, forms α-anilidophenyldihydropyridine bromide. When an aqueous solution of pyridine is treated with a drop of aniline, and then with a trace of fresh cyanogen bromide, a red coloration and a crystalline precipitate immediately appear. The reaction will detect as little as 1 in 350,000 of pyridine, but in such dilute solutions a yellow colour is produced which turns red, and the liquid deposits oily drops after about two days. H. E. C.

New Indicators for Alkaloids. W. J. McGill. (*J. Amer. Chem. Soc.*, 1922, **44**, 2156–2160.)—The Sörensen values of certain alkaloidal salts were determined by the potentiometer method, and test analyses were made with the indicators whose optimum value for the indicator function lies closest to the ascertained value. The Sörensen value of *quinine hydrochloride* is 5·96 to 6·01, that of *cinchonine hydrochloride*, 5·71 to 5·77. As methyl orange shows the most pronounced colour change at P_H4·0 to 4·2, and methyl red at P_H5·4 to 5·6, the results obtained with these indicators are too high. Bromocresol purple, on the other hand, (P_H =6·0) gives slightly low, but more satisfactory results. *Morphine hydrochloride* (P_H 3·98 to 4·00) is usually titrated with cochineal or methyl red (P_H 5·4 to 5·8), hence results are always low (average 1·4 per cent.). The titration of known quantities in presence of bromophenol blue shows good agreement (0·5 to 0·1 per cent.). The remarks on morphine apply also to *atropine* (P_H 3·8 to 3·84), for which bromophenol blue is recommended. *Strychnine hydrochloride* (P_H 5·42 to 5·45) reacts best with methyl red. W. R. S.

Inorganic Analysis.

Estimation of Lead in Lead Amalgam. M. G. Mellon. (*J. Amer. Chem. Soc.*, 1922, **44**, 2167–2174.)—A weighed quantity of amalgam, containing up to 0·4 grm. of lead (which must be in actual solution in the mercury) is covered with water containing one drop of ten per cent. acetic acid, and stirred for at least 30 minutes with 10 c.c. of a 1·0 *M* solution of copper nitrate. The liquid is filtered to eliminate any copper undissolved in the mercury; another drop of acetic acid is added to the filtrate, in which the lead is precipitated under the usual conditions with potassium dichromate. W. R. S.

Reductions with Cadmium and Lead in Volumetric Work. W. D. Treadwell. (*Helv. Chim. Acta*, 1922, **5**, 732–743; 806–818; *cf.* ANALYST, 1921, **46**, 342.)—*Uranium*: When uranyl sulphate solutions are reduced with zinc in Jones' reductor, prior to titration with permanganate, reduction proceeds slightly beyond the tetravalent state. If the reduced solution is allowed to flow, drop

by drop, into an open vessel, the trivalent uranium oxidises spontaneously to the tetravalent state, and stoichiometric results ensue. In the cadmium reductor (7 cm. column; acidity about 3 *N*), the action still proceeds beyond the desired stage, but to a less extent, and the reduced solution re-oxidises as it drops into a beaker, all the uranium being then present in the tetravalent state; the solution should be titrated immediately after the washings have passed the reductor. The process was carefully checked against a gravimetric method and found to be accurate within the limits of experimental error. Electrometric titration of a solution containing uranous and ferrous sulphates gives a curve showing two well-defined breaks, one of which corresponds to the complete oxidation of each metal. *Titanium* can likewise be titrated electrometrically in presence of iron by treatment in the cadmium reductor (8 cm. column), followed by titration with 0·1 *N* dichromate solution. If the relative quantity of titanium is very small, the solution is reduced with sulphur dioxide and cautiously treated with ammonia until a permanent precipitate (containing all the titanium) is obtained. This is filtered off and dissolved in sulphuric acid, and the solution is reduced and titrated electrometrically. A solution of titanium sulphate free from iron can be accurately titrated by reduction in the cadmium column and titration with permanganate until the pink end-point is obtained. *Vanadium* is quantitatively converted into V_2O_2; the whole operation must be conducted with careful exclusion of air. *Indigo* is completely reduced to indigo white, the electrometric titration of which by ferric chloride forms an accurate method of estimation: $C_{16}H_{12}N_2O_2 + 2FeCl_3 = 2HCl + 2FeCl_2 + C_{16}H_{10}N_2O_2$. The indigo is dissolved in sulphuric acid (monohydrate) at 70° C. and the solution diluted to 0·05–0·01 *N* indigo strength and 0·2–0·5 *N* acidity. An aliquot portion is poured, drop by drop, through a 7 to 8 cm. cadmium column, followed by boiled acidulated water, the whole apparatus being fil'ed with carbon dioxide. A platinum electrode is suspended in the solution; the external electrode consists of a silver wire dipping into a suspension of silver chloride in dilute sulphuric acid. The end-point is marked by a sudden drop in the potential. Thioindigo is titratable, after the same treatment, with ferric chloride; methylene blue, with ferric sulphate. *Chlorate* in dilute sulphuric acid solution is easily reduced to chloride in the cadmium reductor. The action of sulphuric acid on cadmium being less pronounced than on zinc, chlorate can be accurately estimated in presence of perchlorate by cadmium reduction and subsequent titration of the chloride by Volhard's method. The estimation of *perchlorate* is effected by boiling the solution, containing 25 per cent. of sulphuric acid and titanium sulphate equivalent to 2·5 millimols per 5 of perchlorate, with finely divided cadmium for at least 30 minutes under reflux. After cooling, the solution is diluted slightly, filtered, carefully treated with permanganate to oxidise any titanous salt, and titrated by Volhard's method. *Columbium.* Solutions of columbic acid prepared with addition of succinic acid, according to Metzger and Taylor's directions (*J. Soc. Chem. Ind.*, 1909, **28**, 818) are unstable, as they deposit a white precipitate on standing. Also, the reducibility of the solutions decreases with increasing age or dilution. It is concluded that columbic acid is present

partly in colloidal solution, and this would explain the irregular results obtained by titrating the reduced solution, since only the dissolved columbic acid would be reduced on passing through the zinc or cadmium column. Concordant results are obtained, however, when the columbium solution is reduced together with measured amounts of titanic sulphate, ammonium molybdate, or vanadate solution. Columbium fluoride dissolved in strong hydrochloric acid (*cf.* ANALYST, **1915, 40,** 204), and reduced in the cadmium column, gives concordant results by permanganate titration in presence of manganous sulphate, also by electrometric titration with ferric chloride. Free hydrofluoric acid prevents the reduction. *Molybdenum* in the form of ammonium molybdate is reduced quantitatively to the trivalent state when the solution, strongly acidified with hydrochloric acid, is passed through a lead reductor. The reduced solution is received in an atmosphere of carbon dioxide and titrated with permanganate, manganous sulphate being present. *Tin.* Stannic chloride in strongly acid, boiling hot solution is quantitatively converted into stannous chloride when passed through two reductors, the upper containing a 3 cm., and the lower an 8 cm., column of lead sponge. This is prepared by precipitating a strong solution of lead acetate with zinc, washing the sponge with water, alcohol, and ether, and drying it *in vacuo.* W. R. S.

Estimation of Arsenic. G. R. Lynch. (*Lancet,* 1922, **203,** 629–630.)—An outline is given of the different methods of estimating arsenic, more especially in tissues. To obtain the arsenic in a suitable form for the Marsh test, the tissue is heated with nitric acid, the dry residue gently charred with sulphuric acid, heated and extracted with hot water, and the extract filtered, reduced with sulphur dioxide (the excess of which is removed by boiling) and concentrated to 25–50 c.c. Objection has been taken to the use of the electrolytic method devised by Thorpe, on the ground that the platinum electrodes may alter in their sensitiveness, with the result that mirrors of different size may be obtained from solutions containing the same amounts of arsenic. This change, however, is not a sudden one, and controls by means of fresh standards may be made from time to time. The sensitiveness of the platinum poles may be improved by passing the current through the apparatus reversed. Lead electrodes are more sensitive than those of platinum, but the objection to their use is that the lead may possibly contain traces of arsenic. The amount of arsenic is always evenly distributed throughout an organ such as the liver, and the intestines are the only parts in the body in which the content is liable to variation, this naturally occurring when the dose of arsenic is passing through the alimentary canal.

Influence of Alkali Metals on the Ferrocyanide Titration of Certain Metals. W. D. Treadwell and D. Chervet. (*Helv. Chim. Acta,* 1922, **5,** 633–639.)—The influence of the presence of various alkaline chlorides on the composition of the precipitated ferrocyanides of three heavy metals was investigated electrometrically. *Cadmium* yields precipitates of the composition $CdRb_2Fe(CN)_6$ and $CdCs_2Fe(CN)_6$; the corresponding potassium compound can be obtained only in very dilute solution, and with higher cadmium concentrations the precipitates

contain more cadmium. Titration with sodium ferrocyanide in neutral solution yields $Cd_2Fe(CN)_6$. *Zinc* solutions titrated with potassium ferrocyanide show a sharp end-point at the stage $Zn_3K_2[Fe(CN)_6]_2$. With sodium ferrocyanide, $Zn_2Fe(CN)_6$ is obtained, but $Zn_3K_2[Fe(CN)_6]_2$ and $ZnCs_2Fe(CN)_6$ are formed when the respective chlorides are present in the solution. A neutral *lead* solution gives, with potassium ferrocyanide, a sharp end-point corresponding to $Pb_2Fe(CN)_6$; rubidium chloride has no effect, but cæsium chloride induces formation of $Pb_3Cs_2[Fe(CN)_6]_2$. The results are connected with the different atomic volumes of the reacting metals. W. R. S.

Separation and Estimation of Cobalt. H. H. Willard and D. Hall. (*J. Amer. Chem. Soc.*, 1922, **44**, 2219–2226, 2226–2231, 2237–2253.)—A detailed and lengthy account is given of a process based on the precipitation of cobalt by phenylthiohydantoic acid. W. R. S.

Estimation of Titanium in Ferrous Products. L. Losana and E. Carozzi. (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 394–396.)—The method described depends on the oxidation of titanous compounds to the titanic state by means of methylene blue (*cf.* Ferrari, ANALYST, 1921, **46**, 66), which is found to be unaffected by the other usual components of irons and steels. Convenient concentrations of the methylene blue solutions are 3·9 and 1·95 grms. per litre, corresponding with about 0·001 and 0·0005 grm. of titanium per c.c.; the exact titre is determined experimentally.

With steels and cast irons, which rarely contain as much as 1 per cent. of titanium and are attackable by acids, 2 to 5 grms. of the sample are heated gently to dryness with hydrochloric acid diluted with its own volume of water, the residue thus obtained being heated on a water-bath for 15 minutes with concentrated hydrochloric acid to dissolve the whole of the titanium. The liquid is diluted to 200–300 c.c. and treated for 30 minutes at 60° C. with 25 c.c. of concentrated hydrochloric acid and a few grms. of zinc dust. A test should be made to ascertain if the iron is completely reduced, since the titanium reacts only after the iron. The liquid is then filtered rapidly through a glass wool plug on which is placed a little granulated zinc, into a flask filled with carbon dioxide, and titrated immediately with the methylene blue solution until a distinct coloration, intensified by two further drops of the solution, appears.

In the case of ferro-titaniums, which are insoluble in acids, 0·5 grm. of the finely-divided metal is disaggregated by means of potassium hydrogen sulphate, the mass being then digested with 50 per cent. hydrochloric acid on a water-bath for 20 minutes and the liquid made up to volume in a measuring flask. An aliquot part, corresponding with 0·1 to 0·2 grm. of the metal, is reduced and titrated as described above. If the reduction, filtration and titration are carried out rapidly, the method gives satisfactory results. T. H. P.

Reactions between Gaseous Nitrogen Oxides and Alkaline Solutions. A. Sanfourche. (*Comptes rend.*, 1922, **175**, 469–472.)—When certain precautions are taken, the absorption of nitrous fumes by concentrated sulphuric acid proceeds

normally, but when alkali hydroxide solution is used as absorbent, only exceptionally are the nitrogen compounds formed of the same degree of oxidation as in the original gaseous phase. The results of the author's experiments show that this behaviour is not due to the oxidation of nascent nitrite to nitrate, since, even in absence of oxygen, the amount of nitrite formed may be less, and that of nitrate more, than corresponds with the composition of the gaseous mixture. This is always the case if there is a deficit of alkali at any point or at any moment, the nitrous acid then reacting with the water to give nitric acid and nitric oxide, the latter either undergoing re-oxidation or remaining unchanged according as the atmosphere does or does not contain oxygen; if, however, the alkali is, always and at every point, in excess, absorption by alkali hydroxide follows the normal course. The replacement of alkali by sulphuric acid in the analysis of gaseous nitrogen oxides is recommended. T. H. P.

Estimation of Silica. R. C. Wells. (*J. Amer. Chem. Soc.*, 1922, **44**, 2187–2193.)—The silica content of sea-water (after removal of suspended algæ and diatoms by filtration) was estimated in the following manner:—Three litres, evaporated to 200 c.c., were treated with 30 c.c. of hydrochloric acid, 0·04 grm. of alumina in the form of alum, a little filter pulp, rosolic acid or phenolphthalein, and ammonia to the formation of a pink colour ($P_H = 7$ to 8). The solution was boiled for 2 minutes, the precipitate filtered off, ignited, and fused with 4 grms. of sodium bisulphate. The fused mass was dissolved in water containing 15 c.c. of sulphuric acid (1:1), the solution evaporated to fumes, cooled, diluted, and filtered at once. The precipitate was strongly ignited, weighed, and evaporated with hydrofluoric and sulphuric acids as usual, silica being found by difference. The above method is applicable in mineral analysis. A single evaporation with hydrochloric acid is sufficient, provided the silica is also determined in the ammonia precipitate. The latter should contain at least two parts of alumina to one of silica. About 0·0003 grm. of silica escapes precipitation, and an equal quantity is generally found in the washings from the ammonia precipitate. Silica cannot be estimated from the loss on evaporation with hydrofluoric acid in the presence of calcium sulphate. W. R. S.

Electrometric Titration of Dichromate with Ferrous Sulphate. M. Eppley and W. C. Vosburgh. (*J. Amer. Chem. Soc.*, 1922, **44**, 2148–2156.)—In the electrometric titration of dichromate with ferrous sulphate, the end-point can be determined without plotting curves (Forbes and Bartlett, *J. Amer. Chem. Soc.*, 1913, **35**, 1535). The practical limits of acidity for this titration are found to be 0·4 to 2·5 *M* hydrochloric, or over 0·4 *M* sulphuric, acid; in more dilute acid, the electromotive force requires some time to become constant. The volume of ferrous sulphate solution required to produce a permanent galvanometer deflection decreases slightly with increasing dilution of the dichromate; hence the concentration of the latter must be kept uniform. An excess of about 0·4 per cent. of ferrous sulphate, standardised against permanganate solution, is required in the

electrometric titration when the dichromate concentration is 0·01 *N*; with a concentration of 0·003 *N*, the quantity of ferrous sulphate consumed is about 0·1 per cent. over the calculated quantity. The results of the titration of ferrous ion with dichromate agree with those obtained in the reverse titration. W. R. S.

Magnesium Perchlorate as a Drying Agent. H. H. Willard and G. F. Smith. (*J. Amer. Chem. Soc.*, 1922, **44**, 2255–2259.)—Anhydrous magnesium perchlorate is as efficient a drying agent as phosphorus pentoxide if the flow of the gas to be dried does not exceed 5 litres per hour. The trihydrate is as efficient a drying agent as the anhydrous salt at 0° C., but less so at higher temperatures. Several advantages are claimed for the salt. It absorbs a greater weight of water per unit weight, does not become sticky, and contracts on absorbing moisture; it can be recovered and re-activated repeatedly, and is a neutral drying agent.

W. R. S.

Physical Methods, Apparatus, etc.

Quantitative Analysis by Measurement of Supersaturation-Time. E. F. Hoppler. (*Chem. Zeit.*, 1922, **46**, 957–958.)—The measurement of reaction velocity can be applied to quantitative analysis by the introduction of the conception of "supersaturation-time," by which is meant the time which elapses between the mixing of two reacting substances and the appearance of the product of their interaction—precipitate or coloration. The supersaturation-time is, in the absence of a catalyst, dependent on temperature and concentration only. The method is only applicable to very dilute solutions, and is well adapted for the analysis of waters and effluents. The maximum concentrations which can be used are about *N*/500 for the precipitation method, and *N*/100,000 for the colorimetric method. In the following examples the temperature was 15° C.; a variation of ± 3° C. may introduce considerable error. For the estimation of sulphate, 10 c.c. of the solution are treated with 5 c.c. of 10 per cent. hydrochloric acid and 5 c.c. of 10 per cent. barium chloride solution; the mixture is compared, over a black ground, with distilled water, and the time taken for a turbidity to appear is noted. The following table shows the concentration in mgrms. per litre:

Sulphate (SO_3), mgrms. per litre	100	90	80	70	60	50	40	30	20	10	5
Time, seconds ..	5·5	6	8	10	14	20	31	48	82	245	495

The maximum experimental error is 10 per cent. Curves showing the relation between supersaturation-time and concentration are also given for the estimation of lime and nitrous acid. Lime is precipitated as oxalate by adding to 10 c.c. of the solution (water) 5 c.c. each of 10 per cent. ammonium chloride and ammonium oxalate solutions; and for the estimation of nitrite, 100 c.c. of the water is treated with 2 c.c. each of starch solution and of a 25 per cent. solution of phosphoric acid and 0·2 grm. of potassium iodide, the time until the production of a blue colour being noted. H. E. C.

Reviews.

SOME PHYSICO-CHEMICAL THEMES. By ALFRED W. STEWART, D.Sc. Pp. xii. +419. London: Longmans, Green & Co. 1922. Price 21s. net.

Within the covers of this volume Professor Stewart attempts to cover some twenty distinct problems in physical chemistry. Three chapters are devoted to the subject of complex salts, their formation and detection; three to somewhat allied subjects, the pseudo acids, the theories of indicators, and to the problem of solution in non-aqueous media. Two chapters are allotted to the subject of colloid chemistry, three to the consideration of molecular movement and atomic dimensions, and one chapter each to the discussion of adsorption and catalysis, and the last five chapters are devoted to the problem of valency and the series and structure of atoms.

The various subjects are presented in a very readable form to those possessing a general interest in science, but to the writer, at least, it appears doubtful whether a volume of this kind serves any useful purpose to the specialist or research student. It is admitted that there exists a large gap between standard text books and recent original work, attempts to bridge which are to be found in various monographs. The result of compression of material, which generally reduces the space of a reasonably large monograph within the confines of one chapter, is not always felicitous. By far the weakest chapters in the book are those dealing with the properties of colloids, and with the phenomena of adsorption and catalysis. In particular, the limitation of the Gibbs equation, the more important adsorption isotherms alternative to those of Freundlich, the recent work on neutral salt action in homogeneous catalysis and its bearing on hydration and ionic activity, have not been included.

The first section of the book, including the first eight chapters, on the other hand, gives an admirable survey of the problems under discussion. In the chapters on atomic structure a brief sketch is given of the dynamic atoms of Rutherford, Bohr, Nicholson, Noyes, and Stewart, and the static atoms of Lewis and Langmuir.

The book is well printed, and its utility is grea ly extended by ample references and a well-compiled bibliography on the specialised literature of each section.

ERIC K. RIDEAL.

AN INTRODUCTION TO THE CHEMISTRY OF RADIO-ACTIVE SUBSTANCES. By A. S. RUSSELL, M.A., D.Sc. Pp. 173. London: J. Murray. 1922. Price 6s. net.

Dr. Russell has collected together a vast amount of useful information in the space of 169 pages in his *Introduction to the Chemistry of the Radio-Active Substances*. Chapters IX. to XII., dealing with the analytical chemistry of uranium and thorium, the separation of the radio-elements individually, and the use of radio-elements as indicators of the behaviour of elements at small concentrations, will be of special value to workers in this field.

The author claims, in his preface, that there is no other book in English on the subject reasonably up to date, and, further on, explains that references are not given, as the reader may speedily be put on the track of the original papers by consulting the indexes of a list of books cited. He cannot have it both ways, and, in the opinion of the reviewer, the value of this book would have been enhanced if more references to recent work had been supplied.

Chapter IV. is the least satisfactory in the book, as it is doubtful if the subjects of atomic number, the periodic system, and the structure of the atom can all be dealt with to advantage in the course of eight pages. The conclusion (p. 32) that Moseley's work has established that hydrogen and the rare earths are not included in the periodic system, is novel, and hardly generally accepted, as inferred on p. 73. That can only be maintained if the periodic table is still adhered to in its form where the elements are arranged in periods of 8, 8, 18, 18, and 18 elements, respectively. Surely the work of Moseley has established the correctness of the Rydberg formula, where the periods are 2, 8, 8, 18, 18, and 32, whence hydrogen and the rare earths fall into the periodic system perfectly.

The data given throughout the book have been carefully compiled, the only error noticed is on p. 96, where the transformation constant of radium emanation is given as 0·75 instead of 0·0075.

The book can be highly recommended as possessing the distinctive merits which the author's name entitles one to expect. JOHN A. CRANSTON.

TESTED METHODS OF METALLURGICAL ANALYSIS (NON-FERROUS). By S. PILE, M.A., and R. JOHNSTON. Pp. 128. London: H. F. & G. Witherby. 1922. Price 7s. 6d. net.

A more suitable title for this book would have been: "The Analysis of Non-ferrous Alloys." To say that the accuracy of an analytical method must be tested before publication is merely to enunciate that which is universally accepted as axiomatic. The preface states that all the methods have been tested, and most of them repeated hundreds of times; but repetition is no guarantee against defect of method, and internal evidence often fails to bear out the claim to reliability implied by the title. The authors add that "other methods equally suitable, or even superior, may exist, and we shall be glad to hear of them, and shall be grateful for criticism, friendly or otherwise." Such invitation the reviewer feels in duty bound to accept, subject to the limitations imposed upon him by the space at his disposal.

The methods given for the estimation of arsenic are out-of-date, and open to the following objections: Procedure A is recommended "in absence of tin, iron, and aluminium" for pure copper, cupro-nickel, brass, etc. The metal is dissolved in nitric acid; the solution is concentrated and boiled with dilute nitric acid, any antimonic acid precipitated at this stage being filtered off. This procedure is not only faulty—for the precipitate usually contains other metals, including arsenic—but unnecessary because the interference of antimony can be prevented in the subsequent operations. A footnote mentions that the weighed magnesium

pyroarsenate contains any phosphorus present, but offers no hints as to its removal. In Procedure B (alternative method for the alloys enumerated under A), after solution in *aqua regia*, the hydrogen sulphide precipitate from 10 to 20 grms. of material (no precautions are indicated to ensure complete precipitation of arsenic) is filtered off and extracted on a Büchner funnel with sodium sulphide solution. The re-precipitated sulphides are evaporated with nitric acid, again with the subsequent needless and risky separation of antimonic acid. Procedure C, for small quantities of arsenic in tin alloys, is distinctly poor. The whole hydrogen sulphide group is precipitated, filtered off, and extracted on a Büchner funnel, as under B; the re-precipitated sulphides of tin, antimony, and arsenic (from 10 to 20 grms. of metal) are dissolved in hydrochloric acid and bromine. An excess of tartaric acid is then added, followed by excess of ammonia, and magnesia mixture. No mention is made of the amount of tartaric acid required in presence of much tin, or of the marked solubility of magnesium ammonium arsenate in strong tartrate solutions. In every procedure the arsenic is finally weighed as magnesium pyroarsenate. The convenient volumetric methods (applicable in presence of phosphate) and the precipitation of arsenic sulphide in strongly acid solution (by which antimony and tin are easily and completely removed) find no place in the book.

For the estimation of "traces of antimony" in commercial copper (p. 29), solution in nitric acid, evaporation to small bulk, and boiling with dilute nitric acid are again recommended. The antimonic acid is filtered off and ignited (apparently with the filter), and the residue assayed for antimony. Apart from the fact that ignition of the precipitate in contact with paper almost inevitably leads to partial reduction and volatilisation, the nitric acid method fails to detect, much more to estimate, quantities of antimony below the order of 0·1 per cent., whereas an amount as small as 0·003 per cent. is objectionable for certain purposes. How this antiquated process has been made to pass muster as a "tested" method quite mystifies the writer, and he would invite the authors to compare their results with those obtained by Hampe's method.

While many of the methods described are serviceable and the directions useful, there is a strong admixture of cases that fall short of up to date standard analytical practice; in others, the desired end could be achieved more neatly and quickly, and with equal, if not greater, accuracy. The gravimetric estimation of iron is a case in point, especially in presence of manganese, aluminium, and phosphorus (p. 58): the precipitation with ammonia and ammonium chloride "is repeated until all the manganese is removed"; aluminium is next eliminated by pouring the chloride solution into caustic soda, and phosphorus, if considerable, by another precipitation of the iron as sulphide. All this labour can obviously be avoided by the use of a volumetric method. The cyanide titration of nickel is also ignored.

The use of Büchner funnels in quantitative work is a practice which few, if any, analysts would advocate. This technique is more especially questionable, on account of the formation of channels, where a constituent has to be extracted

from the precipitate, as in Procedures B and C for arsenic, criticised above. There is also a distinct leaning in the book towards the use of unduly large filters.

As regards the style of the book, the following prefatory statement may be reproduced without comment: "The technical slang of the laboratory has been used in preference to literary English as being more pointed and concise."

W. R. SCHOELLER.

THE VOLATILE OILS. By E. GILDEMEISTER and Fr. HOFFMANN. Second Edition by E. GILDEMEISTER; translated by EDWARD KREMERS. Vol. III. Pp. xx. +777. London: Longmans, Green & Co. 1922. Price 32s. net.

This, the concluding volume of the "magnum opus," produced under the auspices of Messrs. Schimmel & Co., of Leipzig, brings to a conclusion the series of monographs on the various essential oils dealt with. Volume II. concluded with a number of the oils of the *Rutaceæ*, with the remainder of which Volume III. begins. About 540 separate monographs, on as many oils, are included in the present volume.

The high rank in essential oil literature which this work possesses is too well known to be here dwelt upon. Suffice it to say that this volume is fully up to its predecessors in every respect. Subject to one qualification, to be mentioned later, it may be said to be exceedingly full and accurate in its treatment of the oils dealt with, and particularly free from typographical errors. The characteristics, uses and commerce in the oils are fully described, and wherever special methods of analysis are necessary these are fully dealt with. The references and index are full and accurate.

Two clerical errors may be mentioned for the attention of the translator, should a third edition be forthcoming. On page 44, under the "Detection of Pinene according to Chace," the words "assuming that pure *turpentine* oil is, at most, to contain but traces of pinene," should read "assuming that pure *lemon* oil," etc. In the first paragraph on page 168 "A. Macewan" seems strangely unfamiliar. Surely it is meant for a reference to Mr. Peter MacEwan?

There is no unfavourable comment possible on this work, except that it appears to be, unfortunately, a translation of the original German edition published in 1916. The result is that the work of the past eight years is untouched, and to that extent the volume is out of date.

This leads to such statements as that on page 215, where in reference to Maiden's *Critical Revision of the Genus Eucalyptus*, it is stated in a footnote: "Up to the present time two volumes have appeared."

The title page is dated 1922, and it is only by an examination of the text that one finds that it really is the 1916 work translated in 1922.

Messrs. Schimmel & Co. are to be congratulated on bringing the issue of this work to a successful conclusion, especially as it is no secret that it is a labour of love into which the huge expense of publication has not entered.

ERNEST J. PARRY.

THE PROBLEM OF PROOF. By A. S. OSBORN. Pp. xxi. +526. New York: Matthew Bender & Co. London: Sweet, Maxwell. 1922. Price 32s. net.

In some respects this book forms a sequel to the author's *Questioned Documents*, which is now recognised as a standard work all over the world. That book deals with scientific methods of examining documents, whilst the present one is concerned with the presentation of observed facts in such a way as to carry conviction to a judge and jury.

In a Utopian State everyone in a Court of Justice would be anxious to establish the truth or the reverse of alleged facts; but in the world as we know it we have to recognise that attempts are often made to suppress the truth, and that a counsel may be briefed to support a case in which he does not believe, and may attempt to discredit a witness who he knows is speaking the truth. A scientific witness, therefore, must not only be able to demonstrate his facts, but must also have some knowledge of the psychological factors which influence the judgment of his hearers.

This theme is developed in twenty-eight chapters which are full of keen humour and of the wisdom gathered from long experience. Among the phases of a trial which are considered from every point of view are the preparation of the facts, sifting the evidence, co-operation of lawyer and specialist, the specialist as witness, the atmosphere of a trial, cross-examination, advocacy, and practical psychology in Courts of Law.

On almost every page are to be found aphorisms which show a shrewd, though kindly, knowledge of human nature.

For instance, in referring to different types of witnesses, Mr. Osborn remarks (p. 25): "Always and everywhere one of the sure marks of truth, as well as of wisdom, is the admission of ignorance." The specialist, he urges, should use as simple words as possible: "To give the exact shade of meaning to an expression often makes, not simply the difference between clearness and obscurity, but the difference between belief and unbelief. . . . It is always the shallow man who uses showy and unnecessarily long words" (p. 83).

Dealing with some of the difficulties of the specialist, he observes: "The unwise zeal of an advocate often creates an unfavourable air of incredulity surrounding testimony, and a witness may be made to appear an unfair partisan through the reflected influence of an over-zealous advocate."

Not infrequently too, he may be handicapped by having to be examined by an unskilled counsel, who has not even mastered the technical points at issue. It is not given to every lawyer to be a technical advocate, and for an inexperienced man to deal with a scientific case is often to court defeat. "It is," as the author says, "as if every doctor attempted on rare occasions to perform major operations. The legal operating room shows many mangled legal corpses" (p. 108).

In discussing the cross-examination of the witness, he remarks: "Testimony should not be hesitating or weak, but technical testimony is not so apt to be weak as to be dogmatic and over-emphasised."

And again: "When the lawyer through excess of zeal for his client's interests, or now and then, perhaps, in his own interest, forgets that the purpose of testimony

is to elicit the truth, the witness should not also forget the fact. . . . Testimony is often made more damaging when the witness who has given it is unfairly assailed." "If the witness becomes irritated, tense and resentful, he is in danger of getting himself into a vulnerable state of mind that may lead to disaster." "It is always very bad policy, as well as highly improper, for the witness to attempt to punish the cross-examiner by injecting into the record any answers not fully justified by the questions. Punishment can sometimes be inflicted, but it should always be fair."

It is not possible to follow the author with quotations through his consideration of all the other aspects of the problem of proof, but the examples given will show the style of the book and the bearing of its argument.

The work of a large proportion of the members of our Society is closely associated with Courts of Law, and all such would gain much practical help from a close study of this book. But, apart from this, it is well worth reading as an example of clear thinking and logical exposition, even by those who have not this ulterior end in view. It is a masterly work. EDITOR.

Publications Received.

THE CHEMISTRY AND TECHNOLOGY OF GELATIN AND GLUE. By R. H. BOGUE. Pp. xi. +635. London: McGraw Hill Book Co. 1922. Price 30s.

THEORIES OF ORGANIC CHEMISTRY. By F. HENRICH. Translated by T. B. JOHNSON and D. A. HAHN. Pp. xvi. +603. London: Chapman & Hall. 1922. Price 30s. net.

THE MICROSCOPICAL EXAMINATION OF FOOD AND DRUGS. Third Edition. By H. G. GREENISH. Pp. xvii. +386. 207 Illustrations. London: J. and A. Churchill. 1922. Price 18s net.

ATOMIC FORM: With Special Reference to the Configuration of the Carbon Atom. By E. E. PRICE. Pp. 148. London: Longmans, Green & Co. 1922. Price 5s. net.

THE NITROGEN INDUSTRY. By J. R. PARTINGTON and L. H. PARKER. Pp. xv. + 336. London: Constable & Co. 1922. Price 21s. net.

RESEARCHES ON CELLULOSE, IV. (1910–1921). By C. F. CROSS and C. DOREE. Pp. x. +253. London: Longmans, Green & Co. 1922. Price 15s net.

CHEMISTRY FOR BEGINNERS AND SCHOOLS. Fourth Edition. By C. T. KINGZETT. Pp. viii. +237. London: Baillière, Tindall & Cox. 1922. Price 5s. net.

The Institute of Chemistry of Great Britain and Ireland.

PASS LIST.

OCTOBER EXAMINATIONS, 1922.

THE following candidates have passed the Examination for the Associateship:—*In General Chemistry*—G. Chignell, B.Sc. (Lond.); H. French; F. E. Wild, B.Sc. (Birm.); and E. B. Young, B.Sc. (Lond.). *In Branch (d) Organic Chemistry (under Regulations in force prior to March*, 1920)—N. G. Baguley and F. Cole.