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AN extraordinary meeting was held at the Institute of Chemistry on January 16, 1924. 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. Hugh Browning Brown, A.I.C., Sidney Augustus de Lacy, A.I.C., A.M.I.Chem.E., Joseph Henry Lane, F.I.C., B.Sc. (Lond.), Leslie Herbert Lampitt, D.Sc. (Birm.), F.I.C., Reginald Francis Moon, B.Sc. (Bristol), Maximilian Nierenstein, D.Sc. (Geneva), Ph.D. (Berne), William Simpson Shaw, M.Sc., A.I.C., and Robert Norman Wright, A.R.C.S., B.Sc. (Lond.), A.I.C.; Misses Phyllis Honor Price, B.Sc. (Bristol), and Mabel Suzanne Lavinia Snelus, A.I.C.

Certificates were read for the second time in favour of Messrs. Thomas Francis Doyle, George Hogan, F.I.C., Frank Knowles, Archibald Knox, A.I.C., Charles Roger Middleton, B.Sc. (Lond.), A.R.C.S., A.I.C., and Harold Richard Read, A.I.C., A.R.C.Sc. (Dublin).

The following were elected members of the Society:—Messrs. Hubert Thomas Stanley Britton, B.Sc. (Bristol), M.Sc. (Lond.), F.I.C., and Robert Charles Frederick.

The Estimation of Nitrogen in Coal.

BY W. DONOVAN, M.Sc.

(*Read at the Meeting, November* 7, 1923.)

IN 1915, A. C. Fieldner and C. A. Taylor made a comparison of various modifications of the Kjeldahl method with the Dumas method, as applied to the estimation of nitrogen in coal. By the use of the Gunning modification of the Kjeldahl method, and with prolonged heating in the Dumas method to ensure complete combustion of the coal, the difference in average values by both methods was 0·10 per cent. The Dumas results were the higher.

E. Terres, H. Fleischer, and others, in 1919, also investigated the estimation of nitrogen in coal and coke. They found that both methods, as usually conducted, gave low results, the Kjeldahl method by loss of gaseous nitrogen, the Dumas owing to incomplete combustion. A modification of the Kjeldahl method was devised so that the gases evolved in the oxidation of the coal could be collected and the nitrogen, which was invariably present, recovered. The Dumas method was modified to permit of the generation inside the combustion tube of a supply of oxygen in the final stages of the operation.

The results obtained were:

	Percentage of Nitrogen.				
	Peat.	Lignite.	Saar Coal.	Ruhr Coal.	Anthracite.
Kjeldahl	1·70	0·80	1·31	1·33	1·35
,, +free *N*	1·77	1·20	1·76	1·58	1·84
Modified Dumas	1·72	1·08	1·73	1·55	1·72

The Research Sub-Committee of the Gas Investigation Committee of the Institute of Gas Engineers, in a report on the Comparative Economics of Production, from Thermal and Chemical Standpoints, of different Grades of Gas, confirmed the work of Terres as regards the modified Dumas method, but reported adversely on the Kjeldahl method. Some published results were:

	Percentage of Nitrogen.		
	Coal.	Coke.	Tar.
Kjeldahl	1·41–1·67	1·23–1·56	0·83–1·09
Modified Dumas	1·91–2·06	1·74–1·87	1·58–1·79

The procedure for the Dumas method as described in the report makes provision for the removal of carbon monoxide and dioxide, but apparently not for methane. The results are not very concordant and are probably somewhat high.

In the course of a series of analyses of New Zealand coals it was necessary to estimate nitrogen, and with the object of avoiding the more tedious combustion method it was decided to ascertain the relation, if any, between results by the two methods, and whether by applying a correction to the Kjeldahl figure the true result could be obtained. The combustion method followed was that recommended by the Association of Official Agricultural Chemists, as published in *Methods of Analyses*, 2nd edition, page 9. The operation is carried out in a previously evacuated tube, and the gaseous products of combustion removed by means of a mercury pump. This does away with the use of carbon dioxide gas for sweeping out the tube. In addition, the end of the tube was filled with potassium chlorate, to provide oxygen for the completion of the combustion, as recommended by Terres.

A combustion tube, 15–17 mm. internal diameter and 80 cm. long, was sealed at one end and filled as follows:

(A), Ten grms. of potassium chlorate, a small plug of ignited asbestos, then (B), 10 cm. of broken pumice, 4 to 5 mm. in diameter, to insulate the potassium

chlorate from the heat in the first part of the combustion. Then (C), 4 cm. of powdered copper oxide, and (D), the combustion mixture of 1 grm. of coal and 25 grms. of finely powdered copper oxide, prepared from copper wire oxide. Then (E), 1 cm. of fine copper gauze, and (F), 15 cm. of copper wire oxide. (G), 5 cm. copper gauze, and (H), another 10 cm. of copper wire oxide.

The combustion tube was connected with a distilling flask of 100 c.c. capacity, containing 15 grms. of soda lime, moistened slightly and spread over glass wool, to increase the effective absorption surface. This in turn led to a Sprengel pump. The tube and absorption vessel were evacuated and the wire copper oxide and gauze (F, G and H) heated until they were red hot. The heating was gradually extended, until the mixture of coal and copper oxide, D, was reached. This was heated carefully and the products of combustion, passing over the hot copper oxide, were converted mainly into carbon dioxide, and were absorbed by the soda lime. When the evolution of gas had apparently ceased, the tube was evacuated, and the gas collected in a suitable receiver.

The potassium chlorate A was then heated carefully, to generate a slow, steady stream of oxygen. The copper reduced in the first stage of the combustion was re-oxidised and any unconsumed carbon completely burned, the reaction causing a glow by which its progress through the mixture could be followed. When the copper gauze, E, showed signs of oxidation heating was discontinued, and the tube again evacuated. The gas collected was mixed with that obtained in the first stage of the combustion, and the whole transferred to the absorption vessel of a Bone and Wheeler gas analysis apparatus, which was calibrated to measure volume. Oxygen and carbon dioxide were absorbed by means of alkaline pyrogallol, and the volume of unabsorbed gas measured in the water-jacketed tube, over mercury. The volume varied from 20 to 35 c.c. An aliquot portion was exploded with excess of oxygen and electrolytic gas in the usual manner, to remove carbon monoxide and hydrocarbons, the volume of the residual nitrogen was measured, and from it the total volume of nitrogen was obtained by calculation.

That considerable amounts of hydrocarbons may escape oxidation in the combustion tube is shown by the following analyses:

A. Gas resulting from combustion of one grm. of sugar.

B. Gas resulting from combustion of one grm. of coal.

(Gases were freed from oxygen and carbon dioxide prior to analysis.)

	A.	B.
Carbon monoxide	5·2	7·8
Methane	61·9	19·7
Ethane	12·0	4·7
Nitrogen	20·9	67·8
	100·00	100·00

(The nitrogen in A was derived from the copper oxide used.)

It is apparent that, unless provision is made for the removal of hydrocarbon gases, the results for nitrogen may be considerably in excess of the truth.

It is necessary to apply a correction for nitrogen in the copper oxide mixed with the coal. Fieldner and Taylor (*infra*) found that all copper oxide procurable by them contained nitrogen that was not removed by heating *in vacuo* for several hours, but was liberated under the conditions of the experiment. The wire form was much purer than either the lump or powder form.

Blank combustions were therefore carried out with three different samples of copper oxide, with the use of pure sugar instead of coal. The results obtained were:

	Nitrogen c.c.
30 grms. copper oxide powder (Merck)	4·5
30 grms. copper oxide lump form (Merck)	2·42
30 grms. wire oxide powdered (British Drug Houses)	0·50

These confirm Fieldner and Taylor's observations.

Powdered wire oxide ground to pass a 60-mesh sieve was therefore used for mixing with the coal, a correction being applied for the nitrogen content.

A trial estimation in which a mixture containing 0·15 grm. of diphenylamine and 0·85 grm. of sugar was used gave nitrogen 1·256 per cent. (theoretical value, 1·243 per cent.).

For the Kjeldahl process 1 grm. of the coal was taken, 15 grms. of potassium sulphate, and 30 c.c. of sulphuric acid, with 0·4 grm. of mercury as catalyst. The mixture was heated somewhat rapidly at first, and then the heat regulated so that clearing took place in about an hour. The heating was continued for a further three hours. After precipitation of the mercury with sodium sulphide, the ammonia was distilled off into 25 c.c. of 0·1 *N* sulphuric acid. When the mercury was omitted, or when smaller amounts of potassium sulphate were used, less satisfactory results were obtained.

Nitrogen was estimated by both methods in five coals which were known to differ considerably in general properties and in nitrogen content. These had the following proximate analyses:

	1. Per Cent.	2. Per Cent.	3. Per Cent.	4. Per Cent.	5. Per Cent.
Fixed carbon	61·80	56·78	57·37	42·44	43·68
Volatile hydro-carbons	32·75	38·38	39·92	39·06	40·55
Water lost at 100° C.	0·75	2·47	1·08	16·00	11·41
Ash	4·70	2·17	1·63	2·50	4·36
	100·00	100·00	100·00	100·00	100·00
Sulphur, per cent.	0·76	0·27	5·33	0·26	0·96

No. 1 was a bituminous coal, low in sulphur, and yielding a highly swollen coke. No. 2 was similar, but the coke was only moderately swollen. No. 3 was very high in sulphur. Nos. 4 and 5 were brown coals.

The results for nitrogen were:

No. of Coal.	Percentage of Nitrogen. Dumas.		Kjeldahl.		Difference of Average.
1.	2·05	Average	1·92	Average	0·18
	2·07	2·07	1·89	1·89	
	2·09		1·85		
			1·88		
2.	1·77	Average	1·58	Average	0·17
	1·74	1·755	1·62	1·585	
			1·54		
			1·60		
3.	1·02		0·88	Average	0·17
			0·83	0·85	
			0·84		
4.	1·08		0·88	Average	0·21
			0·88	0·87	
			0·85		
			0·86		
5.	1·32	Average	1·09	Average	0·23
	1·29	1·305	1·11	1·075	
			1·05		
			1·05		

The agreement of duplicates by the Dumas method was very good, and by the Kjeldahl method, satisfactory, though not quite so good.

The loss of nitrogen by the Kjeldahl process specified is fairly constant, being 0·17 per cent. for the bituminous coals, and 0·22 per cent. for the brown coals. It could be taken as 0·20 per cent. for both types of coal without serious error.

SUMMARY.—Nitrogen was estimated in five coals by the Dumas method. Complete combustion was assured by a supply of oxygen in the final stage. The greater part of the carbon dioxide formed was absorbed within the apparatus. By means of explosion and absorption in a Bone and Wheeler gas analysis apparatus all hydrocarbons and other extraneous gases were eliminated. The final volume of nitrogen was measured over mercury, in a water-jacketed tube in the same apparatus. The results were corrected for nitrogen in the copper oxide used.

Nitrogen was estimated in the same coals by the Kjeldahl-Gunning process, with the use of mercury as a catalyst.

The Kjeldahl results, plus 0·2 per cent., would give the correct percentage of nitrogen in the coals examined.

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A Comparison of Various Modifications of the Kjeldahl Method with the Dumas Method of determining Nitrogen in Coal. A. C. FIELDNER and C. A. TAYLOR, *J. Ind. Eng. Chem.*, 1915, **7**, 106.

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DOMINION LABORATORY,
WELLINGTON, NEW ZEALAND.

Discussion.

Mr. G. Rudd Thompson said that he considered the paper a most valuable contribution and most explicit. The importance of this question from a technical point of view to-day was the yield of ammonium sulphate the gas-makers were going to get from their coal, and, in his opinion, the paper solved a somewhat difficult question. With the Kjeldahl method one got somewhere about **0·2** per cent. less nitrogen than with the Dumas method, but that nitrogen was not recoverable in the by-product plant. The author had proved this low result to be due to loss of gaseous nitrogen. Further, to obtain his results the author had taken a wide range of coals which would very reasonably cover the average coals used in by-product plants in this country.

Mr. G. N. Huntly noticed that the author had made no mention of the formation of nitric oxide. The addition of electrolytic hydrogen might partially remove it, but he felt the paper would have been more satisfactory had it been mentioned. The presence of methane seemed to have been noticed, and if one could arrange to pass the gas backwards and forwards, as in a gas-analysis apparatus, one would get rid of it, but not otherwise. Another point was that when working in a vacuum one had to look out for leaks. An error of 0·2 per cent., due to occluded nitrogen, did not sound much, but it really was serious.

Mr. R. L. Collett asked whether the author had attempted to find out—by collecting the gas evolved by his Kjeldahl apparatus—if the 0·2 per cent. loss was due to loss of gaseous nitrogen. He suggested that possibly the digestion stage of the process was not carried to completion.

Mr. Raymond Ross enquired what gases were occluded by coal, and how much actual nitrogen was occluded. It was well-known that very different results were obtained, as to the amount of ammonium sulphate, according to the method of carbonisation employed. He asked whether lead chromate could not be used for all ordinary combustions of that kind instead of copper oxide; personally, for ordinary combustion, he preferred rolls of oxidised copper gauze to granular copper oxide.

Dr. H. E. Cox said that he had, for some years, used copper gauze which had been oxidised in the manner now put forward by the author. In his experience the amount of nitrogen in coal was generally about **1·4** per cent.; he considered the author's result of **1·7** per cent. too high; the Dumas method often gave too high results on account of unburnt gases, and the gas evolved in the Kjeldahl digestion was not nitrogen derived from the coal substance.

Mr. Rudd Thompson, replying, said that many years ago methane and ethane were occasionally found sporadically, and it was rather strange that no one had taken the trouble to find out the reason of their presence. Although the joint between the combustion tube and the Sprengel shewn in Mr. Donovan's sketch was a cork joint, very probably in actual use the combustion tube was drawn out, so as to avoid leakage.

Effects of Storage on Artificially Polluted Waters.

By ROBERT C. FREDERICK.

(*Read at the Meeting, March,* 1923.)

In the course of an extensive experience in the analysis of water it became increasingly evident that many of the orthodox ideas regarding the interpretation of water analysis results were erroneous. Doubts as to the correctness of some of these beliefs have already been expressed elsewhere (1), and this paper contains an account of a subsequent detailed investigation into the chemical changes which occur in excretally polluted water, and the significance of these in the interpretation of the results of an analysis.

In addition to enabling a correct interpretation of the analytical results for a sample to be made when the analysis had been conducted soon after collection, the research had for a further object the determination of the utility of an analysis when a long period had elapsed between collection and examination. This study has been made on samples only and, though the conditions with these are not exactly comparable with those in the case of a water supply, doubtless the results also give some indication of the probable occurrences *in situ*. The findings have been co-ordinated with statistics of the results obtained by the author in the analysis of nearly 1000 samples from every kind of supply throughout the British Isles; the samples were limited to this number so as to include only those which had been examined in recent years by a technique improved by the latest modifications.

The investigation was made with reference only to the substances whose presence is indicative of excretal pollution, *i.e.* free ammonia, albuminoid ammonia, nitrites, and nitrates. The chlorine content, the value of which in this respect has already been discredited, has received some minor consideration. The writer has, elsewhere, detailed his reasons for abandoning the "oxygen absorbed from potassium permanganate" process in the routine examination of water (2). The analytical processes employed were Wanklyn's for free and albuminoid ammonia (3), modified Lombard's for nitrites (4), and Frederick's for nitrates (5).

The general principle of the research was the preparation of bulk quantities of polluted water, which were then divided into samples of exactly similar original composition and stoppered bottles were filled with them. These were set aside under pre-determined conditions and their contents analysed after various periods of storage up to 100 days.

The water which formed the basis of the majority of these samples was ammonia-free water distilled from an all-glass apparatus. To reproduce the character of natural water a quantity of fresh suspension of soil taken from underneath growing turf was added, after rough filtration through muslin and, in some series, there were added salts commonly present in natural potable waters. Details of each series of samples are given under the headings below. In every instance free ammonia and albuminoid ammonia is expressed as NH_3, and nitrites and nitrates as N.

SAMPLES STORED IN THE DARK AT ROOM TEMPERATURE (SERIES L, M, AND O.—The object of these series was to determine comparatively the changes which took place when the same wafer was polluted with urine, (L); with an equal quantity of fæces, (M); and with the same weight of a mixture of equal parts of urine and fæces, (O).

Series L.—A large aspirator bottle, graduated at 2500, 5000 and 7500 c.c., was filled to about 6000 c.c. with the distilled water, which was aerated by shaking; 100 c.c. of mineral salts partly dissolved and partly in suspension were then added, with shaking, and then 5 c.c. of soil suspension. The whole was mixed. The 100 c.c. of mineral salts mixture contained: Sodium chloride, 0·225 grm.; calcium chloride, 0·750 grm.; magnesium chloride, 0·150 grm.; calcium carbonate, 0·075 grm.; calcium sulphate, 0·750 grm.; and calcium oxide, 0·225 grm. The samples, as finally prepared, had a total hardness of 10·7 parts per 100,000. Ten c.c. of a dilution of urine, of original specific gravity of 1·030 (5 c.c. with distilled water to 100 c.c.) from a healthy human, equal to 0·5 c.c. of urine (0·515 grm.), were then added, and also (to approximate more closely the conditions of a natural water) 1250 c.c. of an upland surface water of good quality, collected three weeks previously, containing no free ammonia, 0·006 part per 100,000 of albuminoid ammonia, no nitrites, and only a minute trace of nitrates. The whole was made up to 7500 c.c. and thoroughly shaken; 2500 c.c. of this mixed water were removed for the preparation of Series O, and the remaining 5000 c.c. were made up to 7500 c.c. with the distilled water and mixed. This water was that used in Series L, and was polluted with urine to the extent of approximately 1 part in 22,000 by weight. It was put aside in the dark in eleven 500 c.c. and six 250 c.c. bottles, and a daily record was made of the average temperature prevailing in the storage cupboard during the previous 24 hours.

Series M.—This series was prepared and stored exactly as in series L, except that the pollution was by an equal weight of fæces, instead of urine, 0·515 grm. being added after disintegrating 5·150 grms. by shaking with beads and water, and taking 25 c.c. after dilution to 250 c.c. It is to be noted that this degree of pollution with fæces imparted a distinct turbidity and colour to the water.

Series O.—This series was prepared and stored as in series L and M, but contained a mixture of half the quantity of urine in the former together with half the quantity of fæces present in the latter series; the total degree of pollution was therefore the same as in the two previous series.

The analytical results obtained in these series are shown in Table I.

In the first place it is to be noted that the chemical changes in samples take place comparatively slowly, and that quite different results are obtained according to whether the pollution is urinary, fæcal, or a mixture of both. It has always been considered that the chemical evidence of excretal pollution in water samples disappeared so rapidly that if much delay occurred between collection and analysis the results obtained were of little or no value, and that this was also the case, even during a short delay, if the samples were not kept cold. The analytical results

TABLE I. SERIES L, M AND O.

Analytical results after various periods of storage of samples polluted with urine (L): fæces (M): urine and fæces (O). Parts per 100,000.

Number of Days Stored	Average Temperature of Storage space to date	L				M				O			
		Free Ammonia	Albuminoid Ammonia	Nitrites	Nitrates	Free Ammonia	Albuminoid Ammonia	Nitrites	Nitrates	Free Ammonia	Albuminoid Ammonia	Nitrites	Nitrates
Immediately	—	0·0064	0·0164	0·0001	0·0040	0·0008	0·0388	0·0002	0·0040	0·0026	0·0220	0·0002	0·0040
4	18·1° C.	0·0068	0·0158	0·0001	0·0040	0·0011	0·0404	0·0002	0·0040	0·0044	0·0236	0·0002	0·0040
11	16·9 ,,	0·0108	0·0140	0·0001	0·0040	0·0148	0·0246	0·0002	0·0040	0·0096	0·0202	0·0002	0·0040
18	16·8 ,,	0·0108	0·0138	0·0001	0·0040	0·0232	0·0250	0·0002	0·0040	0·0208	0·0182	0·0002	0·0040
21	16·9 ,,	—	—	0·0001	—	—	—	0·0003	—	—	—	0·0003	—
25	16·0 ,,	0·0144	0·0156	0·0001	0·0040	0·0238	0·0256	0·0003	0·0040	0·0216	0·0168	0·0003	0·0040
31	15·3 ,,	—	—	0·0001	—	—	—	0·0005	—	—	—	0·0003	—
35	15·2 ,,	0·0144	0·0144	0·0001	0·0040	0·0272	0·0244	0·0007	0·0040	0·0224	0·0206	0·0005	0·0040
39	15·1 ,,	—	—	0·0001	—	—	—	0·0072	—	—	—	0·0015	—
45	15·0 ,,	0·0168	0·0138	0·0001	0·0040	0·0280	0·0224	0·0010	0·0040	0·0188	0·0212	0·0076	0·0040
49	15·0 ,,	—	—	0·0010	—	—	—	0·0240	—	—	—	0·0070	—
54	15·2 ,,	—	—	0·0100	—	—	—	0·0160	—	—	—	0·0120	—
57	15·3 ,,	0·0160	0·0162	0·0004	0·0040	0·0216	0·0236	0·0047	0·0060	0·0152	0·0198	0·0152	0·0080
63	15·5 ,,	0·0140	0·0154	0·0002	0·0040	0·0004	0·0212	0·0160	0·0080	0·0000	0·0200	0·0001	0·0080
67	15·7 ,,	0·0085	—	0·0043	0·0040	—	—	0·0000	0·0080	—	—	0·0000	0·0120
79	15·8 ,,	0·0188	0·0174	0·0012	0·0060	0·0000	0·0142	0·0000	0·0100	0·0000	0·0154	0·0000	0·0140
100	15·8 ,,	0·0168	0·0152	0·0010	0·0060	0·0000	0·0140	0·0000	0·0120	0·0000	0·0128	0·0000	0·0400

of these series completely disprove this view and, moreover, show that, if pollution of the supply has only been very recent, the evidence in samples would be more pronounced if the analysis were actually delayed for a considerable period.

The statement is reiterated in the literature that animal pollution of water is indicated by a high free and a low albuminoid ammonia content, *i.e.* the quantity of albuminoid ammonia is only a small fraction of that of the free ammonia. The statement appears to be founded on isolated analyses of samples of sewage and sewage effluents. The fallacy is apparent when it is seen that the amounts and proportion of the free and albuminoid ammonia are constantly varying from the moment pollution takes place. In point of fact, the quantity of albuminoid ammonia is at no time a small fraction of that of the free ammonia; it is seldom appreciably less, is frequently in excess, and at some periods very markedly in excess, as will be seen from the table below showing the proportion of albuminoid ammonia to one of free ammonia at different periods.

TABLE II. SERIES L, M, AND O.

Proportion of albuminoid ammonia to one part of free ammonia after various periods of storage.

		Days stored									
Series	Immediate	4	11	18	25	35	45	57	63	79	100
L.	2·6	2·3	1·3	1·3	1·1	1·0	0·8	1·0	1·1	0·9	0·9
M.	48·5	36·7	1·7	1·1	1·1	0·9	0·8	1·1	53·0	—	—
O.	8·5	5·4	2·1	0·9	0·8	0·9	1·1	1·3	—	—	—

Pollution of water with either urine or fæces causes an addition of a marked amount of albuminoid ammonia, which is in evidence from the outset before the production of free ammonia has fully developed, and a large proportion remains even when the free ammonia and nitrites have been converted entirely into nitrates. The albuminoid ammonia is therefore of primary importance as an indicator of excretal pollution.

While it is probable that the production of nitrites is accelerated *in situ* under the conditions of certain water supplies, the results obtained in these series show that, in samples, nitrites are only produced a considerable time after the addition of excretal matter, and it follows, then, that the interpretation of their presence as indicating very recent pollution is unwarranted. Taking 0·0005 parts per 100,000 as distinct evidence by the Lombard test, it will be seen that nitrites did not appear until the 49th day in Series L, the 31st day in Series M, and the 35th day in Series O. In elaboration of this view, it is to be noted that nitrites do not indicate very recent pollution, as their production in quantity is nearly always subsequent to a decrease of the free ammonia content, and this only commences after a considerable period. Similarly, the production of nitrates follows a decrease in the nitrite content, and pollution indicated by nitrates is certainly of remote date. The progressive nature of these changes is demonstrated by the remote date.

It is generally understood that the presence of nitrites is of very short duration, almost fugitive, but the figures in Table I. show this belief also to be untenable.

Adopting the periods and minimum figure above, they were present for 51, 32 and 22 days in Series L, M and O respectively. Shorter periods have been noted in some other series. It is probable that the misconception has originated by the testing of portions from the one bottle instead of single portions from separate full bottles. The former method is fallacious as it does not imitate the conditions of water examination practice, and that it has a destructive action on the nitrite content is seen by the results of Series E.

SERIES E.—In this series the sample water was prepared as in those discussed previously, with 6 litres ammonia-free distilled water and 2 litres tap water of excellent quality from the chalk and free from nitrites, 0·5 c.c. soil suspension, 0·5 c.c. urine, and 2·0 c.c. emulsion of fæces. The whole was thoroughly mixed and divided into stoppered bottles as follows:

E.1. Seven 500 c.c. filled full.
E.2. One winchester quart filled to shoulder.
E.3. One winchester quart filled full.

A separate bottle from E.1. was tested for nitrites at weekly intervals dating from the day of preparation, the Winchester quart E.2 was tested every few days (sometimes daily), and the Winchester quart E.3 was similarly tested after remaining sealed for 16 days. The quantity of nitrite present at various periods is shown in Table III.

TABLE III. SERIES E.

Analytical results; amount of nitrites present in separate sealed samples (E.1), compared with that present in samples of the same water, repeatedly tested (E.2 and E.3), parts per 100,000.

Days stored	Average temperature to date of analysis	Nitrites		
		E.1	E.2	E.3
Immediate.	—	0·0000	0·0000	
1	20·7° C.	—	0·0000	—
2	20·1 ,,	—	0·0000	—
3	19·2 ,,	—	0·0000	—
4	19·0 ,,	—	0·0001	—
5	18·9 ,,	—	0·0001	—
6	18·9 ,,	—	0·0001	—
7	18·9 ,,	0·0001	0·0001	—
8	18·8 ,,	—	0·0001	—
9	18·8 ,,	—	0·0001	—
10	18·5 ,,	—	0·0001	—
11	18·3 ,,	—	0·0001	—
13	18·1 ,,	—	0·0001	—
14	17·9 ,,	0·0002	0·0001	—
16	17·8 ,,	—	0·0001	
17	17·9 ,,	—	0·0001	0·0002
18	17·8 ,,	—	0·0001	0·0002
21	17·8 ,,	0·0010	0·0001	0·0002
24	17·9 ,,	—	0·0001	0·0002
27	18·0 ,,	—	0·0001	0·0004
28	18·0 ,,	0·0010	0·0001	0·0007
30	17·9 ,,	—	—	0·0010
32	17·9 ,,	—	0·0007	0·0030
34	17·8 ,,	—	0·0020	0·0060
35	17·8 ,,	0·0300	—	0·0100
37	17·8 ,,	—	—	0·0100
42	18·0 ,,	0·0300	0·0060	0·0100

In resuming the general discussion it has to be pointed out that the alleged short duration of the presence of nitrites is responsible for the teaching that quantitative examination for them is not worth while; this premise is at fault, for the real explanation is the marked fluctuation in quantity.

It is noteworthy that in the case of very recent pollution, particularly urinary, the free ammonia obtained by distillation is not infrequently evolved in a large number of fractions, each of which, after the first few, contains the same amount as, or very slightly less than, that immediately preceding; in samples in which pollution is more remote the free ammonia is completely evolved in a small number of fractions which progressively show a distinct fall in amount. This phenomenon is illustrated in Table IV., containing the results obtained with Series F—a water polluted with approximately one part of urine in 15,000; the quantity of the sample distilled was 250 c.c. in each case and the speed of distillation was approximately the same throughout.

TABLE IV. SERIES F.

Free ammonia contained in 50 c.c. fractions on distilling 250 c.c. of sample; amount expressed in terms of c.c. of standard ammonium chloride solution (1 c.c. = 0·01 mgrm NH_3).

Days stored.	Fraction. 1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	Total
1	1·0	0·7	0·35	0·3	0·2	0·15	0·15	0·1	0·1	0·05	3·10
5	1·0	0·9	0·8	0·4	0·3	0·2	0·1	0·05	—	—	3·75
33	2·5	2·1	1·2	0·7	0·5	0·1	—	—	—	—	7·10
39	2·5	2·1	1·6	0·7	0·4	0·1	—	—	—	—	7·40

It will be seen that 1 day and 5 days after pollution, the free ammonia was evolved in 10 and 8 fractions respectively, whilst after 33 and 39 days it was completely evolved in 6 fractions, though double the amount of ammonia was present.

The phenomenon also aids in distinguishing very high free ammonia due to recent gross pollution from the high amounts met with in some waters due to the reduction of nitrates. An example is given in Table V. D was a water polluted with urine to the extent of one part in 2500, and No. 720 was from a well in Lincolnshire, 100 feet deep, free from excretal pollution. Both samples were analysed after 2 days' storage.

TABLE V.

Free ammonia contained in 50 c.c. fractions on distilling 100 c.c. of sample; amount expressed in terms of c.c. of standard ammonium chloride solution (1 c.c. = 0·01 mgrm. NH_3). D was a water containing recent urinary pollution; No. 720 a water free from excretal pollution.

	Fractions. 1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	12th	13th	14th	15th	16th	17th	18th	19th	20th	Total
D.	3·0	3·0	2·0	1·5	1·0	0·8	0·7	0·6	0·5	0·4	0·4	0·5	0·5	0·5	0·4	0·4	0·5	0·5	0·4	0·4	18·0
720	10·0	5·5	2·5	1·1	0·6	0·2	0·1	—	—	—	—	—	—	—	—	—	—	—	—	—	20·0

Recent pollution is indicated by distinct evidence of free ammonia, particularly if evolved in the manner described above (sample D), associated with

about an equal amount of albuminoid ammonia; if exclusively fæcal, very recent pollution may not be evident by this figure, although the relatively great albuminoid ammonia content is a compensating indication.

In considering the occurrence of free ammonia, albuminoid ammonia, nitrites, and nitrates in water as indicators of excretal pollution, it has to be remembered that all may be derived from harmless sources. In rain or distilled waters, or those in which reduction of nitrates by contact with metals or particular strata can be presumed, free ammonia and nitrites have no significance, and in water from newly constructed wells or containing decaying vegetable matter, they have a significance only when present in marked quantity. In upland surface waters the albuminoid ammonia has no significance, and in waters which are supplied from small storage tanks or cisterns this figure has commonly no import as it is derived from accumulating débris. In waters from certain strata, *e.g.* the chalk, nitrates have no significance.

In parenthesis some remarks may be made here regarding decaying vegetable matter as a source of free ammonia and nitrites. The high figures which can be obtained from this source alone, and cause an erroneous attribution to the presence of excreta, do not appear to have received adequate recognition. In this connection the results of Series W.1 and W.2 are of interest. W.1.—Three 500 c.c. stoppered bottles were filled with tap water of good quality from the chalk. Freshly gathered green grass was thoroughly washed ammonia-free and pieces of blade (6·0 by 0·3 cm.) were cut. Into the first bottle one blade was placed, and in the second, two; the third bottle contained no grass and acted as a control. These were put aside in the dark until the grass had decayed, as evidenced by the almost complete disappearance of green colour (10 days), and were then analysed for free ammonia, albuminoid ammonia, and nitrites. *W.*2.—This Series was prepared exactly as W.1, except that ammonia-free distilled water, to which a trace of fresh soil suspension had been added, was employed. In this case decay was not sufficiently far advanced until after 32 days. The same determinations were then made as above. The results are shown in Table VI. The marked amount of free ammonia and nitrites which may be derived from decaying vegetable matter is evident.

TABLE VI.

Analytical results of samples showing the effect of the presence of decaying vegetable matter.

Water.	Free Ammonia. Parts per 100,000.			Albuminoid Ammonia. Parts per 100,000.			Nitrites. Qualitative test.		
	1 Blade	2 Blades	Control	1 Blade	2 Blades	Control	1 Blade	2 Blades	Control
Tap (W.1)	0·0234	0·0450	0·0002	0·0050	0·0084	0·0020	Present	Present	Absent
Distilled (W.2)	0·0250	0·0506	0·0005	0·0042	0·0032	0·0008	Present	Present	Minute trace

A small quantity of free ammonia may also be derived from undecayed vegetable matter if contained in the portion distilled for this determination. An extreme case (Series *W.*3) is cited. To each of two quantities of 500 c.c. of ammonia-free

distilled water 25 half blades of freshly washed grass were added. In the one sample, decanted from the grass, free ammonia was absent; in the other, distilled with the grass, a result of 0·0150 parts per 100,000 was obtained.

To resume, in the circumstances detailed in the penultimate paragraph above it is impossible to fix limits, but, if the appropriate source can be excluded as the origin of the presence of any of the substances enumerated, it is possible to formulate limits which, if exceeded, afford evidence of excretal pollution. I consider the present accepted limits for free and albuminoid ammonia too wide, and adherence to these must inevitably result in passing as fit for potable purposes a considerable proportion of water samples which are undoubtedly contaminated with excreta. In this connection the figures obtained (Tables VII. and VIII.) in the statistical investigation referred to in the second paragraph of the introduction are illuminating; in all cases the chemical opinion as to the purity of the samples was formed with full knowledge of the supply and was usually confirmed by independent bacteriological examination.

TABLE VII.

Amounts of free ammonia and nitrites in consecutive samples of water considered, in view of analytical results and topographical conditions of supply site, (1) free from excretal pollution; (2) excretally polluted; excluding those which could contain either free ammonia or nitrites from other than excretal sources.

Constituent	Parts per 100,000	Percentage of samples containing free ammonia and nitrites in excess of amount stated. 1. Free from pollution	2. Polluted
Free Ammonia	Exceeding 0·001	15	84
	,, 0·002	3	73
	,, 0·003	Nil	68
	(Average amount= In unpolluted samples 0·0005 In polluted samples 0·0127)		
Nitrites	Absent	95	3
	Exceeding 0·0001	Nil	86

TABLE VIII.

Amount of albuminoid ammonia in consecutive samples of water considered, in view of analytical results and topographical conditions of supply site, (1) free from excretal pollution, (2) excretally polluted; excluding those which could contain albuminoid ammonia from other than excretal sources.

Albuminoid Ammonia Parts per 100,000	Percentage of samples containing albuminoid ammonia in excess of amount stated. (1) Free from pollution	(2) Polluted
Exceeding 0·002	50	100
,, 0·004	25	98
,, 0·006	9	98
,, 0·008	Nil	84
(Average amount = In unpolluted samples 0·0027 In polluted samples 0·0154)		

It will be seen that, of waters considered fit for potable purposes, none contained free ammonia in excess of 0·003, albuminoid ammonia in excess of 0·008, or nitrites in excess of 0·0001 parts per 100,000, after excluding samples which could have derived these substances from other than excretal sources. Nitrates should not exceed 0·050 parts per 100,000. These then are the limits which, if exceeded and a non-excretal origin can be excluded, I submit provide definite evidence of excretal pollution. Considered with the reservations detailed above, it is not necessary that all these figures should be exceeded to cause suspicion, a distinct excess of any one is sufficient, but the occurrence of only a single abnormality is uncommon. Attention is drawn to the large proportion of unpolluted waters in which the analytical results did not even approach these limits. It will be seen that in polluted waters the limit for free ammonia was not exceeded in 32 per cent. of cases, for albuminoid ammonia in 16 per cent., and for nitrites in 14 per cent. The large proportion of samples in which the free ammonia failed to give evidence of pollution is of interest; examples of such waters are given in Table IX.

The samples included are such as could naturally contain only a small amount of albuminoid ammonia, and the high figures obtained in this determination illustrate its value in detecting pollution. Such waters give free and albuminoid ammonia figures not dissimilar from those yielded by many pure upland surface waters, but the nitrite and nitrate results are totally different, and enable a clear distinction to be made; examples of such waters are shown in Table X.

Emphasis has been laid on the presence of albuminoid ammonia as an indicator of the entry of excretal pollution; its absence is equally valuable in showing freedom from pollution particularly in waters containing high free ammonia and nitrites from reduction of nitrates; examples of such waters are shown in Table XI.

In Series L, M and O, a determination was also made of the addition to the chlorine content caused by the degree of pollution employed (1 in 22,000). By estimating the chlorine in the urine and fæces used it was calculated that in the case of urine the increase was 0·15, and with fæces 0·007 parts per 100,000. It is evident, then, that the chlorine estimation is of no value for providing indication of fæcal and of little value for urinary pollution, unless this is in gross amount.

In a prior paper (6) the writer has given an account of the chemical changes which occur in samples similar to the foregoing under certain particular conditions; on exposure to light (Series C); when containing metallic impurities (Series H); when chlorinated (Series Q, R and S). It may be useful to make brief mention of the findings of this previous research here, as the effect of any of these conditions is very marked, and is an imperative consideration in the interpretation of an analysis.

Samples exposed to light (*Series C*).—It will be seen that exposure to light resulted in an enormous increase in the albuminoid ammonia content (due to growth of algae), but, for all practical purposes, there was no effect on the rate

TABLE IX

Analytical results of polluted waters containing a very small quantity of free ammonia, parts per 100,000.

	1	2	3	4	5	6	7	8	9	10
Free Ammonia ..	0·0003	0·0009	0·0002	0·0011	0·0007	0·0001	0·0017	0·0002	0·0000	0·0004
Albuminoid Ammonia	0·0195	0·0266	0·0196	0·0196	0·0186	0·0257	0·0148	0·0286	0·0174	0·0108
Nitrites ..	0·0010	0·0001	0·0002	0·0002	0·0001	0·0012	0·0011	0·0020	0·0014	0·0001
Nitrates ..	1·4280	2·1050	3·0770	0·3800	2·5000	0·5710	0·5710	0·4700	5·7140	2·0000

(1) Well, 22ft. deep (Kent); (2) Well, 40ft. deep (Lincolnshire); (3) Well, 18ft. deep (Norfolk); (4) Well, 12ft. deep (Cornwall); (5) Well, 20ft. deep (Cornwall); (6) Spring (Essex); (7) Spring (Cornwall); (8) Well, 40ft. deep (Norfolk); (9) Well, 32ft. deep (Devon); (10) Well, 22ft. deep (East Yorks.).

TABLE X.

Analytical results of unpolluted waters containing a large quantity of albuminoid ammonia, parts per 100,000.

	1	2	3	4	5	6	7	8	9	10
Free Ammonia ..	0·0008	0·0021	0·0004	0·0000	0·0018	0·0003	0·0012	0·0019	0·0015	0·0012
Albuminoid Ammonia	0·0130	0·0186	0 0127	0·0168	0·0172	0·0104	0·0136	0·0186	0·0256	0·0196
Nitrites ..	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
Nitrates ..	0·0040	0·0040	0·0060	0·0040	0·0040	0·0020	0·0140	0·0060	0·0160	0·0040

(1) Upland surface water (Linlithgowshire); (2) Moorland stream (Shetlands); (3) Burn (Orkneys); (4) Moorland stream (Orkneys); (5) Lake (Co. Donegal); (6) Mountain stream (Co. Cork); (7) Brook (Dorset); (8) Stream (Dumbartonshire); (9) Brook (Co. Cork); (10) Burn (Orkneys).

TABLE XI.

Analytical results of unpolluted waters containing a large quantity of free ammonia from reduction of nitrates, parts per 100,000.

	1	2	3	4	5	6	7	8	9	10
Free Ammonia ..	0·0974	0·1148	0·9840	0·0456	0·1154	0·0834	0·1054	0·0432	0·0576	0·0824
Albuminoid Ammonia	0·0040	0·0020	0·0033	0·0030	0·0012	0·0023	0·0035	0·0042	0·0016	0·0026
Nitrites ..	0·0001	0·0001	0·0001	0·0000	0·0001	0·0010	0·0000	0·0010	0·0010	0·0005
Nitrates ..	0·0020	0·0040	0·0050	0·0060	0·0020	0·0020	0·0040	0·0020	0·0040	0·0040

(1) Well, 400ft. deep (Essex); (2) Well, 50ft. deep (Hants.); (3) Well, 200ft. deep (Essex); (4) Well, 523ft. deep (Kent); (5) Bore well, 78ft. deep (Yorkshire); (6) Public supply (Essex); (7) Well, 300ft. deep (Hants.); (8) Spring (Orkneys); (9) Public supply (Kent); (10) Well, 400 ft. deep (Lincolnshire).

of production and the amount of free ammonia and nitrites. It has always been recognised that water samples must be stored in the dark, but the reason for this is that otherwise there is a fallacious increment to, not a decrement from, the indications of pollution as is commonly supposed.

Samples stored in the dark; effect of metallic impurities.—The presence of 0·1 part per 100,000 of copper (as sulphate) very greatly restrained the production of free ammonia and entirely inhibited its decomposition into nitrites and nitrates. The creation of evidence of original pollution has therefore been, to a great extent, prevented. In an investigation by Atkinson and the writer (7) on the influence of metallic impurities in water on its bacteriological content, it was found that the effect exerted by the four metals tested for in the routine examination of water was in the order—copper, zinc, lead, iron.

Samples stored in the dark; effect of chlorination.—Chlorination to the extent of 3·0 parts per million completely prevented, for all practical purposes, the production of free ammonia, nitrites, and nitrates, *i.e.* it prevented the formation of the evidence of pollution, and even one-quarter of this amount was only slightly less effective.

ROBERT C. FREDERICK.

ROYAL NAVAL MEDICAL SCHOOL,
ROYAL NAVAL COLLEGE, GREENWICH.

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DISCUSSION.*

Mr. E. HINKS: Some of the author's observations, and, still more, his conclusions, are contrary to general experience. It is generally held that a sewage-contaminated water yields a higher free than albuminoid ammonia: that this is generally the case with sewage and with sewage effluents is beyond doubt. The fate of these ammonias and their relation to each other must surely depend upon the bacterial content, the degree of aeration and so forth, of the soil through which the water passes. What happens in stoppered bottles is unlikely to be a certain guide to what happens during percolation through a soil. Again, the author's observations with regard to the effect of decaying vegetable matter are, I think, contrary to other published experiments.

The whole question is one of bacterial action, as is, indeed, observed by the author at the end of his paper.

In series M. and O. the sudden disappearance of the nitrites after the 63rd day, following on the gradual rise, is remarkable. Possibly the exhaustion of

* Criticisms made, either wholly or in part, subsequently to the meeting, are given in the first person.—EDITOR.

available oxygen is the cause of this. Is this likely to happen under natural conditions?

The slowness of the evolution of the free ammonia from water D. in Table V. is also remarkable. Such a result is not in accordance with that usually found on distilling effluents. I suggest that the later fractions are not free ammonia at all, properly so called, but are the result of the gradual hydrolysis of some nitrogenous constituent.

The author is rather sweeping in his references to data other than the ammonias, nitrites and nitrates. Has the chlorine content been justly discredited? Surely in certain circumstances the chlorine affords most valuable indications. Similarly "oxygen absorbed" figures, likewise discredited by the author, are often of value. Is it correct to say that, as an invariable rule, nitrates have no significance in chalk waters? They may be extremely significant.

Is it not the case that to suggest a general standard by which potable waters can be judged is, in any case, a futility? A standard of 0·05 parts of "nitrates" per 100,000 would condemn the bulk of the water supplies of this country, unless the water were in that privileged class in which "nitrates are of no significance."

In classing certain views which are widely held and, one had thought, well established, as "fallacies based upon isolated analyses of sewage and sewage effluents," the author lays himself open to the retort that his own conclusions are based upon the results of the examination of two particular contaminations in one particular water under one particular set of conditions—and those not natural ones.

Mr. O. HEHNER: This paper is written with the almost total disregard of the immense mass of work which has been done during the last half century on the analysis of potable waters and the interpretation of the analytical results. If anything stands out, it is the clearly recognised fact that no single estimation by itself is of any value, but that all the figures obtained by a somewhat comprehensive examination must be taken together in order that a fair judgment may be possible. It is futile to say, as does Mr. Frederick, that the chlorine content has been discredited, and that the "oxygen absorbed from permanganate" is useless, or that "albuminoid ammonia" has no significance. The interpretation of a water analysis may be likened to the reading of a book; each single word or sentence means nothing; it is the total which counts. This total in all cases should include chlorine, sulphuric acid, nitric acid, nitrite, phosphoric acid, free ammonia, albuminoid ammonia, oxygen absorbed, total solids, hardness, and, wherever possible, a bacterioscopic examination for, at least, *B. Coli*. An excess of chlorine may come from the sea; of sulphates from deposit of gypsum; of nitrates (within limits) from the chalk; of free ammonia from reduction of nitratet through iron pipes, or a spongy iron filter; of albuminoid ammonia from peas or other harmless vegetable matters, and so on. Then the origin of the water must, wherever possible, be taken into account, and the sample be compared with the natural unpolluted water from the same stratum or from the immediately surrounding district. An experienced water analyst can read from his results whether a water is polluted with house drainage, including urine, or with animal and manurial drainage, or with soakings from a churchyard, with brewery or similar washings, or is normal for peat water or river water; whether it comes from the chalk or sandstone, from near the sea, or the strata beneath the London clay, polluted or not polluted. Mr. Frederick would destroy all possibility of such judgment.

It may be noted that he re-discovers the fact, known for nearly 50 years, that urine does not give up its nitrogen, or only a small portion of it, in the form of free ammonia, whilst water polluted with fæcal matter in the natural way nearly always does.

Dr. J. C. THRESH: The results of the experiments detailed are interesting, but I fail to see how they assist in interpreting the results of analyses of natural waters. What would have been preferable would have been the study of some natural waters from sources which had been most minutely examined, and which were kept under observation for a considerable period. It seems to me to be safer to regard all waters as having at some period, however remote, been polluted, and to make such examinations thereof as will justify an opinion as to whether they now are "pure and wholesome" and "suitable for domestic purposes." These words, "pure and wholesome" and "fit for domestic purposes," never occur in the paper. Obviously Parliament, in insisting that potable waters should possess these properties, distinguished between pure and wholesome, and even knew that a pure and wholesome water might be unfit for domestic purposes. The analyst may decide about the purity, and even the fitness for domestic use, but the question of wholesomeness is a medical one, and does not depend on the free or albuminoid ammonia, the nitrites and nitrates, all of which, in the amounts likely to be found in a potable water, are absolutely harmless. I take it that a "pure" water is one which is free from colour, odour, taste, turbidity, free from lead or copper and excess of saline matter of an objectionable nature. The excess would also show whether the water was fit for such domestic purposes as washing and cleaning. The "wholesomeness" depends almost entirely on the bacterial contents—in fact, entirely on these in the absence of any constituent of a poisonous nature. The chemical character of a water can be determined without any attempt at estimating the constituents to the third and fourth place of decimals. The age is passing, if it has not already passed, when upon the chemical analysis alone depend all our conclusions regarding the purity and wholesomeness of water.

Mr. S. F. BURFORD said that experiments *in vitro* were not to be compared with results in the field. No careful men were basing information on water, nowadays, on nitrites, nitrates, and albuminoid ammonia only, for so much depended on the district from which the water came. In his opinion, the question of albuminoid ammonia had been much over-rated, and, within his experience, he remembered only three instances of contamination in which albuminoid ammonia was present. The amount of oxygen absorbed was another factor to be taken into consideration.

He considered that methods that were applicable to one class of water were not applicable to others, as, for instance, river water which contained no chlorine. He mentioned a district he knew where three totally different supplies of water were given to the public—one gave high ammonia, one gave chlorine, and one was highly calcareous water. When the question under consideration was merely the water supplied to one individual on his farm, the author's methods of analysis would be very satisfactory, but he considered the analyst must make a finer mesh, according to the purposes to which the water was to be put.

Mr. R. L. COLLETT pointed out that where the author had added only urine his nitrite determination was very steady, but where he had added fæces great changes were to be found in his results. Further, in the presence of copper or of chlorinated waters, he got very steady readings. In his opinion, the paper emphasised the importance of the bacteriological examination of water in conjunction with the chemical analysis.

Dr. BERNARD DYER: It has long been recognised that the water from a cesspool or drain percolating through but a few feet of subsoil into a well may have its nitrogen so completely oxidised by nitrifying organisms that the well-water, though heavily polluted, may yield but negligibly small traces of free and albuminoid ammonia, whilst its nitric nitrogen may be raised to even 1 part or more per 100,000. On the other hand, pure waters of deep well origin contain nitrates far in excess of the small figure which the author in one part of his paper

suggests as evidence of objectionable impurity—a figure which would class the whole of the London water supply as "non-potable," and probably most of the supplies in the country, excluding the soft upland waters of Wales and the North. This, indeed, the author elsewhere seems to recognise when he makes the surely too sweeping assertion in the other direction, that in waters from certain strata nitrates have no significance.

Chemical analysis, while, if construed in the light of reason and experience, lending valuable aid in judging of the suitability of water for drinking purposes, is often of less assistance than investigation of the bacteriological condition of the water. This often enables the analyst to distinguish between what may be called "proximate" pollution and pollution so remote either in time or in space as to have become presumably innocuous.

Reply by Mr. Frederick.

With regard to the courteous remarks of these authorities I must immediately point out that my standpoint has been fundamentally misconceived. I am considered to have examined a number of polluted artificially prepared samples, and on the results obtained to have founded a thesis on the interpretation of the results obtained in water examination practice. What I actually did was to make a number of experiments in an endeavour to obtain confirmation of opinions tentatively formed as a result of extended practical experience. That this is the correct standpoint is evident, beyond all question, from the opening paragraph of the paper.

It does not appear to be realised that the investigation was primarily directed towards determining the chemical changes which occur in samples during the time which elapses between collection and analysis.

There seems to be a general consensus of opinion that I have failed to realise the importance of the bacteriological examination of water. Even with only an elementary knowledge of the subject, one knows that this is, of course, an absolutely essential complementary examination, but in this paper I am dealing with the chemical aspect only, and specifically stated so. It could, with equal truth, have been pointed out that I did not make a microscopical examination of the sediment, or a spectroscopic examination of the dissolved solids. In point of fact, almost every one of the 1,000 or so samples of water on which this paper is founded was examined independently by a distinguished bacteriologist, and the fact that in approximately 99 per cent. of cases our opinions agreed, is the best proof that the principles on which I work and which I have enunciated in this paper are sound.

I am taken to task for stating that the value of the chlorine figure as an indicator of excretal pollution is discredited. In this paper it is shown that with comparatively gross pollution the chlorine is only increased 0·15 with urine and with fæces 0·007 parts per 100,000, and there does not seem any reason to revise my opinion.

Mr. O. Hehner states that I have disregarded the immense mass of work done during the last half century on the analysis of potable waters and the interpretation of the analytical results. If this work has been done, which I question, it has left little of permanent value, for the ideas of to-day seem much the same as those formed subsequent to the publication of Wanklyn's epoch-making work in 1867.

Dr. Dyer states that the limit for nitrates would class the whole London water supply as non-potable. The only water which can be considered definitely to be free from nitrates derived from strata, and to which therefore the limit is applicable, are collected rain waters and distilled waters; the London supply is obtained from rivers and wells.

The Crystalline Bromides of Linseed Oil.

BY HAROLD TOMS, M.SC. (LOND.), A.I.C.

(WORK DONE UNDER THE ANALYTICAL INVESTIGATION SCHEME.)

(*Read at the Meeting, December* 5, 1923.)

IT is well known that when an ethereal solution of linseed oil is treated with bromine an "insoluble" substance is obtained. When Hehner and Mitchell (ANALYST, 1898, **23**, 310) first drew attention to this, it was suggested that estimation of this compound might be used as the basis of a method for the evaluation of linseed oil. The "oil bromide test," however, has never been satisfactory, for, although many investigations (Ingle, *J. Soc. Chem. Ind.*, 1911, **30**, 344; Eibner, and Muggenthaler, *Chem. Zentralbl.*, 1913, **1**, 567; Sutcliffe, ANALYST, 1914, **39**, 28, 388; Gemmell, *ibid.*, 297; and Davidson, *J. Ind. Eng. Chem.*, 1921, **13**, 801 ANALYST, 1921, 466), have been undertaken with a view to placing it on a sound basis, no method has been evolved for preparing the compound in a chemically pure condition.

The oil bromide is somewhat insoluble in ordinary solvents, and this has prevented previous workers from obtaining it in a pure condition. Hehner and Mitchell (*loc. cit.*) purified their material by subjecting it to a long process of extraction, and in this way obtained a substance which melted at 143·5° to 144° C., and gave, on analysis, the following figures:

Found	C	= 32·97	Calculated for ash-free substance	C	= 33·29
	H	= 5·42		H	= 5·48
	Br	= 56·18		Br	= 56·74
	O	= 4·44		O	= 4·49
	Ash	= ·99			—
		100·00			100·00

Since $C_{57}H_{96}O_6Br_{14}$ requires C = 34·27; H = 4·81; Br = 56·11 and O = 4·81 per cent., it was suggested that the compound is a mixed bromo-glyceride of the composition

$$C_3H_5 \begin{cases} C_{18}H_{29}O_2Br_6 \\ C_{18}H_{29}O_2Br_6 \\ C_{18}H_{33}O_2Br_2, \end{cases}$$

i.e. a glyceride containing one oleic acid and two linolenic acid radicles. More recently Davidson (*loc. cit.*) has pointed out that this composition corresponds equally well with that of linolenin-dilinolin bromide.

In passing, it may be noted that in neither paper is any mention made of the

fact that any glyceride containing two molecules of one acid and one of another can exist in two isomeric forms. Thus:

$$\text{(i)}\quad \begin{array}{l} CH_2.OA \\ | \\ CH.OA \\ | \\ CH_2.OB \end{array} \qquad \text{and (ii)} \quad \begin{array}{l} CH_2.OA \\ | \\ CH.OB \\ | \\ CH_2.OA. \end{array}$$

It will be noted also that a substance having the constitution represented by I can exhibit optical isomerism.

In 1921 Davidson (*loc. cit.*) succeeded, with great difficulty, in crystallising some of the crude bromide from carbon tetrachloride. The product thus obtained melted at 151° C. (corr.), and contained 59·24 per cent. of bromine. This figure, as Davidson points out, approaches that required for dilinolenin-linolin bromide (59·42 per cent.). From other solvents he obtained small amounts of material giving bromine contents varying from 57·38 per cent. to 59·24 per cent. The melting points of these products are not stated. The same writer concludes that the crude oil bromide is mainly dilinolenin-linolin bromide mixed with a small amount of some other (unidentified) bromo-glyceride containing a smaller percentage of bromine.

The experiments recorded below were undertaken with the object of determining the nature of the precipitated "oil bromide," and, if possible, of finding a trustworthy method of testing drying oils by means of bromination.

PART I.

The following preparatory experiments were repeated several times in duplicate, first with a sample of oil of unknown origin, and then with Calcutta oil (iodine value 180·9), kindly given by Messrs. Blundell, Spence & Co., Ltd., of Hull. The products obtained in each case were identical in composition.

Experimental.

The Bromination of Linseed Oil.—In a typical experiment 40 grms. of oil were dissolved in 300 c.c. of ether and 2 c.c. of glacial acetic acid were added. The solution was cooled by means of a stream of water and stirred mechanically while 16 c.c. of bromine (excess) were slowly run in. The stirring was continued for some hours and, after standing overnight, the supernatant liquor was decanted. Ether (100 c.c.) was added, and the mixture stirred vigorously for an hour; after standing, the supernatant liquor was again removed. This process was repeated twice more, but on the last occasion the mixture was filtered through an ordinary filter and left to drain for some hours. The residue was then boiled for several hours with alcohol and again filtered. This gave a white granular product (28 grms.) which, after drying on a porous tile, softened at 130° C. and melted at 140° to 145° C.

The ether residue left, after removing the solvent, a semi-solid sticky mass, which did not set after standing for several months. This has not been further investigated.

PURIFICATION OF THE "OIL BROMIDE."—With the object of finding a suitable crystallising medium, some 25 different solvents, mainly esters, were tried. Of these, ethyl acetate, ethyl formate, ethyl aceto-acetate and amyl acetate were the most successful. The first-named solvent gave the best results in that the product was obtained in a granular form, and could be readily separated by filtration; hence it was used in all subsequent experiments.

The crude "oil bromide" was boiled with ethyl acetate, the solution filtered hot and left to cool. After some hours the fine granular precipitate was collected on an ordinary filter, and when nearly dry was transferred to a flask, boiled with alcohol, and filtered hot. The residue (substance A) was then boiled with ether, filtered, and left to dry on a porous tile. The omission of this last operation usually resulted in the crystals caking together into a hard horny mass.

From 40 grms. of oil there were obtained 28 grms. of crude bromide (70 per cent.); this, on crystallisation, gave 7·5 grms. of pure product (18·7 per cent.). This corresponds with 11·2 per cent. of the unsaturated glyceride in the original oil.

From the ethyl acetate mother liquor there was obtained, on complete removal of the solvent, a large amount of a crystalline material (substance B), which in the crude state melted below 100° C.

SUBSTANCE A.—The substance which crystallises from ethyl acetate appears to be practically insoluble in this solvent in the cold. It melted at 153° C. (corr.), and further crystallisation failed to raise its melting point. A microscopical examination showed that it is microcrystalline, since it reacts to light through crossed Nicols. There were also indications of a biaxial structure.

On analysis the following results were obtained:

Found	Br = 59·40 and 59·50;	C = 31·4 and H = 4·18
Calc.	Br = 59·42 ;	C = 31·7 and H = 4·36.

This corresponds to linolic dilinolenic bromo-glyceride, $C_{57}H_{94}O_6Br_{16}$, which substance can exist either as the symmetrical or the optically active compound. Since neither linseed oil nor solutions of this compound show any rotation, it is put forward tentatively that this glyceride is either a racemic mixture, or more probably, the symmetrical compound.

Several determinations of the solubility of this pure bromide in ethyl acetate show that the figure lies between 0·15 and 0·20 grm. per 100 c.c. at temperatures ranging from 15 to 20° C.

SUBSTANCE B.—The residue obtained from the ethyl acetate mother liquor was dissolved in ethyl formate and decolorised by boiling with animal charcoal, and after many crystallisations from ethyl formate a small amount of material was obtained which melted at 117° C. (corr.) after washing with cold alcohol—an operation which prevented the substance from caking. This material reacts to light through crossed Nicols, and is undoubtedly crystalline, but no information regarding the structure of the crystals was obtainable.

On analysis the following results were obtained:

Found	Br = 52·53 and 52·10 per cent.;	C = 36·8 per cent.;	H = 3·93 per cent.
Calc.	Br = 52·23 per cent.;	C = 37·2 per cent.;	H = 5·33 per cent.

This corresponds approximately to $C_{57}H_{98}O_6Br_{12}$, which may be trilinolic bromo-glyceride or one of the several possible isomers of the mixed glyceride containing the three radicles oleyl, linolyl and linolenyl.

In the analysis of both substances it was found that the lime method of estimating the bromine (which was used by Hehner and Mitchell) gave low results, whereas the Carius method and a modification of the method of Stefanow (described below) gave the required theoretical results.

Modification of the Method of Stefanow.—The substance was decomposed with sodium ethylate, and the bromide precipitated as silver bromide in the usual way, with the use, however, of a known amount of 0·1 *N* silver nitrate solution. The excess on titration with ammonium thiocyanate always gave high results, so the silver bromide was collected on a Gooch crucible, and washed free from "fat" with ether. This gave consistent and theoretical results.

Attempts were made to remove the bromine from Substance A, but these were entirely unsuccessful. This is somewhat remarkable in view of the ease with which α- and β-linolenic acids (*cf.* Erdmann and Bedford, *Ber.*, **1909**, **42**, **1324**, **1334**) are obtained by the hydrogenation of hexabromstearic acid.

Again, all attempts to hydrolyse the material failed completely; hence confirmation of the presence of linolic and linolenic acid residues could not be obtained. Up to the present all efforts to synthesise any of the glyceride containing the acid radicles have also been unfruitful.

PART II.

Estimation of the Crystalline Bromide.—The comparative insolubility of the precipitated bromide in ethyl acetate suggested the idea that the weight of this compound obtainable might bear a definite relation to the drying value of the oil, and hence serve as a rapid means of evaluating linseed oil. Attempts were made, therefore, with several samples of oil, to correlate the percentage yield of bromide with the iodine value. The results obtained are shown below.

Sample number	I.	II.	III.	IV.*
Iodine value	180·9	179·5	184·8	183·3
Series I.				
Percentage of bromides..	19·26	(1) 18·26, (2) 18·50, (3) 18·20	19·15	15·80
$\frac{\text{Iodine value}}{\text{Percentage}}$	9·39	9·83	9·65	11·6
Series II.				
Percentage of bromides	24·31	21·93	25·29	23·26
$\frac{\text{Iodine value}}{\text{Percentage}}$	7·44	8·18	7·31	7·88
Series III.				
Percentage of bromides	22·10	20·10	21·30	19·49
$\frac{\text{Iodine value}}{\text{Percentage}}$	8·18	8·93	8·67	9·40

* Sample IV. was a dull yellow oil containing particles of solid matter which settled out as a sludge, very soluble in ethyl acetate.

In the first series about 1 c.c. of oil was weighed accurately and dissolved in 10 c.c. of ethyl acetate. Liquid bromine (1 c.c.) was then run in slowly, rise of temperature being avoided. After some time the precipitate was collected on a Gooch crucible, washed with ethyl acetate (20 c.c.), and dried at 80° C.

In the second series about 1 c.c. of the oil was weighed and dissolved in 10 c.c. of ethyl acetate. A slight excess of a solution of bromine in glacial acetic acid (1 c.c. =0·595 grm. Br.) was run in slowly to prevent rise of temperature. After standing for some time the liquid was decanted through a Gooch crucible, and the precipitate was washed with ethyl acetate (10 c.c.) and dried to constant weight at 80° C.

In the third series the estimations were carried out as in Series 2, except that the precipitate was washed, finally with alcohol.

Excluding Sample 4, the results obtained in the first series are somewhat more consistent than those in Series 2 and 3. It is interesting to note also that in Series 1 the melting point of the product was in each case about 148° C., whereas in the Series 2 the figure was about 140° to 141° C., and in Series 3, 142° to 144° C. The presence of glacial acetic acid seems therefore to increase the yield of precipitate (*cf.* Davidson, *loc. cit.*), but renders the product less pure. By washing with alcohol some of the impurity is removed, as is shown by the decreasing yield and the rise in melting point.

Summary.

Two definite crystalline compounds have been isolated from linseed oil in the form of their bromides. The analyses indicate that they are (1) a linolic-dilinolenic bromo-glyceride, and (2) the trilinolic bromo-glyceride or an oleic-linolic-linolenic bromo-glyceride.

No synthetic confirmation of these results has yet been obtained. Data have been obtained which indicate that the amount of the most unsaturated glyceride in linseed oil is a constant proportion of the total unsaturated bodies present.

In conclusion, the writer wishes to thank Mr. C. Ainsworth Mitchell, who, with Mr. Otto Hehner, originally discovered the "oil bromide," for having unreservedly placed this investigation in his hands, and also the Society of Public Analysts for the grant which defrayed much of the expense incurred.

King's College, University of London,
Strand, W.C.2.

Discussion.

Mr. C. A. Mitchell said that the author's work was an important contribution to our knowledge of the chemistry of linseed oil. Owing to the great variations in the results obtained in estimating the "insoluble bromide" of linseed oil, there had been a tendency to discard the method in favour of the estimation of the amount of linolenic hexabromide yielded by the fatty acids, but the drawback to this was the risk of oxidation of the fatty acids prior to bromination, so that

the use of the oil itself, if the drawback mentioned could be overcome, was preferable. The author had now shown them the cause of these variations, which was that the "insoluble bromide" was a mixture of two relatively insoluble bromides, and that the proportion of these in the precipitate varied with the conditions, such as solvent used for washing the product, the length of time of purification, and so on. It should now be possible to obtain concordant results by estimating the more insoluble of the two bromides. He was not surprised to hear of the failure of the author to remove the bromine from these compounds. He had, himself, repeatedly tried to displace it by the action of nascent hydrogen continued for days at a time, but without success. Possibly the action of hydrogen in presence of a catalyst might be more effective.

Mr. MITCHELL added that Mr. Hehner had read Mr. Toms' paper, and wished to congratulate him upon the results he had obtained, and to express his regret that he was unable to be present to take part in the discussion.

Mr. TOMS, in reply, said that Dr. Gordon, of King's College, London University, (to whom he had sent the substances), was his authority for saying that the bromides were micro-crystalline; he had reported that they were crystalline and not amorphous—the one was biaxial, the other was of a different structure. With regard to obtaining the molecular weight by freezing, such a thing was obviously impossible, owing to the insolubility of the bromides.

Notes.

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

SPRING WATER OF UNUSUAL COMPOSITION.

RECENTLY we received a sample of water, which was taken from a spring in a wood in the vicinity of Glasgow, the object being to determine its suitability as a water supply. As it has an unusual composition, we give below a complete analysis:

	Parts per 100,000.
Aluminium sulphate	3·81
Ferrous sulphate	·01
Calcium sulphate	1·72
Magnesium sulphate	1·07
Magnesium chloride	·61
Sodium chloride	2·59
Sodium nitrate	·04
Silica	traces
Organic matter	·60
Total solid matter	10·45
Free ammonia	·005
Albuminoid ammonia	·007

There were neither carbonates nor free acid present, and the proportions of the various ingredients were calculated according to the form in which they were most likely to exist on evaporation. Although we have made hundreds of analyses of spring water, this is the only one that we have found to contain aluminium sulphate. We have had various samples of pit water containing large proportions of ferrous sulphate with smaller proportions of aluminium sulphate and free acid, but none giving a similar analysis to the above.

R. T. THOMSON.
JAMES SORLEY.

CITY ANALYST'S LABORATORY,
BATH STREET, GLASGOW.

THE VOLUMETRIC ESTIMATION OF VANADIUM IN STEEL.*

IT has been found that the green colour of chromium sulphate can be considerably reduced, or even destroyed, by a suitable addition of cobalt sulphate, since the two colours are complementary. The best ratio appears to be approximately 2 per cent. of chromium to 3 per cent. of cobalt, *i.e.* in a 1 per cent. chromium steel 1½ per cent. of cobalt would be added as sulphate. In fact, in this case, the solution can be made nearly colourless in a volume of 500 c.c. With 4 per cent. of chromium 6 per cent. of cobalt would be added as sulphate. In this case the colour is a pale green. With higher amounts the colours only partly compensate, and the pink colour of cobalt interferes with the end-points. The blank solution for colour comparison must be treated with the same amount of cobalt sulphate as in the test. The method has been found practicable up to 5 per cent. of chromium.

Conversely, a cobalt steel containing up to about 7 per cent. of cobalt can be treated with chromium sulphate so as to obtain the required ratio mentioned, and to eliminate the pink colour of the cobalt, before proceeding with the volumetric estimation.

A. F. ETHERIDGE.

RESEARCH DEPARTMENT,
WOOLWICH ARSENAL.

* *Cf.* ANALYST, 1923, **48**, 588.

UNCOMMON ANIMAL FATS.

THE writer has personally obtained the fats of the Ceylon wild animals, the analysis of which is recorded below.

The Ceylon leopard, *Felis pardus*, is more often spoken of locally as the cheetah. The usual ground colour of the body is a yellowish brown, although sometimes it is very light, or even so dark as to merit the name of black leopard. In each case the skin is thickly studded with black rosettes with pale centres. A full-grown leopard will measure as much as seven feet from nose to tip of tail, and stand 23 to 25 inches high at the shoulder. It feeds on any kind of smaller animal, and will kill full-grown bulls.

The Sambhur, *Cervus unicolor*, is known in Ceylon as the elk. The usual colour of a buck is dark brown, and that of a female a greyish brown. The fur is very coarse and shaggy, so that the skin makes a poor trophy. A good buck

stands from 13 to 14 hands in height at the shoulder, and will weigh as much as 600 lbs. The antlers are three tined. Irregular heads with extra abortive points are sometimes found, antlers with seven points having been seen.

The spotted deer, *Cervus axis*, is generally considered to be the most beautiful of all the deer tribe. The colour is a light fawn spotted with white. There is a dorsal stripe from the neck to the tip of the tail. The males stand from 34 to 38 inches high at the shoulder. They are gregarious, and are met with in herds up to 40 or 50.

The peafowl, *Pavo cristatus*, is found in the low country of Ceylon.

The particular species of pig found in Ceylon is *Sus cristatus*, the Indian wild boar. It has a short massive body and big head provided with fighting tusks. The colour of the skin is a dark slaty grey, with scanty bristles. It is naturally a vegetable feeder, but is by no means adverse to a meal of carrion.

The fats of the animals are all solids at the ordinary temperature (81° F.), with the exception of that of the peacock, which is a yellow oil. This last is highly valued by the local "vederalas" (native doctors) for use in cases of stiff joints or contracted tendons. The following analytical results were obtained:

FATS.

	Specific Gravity 99/15° C.	Butyro-refractometer reading at 40° C.	Acid value.	Saponification value.	Iodine value (Wijs).	Unsaponifiable matter. Per Cent.
Leopard	0·8592	49·5	1·78	201·1	62·2	0·33
Sambhur	0·8610	45·7	4·37	210·6	22·4	0·56
Spotted deer	0·8640	44·3	4·98	212·3	23·8	0·52
Peacock	0·8947	54·5	8·70	215·3	66·4	0·34
Pig	0·8851	52·0	11·12	216·4	44·8	0·40

MIXED FATTY ACIDS.

	Solidifying point. °C.	Butyro-refractometer reading at 40° C.	Neutralisation value.	Iodine value (Wijs).
Leopard	39·2	38·9	210·3	60·9
Sambhur	48·2	31·6	213·1	21·4
Spotted deer	47·8	31·6	215·6	22·65
Peacock	36·4	46·9	21[illegible]·6	66·7

Leopard's fat does not appear to have been examined before, but its constants closely resemble those of the tiger recorded by Lewkowitsch, who gives m. pt., of fatty acids, 37·5° C.; saponification value, 200·8; neutralisation value of fatty acids, 208·2; and iodine value, 57·7.

The analyses of the fats of the two members of the deer tribe, in spite of their tropical habitat, are very similar to those of European deer quoted in Lewkowitsch, who, for example, gives for the Chamois:—Solidifying point of the fatty acids, 51·5° C.; saponification value, 203·3; neutralisation value of fatty acids, 206·5; and iodine value, 25·0.

European wild boar fat, however, differs considerably from the Ceylon wild boar fat; for example, the saponification value is given as 195·5 and the iodine value as 81.

WILLIAM NORMAN RAE.

CHEMICAL LABORATORY,
CEYLON UNIVERSITY COLLEGE, COLOMBO

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.

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1923.

DURING the 3rd Quarter of the year, 1256 samples were submitted for analysis, of which 1087 were analysed under the Food and Drugs Acts, and 134 for the water department. Of the Food and Drugs samples 1049 were bought informally, and of these 43 were adulterated; 38 were bought under the provisions of the Acts, and of these 7 were adulterated.

MILK.—Of the 539 samples examined 38 were adulterated with water or were deficient in fat, and of these 38 no fewer than 33 contained less than 3 per cent. of fat, which is an unusually large proportion. Thirty-eight samples from 23 different farmers contained less than 11·5 per cent. of total solids.

CREAM.—Four of the 11 samples of cream were adulterated, as they contained from 0·23 to 0·35 per cent. of boric acid. None of them had a declaratory label and one was marked "Thick Rich Cream," although it was preserved cream. Two of the informal samples sold as preserved cream were free from boric acid, and should have been sold as cream.

VINEGAR.—Twenty-six informal samples were genuine, but one contained 3·0 per cent. of acetic acid, and one subsequent formal sample contained 2·9 per cent. Proceedings were taken, and the defendant, who undertook to sell from smaller casks in future, was ordered to pay the costs of the prosecution. (*cf* ANALYST, **1923, 48,** 544).

ZINC OINTMENT.—One of 5 informal samples contained 17·3 per cent of zinc oxide, instead of 15 per cent., the proper amount.

BORIC ACID POWDER.—One informal sample contained 80 parts of lead per million, being more than three times the limit of the B.P., and the vendor was cautioned. Nine other samples were genuine, containing from 4 to 24 parts of lead per million.

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.

SALE OF A BUTTER MIXTURE.

JUDGMENT was given by the Justiciary Appeal Court at Edinburgh, on December 15, 1923, in a stated case in which a judgment by Sheriff-Substitute W. J. Robertson, of the County of Ayr, was submitted for review.

The proved facts were that J. and J. McKay, grocers, of Dalry, had sold to an inspector 1 lb. of margarine, in reply to a demand to be supplied with a certain

butter mixture exposed in their window and labelled "Butter mixture, 1s. 2d. per lb." The analysis had shown the sample to be margarine containing less than 10 per cent. of butter fat.

The respondent had been charged with a breach of the Sale of Food and Drugs Acts for the sale of the sample, and also of the Margarine Act, in that the paper wrapper had not the word "margarine" upon it.

The Sheriff-Substitute had acquitted the respondent on the ground that the inspector asked for a particular article and received it, and that any misdescription was the misdescription of the buyer, and not of the seller. He had also acquitted him on the second charge, since the butter mixture was not delivered to the purchaser in any wrapper, and the fact that he had no wrapper in his shop was not relevant to the charge.

The Court, by a majority of two to one, upheld the appeal of the Procurator-Fiscal, and remitted the case to the Sheriff-Substitute with instructions to proceed.

Lord Cullen thought that the Sheriff was not entitled from the facts proved to infer that the purchaser's demand for "1 lb. of that butter in the window" was not truly a demand for butter.

Lord Sands considered that the merchant was guilty of a contravention of the Act, if, when asked for "that butter," he supplied a customer with a mixture resembling butter, without satisfying himself that the customer knew that it was not butter.

The Lord Justice-General pointed out that the Sheriff-Substitute had reported that it had been proved that, at the time of the purchase, the inspector had knowledge of the terms of the ticket. The exposure of the article for sale was an offer of a mixture not of any single article, nor of an article of any single "nature, substance and quality." The respondent was probably committing an offence under the Margarine Acts by selling, otherwise than as margarine, a compound resembling butter, but he was not charged with an offence under those Acts, but under the Food and Drugs Acts, for selling "butter" which was not of the nature, substance and quality of butter. It did not seem just or reasonable to hold, on the facts proved, that the purchaser's demand for "that butter" was a demand for "butter," in view of the fact that the purchaser was aware that what he was asking for was not "butter," but a "butter mixture." His Lordship was, therefore of opinion that the Sheriff-Substitute was justified in acquitting the respondent.

Department of Scientific and Industrial Research.

FOOD INVESTIGATION BOARD.

RED DISCOLORATION (SO-CALLED "PINK") ON DRIED SALTED FISH.*

THE state known as "pink" is one to which dried, salted fish is liable.

The report begins with a full history of the subject, from which it appears that "pink" was first investigated in 1878. Much has since been written on the state, and the views as to its cause and hygienic significance are divergent.

The conditions necessary for the appearance of the condition are a temperature high for our latitude, and moist air. Hence "pink" with us is practically limited to the hottest months of our summer, but it is said that consignments of salt fish

* Special Report, No. 18. By P. C. Cloake, M.D., D.P.H. Pp. 22. 1923. H.M. Stationery Office. Price 1s. net.

leaving us for the Mediterranean countries in an apparently sound condition not infrequently become badly affected with "pink" when they come into warm climates.

Owing to the water-attracting qualities of the salt used in curing, moisture condenses in the cracks on the surfaces of salt fish, and between the apposed surfaces of fish when they are stacked. It is there, especially in the surface cracks, that "pink" begins.

In the process of drying and salting, the fish are handled freely and exposed to the dust from the air. Therefore the surfaces are, as might be expected, generally infected. The bulk of the organisms present, however, have nothing to do with "pink." They are for the most part the ordinary common forms of bacteria and exert no undesirable action.

"Pink" is due to at least two organisms—a "red coccus," which occurs in well-defined coccus and sarcinal growths, and an organism of a striking type, so far unidentified, to which the name organism X might for convenience be given. An alga is also present in great abundance on the surface of dried and salted fish. This occurs in uncoloured areas, as well as in the patches of "pink." It is therefore not held to be responsible, even in part, for the discoloration.

The "pink"-forming organisms, the red coccus and organism X, are remarkable in that they grow only in the presence of a large quantity of salt—over 15 per cent. They belong, therefore, to the group of organisms called, from their liking for salt, halophilic. Both have the further peculiarity that they grow slowly and need a moderately high temperature. At 77° F. it is about three weeks before visible colonies appear. Growth was found to be much more rapid at 99° F.

Organism X was recognised with difficulty, owing to the fact that it is destroyed by the procedure ordinarily adopted by a bacteriologist, who begins by dispersing his suspected substance in dilute solution of salt. This completely destroys X, since it breaks up in dilute solutions of salt into an amorphous slime. It was found, however, to preserve its character and to remain alive in strong brine. No signs of the spirochæte which earlier writers had described as a cause of "pink" were found.

The experiments described in the report seem conclusively to prove that "pink" is due to the use of salt, and more particularly solar salt, contaminated with these "pink"-forming organisms. The salt, as used by curers, becomes contaminated with them, as they are present on the salt-encrusted walls of stores, and on the surfaces of tables used by the operatives. The method of prevention is therefore simple, namely, to sterilise the salt, the utensils, and the rooms. Whether it is commercially feasible only those who know the magnitude of the losses which "pink" entails upon the industry can say.

Salt can be sterilised by heating for thirty minutes to 248° F.—a lower degree of heat will not suffice. Salt can also be sterilised, so far as these "pink"-producing organisms are concerned, by adding to it 5 per cent. of sodium bisulphite, but this is not to be recommended for hygienic reasons.

There is still another possibility, namely, drying the fish further than is done at present. Fish dried so that little moisture remains seems incapable of growing "pink." Unfortunately, as is shown in an appendix by Dr. Moran and Mr. Piqué on the absorption of water by salted and dried cod, the capacity for reabsorbing water, so as to become again palatable, is lost when drying is excessive. The appendix throws light upon the irreversible nature of the drying process. Curves are given which show that the rate of drying is also an important factor. The pieces of fish most rapidly dried showed the greatest capacity for reabsorbing water.

The Government Laboratory, Bangkok, Siam.

FIRST REPORT FROM NOVEMBER, 1917, TO MARCH 31, 1922.

THE Director of the Government Laboratory at Bangkok, Mr. A. Marcan, F.I.C., has issued his first report on the work of the year ending in March 31, 1922.

In November, 1917, the Department of Commerce took over the chemical work then being carried out at the Royal Mint, with the object of establishing a central laboratory for the whole country. The work outgrowing the accommodation available at the Mint, a new building was erected on a central site, and was occupied in September, 1919, and all Government Departments were invited to submit their chemical work, and analyses were made for the public on payment of fees.

This laboratory is fitted with modern equipment, including coils, chilled by ice, connected with the main water supply, electric heating and power, and exhaust fans for ventilation. During the period under review 26,140 analyses were made, consisting principally of coinage silver and bronze for the Mint.

CHEMICO-LEGAL WORK.—This included toxicological analyses of drugs, foods, stomach contents, etc., and the examination of stains for blood. The materials chiefly used for poisoning are plants which are of common occurrence throughout the country.

Much work is needed to obtain accurate knowledge of the poisonous active principles of some of the indigenous plants, and the Laboratory would be grateful to anyone who could give authoritative information as to some of these plants and their properties.

One narcotic drug, a species of *Dictyophora*, is not known to have been reported elsewhere. It is dried and burnt, and the fumes blown on to the sleeping victim, with the result that a sound sleep is produced and theft can be committed in safety.

In the period reviewed 16 cases were submitted, involving the analysis of human viscera, and 83 miscellaneous materials suspected to contain poison. Positive results were obtained in 33 per cent. of the cases submitted.

Atropine, one of the active principles of *Datura* species, was detected in 12 of the cases, arsenic in 8, corrosive acids in 3, mercury in 2, arsenic with nicotine in 2, strychnine, opium, atropine with morphine, chloroform, *Gloriosa superba*, and sulphur (for producing suffocating fumes) in one case each.

POISONOUS PLANTS IN SIAM.—The following is a preliminary list of the plants known to contain powerful or poisonous principles. Three are known to have been used, and others are likely to be used, for criminal purposes:—*Abrus precatorius*, Linn. (seeds); *Allamanda cathartica*, Linn. (juice and leaves); *Nerium odorum*, Soland (root and bark); *Cerbera odollam*, Gaerta (seeds); *Thevetia neriifolia*, Juss. (juice); *Calotropis gigantea*, Br. (juice); *Datura*, Spp. (seeds); *Euphorbia*, Spp. (juice); *Jatropha curcas*, Linn. (seeds); *Croton tiglium* (seeds); *Excoecaria agallocha*, Linn. (juice); *Cannabis indica*, Linn. (dried plant); *Antiaris toxicaria*, Lesch. (juice); *Gloriosa superba*, Linn. (rhizome); and *Dictyophora*, Sp. (dried plant burned). Imported: *Strychnos nux vomica* beans.

OTHER WORK.—This included 57 cases of counterfeit coining, 38 samples of drugs for the Government Medical Depot, 54 drugs under the Morphine and Cocaine Act, and 29 samples of suspected illicit opium, for which a rapid and accurate method of dialysis was devised.

The mixed ethyl esters of chaulmoogra oil were prepared from native oil, and were used with satisfactory results in the treatment of leprosy, and extract

of rice (vitamin extract) was made on a small scale for use in cases of beri-beri. Provision has now been made for the preparation of these extracts on a technical scale, and also for the establishment of a laboratory for the examination of natural products, such as oil seeds, tanning materials, drugs, etc., on a semi-technical scale.

Ministry of Health.

THE following circular has been sent to the clerks of Authorities administering the Food and Drugs Acts:

SALE OF FOOD AND DRUGS ACTS.

Public Health (Milk and Cream) Regulations, 1912 and 1917.*

CIRCULAR 462.

SIR,

1. I am directed by the Minister of Health to request that a copy of the report of the Public Analyst for the fourth quarter of the present year may be transmitted to this Department during the month of January, together with a copy of a report by the Medical Officer of Health upon the administration of the Public Health (Milk and Cream) Regulations for the year 1923. In this connection I am again to draw attention to Memorandum 36/Foods, a copy of which was forwarded to the Council in January, 1921, and to ask that the reports may be prepared on the lines indicated in that memorandum.

2. In view of the increasing practice of selling milk in sealed bottles it is desirable that the attention of sampling officers should be drawn to the difficulty which is sometimes found in dividing a sample of bottled milk so as to secure the uniform distribution of the milk fat throughout the three parts of the sample. Where the cream has risen freely in the bottle or where some of it adheres to the sides it may be found useful to decant the milk into a larger vessel and to return a small quantity in order to rinse out the bottle before the final mixing and division are effected.

3. The Minister desires to recommend to the consideration of the Council the following suggestions which he has received from the Society of Public Analysts with regard to the sampling of prescribed medicines:—

"(i) That the inspector be instructed, prior to dividing the sample into three parts, to mark, in the presence of the vendor, the height the contents reach in the bottle in which the medicine is originally supplied to him by the vendor. That the bottle so marked be submitted to the Analyst in order to enable him to determine the total quantity of medicine supplied.

"(ii) That the Analyst and the Medical Officer of Health be both consulted as to the type of prescription it is desirable to use for the purpose of checking the accuracy of dispensing, and that, in the event of any substantial inaccuracies being disclosed by analysis, both these officers be consulted as to the desirability of instituting proceedings."

The object of the first suggestion is to enable the Analyst to ascertain the total quantity of each of the ingredients (including the water or other "vehicle") present in the medicine. If he receives only a portion of the sample, representing an unknown fraction of the whole, he is only able to ascertain the relative percentages of the several ingredients; but if he is also provided with information as to the total quantity of the medicine dispensed he can then deduce the total amount of each of the ingredients as supplied by the Chemist. These particulars will obviously be of importance to the Council in considering what action they should take in regard to a medicine which has been inaccurately dispensed.

The Minister believes that the second suggestion is in accordance with the practice which is already largely adopted by Local Authorities. It is clearly desirable that, where a sample of medicine is taken for the purpose of checking the accuracy of dispensing, it should be so chosen as to be capable of accurate analysis. It is also desirable in considering whether or not proceedings should be taken under the Sale of Food and Drugs Acts that proper regard should be paid both to the degree of accuracy obtainable in the analysis of the article in question and to the margin of error allowable in ordinary dispensing operations.

I am, sir, your obedient servant,

R. B. CROSS, *Assistant Secretary.*

* With regard to the dispensing of medicines, somewhat strangely included in these Regulations, *see* ANALYST, 1923, **48**, 492.—EDITOR.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Proteins of Wheat Bran. D. B. Jones and C. E. F. Gersdorff. (*J. Biol. Chem.*, 1923, **58**, 117–131.)—From wheat bran, by which is meant the outer seed coats together with the under-lying layer of cells which contains the protein, three proteins, *viz.*, an albumin, a globulin and an alcohol-soluble protein have been isolated. The bran, which was exceptionally clean, was rapidly washed in cold water and dried at a low temperature to remove the adhering particles of other portions of the wheat kernel and ground to a powder. This contained 17·25 per cent. of protein (N × 6·25). By successive exhaustive extractions with distilled water, 4 per cent sodium chloride solution, boiling 70 per cent. alcohol and 0·5 per cent. sodium hydroxide solution, 86·61 per cent. of the total protein in the bran was extracted (N × 6·25). The preparations and properties of the three proteins isolated are described. Their percentages, expressed in terms of the total protein in the bran, were as follows:—Albumin, 16·64; Globulin, 13·62; Alcohol-soluble protein, 31·01 per cent. Analyses showed them to have the following average elementary percentage composition:—Albumin: N, 15·42; C, 53·21; H, 6·71; S, 1·35. Globulin: N, 17·76; C, 53·43; H, 7·40; S, 0·91. Alcohol-soluble protein: N, 15·35; C, 54·25; H, 6·75; S, 1·35. P. H. P.

Estimation of Reducing Sugars by means of Cupro-potassium Solution. L. Maquenne. (*Bull. Soc. Chim.*, 1923, **33**, 1681–1692).—The method here considered (*cf. Bull. Soc. Chim.*, 1898, **19**, 926; *Compt. rend.*, 1915, **161**, 617; 1916, **162**, 145, 207, 277) consists essentially in estimating by means of potassium iodide and sodium thiosulphate in an acid medium and, without separation of the cuprous oxide, the copper remaining in solution in the cupro-potassium solution reduced by Haen's method. The criticisms advanced against this method by Fleury and Boutot (*Bull. Soc. Chim. Biol.*, 1922, **4**, 361) are refuted, and it is shown that the method gives results as accurate as those obtained by the procedure recommended by these authors, and is to be preferred for various reasons. T. H. P.

Clarification of Solutions in the Analysis of Sugar Products. L. Eynon and J. H. Lane. (*J. Soc. Chem. Ind.*, 1923, 463T.)—The authors have previously found that the estimation of sugars by Fehling's solution is vitiated by the presence of calcium, and that this can be overcome by the use of potassium oxalate instead of sodium sulphate to remove the lead. This was not known when the experiments were carried out on which is based the view that normal lead acetate, unlike the basic acetate, does not precipitate invert sugar from solutions of raw sugar-products, although it does appear to remove a small proportion of reducing

non-sugars. The authors have accordingly re-investigated these points in the light of their previous discovery.

They find that in the clarification of solutions of raw sugar-products no reducing sugar is co-precipitated by the normal lead acetate in the presence of either tannic acid, egg albumin, or the organic non-sugars of cane molasses and beet molasses. (These were specially prepared by suspending the washed lead precipitate in water and passing through it sulphuretted hydrogen, filtering from the lead sulphide and boiling off the excess of gas from the filtrate.) They also show that no reducing sugar is co-precipitated by precipitation of the lead by means of potassium oxalate. They are unable to confirm the experience of A. H. Bryan who states that if a solution of dextrose, magnesium sulphate and ammonium tartrate is treated with lead acetate and then with potassium oxalate, 0·9 per cent. of the dextrose is removed. The estimation of sugar-products without preliminary clarification involves two errors, that due to reducing non-sugars precipitable by lead and that due to the presence of calcium salts. The nett effect of these errors in the case of raw sugars is generally negligible, but may be serious in the case of sugar-syrups and molasses. The following procedure is therefore recommended for low grade products:—The sample (12·5 grms.) is dissolved in water, treated with 25 c.c. of a 10 per cent. solution of normal lead acetate and with a little alumina cream, if necessary, and made up to 250 c.c., the whole being thoroughly shaken and filtered. One hundred c.c. of the filtrate are treated with 10 c.c. of a 10 per cent. solution of potassium oxalate, made up to 500 c.c., shaken and filtered. This one per cent. solution of the sample is used for the estimation of invert sugar and sucrose, as under (*a*) and (*b*), respectively. (*a*) The solution is titrated as previously described (*ibid.*, 1923, 32T.) (*b*) One hundred c.c. of the solution are treated with 15 c.c. of normal hydrochloric acid, diluted to about 150 c.c., heated to boiling and boiled for two minutes. The solution is then cooled, neutralised with sodium hydroxide, diluted to 200 c.c., and titrated as under (*a*). R. F. I.

Application of Miscibility to the Detection of Adulteration of Cacao Butter and to the Identification of Various Pure Products. H. Rosset, Marange and Vinter. (*Ann. Falsificat.*, 1923, **16**, 454–468.)—Two simple forms of apparatus are described for determining low and high miscibility temperatures. With a suitable liquid, such as pure aniline, which may be identified by its miscibility curve with a well-defined liquid like 50 per cent. aqueous alcohol (1) pure cacao butters yield virtually identical miscibility curves, the extreme differences of temperature being 2·7° C.; (2) with the exception of illipé butter, the common adulterants of cacao butters, do not exhibit the phenomenon of miscibility; and (3) the presence of minimum proportions of such adulterants in cacao butter may be detected by means of the temperatures of reciprocal miscibility.

The fat or chocolate to be examined is extracted with ether, preferably anhydrous, in a Soxhlet extractor, the solution obtained being concentrated by distillation at the ordinary pressure and then evaporated at 50° C. under 12 mm. pressure for 4 to 5 hours, to eliminate moisture and ether; fatty matters, simply

melted and filtered, may be used directly without appreciable error. The results of measurements of the miscibility of aniline with various samples of pure and adulterated cacao butters, etc., are given.

The presence of small proportions of nitrobenzene in aniline and of benzene in chlorobenzene may be detected similarly by investigating the miscibility with aqueous alcohol. T. H. P.

Detection of Saccharin and Dulcin in Vinegar and Products containing Acetic Acid. G. Reif. (*Zeitsch. Unters. Nahr. Genussm.*, 1923, **46**, 217–223.)—A new German food law limits the amount of dulcin in foodstuffs to 0·2 grm. per litre or per kilo. The following method is advocated for the detection of dulcin and saccharin:—One hundred c.c. of the liquid, or 100 c.c. of extract in the case of a solid substance, are made just alkaline with sodium bicarbonate and shaken out for half an hour with two successive quantities of 100 c.c. of ether. The ether extract is distilled, the residue dissolved in hot water in a test tube, a few drops of mercuric nitrate solution added, and the mixture warmed for a few minutes; in the presence of dulcin a violet colour is produced which is darkened by the addition of lead peroxide. The alkaline liquid is now acidified with sulphuric acid and extracted with ether. Then the ether extract is washed with a little water, evaporated, and tested for saccharin as usual. If the substance contains benzoic acid or much fat it should be first extracted with about 10 c.c. of ether before being made alkaline for the dulcin test. Should salicylic acid be present, it must be eliminated by oxidation with alkaline permanganate. The acid ether extract is therefore evaporated at a low temperature, and the residue dissolved in weak alkali, warmed, and potassium permanganate added in slight excess; the mixture is now acidified and excess of permanganate is discharged by the cautious addition of sulphurous acid. The clear solution is next extracted thrice with ether, and the residue, after evaporation, converted into salicylic acid by fusion at about 250° C. in a silver crucible with sodium hydroxide, after which it may be identified by means of ferric chloride in the usual way. H. E. C.

Polarimetric Estimation of Malic Acid. F. Auerbach and D. Kruger. (*Zeitsch. Unters. Nahr. Genussm.*, 1923, **46**, 97–154.)—The greatly enhanced optical activity of malic and tartaric acids in combination with uranium or molybdenum affords an accurate method for their estimation, either alone or in the presence of each other (*cf.* ANALYST, 1923, **48**, 346). Essential conditions are the presence of an excess of the activating metal and a suitable P_H value, which is secured by the addition of a suitable buffer substance. The molecular rotations are to some extent dependent on concentration, and have the following values at about 0·1 mol/litre for the sodium flame; temperature 18° to 20° C. uranium tartrate, +650°; uranium malate, −700°; molybdenum tartrate, +1044°; molybdenum malate, +1020°. For the estimation of malic acid the solution is exactly neutralised with sodium hydroxide, 0·1 mol/litre of di-sodium citrate added, the mixture shaken for about four hours with 3 grms. of uranyl acetate in 25 c.c. of the solution, and the rotation then observed. If molybdenum is to be used,

the concentration of malic acid should not be less than 0·02 mol/litre; sodium acetate 2·5 mgrm. mol., or 1 c.c. of glacial acetic acid and 0·4 grm. atoms per litre of molybdenum as ammonium molybdate, are added to 25 c.c., and the rotation is observed as before. In the case of tartaric acid the solution, which should contain between 0·1 and 0·15 mol/litre, is neutralised and treated, as before, with uranium acetate and sodium citrate solution: if the solution is of less strength than 0·1 mol. per litre the molybdenum method may be used by adding glacial acetic acid and ammonium molybdate in the proportions already quoted. When both acids are present in the same solution advantage is taken of the fact that there is a change of sign in the rotation of malic acid with uranium and molybdenum. The rotation is therefore observed after treating portions of the solution with uranium acetate and ammonium molybdate respectively, and the proportions of the two acids calculated with the help of graphs which are given in the text. The presence of other organic acids, or of considerable quantities of alkali salts, does not materially affect the rotation of uranium malate or of molybdenum tartrate, but interferes with that of the other two compounds, so that the process is not applicable directly to malic and tartaric acids together in the presence of such substances. The method may be applied to the estimation of both acids in fruit juices or extracts by the precipitation of the proteins, pectins, etc., then separation of the organic acids by means of their barium salts. The rotation of the barium salts on the addition of uranium or molybdenum is given, and details of the application and the calculations are also shown. H. E. C.

Estimation of Malic Acid in Fruit Products. F. Auerbach and D. Krüger. (*Zeitsch. Unters. Nahr. Genussm.*, 1923, **46**, 177–217.)—The practical application of the barium malate method of separation of malic acid and its polarimetric estimation by means of uranium and molybdenum salts is described in detail (*cf.* preceding abstract). For the estimation of malic acid in fruit juices, jams and similar products, the alkalinity of the ash is first determined, then slightly more than the required quantity of hydrochloric acid is added to 25 c.c. of the extract, and the pectins precipitated by diluting the liquid to 100 c.c. with alcohol. After filtration, 75 c.c. are neutralised by the addition of barium carbonate, then 2 c.c. of a saturated solution of barium acetate are added, the barium malate is precipitated by diluting the liquid to 250 c.c. with alcohol, warming, and allowing the mixture to stand overnight. The barium malate precipitate is filtered off, washed with alcohol, dried and brushed into a 50 c.c. flask, and to it are added 0·05 grm. of barium tartrate, 0·1 grm. of barium citrate, and water to the mark. The solution is shaken for several hours, filtered, and the rotation of the filtrate observed after treatment with uranium and molybdenum as follows:—(*a*) To 20 c.c. 2·5 mgrms. mol. of disodium citrate and 3·5 grms. of uranyl acetate are added, and the mixture shaken for four hours and made up to 25 c.c. (*b*) To 10 c.c. are added 10 c.c. of a saturated solution of ammonium molybdate and 2 c.c. of acetic acid, then the mixture is allowed to stand in the dark for three hours and diluted to 25 c.c. If the solutions are coloured, they may be decolorised with

animal charcoal as usual. The malic acid content is calculated from the observed rotations in the manner already described (*loc. cit.*). Corrections are given for the volume of the precipitates. Dextrin, sucrose, dextrose and fructose are not precipitated with the barium malate in the above process, and do not interfere unless present in large proportions. Preservatives, such as formic, benzoic or salicylic acid, do not affect the accuracy of the method. The following results were obtained with fruit juices:

	Per Cent.		Per Cent.
Pear juice	0·32	Apple juice	0·60–0·73
Cherry juice	0·56–0·67	Red current juice	0·052
Gooseberry juice	0·088	Raspberry juice	trace
Bilberry juice	0·044	Cranberry juice	none
Juniperberry juice	0·013	Tomato juice	0·013

H. E. C.

Mustard Flour and Oil in the Wine Industry. J. C. Delage. (*Ann. Falsificat.*, 1923, **16**, 483–491.)—Ground black mustard, either untreated or after being washed with 5 times its weight of water, exhibits marked antiseptic properties, and is also able to destroy unpleasant flavours. Thus, a quantity of the mustard containing 0·0014 grm. of allyl mustard oil is sufficient to render a litre of wine aseptic. This effect is not only far greater than that of sulphurous acid, but also more permanent, as yeasts do not develop tolerance towards the mustard oil. In white wines the ground mustard produces a slight turbidity which renders filtration of the wine necessary, so that the mustard oil itself should be used in such cases. The oil is best employed in a 3 per cent. solution in 50 per cent. aqueous alcohol. T. H. P.

Iodimetric Estimation of Thiosinamine. Morvillez and R. Meesemaecker. (*J. Pharm. Chim.*, 1923, **28**, 442–445.)—An aqueous potassium iodide solution of iodine is decolorised by a solution of thiosinamine, and the estimation is carried out by acidifying 10 c.c. of the thiosinamine solution in an Erlenmeyer flask with sulphuric acid, adding 20 c.c. of 0·1 *N* iodine solution, and leaving the mixture in the dark for 15 minutes. The non-combined iodine is then estimated by titration with 0·05 *N* sodium thiosulphate solution in the presence of starch, as indicator, and 12 c.c. of chloroform. If A is the number of c.c. of thiosulphate solution required, the strength of the thiosinamine solution is found from the formula:—$(A - n/2) \times 0{\cdot}0058 \times 10$. As a result of experiments with different lengths of reaction time (5 to 90 minutes) in neutral and acid solutions, it was found that the best conditions are 15 minutes in acid solution. The results obtained by this method are in close agreement with those by the Charpentier-Volhard and Denigès methods of estimation, which both depend on the decomposition of silver nitrate by the thiosinamine with the formation of silver sulphide, and the present method effects a great saving of time. The method is also applicable to the estimation of volatile mustard oil in essential oil of mustard. D. G. H.

Autoxidation of Chloroform. A. M. Clover. (*J. Amer. Chem. Soc.*, 1923, **45**, 3133–3138.)—Chloroform undergoes oxidation in diffused light, with the formation of a peroxide, which is probably dichloro-carbon-peroxide. This substance is formed at a gradually increasing rate, and its accumulation proceeds up to a certain point, where rapid decomposition sets in. Beyond this point the oxidation of the chloroform continues, although very little peroxide is found in the solution. The phosgene, carbon dioxide, chlorine and hydrochloric acid present in the oxidised product are derived from the decomposition and hydrolysis of the peroxide. The presence of 0·1 per cent. of alcohol retards the autoxidation, and in a test experiment with that amount only a trace of peroxide was found after 6 weeks. With 0·05 per cent. of alcohol autoxidation was only prevented for about a week. Phenol benzyl alcohol, petroleum spirit, and purified paraffin oil have also been found effective preservatives. The preservative acts as an anti-catalyst.

Eucalyptus Oils as Germicides. A. R. Penfold and R. Grant. (*J. Roy. Soc., N.S. Wales*, 1923, **57**, 10; *Chem. Trade J.*, 1924, **74**, 10.)—One per cent. suspensions of crude eucalyptus oils and their pure constituents in 7·5 per cent. resin soap solution were tested by the Rideal-Walker method. Of the ten commercial eucalyptus oils examined, that of *E. radiata* had the strongest germicidal value, its coefficient being 10 to 12; its active principle was piperitol. The pure active principles of the oils gave the following Rideal-Walker coefficients:—Australol, 22·5; geraniol, 21; citral, 19·5; and piperitol, 13. It was found that a concentrated preparation diluted with water gives a lower coefficient than an original dilute preparation of the same strength, probably owing to dilution disturbing the emulsion in the case of a concentrated suspension.

Biochemical, Bacteriological, etc.

Physiological Assay of Insulin Preparations. H. Penau and H. Simonnet. (*J. Pharm. Chim.*, 1923, **28**, 385–395.)—After investigating various methods of examination which have been put forward the authors eliminated all chemical methods, having found physiological methods, particularly those in which rabbits and dogs are used, to be the most reliable. Since the physiological response of individual animals varies somewhat, a minimum of four animals should be used in all experiments and the physiological unit for insulin is defined, according to the Toronto workers, as the quantity of active principle which, injected into rabbits weighing about 2 kilos. and fasting for 16–24 hours, depresses the blood sugar from 0·11 per cent. to about 0·045 per cent. The clinical unit is taken as a third of this. Objectively, the hypoglycæmia is accompanied by characteristic convulsions which, however severe, can be cured in a few minutes by intraperitoneal injection of dextrose, the dose being to a certain extent proportional to the amount of insulin injected.

Since the physiological and therapeutic values of a given insulin preparation are not always identical (which may be accounted for by regarding insulin as a

polyvalent complex of which the various parts have different pharmacodynamic properties), the effect of various preparations on depancreated dogs was tried. The authors conclude that the pharmacodynamic activity of insulin is best investigated by the Canadian rabbit method, supplemented by the effect produced on the sugar content of the blood and urine of depancreated dogs—an action perhaps more comparable with that which occurs in the case of the human patient.

D. G. H.

Aqueous Extracts of Pancreas. II. New Facts. H. A. Piper, R. S. Allen and J. R. Murlin. (*J. Biol. Chem.*, 1923, **58**, 321–336.)—Insulin is not a protein. This refers to the product obtained from the pancreas of the ox and pig. A subsequent paper will give the method of preparing it protein-free. It has been obtained as a white or greyish-white amorphous powder. The insulin molecule, if it be a chemical entity, must be large, for it withstands dialysis in thin vegetable parchment for many hours; thus it can be separated from diffusible salts. Insulin is only with difficulty separated from protein, since it is adsorbed by this class of substance. The hypoglycæmic action of insulin varies with different conditions. There is an apparent development of potency. Where the first injection sometimes gives no reaction an injection from the same solution the next day yields a satisfactory test. The potency is not reduced when the filtrate, after standing, shows a growth of bacteria, and remains even when a hydrogen sulphide odour is apparent. The development of the hypoglycæmic reaction in rabbits has much to do with the exact reaction to which the neutralisation is carried after extraction in 0·2 *N* hydrochloric acid. Insulin is fairly stable. Practically protein-free, it has been kept for 4 months. The lowest acidity at which it has been observed to keep well is $P_H = 5{\cdot}7$. To obtain large yields the range of acidity between $P_H = 4{\cdot}3$ and 5·7 at any stage just preceding filtration should be avoided. Insulin is not a concentrated form of glutathione.

P. H. P.

Aqueous Extracts of Pancreas. III. Precipitation Reactions. C. P. Kimball and J. R. Murlin. (*J. Biol. Chem.*, 1923, **58**, 337–346.)—Rapid preparation of insulin for medicinal purposes requires that it should be removed from solution by some method more expeditious than that of drying. In this attempt to find a method of precipitation the preparations used were as protein-free as possible; many reagents which are well known protein precipitants failed to give any precipitate. A specific amount of the reagent to be tested was added to the preparation, and the precipitate was thrown down by centrifugal action, taken up in distilled water and tested as soon as possible on rabbits. The supernatant liquid was dried, with or without dialysis, depending upon the nature of the additive, and similarly dissolved and tested. Tables of the results are given. Positive reagents were:—Ammonium sulphate, sodium chloride, trichloroacetic acid, acetone and methyl, ethyl, isopropyl, *n*-butyl, isoamyl and caprylic alcohols. Probably insulin, when pure, is insoluble in neutral water. It gives no protein reactions and the most potent preparations that have been analysed have had a low nitrogen content, 4 to 6 per cent. dry weight.

P. H. P.

Oxidation of Dextrose by means of Iodine in Presence of Insulin. G. A. Alles and H. M. Winegarden. (*J. Biol. Chem.*, 1923, **58**, 225–234.)—This investigation was carried out to discover whether insulin, alone or in the presence of certain animal fluids, has any influence upon dextrose *in vitro*. It was known before, and is confirmed here, that the rate of oxidation of various sugars by iodine in solutions of sodium bicarbonate or sodium phosphate varies greatly with the nature of the sugar; thus a study of the relative rates of oxidation of dextrose, before and after treatment with insulin, should give a sensitive means of finding whether any of the dextrose has been transformed by it into any other substance, even into a stereomeric hexose. Experiments, which are described, were made with dextrose alone, with mixtures of dextrose and insulin, with insulin and liver extract, and with insulin and blood serum or oxalated blood. Tables of results are given. In no case was any difference detected in the rate at which the iodine is consumed. Therefore no appreciable reaction takes place between dextrose and insulin, even in the presence of the animal fluids mentioned; thus the metabolic process must be more complicated in character; also, there is little promise of developing a method of assay for insulin on the basis of its action on dextrose outside the body. P. H. P.

Fat-Soluble Vitamins. XIV. H. Steenbock, E. B. Hart, J. H. Jones and A. Black. (*J. Biol. Chem.*, 1923, **58**, 59–70.)—Additional justification is given for speaking of the fat-soluble vitamins rather than of a fat-soluble vitamin, as support, by experiments carried out upon dogs and chickens, is lent to the idea that the anti-rachitic vitamin is an entity distinct from vitamin *A*, the anti-ophthalmic substance. Pups were weaned and fed on a standard rickets-producing diet, whereby the inorganic phosphate and calcium of the blood were reduced. By the administration to 3 dogs of 1 c.c., 4 c.c. and 12 c.c. daily respectively of cod liver oil, freed from vitamin *A* by aeration, the blood phosphorus and calcium were restored to normal, and the ash content of the bones was increased. One dog was kept as a control. The cod liver oil was not able to correct growth interference; vitamin *A* was probably needed. Some butter fat, in addition to its ration of cod liver oil, caused the first dog to become normal. The dog receiving 4 c.c. of cod liver oil per day developed a purulent rhinitis, and the one having 12 c.c. a keratitis, thus furnishing additional proof that the cod liver oil was free from vitamin *A*. The aerated cod liver oil increased the inorganic phosphates and calcium of the blood of chickens and re-initiated growth, but it must not be inferred that the birds do not need vitamin *A*, since they were put upon the experimental ration at an advanced age and weight and had had opportunity to store this vitamin. P. H. P.

Fat-Soluble Vitamins. XV. R. M. Bethke, H. Steenbock and M. T. Nelson. (*J. Biol. Chem.*, 1923, **58**, 71–103.)—Experiments are described by means of which the inorganic relations in the bloods and bones of rats when fed on various deficient diets were studied. Poor calcification of bone occurred in rats on a synthetic ration of purified food constituents deficient in fat-soluble vitamins,

even with the addition of 15 c.c. of skimmed milk or 0·5 c.c. of whole milk per rat per day. Normal calcification occurred with 20 c.c. of skimmed milk or 1 c.c. of whole milk. Data were accumulated on the variation in composition of blood and bone with age in the rat, preliminary to further studies. The ash content of the femurs and humeri totalled 66 per cent., a maximum value, when the animals weighed 375 to 425 grms. The blood phosphates and calcium were slightly higher in the very young than in the older animals. Additions of calcium to a basal ration caused a similar increase of growth to that caused by additions of fat-soluble vitamins, as found in cod liver oil, thus indicating the existence of a quantitative relation between vitamin and calcium in effecting the assimilation of the latter. Probably the beneficial results from the feeding with calcium salts are due to the mass action of the calcium counteracting the effects of a vitamin deficiency. Absence of normal growth tended to give a reduction of the calcium content of the blood and ash content of the bones. The phosphorus of the blood was more constant, but was depressed as the calcium increased. With casein as the protein, given in the proportion of 18 per cent. of the ration, the phosphorus requirements of the rat appeared to be complied with. Increased growth did not result from the addition of a neutral mixture of sodium and potassium phosphates. This was reflected in the composition of the blood and bones. The calcium of the blood was consistently depressed where no fat-soluble vitamins were added, the greatest depression being where the most phosphate was added. Radiations with ultra-violet light for 10 minutes daily in the absence of fat-soluble vitamins in the diet brought up both the calcium and phosphorus of the blood. P. H. P.

Presence of Vitamin *A* in Frozen Pork. A. M. Wright. (*J. Soc. Chem. Ind.*, 1923, **42**, 509T.)—Following work on the presence of vitamin *B* in Frozen Flesh Food (ANALYST, 1923, **48**, 611), the author has investigated a point which has long been a matter of dispute, namely, the presence of vitamin *A* in lard. The experimental work is on the same lines as in the former investigation, and the diet given to the cockerels consisted of pork containing 25 per cent. of fat which had been in cold storage for 9 years, starch (with or without butter fat for control purposes), the same salt mixture as before, and the juice of swede turnips. The following results were obtained:

	Controls A. B. & C Vitamin present. Grams.	Controls Vitamin A deficient. Grams.	Pork with butter fat. Grams.	Pork: no butter fat added. Grams.	Pork; butter fat first 28 days only Grams.
Original weight	161	164	179	169	168
7–10 days ...	165	166	195	201	197
10–14 ,, ...	177	173	206	225	213
21 ,, ...	214	161 (died)	241	268	258
28 ,, ...	247	—	277	279	290
35 ,, ...	300	—	279	296	302
42 ,, ...	302	—	295	300	315
49 ,, ...	321	—	346	338	342
60 ,, ...	333	—	350	347	360

It is evident, therefore, that even after 9 years in cold storage at a temperature varying between 2° and 15° F. vitamin *A* is present and remains active in pork fat. D. G. H.

Differentiation of Vitamin *A* from the Anti-rachitic Factor. E. Lesné and M. Vagliano. (*Comptes rend.*, **1923, 177,** 711–712.)—The results of experiments on the administration of cod liver oil to rats subjected to an anti-rachitic diet confirms the non-identity of the anti-rachitic factor of the oil with the fat-soluble vitamin *A*. The latter may be introduced into the organism in any way, but the former is active only when ingested. T. H. P.

Preservation of Blood for Analysis. F. V. Sander. (*J. Biol. Chem.*, **1923, 58,** 1–15.)—The data experimentally obtained show that samples of human blood can be preserved for 5 to 6 days, and that the values for non-protein nitrogen, urea, uric acid, creatinine, creatine and sugar will have the same clinical significance as those values obtained by an immediate analysis of the blood. The urea, uric acid, creatinine, creatine and sugar content of blood can be kept constant for at least 2 weeks, but the non-protein nitrogen value slightly increases, and this cannot be accounted for by an increase in ammonia and amino-acid content. A mixture of 0·01 grm. of sodium fluoride and 0·001 grm. of thymol for each c.c. of blood is recommended for the preservation of blood for 6 to 14 days, and, with the use of this, the blood need not be drawn under sterile conditions, except with regard to the patient. Sodium fluoride or thymol alone will not preserve the blood constituents investigated for a period of 5 to 6 days, but the above mixture is apparently very efficient. Both have but little effect upon the reagents used in each analysis and cause no interference with methods. Higher concentrations of the preserving materials are not necessary for preservation, and do not upset the analysis, but cause hæmolysis to take place in much less time. No single preserving substance can be relied upon to maintain unchanged the values for non-protein nitrogen, urea, uric acid and sugar for a period of 48 hours; creatinine and creatine remain constant for several days in unpreserved blood and in blood containing many of the common preservatives. P. H. P.

Identification of Blood Meal of Mosquitoes. C. G. Bull and W. V. King. (*Amer. J. Hygiene*, **1923, 3,** 491–496.)—The blood meals of mosquitoes can be identified easily by the precipitin test if the specimen is collected within an hour after the mosquitoes have fed, and fairly well up to 12 hours afterwards, but specimens collected up to 24 hours afterwards usually give negative or non-specific reactions. Identification is possible 36 hours afterwards if the fed mosquitoes are kept in an ice box. Blood in an advanced stage of digestion fails to react with any of the precipitin sera. The sera preparations, the collection of the blood specimens, and the test are described in detail. Specimens collected as described may be kept for 3 or 4 months before being tested, since they undergo no further disintegration. Known specimens were obtained as controls by allowing mosquitoes to feed on man and different domestic animals. Control tests

reproduced show the weakest point in the method to be the failure of reactions with the anti-human serum. A highly potent anti-human serum could not be obtained. P. H. P.

Qualitative Tests for Acetone Bodies. E. J. Bigwood and W. S. Ladd. (*J. Biol. Chem.*, 1923, **58**, 347–361.)—The authors made both quantitative and qualitative analyses on the same samples of diabetic urine and carried out experiments to throw light upon the selectivity, sensitivity and quantitative significance of these tests. The following is the technique used. *Sodium nitroprusside test.*—Add 20 drops of a mixture of 10 c.c. of glacial acetic acid and 10 c.c. of a 10 per cent. sodium nitroprusside solution to 10 c.c. of urine in a test-tube, shake, and layer on this 1 to 2 c.c. of concentrated ammonium hydroxide solution. At the contact of the fluids a purple ring appears. *Ferric chloride test.*—To 10 c.c. of urine 10 c.c. of a 10 per cent. ferric chloride solution are added, but more if necessary to clear the precipitate. A brown colour appears. Readings are taken at intervals with both these tests as the colours deepen. It was found that a pure acetone solution and a solution of diacetic acid free from acetone each gives a colour reaction with sodium nitroprusside. Only the latter solution gives a colour reaction with ferric chloride. Electrolytes present in urine, especially sodium chloride, tend to intensify the colour of the ring in the sodium nitroprusside test. Quantitatively the tests serve only as crude approximations in indicating the amounts of acetone and diacetic acid present. Of the two, the ferric chloride test appears to give less eccentric results. P. H. P.

Anaerobes from Water Samples. P. D. Meader and E. A. Bliss. (*Amer. J. Hygiene*, 1923, **3**, 394–400.)—The presence of gas in broth containing 1 per cent. of lactose is regarded in the *Standard Methods of Water Analysis* of the American Public Health Association (1920) as a presumptive test for the presence of *B. coli* in the water under examination. Sometimes gas is found when *B. coli* cannot be isolated. The origin of this gas is important. There appears to be a variety of organisms, morphologically unlike *B. coli*, which may be a source of error and difficulty in water analysis, because of gas production in lactose broth. Anaerobes have been isolated from 16 to 21 per cent. of 76 tubes of lactose broth, inoculated with samples of water. These tubes showed gas production, but no *B. coli* could be isolated. Of 25 strains of anaerobic bacilli tested, 2 fermented lactose, with evolution of gas. Anaerobic bacilli were isolated from raw water and from water subjected to various methods of purification, but the presence of these organisms in water appeared to bear no relation to the aerobic count. Anaerobic organisms appear to have been an unimportant factor in the fermentation of lactose in the samples investigated. P. H. P.

Survival of Bacteria in Flies. R. W. Glaser. (*Amer. J. Hygiene*, 1923, **3**, 469–480.)—The biting stable fly, *Stomoxys calcitrans*, the cattle horn fly, *Lyperosia irritans*, and the house fly were used in this work, the last for purposes of comparison, since it would be unsafe to compare the results obtained on the first two with the published data on *M. domestica*, owing to the region in which the work

was done. The experiments are described. Results showed that the intestine of a house fly at any age is always a veritable reservoir for bacteria. *Stomoxys* harbour bacteria within them, but the number is much smaller. New bacteria are not present in the daily food of *Stomoxys*, as is the case with the omniverous house fly, for the former feeds on sterile vertebrate blood, which may have an inhibiting effect on the bacteria already inside the fly. Recently emerged horn flies contain very few bacteria, and adults practically none. The practical sterility of the adult intestine is strange, since the larvæ live in cow dung and ingest quantities of bacteria. Probably the bacteria are inhibited and destroyed as the fly is transformed and assumes adult life. P. H. P.

Moulds on Frozen Meat. A. M. Wright. (*J. Soc. Chem. Ind.*, 1923, 488T.)—Several workers have proved that the moulds they have found on frozen meat have included *Mucor mucedo*, a *Rhizopus*, *Penicillium glaucum*, *Thamnidium elegans*, and *Cladesporium herbarum*, and that in several cases of "black spot" one or other of these (except *Thamnidium*) has been found to be the cause. Brown spots have been caused by a saccharomyces which grew at −2° C., but not at −9° C. *Cladesporium herbarum* has been found to produce "black spot" on meat kept at −5·5° C., but in New Zealand this appears to be the least common cause. The author has found that if *Mucor mucedo* has been grown on meat at from −2° to −1° C. till well established and then placed in cold storage at −12° to −15° C., a black spot has developed. Similar results have been obtained with *Penicillium glaucum*, but the initial temperatures were about 4° C. The author therefore concludes that no one species of fungus is responsible for "black spot" on frozen meat. In every case that the author has investigated he has shown that at some time during the cold storage the temperature has risen above 0° C., as a result of defective insulation, and, in some cases, sufficiently high and for a sufficiently long period to allow actual putrefaction to take place. It has been said that prolonged cold storage in itself is the responsible factor in producing moulds and "black spot." The author, however, can produce mould on cold-stored meat in one month; on the other hand, he has found meat free from moulds after nine years' cold storage under strict conditions of temperature and sound insulation. Two cases came before his notice of a feathery growth being diagnosed by an authority as "mould," which were subsequently proved to be not mould at all. One consisted of crystals of salts and organic compounds which separate from meat juices during freezing, and the other was composed of the cotton fibre from the bagging which had adhered to the carcase as fluff. The temperature in the cold storage of meat should never rise above −9° C. (*Cf.* ANALYST, 1923, **48**, 549.) R. F. I.

Toxicological and Forensic.

A Case of Poisoning by Sodium Arsenate. M. Bridel. (*J. Pharm. Chim.*, 1923, **28**, 395–397.)—The maximum dose of sodium arsenate given by the French Codex is 1 cgrm. at a time and 2 cgrms. in 24 hours, but the toxic dose for

a man is 0·252 to 0·263 grm., this being based on Kohn Abrest's figure of 0·115 to 0·120 grm. of arsenic acid. If prescribed in a solution containing 0·1 grm. in 300 c.c., 5 mgrms. in a dose and 1 cgrm. in 24 hours is generally ordered. Notes of a case are given in which a woman took 4 spoonfuls at 24 hour intervals of a solution containing 0·261 grm. per spoonful, *i.e.* 1·044 grm. of sodium arsenate in 72 hours. After the third dose headache, puffiness of the face and sore throat supervened, together with jaundice. Diarrhœa and vomiting followed, but only lasted two or three days, and gradual recovery took place. D. G. H.

The Swedish Commission on Arsenical Poisoning. Petrén. (*Acta Med. Scand.*, **1923**, **58**, *Fasc.* II.–III; *Lancet*, 1923, **205**, 531–532.)—A summary is given of the work of the Commission of chemists and doctors appointed by the Swedish Government to investigate the questions of domestic poisoning by wall-paper, clothing, etc., due to arsenic. It was found necessary to fix certain standards for this class of poisoning. Thus, for arsenical house poisoning to be diagnosed, it must, among other things, be proved that the symptoms began within 1 to 3 months of exposure, and ceased within 3 months of the cessation of such exposure to house poisoning. When these criteria were applied, very few of the 91 cases reported to the Commission were authenticated.

Differences in Poisoning by Arsenic from Different Sources.—When arsenic is taken in large doses by the mouth, melanosis and polyneuritis are prominent sequelæ, whereas melanosis has never, and polyneuritis has rarely, been observed in cases of house poisoning. On the other hand, workers in arsenic, in contact with Schweinfürth's green, are liable to suffer from cutaneous lesions, which are practically unknown in cases of poisoning with arsenic given by the mouth. In the case of house poisoning, volatile compounds of arsenic appear to be responsible for the symptoms. The chemical investigations of Prof. Ramberg, a member of the Commission, have shown that the composition of the arsenical gases developed by the action of certain moulds is inconstant, and do not support Biginelli's hypothesis that the arsenical gas generated under these conditions is diethylarsine.

Other Findings of the Commission.—Much stress is laid on the great differences in the reaction of the body to the same compound. In the case of salvarsan, for instance, the reaction of the body would seem to depend to a certain extent on the nature of the pre-existing infection, and the reaction of syphylitics to salvarsan is probably peculiar to this class of case. In the case of influenza patients, however, the first and only toxic effect of salvarsan was vomiting. Confirmation has been obtained of the observations of Tinel and Leroid, who found that, whilst arsenic cannot reach the cerebro-spinal fluid through healthy membranes, it may do so when these membranes show morbid changes.

Agricultural Analysis.

Soil-point Method for Directly Estimating the Water-supplying Power of a Soil in the Field. F. Hardy. (*J. Agric. Sci.*, 1923, **13**, 355–360.)—The method is designed to show the actual water-supplying power of a soil to

plant roots *in situ*; this power bears no relation to the total moisture content, and is largely dependent on the nature of the contact between the soil and the experimental point. One hundred ordinary hard graphite pencils (Hardtmuth's 4H.) are sharpened in a rotary mechanical sharpener, and the points then blunted by rubbing on sand paper; they are separated into 20 marked sets of 5, each set is weighed and at once placed in a celluloid case. Ten of the sets are planted out in a transverse across the field, the pencils of each set being inserted at right angles to the transverse. The planting is done by pressing a stout nail into the soil and inserting the pencil to a depth of 5 inches into the hole thus made. The planting is timed so that the points may be in contact with the soil for three hours, at the end of which time the sets are withdrawn, immediately replaced in their cases, and weighed as soon as possible. The experiment should be made in duplicate. The water-supplying power is expressed in hundredths of a grm. absorbed by one soil-point; soils on which sugar-canes grew vigorously had water-supplying power between 2·7 and 4·7; normal growth coincides with values between 2·7 and 2·3, and soils below 2 showed distinct wilting. H. E. C.

Effect of Movement of Soil Salts on the Standardisation Values of Electrodes used in Moisture Estimations. T. Deighton. (*J. Agric. Sci.*, 1923, **13**, 440–446.)—Electrodes were buried at various depths in a large mass of soil kept on a constant-level water table and protected from rain so that the moisture content at any depth varied only with the temperature and humidity of the atmosphere. Under these conditions movements of the soil and salts would be indicated by altered resistances. After making allowance for observed differences of temperature, the results show that the humidity of the atmosphere is without effect on the moisture content at depths greater than 3 inches. After several months water was added by means of a fine spray equivalent to 1 mm. rainfall, this had no effect on the resistance, but increasing amounts of water caused a lowering of the resistance. It is concluded that standardisation values in normal soils are not materially affected by showers. H. E. C.

Cause of Error in the Jodlbauer Process for the Estimation of Total Nitrogen. J. Bordas. (*Comptes rend.*, 1923, **177**, 696–697.)—Estimation of the total nitrogen in a fertiliser containing leather by Jodlbauer's modification of Kjeldahl's method gives low results, loss of nitrogen being caused by the reducing action of the tannin on the nitrate. Similar errors are encountered if pyrogallol, hydroquinone or pyrocatechol is present, but the non-reducing resorcinol is without effect. Hence when both tannin and nitrate are present, the total nitrogen must be estimated either by the Dumas method, or by Salle's or Desvarda's method (reduction in an alkaline medium), followed by Kjeldahl treatment of the residue of the distillation. This modification must be applied also to vegetable matter containing both tannin and nitrates. T. H, P.

Water Analysis.

Estimation of Dissolved Air in Small Quantities of Water. H. G. Becker and W. E. Abbott. (*J. Soc. Chem. Ind.*, 1923, 484T.)—On dissolving potassium hydroxide in tap water a vigorous evolution of dissolved air can be seen, and this observation is the basis of the method described. Twenty to thirty c.c. of the water to be tested are introduced into a simple special apparatus of which a sketch is given, allowed to dissolve the potash and the small bubble of air evolved is measured, passed through pyrogallol and again measured all in the same apparatus. As the potash would be expensive if the method were used regularly, a cheaper alternative was looked for. After several trials, choice was made of ammonium sulphate in the form of specially prepared air-free pellets. The methods of Letts and Blake or of Winkler are designed for use with 250 c.c. of the water, and are not accurate for quantities under 50 c.c. R. F. I.

Organic Analysis.

Detection of Halogen in Organic Compounds. J. Piccard and F. de Montmollin. (*Helv. Chem. Acta*, 1923, **6**, 1020.)—In the case of volatile compounds, the flame test on copper wire is modified by introducing into the flame, 1 cm. above the substance, a small piece of copper wire gauze, which is attacked by the halogen acid. If the substance is rich in carbon and renders the flame luminous, it is held in the small flame of a Bunsen burner by means of copper wire; the combustion gases are made to traverse the flame of a second burner, inclined above the small flame, where the green coloration becomes visible. A sensitive reaction for the detection of small quantities of halogen in volatile liquids (*e.g.* benzene) is carried out in a vertical combustion tube, the upper end of which holds a filter paper impregnated with the liquid. The lower end of the tube is drawn out and bent upwards. The vapour issuing from the narrow tube is ignited, and a tiny piece of copper gauze held in the flame; the green coloration will develop in the colourless burner flame held over the small flame. W. R. S.

Estimation of Fluorine in Organic Compounds. J. Piccard and C. Buffat. (*Helv. Chim. Acta*, 1923, **6**, 1047–1048.)—The substance is heated with potassium to about 400° C. *in vacuo*. From 0·1 to 0·2 grm. (*e.g.* phenyl fluoride) is sealed in a small thin-walled glass bulb so that the bulb is almost completely filled. The bulb is transferred to a pressure tube together with 20 c.c. of absolute ether and 0·5 grm. of potassium. The tube is drawn out to a capillary and evacuated completely, after which the capillary is closed. The bulb is then broken by shaking, and the tube heated some time over a free flame, with shaking, to expose fresh surfaces of the fused metal. For the completion of the reaction, the tube is heated in a tube furnace to about 400° C. After cooling, the tube is opened, and its contents taken up with alcohol and with water, any insoluble matter (carbon) being filtered off. The authors use conductometric titration with calcium chloride for the estimation of the fluoride in the solution. W. R. S.

Benzidine as a Reagent for Aldehydes. P. N. van Eck. (*Pharm. Weekblad.*, 1923, **60**, 1204–1208.)—Benzidine gives distinctive colour reactions with groups of aldehydes and with individual aldehydes dissolved in glacial acetic acid. For example, it gives colorations ranging from yellow to orange with aliphatic aldehydes; with benzaldehyde it forms a crystaline yellow deposit; with anisaldehyde, orange crystals; and with phenylacraldehyde, blood-red crystals. It affords a delicate test for vanillin, with which it gives an orange-red coloration, changing to red on diluting the solution with water.

Composition and Constitution of Elæostearic Acid. L. Maquenne. (*Bull. Soc. Chim.*, **1923, 33,** 1654–1655.)—Vercruysse's conclusion that the structural formula of elæostearic acid contains two multiple linkings (*Bull. Soc. Chim. Belg.*, **1923, 32,** 151) was also arrived at by the author (*Compt. rend.*, **1902, 135,** 696), who showed that this acid is extremely liable to undergo oxidation, and that it is both acetylenic and ethylenic in character. The melting point, 48° C., is confirmed for the acid. T. H. P.

Estimation of the Iodine Value of Oils and Fats by means of Pyridine Sulphate-bromide. K. W. Rosenmund and W. Kuhnhenn. (*Zeitsch. Unters. Nahr. Genussm.*, 1923, **46,** 154–159.)—Pyridine-sulphate-bromide ($C_6H_5N.H_2SO_4.Br_2$) is recommended for the iodine absorption test, as it forms additive compounds with oils without any substitution or oxidation. The reagent is prepared of 0·1 *N* strength by dissolving 8 grms. of pyridine and 10 grms. of sulphuric acid in 20 c.c. of glacial acetic acid (kept cool meanwhile), adding 8 grms. of bromine dissolved in another 20 c.c., and diluting the mixture to 1 litre with glacial acetic acid. The solution keeps well, but if stored in a large flask frequently opened in warm weather it should be periodically standardised. The oil or fat is dissolved in 10 c.c. of chloroform, a small excess of the pyridine-sulphate-bromide solution is added, and the mixture allowed to stand for 3 to 5 minutes. After this time the excess is determined either by adding potassium iodide solution and titrating the liberated iodine with thiosulphate, or by direct titration with standard arsenite solution. Tables of results show that the iodine value so estimated is strictly comparable with that given by the more usual iodine tri-bromide method. With the latter the value obtained is to some extent dependent on the excess added, but with the proposed reagent quite a small excess is sufficient and a large one is not deleterious. The reagent prepared in the above manner is also suitable for the estimation of arsenious acid; the acidified arsenic solution is coloured red with methyl orange, and the standard pyridine solution run in until the methyl orange is oxidised and its colour destroyed. Phenol may be estimated as tribromphenol by adding excess of the reagent and titrating back with arsenite solution. H. E. C.

Analysis of Soap Powder. F. F. Flanders and A. D. Truitt. (*J. Ind. Eng. Chem.*, 1923, **15,** 1232.)—The following method is recommended for the rapid estimation of soap and sodium carbonate in soap powders. Two grms. of the

sample are dissolved in 100 c.c. of hot water, and the solution is titrated with 0·5 *N* hydrochloric acid, with the use of methyl-red as indicator; 2 c.c. of 0·5 *N* hydrochloric acid are then added, the mixture is boiled for ten minutes to expel carbon dioxide, and the excess of acid is titrated with 0·1 *N* sodium hydroxide solution. A further quantity of 2 c.c. of 0·5 *N* hydrochloric acid is added, the mixture is cooled, and extracted with three successive quantities of 25 c.c. of neutral chloroform; the chloroform extracts are filtered, the filter washed with 25 c.c. of chloroform, the filtrate boiled to expel carbon dioxide, and the hot solution titrated with 0·1 *N* sodium ethylate solution, phenolphthalein being used as indicator.

$$Na_2CO_3 = \frac{(\text{cc. } 0{\cdot}5\,N \text{ HCl}) - (\text{cc. } 0{\cdot}1\,N \text{ NaOH}) - (\text{cc. } 0{\cdot}1\,N\ C_2H_5ONa)}{2} \times 0{\cdot}0053.$$

$$\text{Anhydrous soap} = \frac{(\text{cc. } 0{\cdot}1\,N\ C_2H_5ONa)}{2} \times 0{\cdot}0306.$$

W. P. S.

Lubricant and Asphaltic Hydrocarbons in Petroleum. C. F. Mabery. (*J. Ind. Eng. Chem.*, 1923, **15**, 1233–1238.)—The author has investigated the nature of the petroleum hydrocarbons which cannot be distilled without undergoing decomposition; the crude oil was first distilled under 30 mm. pressure up to 300° C., and the undistilled residue subjected to fractional solution in a hot mixture of ether and alcohol. The specific gravity, molecular weight, and percentage composition of each fraction were then determined. The method was applied to petroleums from W. Virginia, Pennsylvania, Ohio, Texas and Russia. A comparison of the results shows that there is a difference between the lubricant and asphaltic hydrocarbons, and the higher specific gravity of the Texas and Russian lubricant hydro-carbons is due to their structure. Determinations of the iodine values show that the ring form of unsaturation applies only to the lubricant hydrocarbons, and these do not appear to enter into the formalite reaction of the Marcusson method. W. P. S.

Chemistry of Wood. Relation between Methoxyl and Lignin in Wood. G. J. Ritter. (*J. Ind. Eng. Chem.*, 1923, **15**, 1264–1266.)—The lignins isolated from soft and hard woods differ in composition, since a larger percentage (80 to 90) of the total methoxyl content of the wood can be recovered from soft wood lignin than from hard wood lignin (62 to 80 per cent. recovery). When the woods are heated with dilute alkali solution under pressure they yield the same percentage (approximately 63) of methoxyl in the form of methyl alcohol, but the composition of the residues differs; the hard wood residue contains the remaining methoxyl, whilst the soft wood residue contains none. This fact also suggests a different methoxyl linkage in the two lignins. W. P. S.

Estimation of Pentoses and Pentosans. II. Estimation of Furfuraldehyde. N. C. Pervier and R. A. Gortner. (*J. Ind. Eng. Chem.*, 1923, **15**, 1255–1262.)—Titration with potassium bromate solution, in the presence of

hydrochloric acid and potassium bromide, is recommended for the estimation of furfuraldehyde in the distillate obtained when a pentose or pentosan is distilled with hydrochloric acid (*cf.* ANALYST, **1924, 49,** 47). Five c.c. of 20 per cent. potassium bromide solution are added for every 100 c.c. of the furfuraldehyde solution (distillate) and the acidity is adjusted to about 4 per cent. by weight of HCl by the addition of acid or alkali, as required. The mixture is stirred and 0·1 *N* potassium bromate solution is added from a burette at such a rate that the production of a yellow colour throughout the solution is avoided. When the end-point is approached, the bromate is added in quantities of 0·2 c.c., and the time required for the disappearance of the free bromine is determined electrometrically. A rather large increase in the time required is noted at the end-point of the titration, and the observations are carried slightly beyond this point. The ratio of increment of time to increment of bromate solution is plotted against the total volume of bromate solution already used, and the end-point of the titration is found from this curve. Each c.c. of 0·1 *N* bromate solution is equivalent to 0·004803 grm. of furfuraldehyde. The amount of the aldehyde present does not affect the accuracy of the method; hydroxymethylfurfuraldehyde and lævulinic acid, decomposition products of hexoses, do not interfere, but methylpentoses (*e.g.* rhamnose) and methylpentosans have an influence on the results obtained since they yield methylfurfuraldehyde which is titrated by the bromate solution.

W. P. S.

Oil from Kauri Copal. A. G. Hill and D. Nishida. (*J. Ind. Eng. Chem.*, **1923, 15,** 1276–1277.)—A dark yellow, viscous oil is obtained when Kauri copal is distilled at 330 C. under reduced pressure; the oil, known by the commercial name of "gum spirits," has the following characteristics:—Sp. gr. at 20° C., 0·9667; flash point, 85–86° C.; $[\alpha]_D^{20}$, +3·66°; n_D^{25}, 1·5128; acid value, 69·0; saponification value, 83·0; iodine value (Hanus), 114·0. After the oil has been washed with alkali solution, dried, and re-distilled under reduced pressure it has sp. gr., 0·9280; $[\alpha]_D^{20}$, +2·76°; n_D^{25}, 1·5102; iodine value (Hanus), 104. The oil, when exposed for six days in the form of a thin layer to the atmosphere, gives the colour reaction of rosin oil with the Liebermann-Storch test, and solidifies to a resinous film.

W. P. S.

Inorganic Analysis.

Estimation of Carbon Disulphide by Iodimetry. É. André. (*Bull. Soc. Chim.*, **1923, 33,** 1678–1681.)—The quantity of carbon disulphide corresponding with 1 c.c. of iodine solution is found to depend on the length of time during which the carbon disulphide and the alcoholic potassium hydroxide solution react. The reaction is evidently neither so simple nor so rapid as generally thought.

T. H. P.

Volumetric Micro-Estimation of Sodium. H. Müller. (*Helv. Chim. Acta*, **1923, 6,** 1152–1161.)—The serum (0·1 c.c.) is diluted with water to 1 c.c. in a small centrifugal tube, and treated with one c.c. of potassium pyroantimonate

solution (2 grms. per litre), and, drop by drop, with 0·4 c.c. of 95 per cent. alcohol. The solution is centrifuged after 2 hours' standing, and the clear solution pipetted off. The precipitate is shaken three times with 2 c.c. of 30 per cent. alcohol, centrifuged each time, and the washings removed as before. The tube is heated at 80° to 100° C. on a water bath for the complete removal of alcohol. After cooling, the precipitate is treated with 1 c.c. of 2 per cent. potassium iodide solution per mgrm. of sodium assumed to be present, 1 c.c. of strong hydrochloric acid, and 2 c.c. of water; the solution is titrated, after ten minutes, with 0·01 *N* thiosulphate solution; the number of c.c. multiplied by 0·115 give mgrms. of sodium. Albumin need not be removed before the estimation, and the presence of phosphate, calcium, or magnesium does not affect the results. W. R. S.

Estimation of Sulphonitric and Sulphonitrous Acids. A. Graire. (*Comptes rend.*, 1923, **177**, 821–823.)—The estimation of the nitrogen compounds in impure sulphuric acid cannot be effected by the permanganate method or by means of the nitrometer, since such procedure leads either to reduction phenomena or to the formation of complex salts with nitric oxide. On the other hand, Schlœsing's method, in which ferrous chloride is used, gives satisfactory results for the acids and oxides of nitrogen present. T. H. P.

Physical Methods, Apparatus, etc.

Identification of Minerals by Microscopic Examination of their Traces left on a Hard Body. P. Gaubert. (*Comptes rend.*, 1923, **177**, 960–962.)—Information serving to characterise a mineral, partially or completely, is often obtainable by microscopic examination of the trace obtained by rubbing a fragment of the mineral on a ground glass slide or, for harder minerals, on a quartz plate cut perpendicularly to the axis and roughened with emery on one face. The transparency of the slide is restored by covering the trace with a liquid of about the same refractive index as the glass or quartz. Microscopic examination of the trace indicates the malleability, cleavage, friability, fracture, transparency, polychroism, bi-refraction, etc., of the mineral, and the refractive index may be estimated by using liquids with known indices. Further, in many cases, the degree of purity may be estimated from the appearance of the trace. This may also be treated with ordinary reagents and subjected to microchemical reactions. Thus, the presence of lead may be determined, from the form of lead nitrate crystals, in less than 0·00001 mgrm. of galena. Where doubtful results are obtained, comparison may be made with the traces left by known minerals.
T. H. P.

Burner for Producing Monochromatic Light. A. O. Jones. (*J. Soc. Chem. Ind.*, 1923, 459T.)—A one-inch Meker burner is arranged in such a way that its gas-supply has passed through a steel crucible heated by the burner and containing the desired volatile salt (sodium nitrite is convenient for a yellow flame).

The crucible has a screw cap with asbestos washer and is provided with steel side-tubes which support the crucible at a convenient height above the burner, and at the same time are connected directly with its gas-supply (sketch given). A short time after lighting the gas a strong monochromatic light is obtained.

R. F. I.

New Light Filter. L. W. McCay. (*J. Amer. Chem. Soc.*, 1923, **45**, 2958).—A filtered solution of ordinary chrome alum (310 grms. per litre) placed in glass bottles of square prismatic form (about 10 cm. high and 4·7 cm. at the lateral edge) forms an efficient light filter for observing the potassium flame. It absorbs completely not only the sodium light, but also that of lithium, strontium, calcium and barium. The solution is not only very sensitive, but will also keep indefinitely. It also shows the light of the rubidium and cæsium flames.

New Method of Gas Analysis. R. Geberth. (*J. Ind. Eng. Chem.*, 1923, **15**, 1277–1278.)—The method depends on the principle that mechanical energy impulses, such as sound waves, produced by a vibrating element, differ in character with the chemical composition of the gas through which they are transmitted. The apparatus used consists of a closed cylinder, adjustable as to length, through which the gases are passed, and having at one end a diaphragm coupled to a tuning fork and ammeter, the latter measuring the electric current operating the tuning fork. A graduated dial indicates the length of the gas chamber. The tuning fork is oscillated at a constant rate by an electro-magnet having a carbon transmitter as a variable resistance; as the column of gas is brought near to the resonance point, the ammeter, in series with the electro-magnet, indicates a very sharp rise in the current.

A change in the density of a gas sufficient to cause a change of 0·01 per cent. in the resonance length is readily indicated, and if the resonance length of one of the gases in a binary mixture is known, the composition of the mixture can be estimated. For instance, it is possible to indicate the presence of less than 0·1 per cent. of hydrogen in electrolytic oxygen, or of less than 1 per cent. of sulphur dioxide in air. W. P. S.

Analysis of Mixed Salts by the Freezing Point Method. H. E. Batsford. (*J. Ind. Eng. Chem.*, 1923, **15**, 1272–1273.)—The method consists in fusing the salt mixture in an iron crucible and determining the freezing point by means of a thermocouple and recording instrument. A curve is plotted from the results obtained with mixtures of known composition, and this curve is used for reference in the analysis of mixtures of unknown composition. The triangular method of plotting ternary mixtures is illustrated. For example, a mixture of sodium chloride, calcium chloride and potassium chloride had a freezing point of 620° C. and contained 14·43 per cent. of calcium equivalent to 40·00 per cent. of calcium chloride; reference to the curve shows that the mixture also contained 46 per cent. of sodium chloride and 14 per cent. of potassium chloride. W. P. S.

Method for Reproducing Graphs in Quantity. W. C. Greene and R. S. Hunt. (*J. Amer. Chem. Soc.*, 1923, **45**, 2961).—The graphs are plotted with waterproof drawing ink on the ordinary graph (or co-ordinate) paper. This is dipped into a saturated solution of a purified, colourless paraffin oil in chloroform, and, after about one minute, is withdrawn and allowed to drain. The excess of oil is then wiped off and the sheet left to dry in the air. The prepared paper is used as a negative for the reproduction of photographic copies on any of the bromide or blue print papers by direct printing.

Reviews.

ANALYTISCHE CHEMIE DER ALKALOIDE. By Professor K. H. BAUER. Pp. 425. Berlin: Gebrüder Borntraeger. Price 30s.

This volume deals in a systematic way with methods for the recognition and the quantitative estimation of alkaloids, and it also contains a concise account of what is known of the chemistry of the alkaloids with which it deals. The author, perhaps wisely, makes no attempt to correlate the alkaloids in accordance with their chemical constitution, but classifies them by the source of origin, and the various groups of alkaloids are dealt with in haphazard succession.

The opening Sections deal with the many reagents which give precipitates with alkaloids, and the behaviour of the more important alkaloids with them. Colour reactions are also described, as well as other qualitative methods of identification.

In regard to methods of titration, the best indicators for use with the different alkaloids are given, and also some account of the varying neutral points obtained with different indicators. It is a pity that no reference is made to hydrogen ion concentration, or to the use of the newer indicators for this purpose.

To an English reviewer the book seems singularly incomplete, because it deals so very scantily with the important contributions which English chemists have made to this subject; indeed, the author does not appear to have had access to the Journal of the Chemical Society or to the ANALYST. We take haphazard two instances of the neglect of English work: no reference whatever is made to Dunstan's work on the aconitines, nor to that of Pyman on the emetine alkaloids. The old formula for emetine is employed notwithstanding the fact that it was corrected in 1914.

Professor K. H. Bauer has produced a book on a subject which is of importance to, and a book on which is needed by most analytical chemists. The volume is of the right size and is well printed. It is therefore disappointing to find that he has in a large measure failed to produce what is really wanted.

F. H. CARR.

THE MICRO-ORGANISMS OF THE SOIL. By Sir JOHN RUSSELL, F.R.S., and Others. Pp. viii. + 188. London: Longmans, Green & Co. 1923. Price 7s. 6d. net.

Sir John Russell and his collaborators are to be congratulated on having brought together, in a small space and in an attractive style, the present knowledge of the interrelationship of the micro-organisms of the soil. The work is much enriched by an able historical review of the subject, and is illuminated by the contributions of the group of workers who have focussed their special knowledge on the soil problems.

In the words of the introduction, the purpose of the volume "is to give the broad outlines of our present knowledge of the relationships of the population of living organisms in the soil to one another and to the surface vegetation"; the text actually contains considerable detail which is augmented by a valuable bibliography. Of special importance is the work at Rothamstead, which has thrown so much light on the availability of the nitrogenous constituents of the soil. The influence of partial sterilisation on increasing the rate of oxidisation of the soil and the recognition of the important part played by the protozoa as a limiting factor in the bacterial numbers present in the soil, is of especial interest, and is dealt with in detail in the second chapter, on Soil Protozoa. Arising from this painstaking and laborious work great advances have been made in our knowledge of the distribution and activities of soil bacteria, ciliates, amœbæ and flagellates.

The "elective" methods of differentiating between the different groups of soil bacteria have made possible the study of many interesting groups in the "20,000,000 bacteria per grm. of soil which is now considered a fair average number."

The study of the organisms decomposing cellulose and their need for combined nitrogen has resulted in the development of a commercial process for making synthetic farmyard manure from straw, another contribution to practical agriculture from Rothamstead which may have a great economic future.

The complexity of the subject of nodule formation on leguminous plants, as disclosed by further work, still leaves room for improvement in our methods of legume cropping, conditions of which it is stated are being thoroughly worked out.

The Soil Algæ, Soil Fungi and the Invertebrate Fauna of the soil are ably discussed in other chapters of the book.

Much original work appears in the text, and it is obvious that full advantage is being taken of the unique facilities at Rothamstead for supplying historical, statistical and analytical data covering a long period of years.

In the final chapter, the Chemical Activities of the Soil Population and their Relation to the Growing Plant, are summarised in a very masterly manner.

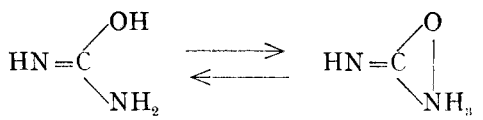
It is of special interest to note that each acre of dunged land loses, on an average, 41,000 calories per day, while each acre of unmanured land loses 2,700 calories per day. The human food produced on the dunged land yields only 7,000 calories per day.

The control of the soil population is still only in its infancy, but this useful contribution to our knowledge of the subject indicates the road and gives inspiration and a promise of useful development in future research work.

J. GOLDING.

THE CHEMISTRY OF UREA: THE THEORY OF ITS CONSTITUTION, AND OF THE ORIGIN, AND MODE OF ITS FORMATION IN LIVING ORGANISMS. By Prof. EMIL A. WERNER, M.A., Sc.D., F.I.C. (Monographs on Biochemistry). Pp. xii. + 212. London: Longmans, Green & Co. 1923. 14s. net.

There is no one more competent to write on urea than Prof. Werner, and any book written by him on the subject must perforce be a valuable addition to the literature. It is, however, much to be regretted that Prof. Werner sets out mainly to prove his tautomeric formula



and to show that the old carbamide formula $CO(NH_2)_2$ is "quite untenable." Although it cannot be denied that he has made a good case for his formula, it must be left to the future to decide how far Prof. Werner has succeeded in convincing the chemical world at large as to the correctness of his views. There is, however, but little doubt that a more general treatment of the subject would have added greatly to the value of this monograph. As it stands, it is not the "Chemistry of Urea," but the case for the Werner formula.

M. NIERENSTEIN.

The Institute of Chemistry of Great Britain and Ireland.

PASS LIST.

JANUARY EXAMINATIONS, 1924.

THE following candidates have passed the examination for the Associateship:—*In General Chemistry:* D. S. Cohen, R. C. Doyle, H. C. Exell, H. H. Goldthorpe, B.Sc. (Lond.), A. T. S. Hare, F. P. Hornby, J. Johnston, B.Sc. (Lond.), A. N. D. Pullen, W. H. Radford, R. W. Watridge, B.Sc. (Lond.), and R. J. Wood.

(Nineteen candidates failed to satisfy the examiners.)