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THE EXAMINATION OF COMMERCIAL SAMPLES OF NICOTINE.

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(Read at the Meeting, June 4, 1919.)

CONCENTRATED nicotine is now manufactured in this country and in America, and is sold retail through agents at approximately 95 per cent. strength, the remainder being water. It contains also the alkaloids nicoteine, nicotellin, nicotimine, which for analytical purposes are reckoned as nicotine. Nicotine is employed almost exclusively as an insecticide for agricultural purposes, especially for the destruction of green fly (or aphis) and plant bugs (*Hemiptera*) on fruit and hops. It is, therefore, of national importance that it should be sold of the guaranteed strength and be free from adulteration.

During the last few years there has been a world-scarcity of nicotine, due not only to difficulties of labour, but also to the diminished imports of tobacco and to the consequent use of lower grades of tobacco and stalks for smoking purposes, these having previous to this been used only for nicotine extraction. In consequence of this there is a great inducement at the present time to adulterate the concentrated product, and the grower to whom the nicotine is sold will be well advised to submit samples of his purchase to analysis.

Since nicotine is miscible with water, it is easily adulterated in this way. The authors have found many samples containing less than 95 per cent. which should have been up to this standard. It must, however, be remembered that, as nicotine is very hygroscopic, water absorption is likely to occur if the material be not kept in tight packages.

The usual method for estimating nicotine is titration with a standard acid, using an indicator such as methyl orange, cochineal, phenacetolin, etc. Incidentally, the authors have found that *methyl red* is by far the most sensitive indicator to employ. Each c.c. of $\frac{N}{1}$ acid corresponds to 0·162 grm. of nicotine. This test readily reveals any excess of water, though it cannot be relied on to give an accuracy of over 1 per cent. in the concentrated material, even with methyl red as an indicator,

unless the analyst has had some considerable experience in judging the colour change against a sample of known strength.

One of the objects of this paper is to insist upon the great utility and value of the refractive index as a ready means of estimating the strength of nicotine solutions. In this respect it is, in our view, much superior to the polarimeter, since, as recently shown by Jephcott, the optical rotation of nicotine solutions is very irregular (owing to the formation of hydrates).

Since the refractive index of commercial nicotine is about 1·525, compared with water 1·334, it is obvious that there is a very wide difference to work upon. Taking the usual model of the Abbé refractometer as capable of reading readily to within 2 units in the fourth decimal place, this gives an attainable accuracy in reading of $\frac{1}{10}$th per cent., provided that the temperature be carefully adjusted. The authors have determined the refractive indices for commercial nicotine and water throughout a large range, and from the curve so obtained the table on p. 365 was constructed, giving the refractive indices for all percentage strengths of the commercial article.

A further advantage of the use of the refractive index is that adulteration with weak ammonia, which is a very convenient adulterant in the hands of unscrupulous people, and which would give a high value in the acidity test, has little effect on the true refractive index, that of ammonia solutions being very low. The same remarks also apply to an addition of other alkaline hydroxides or carbonates —e.g., sodium and potassium.

The best method for the analysis of " pure " nicotine is that proposed by Bertrand and Javillier (ANALYST, 1909, 34, 219). The precipitant employed is an acid solution of silico-tungstic acid, a bulky precipitate being formed which has ten times the mass of the nicotine. It is filtered, dried, and incinerated, the factor used being 0·1139.*

The problem of the adulteration of nicotine would not be a difficult one if these were the only adulterants likely to be used. Unfortunately, there is one substance which has unquestionably been used in the past without detection and without even arousing suspicion. We refer to Pyridine. Pyridine has also feeble insecticidal properties; it is miscible with nicotine and water, and is precipitated by the usual reagents used for nicotine estimation, such as gold chloride, picric acid, zinc, and mercuric chloride. It is precipitated by silico-tungstic acid,† a fact which renders this otherwise excellent method of no value in the case of adulteration with pyridine. It is also soluble in the same solvents to about the same degree as nicotine, and, being powerfully basic, would not be detected in the usual method of titration with acid. The importance of this question led the authors to investigate carefully the question of pyridine adulteration.‡

In the first place, we find an indication of pyridine adulteration is given by the odour of the product in the titration test when almost all the bases have been

* Allen (supplement, p. 485) states this factor incorrectly as 0·1071.

† Although the pyridine silico-tungstate is not wholly insoluble in water, as is the nicotine salt.

‡ The advantage obtained by the adulteration of nicotine with pyridine may be judged by their present respective values :

Pyridine quoted at 2s. 10d. per gallon.
Nicotine quoted at 16s. per pound.

neutralised. It is not easily detected in the concentrated product, but before neutralisation is quite perceptible. This may then be confirmed by the comparison of the titration figure with acid, calculated to nicotine (which, since pyridine requires more acid, will be too high), with that obtained by reference to the table of refractive indices. In the case of pyridine adulteration this latter figure will be too low, since the refractive index of pyridine is less than that of nicotine. We have made observations of the refractive indices of various strengths of pyridine solution,

TABLE I.—REFRACTIVE INDICES OF AQUEOUS SOLUTIONS OF NICOTINE.

Per Cent. Nicotine.	Refractive Index, 15° C.	Difference.	Per Cent. Nicotine.	Refractive Index, 15° C.	Difference.	Per Cent. Nicotine.	Refractive Index, 15° C.	Difference.
100	1·5300		66	1·4765	22	32	1·4018	·21
99	1·5293	7	65	1·4743	22	31	1·3997	22
98	1.5285	8	64	1·4721	22	30	1·3976	21
97	1·5276	9	63	1·4699	22	29	1·3954	22
96	1·5266	10	62	1·4677	22	28	1·3933	21
95	1·5255	11	61	1·4655	22	27	1·3911	22
94	1·5244	11	60	1·4633	22	26	1·3889	22
93	1·5232	12	59	1·4511	22	25	1·3868	21
92	1·5219	13	58	1·4589	22	24	1·3846	·22
91	1·5206	13	57	1·4567	22	23	1·3824	22
90	1·5193	13	56	1·4545	22	22	1·3803	21
89	1·5179	14	55	1·4523	22	21	1·3781	22
88	1·5165	14	54	1·4501	22	20	1·3760	21
87	1·5150	15	53	1·4479	22	19	1·3738	22
86	1·5134	16	52	1·4457	22	18	1·3717	21
85	1·5118	16	51	1·4435	22	17	1·3695	22
84	1·5102	16	50	1·4413	22	16	1·3674	21
83	1·5086	16	49	1·4391	22	15	1·3652	22
82	1·5069	17	48	1·4369	22	14	1·3631	21
81	1·5052	17	47	1·4347	22	13	1·3609	22
80	1·5035	17	46	1·4325	22	12	1·3588	21
79	1·5018	17	45	1·4303	22	11	1·3567	21
78	1·5001	17	44	1·4281	22	10	1·3546	21
77	1·4984	17	43	1·4259	22	9	1·3525	21
76	1·4967	17	42	1·4237	22	8	1·3504	21
75	1·4950	17	41	1·4215	22	7	1·3483	21
74	1·4932	18	40	1·4193	22	6	1·3463	20
73	1·4913	19	39	1·4171	22	5	1·3443	20
72	1·4893	20	38	1·4149	22	4	1·3422	21
71	1·4873	20	37	1·4127	22	3	1·3402	20
70	1·4852	21	36	1·4105	22	2	1·3382	20
69	1·4831	21	35	1·4083	22	1	1·3362	20
68	1·4809	22	34	1·4061	22	0	1·3341	21
67	1·4787	22	33	1·4039	21			

TABLE II.—REFRACTIVE INDICES OF AQUEOUS SOLUTIONS OF PYRIDINE.

Per Cent. Pyridine.	Refractive Index, 15° C.	Difference.	Per Cent. Pyridine.	Refractive Index, 15° C.	Difference.	Per Cent. Pyridine.	Refractive Index, 15° C.	Difference.
100	1·5136		66	1·4635	19	32	1·3966	20
99	1·5128	8	65	1·4616	19	31	1·3947	19
98	1·5119	9	64	1·4597	19	30	1·3927	20
97	1·5109	10	63	1·4577	20	29	1·3907	20
96	1·5099	10	62	1·4557	20	28	1·3888	19
95	1·5088	11	61	1·4537	20	27	1·3868	20
94	1·5077	11	60	1·4516	21	26	1·3849	19
93	1·5065	12	59	1·4496	20	25	1·3829	20
92	1·5053	12	58	1·4475	21	24	1·3809	20
91	1·5041	12	57	1·4454	21	23	1·3790	19
90	1·5028	13	56	1·4434	20	22	1·3770	20
89	1·5015	13	55	1·4414	20	21	1·3750	20
88	1·5002	13	54	1.4394	20	20	1·3731	19
87	1·4988	14	53	1·4375	19	19	1·3712	19
86	1·4974	14	52	1·4356	19	18	1·3692	20
85	1·4960	14	51	1·4337	19	17	1·3672	20
84	1·4945	15	50	1·4317	20	16	1·3652	20
83	1·4930	15	49	1·4297	20	15	1·3632	20
82	1·4915	15	48	1·4277	20	14	1·3612	20
81	1·4900	15	47	1·4258	19	13	1·3592	20
80	1·4884	16	46	1·4239	19	12	1·3572	20
79	1·4867	17	45	1·4219	20	11	1·3552	20
78	1·4850	17	44	1·4200	19	10	1·3532	20
77	1·4833	17	43	1·4181	19	9	1·3512	20
76	1·4816	17	42	1·4162	19	8	1·3492	20
75	1·4799	17	41	1·4142	20	7	1·3473	19
74	1·4782	17	40	1·4123	19	6	1·3454	19
73	1·4764	18	39	1·4103	20	5	1·3435	19
72	1·4746	18	38	1·4084	19	4	1·3416	19
71	1·4728	18	37	1·4064	20	3	1·3397	19
70	1·4710	18	36	1·4045	19	2	1·3378	19
69	1·4792	18	35	1·4025	20	1	1·3359	19
68	1·4673	19	34	1·4005	20	0	1·3341	18
67	1·4654	19	33	1·3986	19			
		19			20			

and a comparison of these two tables gives an approximate figure for the pyridine present (see Method I., p. 367). When, by proceeding in this manner, nicotine is suspected of adulteration with pyridine, two methods may be employed for confirmation.

The one which we suggest as being the most ready of application by the analyst depends on the fact that nicotine in certain concentrations separates almost wholly from its solutions on being heated to 100° C., whereas under these circumstances pyridine remains soluble.

If, therefore, on heating to this temperature the aqueous liquid is tested, it will be found to have a high refractive index when adulterated with pyridine. The authors have investigated the effect of additions of pyridine, and are able to give figures showing the percentage adulteration corresponding with the refractive indices found (see Method II.).

The second method depends upon the diversity of b.-pt. of the two substances :

Nicotine	...	...	...	B.-pt., 246·7° C. at 745 mm.
Pyridine	...	...	...	B.-pt., 115·5° C. at 760 mm.

A definite volume is distilled up to a certain temperature in a standard flask (see p. 368) and the refractive index and volume of the distillate noted.

We hope to give a supplementary paper on the examination of tobacco extracts and other forms of the alkaloid, such as the American " black leaf 40 " (crude nicotine sulphate), and also of the pure oxalate and sulphate of nicotine.

METHOD I.

Determination of the Adulteration of Nicotine with Pyridine by Titration with Acid, and Reference to Table of Refractive Indices.

1. The refractive index of the sample of concentrated nicotine (also the dispersion figure *) is ascertained, and the corresponding percentage of nicotine (a) given by Table I. noted.

2. About 5 grms. of the sample are weighed accurately, diluted to 200 c.c. with distilled water, and titrated with $\frac{N}{1}$HCl, using methyl red as indicator.

If pyridine is absent, the end-point is fairly sharp, but in presence of over 2 per cent. of pyridine it becomes much less distinct. This is a good preliminary indication of adulteration.

3. The result is calculated to nicotine (each c.c. $\frac{N}{1}$ acid = 0·162 grm. nicotine) (b).

4. In case of pyridine adulteration (b) will be greater than (a), and $(b-a)$ will give the approximate percentage of pyridine present.

Example.

Nicotine employed showed 95·1 per cent. by silico-tungstate method.

To this was added 5 per cent. of pyridine (testing 95·1 per cent. purity).

The refractive index of the mixture was 1·5240 (15° C.), showing on Table I. 93·6 per cent. nicotine (a).

On titration with $\frac{N}{1}$ HCl, using methyl red, and calculating to nicotine, the figure 98·5 per cent. nicotine was obtained (b).

$(b-a) = 4·9$.

* An indication of pyridine adulteration is given by a *lower dispersion figure* on the instrument. With the Abbé refractometer used by the authors, the following figures were given on the scale :

				15° C.
Nicotine, 95 per cent.	..	..	..	38·0
Pyridine, 95 ,, ,,	..	..	..	36·2
Water	..	..	..	42·2

METHOD II.

By Heating to 100° C. and Examining the Aqueous Liquid after the Separation of Nicotine from the Solution

(This is a simple and rapid method, but not suitable unless over 10 per cent. of pyridine be present.)

1. Into a conical flask of 150 c.c. capacity, exactly 25 grms. of the suspected sample of nicotine are weighed out and diluted with water to 100 c.c.

2. A cork carrying a thermometer dipping into the liquid, and the flask heated in a water oven till the temperature attains 99° C. when it is kept at that temperature for ten minutes.

3. The flask is now removed carefully from the oven and placed on one side to cool; the thermometer is then removed and the flask tightly corked, using great care not to agitate the liquid.

4. The flask is left for a period not exceeding twelve hours, and, when cold, a drop of the surface aqueous fluid (the nicotine will have separated on the bottom as an oily liquid) is taken and the refractive index ascertained.

5. In the case of pure nicotine, the refractive index obtained shows by the Table I. a percentage of 9·7 nicotine in the aqueous liquid. If pyridine is present to the extent of over 10 per cent., this figure is increased. Reference to the following table will show the approximate extent of adulteration (below 10 per cent. the solubility of the nicotine is apparently decreased):

Pyridine Present per Cent.	Refractive Index (15° C.) of Aqueous Liquid.	Difference per 1 per Cent. Pyridine.
0	1·3540	
5	1·3538	
10	1·3558	
15	1·3587	5·6
20	1·3616	5·8
25	1·3640	4·8
30	1·3662	4·4
35	1·3684	4·4
40	1·3705	4·2

METHOD III.

By Fractional Distillation.

(The exact procedure must be followed, as the method is entirely an arbitrary one.)

1. The refractive index of the sample is ascertained and the corresponding percentage of nicotine noted by reference to Table I. If this exceeds 95 per cent., the requisite amount of distilled water to bring it to this strength * is added.

2. One hundred c.c. of the sample (adjusted as above, if necessary) are placed in a STANDARD ENGLER FLASK,† and a thermometer with a cork inserted so that the top

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If under 95 per cent. strength (by Table I.), the results will not correspond with the figure given. In such cases place about 150 c.c. of the nicotine in a basin inside a desiccator, preferably evacuated over sulphuric acid, and leave until it has exceeded this figure in concentration, when adjust as before.

† The standard flask for petroleum distillation. For details, see Technical Handbook of Oils, Fats, and Waxes. Fryer and Weston. Vol. II., p. 214.

of the bulb is level with the side tube.   A condenser of 30 cm. length is used, and the distillate caught in a 50 c.c. cylinder.

3. The flask is heated with a small Bunsen flame (3 cm. in height) until the temperature reaches 150° C.   At this point the flame is immediately withdrawn.

4. The volume of the distillate is noted,† and its refractive index ascertained. Reference to the following table gives the percentage of pyridine present:

Refractive Index of Distillate.	Difference for 1 per Cent.	Percentage of Pyridine Present.	Refractive Index of Distillate.	Difference for 1 per Cent.	Percentage of Pyridine Present.
1·357		0	1·448		13
	9			3	
1·366		1	1·451		14
	9			3	
1·375		2	1·454		15
	9			3	
1·384		3	1·457		16
	9			3	
1·393		4	1·460		17
	8			3	
1·401		5	1·463		18
	8			2	
1·409		6	1·465		19
	8			2	
1·417		7	1·467		20
	7			2	
1·424		8	1·469		21
	6			2	
1·430		9	1·471		22
	6			2	
1·436		10	1·473		23
	5			2	
1·441		11	1·475		24
	4			2	
1·444		12	1·477		25
	4				

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NOTES.

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

NOTE ON COMPOUND TINCTURE OF RHUBARB.

In the preparation of compound tincture of rhubarb, the 1898 British Pharmacopœia directed the use of 60 per cent. alcohol for the extraction of the rhubarb "root," cardamom seeds, and coriander fruit.   In the 1914 edition the strength of the alcohol to be employed is altered to 45 per cent.

No.	Sp. Gr.	Total Solids. Grms. per 100 c.c.
1	0·9622	13·0
2	0·9777	17·0
3	0·9915	15·6
4	0·9918	15·2
5	0·9935	16·9
6	0·9946	16·5
7	0·9945	16·3
8	0·9976	16·8
9	1·0050	18·4
10	—	15·4 (3·7)
11·	—	15·5 (3·9)

† This volume should not exceed 5 c.c. in the case of genuine nicotine if the conditions are correctly adhered to, and the strength accurately adjusted (see §1 above).   The volume increases with the extent of the adulteration.

The samples dealt with in the following table were purchased in London during October, 1919, except those numbered 10 and 11, which were prepared in the laboratory. The figures in brackets show the amounts of solids exclusive of glycerol. The prices of purchased samples ranged from 4d. per ounce (No. 3 and No. 5) to 1s. for No. 4.

No. 2 has obviously not been prepared according to the directions of the 1914 edition of the Pharmacopœia. The figures are consistent with an 1898 tincture, but it is more likely that an addition of an appropriate amount of glycerol has been made to some *Tinctura Rhei Composita* (war emergency formula) since the ban on the use of glycerol for such articles has been removed. No. 1 is decidedly below strength.

C. G. Moor ("Suggested Standards of Purity for Foods and Drugs") gave figures of 0·964 to 0·977 sp. gr. and of 13·3 to 17·0 grms. total solids per 100 c.c. for the 1898 tincture. The reduction in alcoholic strength in the 1914 tincture has, of course, resulted in a rise in sp. gr., but the total solids figure has not appreciably altered. Except No. 1, all tinctures dealt with in this Note exceed the minimum total solids of 14·8 (*i.e.*, for the 1898 tincture) mentioned in "Suggested Standards for Pharmacopœial Preparations" issued by the Local Government Board for Ireland (August, 1902).

Squire's "Companion" (nineteenth edition) gives as tests: "Compound tincture of rhubarb has a sp. gr. of about 1·003; it contains about 17·5 per cent. w/v of total solids and about 39 per cent. v/v of absolute alcohol." Only one of the samples reaches either sp. gr. or total solids of these requirements, and the results seem to show that, while they are sometimes met, it is only in exceptional cases. It looks as if, to reach them, a manufacturer would have to restrict himself to selected parcels of rhubarb.

Evidence that Squire's tests are not usually attained can be obtained from a survey of figures published, not only on the 1898 tincture, but also from those on the 1885 preparation. Though the latter was made with proof spirit, it seems unlikely that the extract to 45 per cent. alcohol would be much greater, while the presence of the extractives of saffron in addition would have an effect in increasing the solids. No glycerol was used for this 1885 tincture. J. Spilsbury (ANALYST, 1889, **14**, 208) certainly reported 5·38 grms. of total solids per 100 c.c., but this was characterised by Macfarlane (Canadian "Bulletin," No. 34) as "abnormally high²— perhaps imperfectly dried." Macfarlane himself quotes figures of 3·31 to 4·26 for total solids.

In compound tincture of rhubarb glycerol is present in too small an amount to have appreciable medicinal action (White and Humphrey in their "Pharmacopedia" say it is probably added to prevent the formation of a deposit on keeping), but it forms the major part of the residue. If allowance be made for it, the results obtained show that some tinctures may be expected to have more than twice the medicinal value of others

WILLIAM PARTRIDGE.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Acidity of Chaulmoogra Oil. V. Cofman. (*Pharm. J.*, 1919, **103**, 269.)—Two samples of chaulmoogra oil, one expressed and the other extracted from the seeds, had acid values of 8·3 and 7·7 respectively, whilst five commercial samples had acid values ranging from 18·5 to 76·7. The acidity of the oil was found to vary with the mode of preparation and time of keeping. For example, in the case of the expressed sample this value had risen to 9·2 in four months and to 19·2 in a year. In the process of the U.S. Dispensatory, in which the seeds are crushed and boiled with water prior to the extraction with ether, the acid value was 15·6 as compared with 7·7 in the case of the oil extracted directly with ether from the same seeds. From these results the conclusion is drawn that the limits for the acidity of chaulmoogra oil prescribed by the B.P. are too narrow, and are of no value as an identification test. They should, therefore, be altered or (preferably) omitted.

C. A. M.

Estimation of Fat in Cocoa and Chocolate. E. B. Hughes. (*Chem. News*, 1919, **119**, 104.)—The method is based on that of Bordas and Touplain for the rapid analysis of milk. A Leffmann-Beam centrifugal machine fitted with glass cylinders holding about 40 c.c. may be employed, and, in the case of chocolate, the material should be ground sufficiently finely to pass through a 30-mesh sieve. Two grms. of the finely powdered substance, or 1 grm. in the case of whole-fat cocoa, are mixed with about 30 c.c. of 50 per cent. alcohol, and then twice spun, the clear liquid being decanted off and rejected; to the residue are added 25 c.c. of a mixture of equal volumes of sulphuric and petroleum ether, the whole well stirred and mixed for about fifteen minutes, spun, and the clear liquid decanted into a weighed flask. This process is repeated, the ether distilled off, and the fat and the flask weighed. The extracted fat is free from impurity. In materials examined by this method, and also by the usual Soxhlet extraction, the differences in the fat content obtained were extremely small, while in most cases, when using the Soxhlet apparatus, the fat was impure and had to be taken up again in ether.

H. F. E. H.

Influence of the Oxidation of Lactose and Lactic Acid on the Results of the Analysis of Milk preserved with Potassium Dichromate. Marchadier and Goujon. (*Ann. Chim. anal.*, 1919, **1**, 288-290.)—The total solids of milk preserved with potassium dichromate frequently differ from the sum of the individual constituents. For example, in one case the total solids were 122·6 grms., whilst the sum of the constituents was 111·4 grms. per litre. This is shown to be due to the oxidation of the lactose and lactic acid with the formation of acetic acid, water, and carbon dioxide, and, in some cases, of oxalic acid. In the case of the sample mentioned, potassium dichromate was no longer present, but had reacted to

form the blue double oxalate of potassium and chromium, $(C_2O_4)_6Cr_2K_6 + 6H_2O$, the aqueous solution of which, when treated with lead acetate, yielded a precipitate of the double blue oxalate of chromium and lead, $(C_2O_4)_6Cr_2Pb_3 + 15H_2O$.   C. A. M.

Use of the Simplified Molecular Constant in the Analysis of Coagulated Milk. Fonzes-Diacon. (*Ann. Falsific.*, 1912, **12**, 202-203.)—The acidity of the whey in excess of the normal acidity is calculated into lactose and added to the amount of lactose estimated by the usual method. The chlorides are then estimated in the same whey, and translated isotonically into lactose. The sum of these results in grms. per litre is the simplified molecular constant, and should it be much below 70, watering of the milk is indicated, and its amount may be approximately calculated. The results thus obtained in test analyses agreed approximately with those calculated from the analysis of unaltered milk.   C. A. M.

Estimation of Small Quantities of Nitrites in Pickled Meats. F. Auerbach and G. Reiss. (*Arbeit. Reichsgesundheitsamte*, 1919, **58**, 532-555.)—The method depends on the extraction of the nitrite with dilute sodium carbonate solution, separation of soluble proteins by means of colloidal ferric hydroxide, and the colorimetric estimation of the nitrite with *m*-phenylenediamine. In the case of pickled meat the piece is washed with water, and portions about 1 cm. thick are then cut off and passed through a mincing machine; minced meat, sausage meat, etc., may also be passed through the machine to insure thorough mixing. Ten grms. of the minced sample are mixed with 150 c.c. of water containing 6 drops of 25 per cent. sodium carbonate solution, and shaken occasionally for ninety minutes. The mixture is then diluted to 200 c.c., filtered, and 10 c.c. of the filtrate are treated with dilute sulphuric acid and zinc iodide-starch solution. If no blue coloration develops, the samples are free from nitrite, but if a distinct coloration is produced within a few minutes, nitrite is present, and its quantity is estimated as follows : 75 c.c. of the filtered extract are treated with 20 c.c. of colloidal ferric hydroxide solution, the mixture is diluted to 100 c.c., and filtered. To 50 c.c. of the colourless filtrate are then added 1 c.c. of 10 per cent. sodium acetate solution, 0·2 c.c. of 30 per cent. acetic acid, and 1 c.c. of *m*-phenylenediamine hydrochloride solution (0·5 grm. of the salt dissolved in 100 c.c. of water and a few drops of acetic acid). The yellowish or red coloration obtained is compared with those produced by known amounts of nitrite under similar conditions. When meat is pickled for several weeks with potassium nitrate, a portion of the nitrate may be reduced to nitrite. The quantity of nitrite thus formed is only a few mgrms.—at most 10 mgrms.—per 100 grms. of meat ; the nitrate itself may contain a small quantity of nitrite, and, taking these sources of nitrite into consideration, it may be concluded that the sample contains added nitrite when the nitrite content (as $NaNO_2$) exceeds 15 mgrms. per 100 grms. of meat. The use of nitrites in the preparation of pickled meats has recently been forbidden in Germany.   W. P. S.

American Tomato-Seed Oil. G. S. Jamieson and H. S. Bailey. (*J. Ind. and Eng. Chem.*, 1919, **11**, 850.)—Air-dried tomato seeds give a yield of about 25 per

cent. oil when extracted with ether, and about 18 per cent. when the seeds are pressed. The Renard test indicates the presence of a considerable amount of arachidic acid, but full investigation shows that this is an unreliable indication, as extreme care failed to prove the presence of more than 0·4 per cent. of this acid. The following constants were obtained from the analysis of nine authentic and genuine samples of tomato-seed oil from seed grown in various parts of the United States:

	Highest.	Lowest.	Average.
Sp. gr. at 25° C.	0·9196	0·9184	0·9190
Refractive index at 25° C.	1·4728	1·4715	1·4722
Iodine number (Hanůs)	125·0	117·5	122·5
Saponification number	192·0	187·0	189·5
Reichert Meissl number	0·3	0·1	0·26
Polenske number	0·6	0·4	0·55
Acetyl value	20·5	10·0	14·2
Insoluble fatty acids, per cent. ...	96·6	95·0	98·5
Soluble ,, ,, ,, ,, ...	0·7	0·44	0·52
Unsaturated (liquid) acids, per cent. ...	80·6	76·1	78·5
Saturated (solid) ,, ,, ,, ...	18·0	15·0	16·4

H. F. E. H.

Reactions between Potassium Sulphate and Tartaric Acid under Various Conditions. A. Borntraeger. (*Annali Chim. Applic.*, 1919, 12, 1-23.)—Bussy and Buignet (*Comptes rend.*, 1865, 60, 200) concluded that when wines and musts were plastered, potassium bisulphate was formed, and that this was decomposed by the alcohol into the normal sulphate and free sulphuric acid. The author concludes, however, that the reaction between calcium sulphate and potassium bitartrate takes place in accordance with the equation—

$$2C_4H_5KO_6 + CaSO_4.2H_2O = C_4H_4CaO_6 + K_2SO_4 + C_4H_6O_6 + 2H_2O.$$

As was also shown by Bussy and Buignet, the system ($K_2SO_4 + C_4H_6O_6$) is readily converted into the system ($KHSO_4 + C_4H_5KO_6$). When a solution containing potassium bisulphate and bitartrate in equimolecular proportions is evaporated, the normal sulphate and tartaric acid are first formed, but, on continuing the evaporation, potassium bitartrate separates out, leaving potassium bisulphate in solution. When the solution is concentrated still further the reverse reaction takes place, $KHSO_4 + C_4H_5KO_6 = K_2SO_4 + C_4H_6O_6$. In like manner, a solution of potassium sulphate and tartaric acid in equimolecular proportions, when incompletely evaporated, leaves a residue of potassium bitartrate with potassium bisulphate in solution, whilst the final dry residue consists of potassium sulphate and tartaric acid. If free sulphuric acid were present the final residue would be moist. In an experimental study of the methods used for the investigation of this question in the examination of plastered wines it was found that neither ether nor anhydrous alcohol has any action upon potassium

bisulphate, but that alcohol containing a trace of water acts slowly upon the bisulphate, partially decomposing it into the normal sulphate and free sulphuric acid. Ether and absolute alcohol extract only tartaric acid from a dry mixture of that acid with potassium sulphate, but dilute alcohol causes a partial reaction to take place, with the formation of potassium bitartrate and bisulphate, and the partial decomposition of the latter into the normal sulphate and free sulphuric acid. The influence of the salts of weak acids in wines must be taken into account when the liquid is evaporated for the detection of free sulphuric acid. These will interfere with the test except in the case of wines to which a large amount of acid has been added or of wines extraordinarily heavily plastered.   C. A. M.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Contribution to the Study of Milk Serum. R. Ledent. (*Ann. Falsific.*, 1919, **12**, 197-201.)—The sp. gr. of milk serum obtained by spontaneous coagulation ranges between 1·027 and 1·030 at 35° to 40° C. in the case of Belgian and Dutch milks, and from 1·026 to 1·031 in the case of milks of other countries. The following method enables a serum of sufficiently constant composition for comparison to be obtained: 75 c.c. of the milk are heated for five minutes at 70° C. (not more) with 1·5 c.c. of 20 per cent. acetic acid, and then filtered, and the first 30 c.c. of the filtrate rejected. From the results obtained with over 100 samples of milk from the provinces of Liège and Luxemburg it was found that the sp. gr. of pure milk serum ranged from 1·027 to 1·029 at 15° C., whilst the sera from milk of doubtful purity had a sp. gr. of 1·026 to 1·027, and that from milk containing 10 per cent. of water 1·0255 or less.   C. A. M.

ORGANIC ANALYSIS.

Estimation of Arsenic in Substituted Phenylarsinic Acids and their Reduction Products. R. G. Fargher. (*J. Chem. Soc.*, 1919, **115-116**, 982-992.)—Ewins (ANALYST, 1917, **42**, 50) considers that the method devised by Lehmann (*Apoth. Zeit.*, 1912, **27**, 545; ANALYST, 1912, **37**, 415) for the estimation of arsenic in salvarsan and neosalvarsan, whilst applicable to some derivatives, fails entirely in many cases owing to the fact that the preliminary treatment with sulphuric acid and permanganate fails to bring about complete oxidation. It has now been found possible by the use of the modification described below to extend this estimation to many substituted phenylarsinic acids containing nitro-, amino-, hydroxy-, methoxy-, bromo-, and other groups. Some of the powdered substance (0·2 grm.) is weighed and intimately mixed in a 250 c.c. flask with 1 grm. of potassium permanganate. Five c.c. of 50 per cent. sulphuric acid are added, followed by a further 10 c.c. of concentrated sulphuric acid when the first reaction has ended. After a few minutes, 10 c.c. of water are added, and the mixture is heated for half an hour to gentle boiling, precautions being taken against loss by spraying. The manganese dioxide is then removed by a slight excess of hydrogen peroxide, 30 c.c. of water are added, and the solution is again boiled for ten minutes, after which a dilute solution of potassium permanganate is added drop by drop until a faint, permanent pink tinge is obtained. This is discharged by the addition of a drop of a dilute solution of oxalic

acid. The solution is then cooled, 2·5 grms. of potassium iodide are added, the whole being allowed to remain for an hour, and the liberated iodine titrated by means of thiosulphate. A blank experiment should be carried out alongside each estimation, and the final reading corrected accordingly. The following are examples of the results obtained :

Substances.				As Found.	Calc.
3-Nitro-4-hydroxyphenylarsinic acid	...	...		28·4, 28·4	28·5
p-Aminophenylarsinic acid	...	...	...	34·5, 34·5	34·6
1 : 2-Dihydrobenzoxazolone-4-arsinic acid ...		...		28·6	28·9
3-Nitro-4-aminophenylarsinic acid		...	...	28·9, 28·8	28·6
3 : 3'-Dinitro-4 : 4'-dihydroxydiphenylarsinic acid		...		19·6, 19·5	19·5
p-Bromophenylarsinic acid	...	...	...	26·5	26·7

H. F. E. H.

Titration of p-Aminoazo Benzene. F. Neitzel. (*Chem. Zeit.*, 1919, **43**, 472.)—

The analysis of p-aminoazo-benzene by diazotisation with nitrite in acidified aqueous solution gives untrustworthy results, but by diazotising in an alcoholic acid solution the method is rendered accurate. One grm. of the sample is dissolved in 100 c.c. of alcohol and 5 c.c. of hydrochloric acid (sp. gr., 1·19), and the solution immediately titrated with $\frac{N}{5}$ or $\frac{N}{1}$ nitrite solution at 5° to 8° C. The end-point of the reaction is found by applying a drop of the liquid to moistened starch-iodide paper.

C. A. M.

Selective Combustion of Carbon Monoxide in Hydrogen. E. K. Rideal.

(*J. Chem. Soc.*, 1919, **115-116**, 993-1006.)—In the ANALYST (1919, 89) the author has described the method and apparatus employed for the preferential oxidation of small quantities of carbon monoxide in hydrogen when such a mixture is passed, together with small quantities of oxygen, over certain catalytic materials maintained at suitable temperatures. It was established that complete elimination of the monoxide was possible, though there was also oxidation of some of the hydrogen. In the present work, in addition to recording some experimental results, there is a full theoretical and mathematical discussion of the subject. The catalytic materials and the methods for their preparation, which were only briefly referred to in the ANALYST (*loc. cit.*), are now described, comprising : (1) Iron oxide prepared by the gentle ignition of the nitrate, and used in uniform pieces about 0·2 c.m. in diameter ; (2) iron oxide containing 2·5 per cent. of chromium oxide and 0·5 per cent. of cerium oxide ; (3) copper oxide prepared from copper wire by alternate oxidation and reduction with air and hydrogen respectively ; this, when suitably prepared, is capable of forming appreciable quantities of water when hydrogen is passed over it at 120° C.; (4) nickel prepared by soaking small pieces of diatomite in nickel nitrate, followed by gentle ignition and heating in superheated steam ; the finished product contains 5 per cent. of nickel; (5) palladiumised asbestos. It is extremely difficult to prepare two specimens of catalytic material identical in activity, and it is also found that the activity of the catalyst undergoes marked fluctuations in the course of an experiment. The ap-

paratus as now employed is made of silica in place of glass, temperatures in all cases being accurately controlled by means of a thermometer, around the bulb of which the catalytic material is built up, a temperature between 150° and 380° C. being employed. The selective combustion of carbon monoxide in hydrogen is shown to be a case of two simultaneous reactions. Elevation in temperature causes a decrease in the apparent selective character of the reaction. The results are in agreement with Langmiur's theory of adsorption, but the surface concentration of each gas is found to be dependent not only on the nature of the gas, but also on that of the absorbing surface.   H. F. E. H.

Analysis of the Residual Acids from the Manufacture of Ether.   E. C. **Carron.**   (*Ann. Chim. anal.*, 1919, **1**, 282-288.)—After determining the sp. gr. of the liquid, the free sulphuric acid is estimated by diluting 5 c.c. of the sample to 100 c.c. with water below 15° C., raising the temperature to 15° C., treating 5 c.c. of the dilute solution with 15 c.c of 6 per cent. barium hydroxide solution, and centrifuging the mixture for thirty minutes. The clear liquid containing the barium sulphovinate in solution is decanted, and the precipitate washed with 10 c.c. of $\frac{N}{5}$ hydrochloric acid to dissolve the excess of barium and any barium carbonate, again centrifuged with water, washed, and finally centrifuged with water, ignited, and weighed. The amount of free sulphuric acid is calculated from the weight of barium sulphate. *Distillation :* 150 c.c. of the sample are distilled between 85° and 90° C., and the distillate collected in a condenser chilled with a freezing mixture to −10° to −15° C. The distillate is brought to 15° C., the volume read, and water then added drop by drop with continual shaking until a permanent turbidity is produced, when the volume is again read. From these data the relative amounts of water, alcohol, and ether are found by reference to a graph constructed by Hascoet from empirical determinations. *Acidity in the Residue :* An aliquot portion of the residue in the flask is titrated with standard alkali, with methyl orange as indicator, and the results are expressed as sulphuric acid. The difference between this result and the free sulphuric acid previously estimated, multiplied by 1·285, gives the amount of sulphovinic acid. *Ether* is estimated by distilling 25 c.c. of the sample from an ether bath, provided with a reflux condenser, at 35° C., with the aid of a slow current of air, and collecting the distillate in a U-tube with one very narrow limb. This contains 8 c.c. of a nitro-chromic reagent, and is immersed in ice-water. The reagent consists of 1·2 grms. of sodium and ammonium dichromate, 20 c.c. of water, and 180 c.c. of nitric acid (sp. gr., 1·33). The depth of the coloration produced through the formation of chromic nitrate is compared with that given by a range of colorations produced under the same conditions by mixtures of 15 per cent. alcohol with variable quantities of ether. The readings should be made within ten minutes after the ether has distilled, and at a temperature of about 0° C., and it is essential that the current of air should always be drawn through the reagent tubes at the same speed.

                                    C. A. M.

Detection and Estimation of Small Amounts of Certain Organic Nitro-Compounds.   E. **Elvore.**   (*J. Ind. and Eng. Chem.*, 1919, **11**, 800-864.)—The author

has applied the Webster alkali colour test (*Brit. Med. J.*, 1916, **2**, 845) for T.N.T. in urine as a quantitative method for air testing in munition plants, etc. Preliminary work showed that the colours obtained were very sensitive to variations in the strength of alkali employed, and in the solvent (alcohol or ether) for the T.N.T. a definite volume of the air is passed through a series of three small test-tubes each containing 5 c.c. of absolute alcohol. The contents of these tubes or a suitable aliquot are nesslerised against standard T.N.T. solutions, using 5 c.c. of $\frac{N}{10}$ NaOH to each jar, the total volume being 50 c.c. The T.N.T. standards ranged from 0·01 to 0·1 mgrm. of the pure material in absolute alcohol.

A weakness of the Webster test as applied to urines is the production of similar colours by other substances, such as rhubarb, senna, and cascara, which may be present. The author has therefore developed the application of the Griess nitrite test to the detection and estimation of small amounts of T.N.T. or its hydroxylamine derivative in urine. Twenty c.c. of the urine are acidified in a separating funnel with 10 c.c. of 2N. H_2SO_4. Ten c.c. of ether are then added and shaken for three minutes. Five c.c. of $\frac{N}{1}$ caustic soda are added to the ethereal extract and shaken again. The two layers are allowed to separate, and the aqueous alkaline layer is drawn off into a 100 c.c. measuring flask. The ethereal layer is washed twice with 1 c.c. of caustic soda and the washings added to the flask. The combined alkaline extracts are diluted with 50 c.c. water and acidified with 2 c.c. of 5 N acetic acid and made up to 100 c.c. A series of standards are prepared by adding known amounts of an ethereal solution of pure 2,6-dinitro-4-hydroxylamino-toluene to 20 c.c. portions of normal human urine. The hydroxyl compound is used, since T.N.T. is converted into this substance when passing through the body (Special Report Series, No. 11, Medical Research Committee of Great Britain, 1917, p. 18). (*Cf.* ANALYST, 1917, **42**, 89.)　　　　H. F. E. H.

Examination of Hydrogenated Oils, with Special Reference to the Detection and Estimation of Nickel and Arsenic in the Same. G. Reiss.

(*Arbeit. Reichsgesundheitsamte*, 1919, **51**, 521-531.)—Eight samples of hydrogenated vegetable oils (cotton-seed, earth-nut, linseed, and sesame oils) and six samples of hydrogenated fish oil were examined; their chemical and physical characters were similar to those of ordinary edible fats, and their suitability for human consumption was confirmed by the results of feeding experiments. The quantities of nickel and arsenic present in the samples were usually negligible; the largest quantity of nickel found was 0·36 mgrm. per kilo of hydrogenated earth-nut oil, whilst the largest quantity of arsenic was 0·1 mgrm. (As_2O_3) per kilo. The following extraction method was found to be more sensitive than the usual incineration method for the detection and estimation of nickel: 200 grms. of the fat are melted in a flask, 100 c.c. of 12·5 per cent. hydrochloric acid and a small quantity of potassium chloride are added, and the mixture is heated in a boiling water-bath for one hour with frequent agitation. After cooling, the liquid is separated from the solidified fat, filtered, and an aliquot portion of the filtrate evaporated to dryness in a porcelain basin. The residue is dissolved in 20 c.c. of water, the solution rendered ammoniacal, boiled, filtered, and the filtrate treated in the usual way with dimethylglyoxime

solution. The precipitate obtained—if nickel is present—is collected and weighed; it contains 20·31 per cent. of nickel. To detect and estimate arsenic, 20 grms. of the sample are melted in a porcelain basin, and 20 c.c. of a mixture of 10 parts of fuming nitric acid and 1 part of concentrated sulphuric acid are added drop by drop while the fat is stirred. After the contents of the basin have been heated for some time on a water-bath, they are mixed with 30 grms. of a mixture of equal parts of sodium nitrate and potassium nitrate, and the mass is transferred, in small portions at a time, to a platinum basin containing 5 grms. of the sodium-potassium nitrate in a molten condition. When the incineration is complete, the mass is cooled, dissolved in about 200 c.c. of water, the solution acidified with dilute sulphuric acid, boiled to remove carbon dioxide and nitrous acid, and filtered. The filtrate is treated with 10 c.c. of 11·12 per cent. crystallised aluminium sulphate solution, then rendered ammoniacal, heated for thirty minutes on a water-bath, and filtered. The precipitate is washed with dilute ammonia; the filtrate is acidified with sulphuric acid, and again treated with aluminium sulphate and ammonia. The two precipitates are united, dissolved in 35 c.c. of 10 per cent. sulphuric acid, and the solution heated on a water-bath until all nitric acid has been expelled (diphenyl-amine test). Ten grms. of concentrated sulphuric acid are then added, together with sufficient water to make the total weight about 50 grms., and the solution is transferred to a Marsh apparatus, and the estimation carried out in the usual way.

W. P. S.

Estimation of Oxygen in Organic Substances. R. Strebinger. (*Zeitsch. anal. Chem.*, 1919, **58**, 97-114.)—The method depends on the estimation of the weight of potassium iodate required to oxidise a known weight of the substance to carbon dioxide, water, ammonia, and sulphuric anhydride. It also involves the direct estimation of carbon, hydrogen, nitrogen, and sulphur. It breaks down if nitrogen is present in any combination other than as amino-nitrogen. About 2 grms. of potassium iodate are accurately weighed into a 300 c.c. flask, a few drops of water and 30 c.c. sulphuric acid added, and the flask rotated to wet as much as possible of the inner surface. A weighed quantity of the substance (0·1 grm.) is next added, and the mixture heated on a sand-bath at about 200° C. until iodine vapours have disappeared and the solution becomes green in colour, due to complete oxidation of the substance and the presence of a little dissolved iodine. The cooled solution is diluted, when it assumes the brown colour of a solution containing iodine. This is expelled by boiling, after which the solution is cooled and made up to 300 c.c., or other convenient known bulk. Of this, 50 c.c. are mixed with potassium iodide solution and titrated with thiosulphate. The amount of potassium iodate consumed in oxidising the substance is then calculated. As the net result of the series of reactions in the digestion-flask is that 6 molecules of iodate liberate 6 atoms of iodine (driven off in the process), and render 15 atoms of oxygen available for oxidising the substance under analysis, the amount of oxygen consumed (O_1) is calculated from the relation $6KIO_3 = 150$. The percentage of oxygen in the substance is then given by the formula—

$$\% \text{ O} = 2\cdot667 \text{ C} + (1 - 0\cdot2159 \frac{N}{H})7\cdot937 \text{ H} + 1\cdot497 \text{ S} - 100 \frac{O_1}{E},$$

where C, N, H, and S represent the percentages of those four elements, and E is the weight of substance taken for analysis. Of twenty-three test numbers given, only two show errors greater than 0·3 per cent. on the substance. G. C. J.

Determination of Nitrobenzene in Commercial Nitrobenzenes. C. **Simpson and W. J. Jones.** (*J. Soc. Chem. Ind.*, 1919, **38**, 325-326.)—A cryoscopic method. The authors have determined accurately the freezing-points of binary mixtures of pure nitrobenzene (saturated with water) with varying quantities (up to 10 per cent.) of paraffin, carbon disulphide, benzene, *m*-dinitrobenzene, toluene, *o*-nitrotoluene, and *p*-nitrotoluene. Unless the amount of toluene in the original benzol is large, there will be no free toluene in the nitrated product, and if the benzol used for nitration be of fair quality, and nitration carried out under normal conditions, the impurities in the crude product after washing to remove acids will be present in approximately the following ratio: Benzene : paraffin : carbon disulphide : *m*-dinitrobenzene : *o*-nitrotoluene : *p*-nitrotoluene :: 0·5 : 0·8 : 0·2 : 4·3 : 1·0 : 0·5. On this assumption and the authors' figures for the freezing-points of binary mixtures, the percentage of nitrobenzene in crude washed nitrobenzol may be calculated from the freezing-point by the following equation—namely, $x = 90 \cdot 2 + 1 \cdot 87 \, t$, where t is the freezing-point in degrees C.

For nitrobenzene freed from benzene, paraffin, and carbon disulphide by steam distillation, the appropriate equation is $x = 89 \cdot 0 + 2 \cdot 11 \, t$, whilst for distilled nitrobenzene which contains *o*-nitrotoluene as its sole impurity the equation is $x = 90 \cdot 0 + 1 \cdot 87 \, t$.

The test is made by shaking some of the nitrobenzene with 2 drops of water in a test-tube and placing this test-tube inside a larger one containing melting ice. The temperature falls slowly and then rises suddenly, the highest point attained being taken as the freezing-point. The thermometer, graduated in tenths, may be conveniently corrected for the purpose by means of melting ice (0° C.) and freezing, wet, purified nitrobenzene (5·22° C.). The latter is prepared by partially freezing a good commercial sample, separating the crystals from the mother liquor, melting them, and repeating the fractionation until the melting-point of three successive products shows no further rise. G. C. J.

Analysis of Vaseline. G. Armanni and A. G. Rodano. (*Annali Chim. Applic.*, 1919, **12**, 50-51.)—A method of distinguishing between natural and artificial vaseline has been based upon the different solubilities of the two substances in a mixture of benzene and absolute alcohol (1 : 1). One part of the vaseline is dissolved in 20 parts of the hot solvent, and the solution allowed to stand for twenty-four hours in a cold place. If the vaseline be natural, there will only be a slight oily deposit, whilst artificial vaseline yields a flocculent or crystalline deposit resembling paraffin wax. In the case of mixtures the amount of precipitate is proportional to the quantity of artificial vaseline present, and the method will detect less than 20 per cent. of the latter. C. A. M.

INORGANIC ANALYSIS.

Estimation of Small Quantities of Alkali Iodides in Presence of Bromides and Nitrites. E. Lasausse. (*J. Pharm. Chim.*, 1919, **20**, 177-181.)— The solution, containing 2 to 3 mgrms. of iodine in the form of iodides, is neutralised with phosphoric acid, diluted to about 150 c.c., transferred to a large beaker, and treated with 4 c.c. of officinal (French) 50 per cent. phosphoric acid. A slight excess (1 to 3 c.c.) of a 5 per cent. solution of potassium permanganate is then added until a pink coloration, first in the cold and then at 40° C., is obtained, after which sodium bisulphite solution is introduced drop by drop until the liquid is decolourised. It is then neutralised to turmeric paper with 25 per cent. potassium hydroxide solution, an excess of 5 c.c. added, and then an excess of 10 c.c. of potassium permanganate solution, and boiled for ten minutes. The oxidation in the acid medium at 40° C. oxidises nitrites and cyanides, whilst the second oxidation in alkaline medium converts the iodides into iodates, but does not affect the bromides or bromates. After the ten minutes' boiling, 25 grms. of crystalline sodium sulphite are added, and then, drop by drop, 10 c.c. of alcohol, and the boiling is continued for two minutes to obtain a compact precipitate of manganese oxide. After cooling, the liquid is made up to 220 c.c. and filtered, and 200 c.c. of the filtrate acidified with 8 c.c. of phosphoric acid, treated with 2 c.c. of 10 per cent. potassium iodide solution, and the iodate immediately titrated with $\frac{N}{100}$ thiosulphate solution :
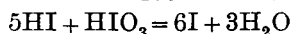
$$5HI + HIO_3 = 6I + 3H_2O \qquad \text{C. A. M.}$$

Electrometric Titrations, with Special Reference to the Estimation of Ferrous and Ferric Iron. J. C. Hostetter and H. S. Roberts. (*J. Amer. Chem. Soc.*, 1919, **41**, 1337-1357.)—The advantages of the electrometric method for oxidising and reducing reactions are shown to be many. The method permits the use of dichromate with its attendant advantages. The reduction of the solution with electrometric control eliminates the removal of excess reducing agent, which must be done with the usual methods of reduction. Conditions, such as acidity, need not be controlled except within very wide limits, and hydrochloric, sulphuric, or hydrofluoric acids, or mixtures of these, may all be used. The sensitiveness and accuracy of the method make possible (*a*) the estimation of a few tenths of a mgrm. of tin, chromium, ferrous or ferric iron in presence of large quantities of some other element, and (*b*) the determination of blanks involved in some of the ordinary estimations by reducing or oxidising agents. The time within which an estimation can be carried out is greatly shortened. The content of ferrous or ferric iron in a silicate, for instance, can be determined in less than half an hour. The precision attainable is comparable with that attained by the best of the ordinary volumetric methods. G. C. J.

Volumetric Estimation of Hydroxylamine. W. C. Bray, M. E. Simpson, and A. A. Mackenzie. (*J. Amer. Chem. Soc.*, 1919, **41**, 1363-1378.)—The authors have investigated three methods for the estimation of hydroxylamine : (1) Reduction to ammonia by excess of titanous salt in acid solution ; (2) oxidation to nitrous oxide

by excess ferric sulphate in sulphuric acid solution, with titration of the ferrous salt by permanganate solution; and (3) oxidation to nitrous oxide by iodine in a solution kept neutral by means of disodium hydrogen phosphate. The titanous salt and ferric salt methods were found to be accurate, but the iodine method was unsatisfactory. In addition to the known positive error in the ferric salt method, which is due to the addition of permanganate while some hydroxylamine or an intermediate product (nitroxyl) is still present, a negative error due to oxygen of the air was found under certain conditions. It is shown that both errors can be easily avoided. In the iodine method three errors were encountered: (1) Due to incomplete reaction, avoided by the use of sodium phosphate; (2) nitrite formation, which occurs under all conditions investigated, and corresponds to a positive error; and (3) absorption of oxygen of the air, which corresponds to a negative error. An empirical method was developed for obtaining theoretical results, but it is shown that these depend on a compensation of errors. G. C. J.

Estimation of Phosphorus in Presence of Tungsten. G. W. Gray and J. Smith. (*Iron and Steel Inst.*, 1919; through *J. Soc. Chem. Ind.*, 1919, **38**, 538 A.) —In the estimation of phosphorus in presence of tungsten low results are frequently noted. In methods in which tungstic acid is separated by evaporating to dryness with hydrochloric acid a large amount of phosphorus is precipitated with the tungstic acid as phosphotungstic acid, and so escapes estimation. The authors have devised a method of estimating phosphorus in ferro-tungsten, tungsten powder, and tungsten ore, which has proved accurate during some years of use. Two grms. of the powdered sample are fused with 10 grms. of a mixture of sodium carbonate and potassium nitrate in molecular proportions in a platinum crucible, the melt is dissolved in the least possible quantity of water, filtered, and the residue washed free from tungstates with boiling water containing a little ammonium nitrate. The residue is ignited in the original crucible, dissolved in hydrochloric acid, and the solution evaporated to dryness. The filtrate is treated with 20 c.c. of hydrochloric acid and 2 c.c. of bromine, ammonia is added until the precipitated tungstic acid is dissolved, and then a further quantity equal to one-fourth of the original volume of the liquid. The phosphorus is then precipitated with magnesia mixture. This method may also be used for estimation of phosphorus in alloy steels with satisfactory results.

Electrolytic Resistance Method for Estimating Carbon in Steel. J. R. Cain and L. C. Maxwell. (*J. Ind. and Eng. Chem.*, 1919, **11**, 852-860.)—The method depends on passing the carbon dioxide produced by direct combustion of the steel into a solution of barium hydroxide of known electrical resistance; after complete absorption of the gas, the resistance is again determined, and from the increase in this (due to precipitation of barium ions) the percentage of carbon is deduced. Special resistance measuring apparatus has been developed (and is figured in the paper) which simplifies the measurements by dispensing with tuned telephones, high-frequency generators, and balanced inductances and capacities. A convenient nomographic method of applying necessary temperature corrections to resistance

measurements has also been developed. A suitable absorption vessel with electrolytic resistance cell incorporated is illustrated and described. Resistance measurements of twelve barium hydroxide solutions varying in concentration from 5·8 grms. to 7·3 grms. per litre have been carried out accurately to within 0·1 ohm, and temperature coefficients of resistance of these twelve solutions have been determined over the range 20° to 30° C. As a means of estimating carbon in steel the method is very rapid, and the results are accurate to within 0·01 per cent.   G. C. J.

Estimation of Uranium, Zirconium, Chromium, Vanadium, and Aluminium in Steel. C. M. Johnson. (*Chem. and Met. Eng.*, 1919, **20**, 523-524, 588-589; through *J. Soc. Chem. Ind.*, 1919, **38**, 537 A.)—The feature of the method is the separation of the elements to be estimated from the bulk of the iron by fractional precipitation with ammonia, which enables larger weights of sample to be taken. For the estimation of uranium in plain steel, 5 grms. of drillings are dissolved in sulphuric acid (1 : 3), filtered, and the insoluble residue ignited, cooled, heated with hydrofluoric and sulphuric acids, and the clear solution added to the first filtrate. This is then diluted and ammonia solution added until the precipitate turns blackish. The precipitate is filtered off, redissolved in hydrochloric acid (1 : 1), and oxidised with sodium peroxide until all the iron is precipitated and the solution is alkaline. After adding sodium and ammonium carbonates to keep the uranium in solution, the solution is boiled and the iron filtered off. Hydrochloric acid (1 : 1) is then added till the solution no longer turns turmeric paper faint brown, the solution is boiled to expel carbon dioxide, made acid with hydrochloric acid (1 : 1), cooled, treated with 5 grms. of diammonium phosphate and excess of ammonia, and acidified with acetic acid (1 : 1). The uranium is filtered off, redissolved in hot sulphuric acid (1 : 3), boiled, and potassium permanganate added till a permanent pink colour is produced. The uranium is reduced in a zinc "reductor," and titrated with a standard solution of permanganate. For uranium in chrome-tungsten steel 5 grms. of steel are dissolved as before, the solution filtered, diluted, and ammonia added till the precipitate turns bluish-white; after filtering, the estimation of the uranium is finished as in the case of plain uranium steel. The insoluble residue is washed off the filter with dilute sulphuric acid and oxidised with nitric acid (sp. gr., 1·20). The tungsten is filtered off, the filtrate peroxidised, and, after separation of the iron, finished as with plain steel. For the estimation of aluminium and zirconium the procedure is the same as above for uranium as far as the addition of sodium carbonate; the precipitate then contains the iron and zirconium and the filtrate the aluminium. Hydrochloric acid (1 : 1) is added and the precipitated aluminium is allowed to settle, filtered off, and redissolved in hydrochloric acid (1 : 1). Ammonia is added, the precipitated aluminium filtered off and ignited in a weighed crucible. The iron and zirconium left on the filter are dissolved in sulphuric acid (1 : 3), a saturated solution of disodium phosphate added, then ammonia till a precipitate starts to form. After standing some hours, the precipitate is filtered off and ignited in a weighed crucible. It is then evaporated with sulphuric and hydrofluoric acid till fumes of sulphur trioxide appear, in order to remove silica. The zirconium phosphate is then filtered off and

ignited to a constant weight. For aluminium in plain steel the procedure is the same as before until after peroxidation. Hydrochloric acid (1 : 1) is then added, and the aluminium filtered off and washed with ammonium nitrate, redissolved in hot hydrochloric acid (1 : 1), and precipitated with ammonia, then ignited in a platinum crucible. For the estimation of chromium and vanadium 5 grms. of the steel are dissolved in sulphuric acid (1 : 3), filtered, and the insoluble residue washed off. The filter-paper is incinerated, the ash dissolved in concentrated hydrochloric acid, evaporated with sulphuric acid (1 : 1), and added to the original solution. This is diluted and ammonia added till a black precipitate forms, filtered, the precipitate redissolved in sulphuric acid (1 : 3), and poured on the original insoluble residue. The mixture is heated, treated with nitric acid (1 : 20), and permanganate added till a brown precipitate of manganese oxide forms. The solution is boiled, filtered, and chromium and vanadium estimated as usual with ferricyanide as internal indicator. Tables are given showing results obtained by the method on known steels. The method will probably answer for titanium and tantalum and small amounts of copper and nickel.

Estimation of Sulphates in Concentrated Electrolytes and Estimation of Sulphur in Foods. V. K. Krieble and A. W. Mangum. (*J. Amer. Chem. Soc.*, 1919, **41**, 1317-1328.)

—The method is long and tedious, and it is not recommended that it should be used indiscriminately. Where, however, the sulphur content of the material is low, and when difficulties from fires and explosions are encountered, the method is a decided improvement both in the oxidation process and in the final estimation of sulphates in presence of much sodium chloride.

The material (2 to 3 grms.) is moistened with 2 to 3 c.c. of water in a 100 c.c nickel crucible. Sodium carbonate (5 grms.) is next added, and the whole mixed with a nickel rod. Sodium peroxide is next added until the whole mass becomes dry and granular. The crucible is then heated over a spirit lamp until the mixture becomes a homogeneous brown mass. It is then allowed to cool somewhat, after which more sodium peroxide, making 25 grms. in all, is added. The crucible is then heated strongly at one point opposite the level of the contents until oxidation begins, when the flame is removed and the crucible covered. Heating is continued for ten minutes after the mass is fused. The cooled mass is dissolved in 100 c.c. of hot water, the solution acidified and filtered if necessary. If silica is present in appreciable amount, appropriate steps must be taken for its removal. About 50 c.c. of hydrochloric acid are added to the solution, which is brought to about 350 c.c. and heated to boiling. About 10 c.c. of 10 per cent. barium chloride solution are added at the rate of 10 c.c. in four minutes and after forty-eight hours the solution is evaporated to dryness and the residue taken up in water. About 1 or 2 c.c. of hydrochloric acid are added, and after eighteen hours the precipitate is collected on a Gooch crucible, washed, dried, ignited, and weighed. The results are high, and must be corrected by a control experiment with a known weight of potassium sulphate, such as will give approximately the same amount of barium sulphate as is obtained from the food. (*Cf.* Johnston and Adams, ANALYST, 1911, **36**, 426.)   G. C. J.

Estimation of Sulphur in Illuminating Gas by Means of Iodine Solution.
M. Hirsch. (*Chem. Zeit.*, 1919, **43**, 482.)—A measured quantity (30 to 40 litres) of
the gas is burned in Drehschmidt's combustion apparatus in which the drying-tower
is charged with solid potassium hydroxide instead of with the potassium carbonate
solution of bromine. The absorption flask is charged with 15 c.c. of $\frac{N}{10}$ iodine
solution, and is followed by a flask containing 15 c.c. of $\frac{N}{10}$ sodium thiosulphate
solution. A rapid current of air is drawn through the flasks, and the gas collector
then fixed over the burner. The reaction is as follows :

$$SO_2 + I_2 + 2H_2O = 4H + 2I + SO_4.$$
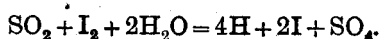
After the combustion, both flasks are emptied into an Erlenmeyer flask, and the
liquid titrated with $\frac{N}{10}$ iodine solution. As a control the sulphuric acid may be
estimated as barium sulphate.   C. A. M.

Estimation of Uranium in Carnotite. C. E. Scholl. (*J. Ind. and Eng.
Chem.*, 1919, **11**, 842.)—Iron, aluminium, and vanadium are the chief impurities
which cause errors in the analysis of carnotite. Hydrogen peroxide, which is often
employed, causes uranium in nitric acid solution to assume a kind of non-ionic con-
dition in which it reacts with extreme slowness. The elements producing difficulties
are eliminated by adding ferric iron, followed by precipitations with sodium carbonate
without boiling, and sodium hydroxide *with* boiling. To a sample of the material
containing about 0·2 grm. uranium oxide are added 25 to 50 c.c. nitric acid (1 : 1),
the whole heated until all uranium is dissolved, the solution being then diluted to
about 250 c.c. and filtered. To the filtrate is added ferric chloride equivalent to about
three times the weight of vanadium present, solid sodium carbonate being then
slowly added to the cold solution in amount about 1 grm. in excess of neutrali-
sation. The solution is next heated to about 90° C. for fifteen minutes, but not
allowed to boil, and filtered. The precipitate contains all the iron and vanadium,
and most of the aluminium. The filtrate is neutralised slowly with nitric acid until
the uranium begins to precipitate, and is then boiled to drive off CO_2. Sodium
hydroxide is then added in excess, and the whole boiled for fifteen minutes. The
filtrate contains the rest of the aluminium and any vanadium previously escaping.
The precipitate is dissolved in dilute nitric acid and heated to about 90° C., an excess
of ammonia added, and then boiled. The precipitate is filtered off, ignited, and
weighed as U_2O_3. In case of doubt as to purity, the precipitate may be dissolved in
dilute warm nitric acid, any residue being filtered off, ignited, and deducted.
                                                                H. F. E. H.

APPARATUS, ETC.

Anti-Suck-Back Device Applicable to Evolution Methods of Analysis.
P. L. Robinson. (*Chem. News*, 1919, **119**, 159.)—In the volumetric estimation of
sulphur in steel difficulty is often encountered due to the suck-back of the absorbing
fluid towards the end of the reaction. To obviate this, the author has devised two
forms of anti-suck-back heads, described and illustrated with diagrams. The first is
a liquid trap joint made with a piece of 1″ diameter glass tube and two rubber

bungs, which is to be had in an improved form made with only one bung by Messrs. J. Preston, Sheffield (price, 18s. per dozen). This consists of a piece of glass tubing about $4\frac{1}{2}''$ long, wide enough to take a $1''$ bung at the bottom, and closed at the top except for two apertures, one of which is the delivery tube, the other containing the stem of a small thistle-headed funnel reaching to within $\frac{3}{4}''$ of the bottom of the wide tube, and just not touching the rubber bung at the bottom, through which passes the delivery tube from the flask. The upper end of this latter tube rises $1''$ above the lower end of the thistle-funnel tube, thus determining the volume of liquid in the trap. When, in working, the pressure of the enclosed case is above atmospheric, the liquid is forced up the funnel stem, but when the pressure is reduced by more than $1''$ of

To Delivery Tube

A

C

B   B

FIG. 1

$4\frac{1}{2}''$

D

To Flask

To Delivery Tube

A

C

B

E   E   FIG. 2.

F   D

H
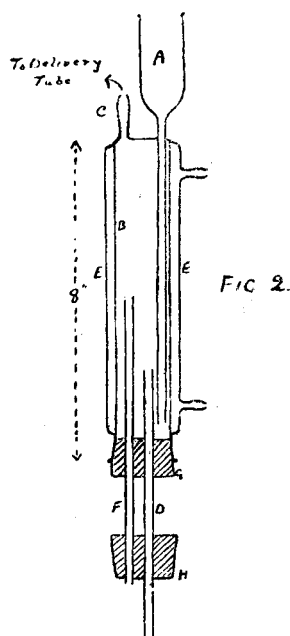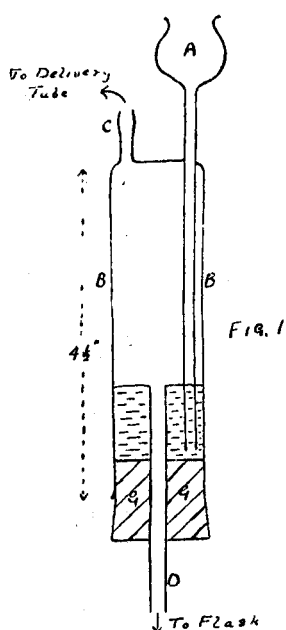
water below atmospheric, air is drawn into the apparatus. The device also acts as a trap for splashing. (2) *Anti-Suck-Back Condenser Head for Evolution Sulphur in Steel*: This apparatus was designed to meet the case of steel which, either by its nature or the size of the drillings, dissolves very slowly. It consists of condenser and an acid delivery funnel, together with an anti-suck-back head, similar in idea and construction to that already described, the wide tube in this case functioning as a condenser, being fitted with inlet and outlet tubes for circulation of cold water. It is made by Messrs. Orme and Co., Manchester (price 10s. 6d.) The thistle-headed funnel is much larger, and is used to deliver the acid direct on to the steel. Through the bung closing the lower end of the wide tube pass two tubes, the first having its upper end an inch above the end of the funnel stem and passing $3''$ below the bung in the flask, which is attached beneath the condenser, the other having its upper end $3''$ above the end of the funnel stem, while its lower end passes only just through the flask bung.

The acid mixture is poured into the funnel, and passes down the tube into the flask, while the air and the immediate products of the reaction escape by means of the second tube. which passes only just below the bung of the flask. A little water is then run down the funnel to wash the last of the acid into the flask, thus preventing the action of acid on the bung.   H. F. E. H.

Automatic Extraction Apparatus. J. Tcherniac. (*J. Chem. Soc.*, 1919, **115-116**, 1090.)—In the examination of thiocyanoacetone and its derivatives (*J. Chem.*
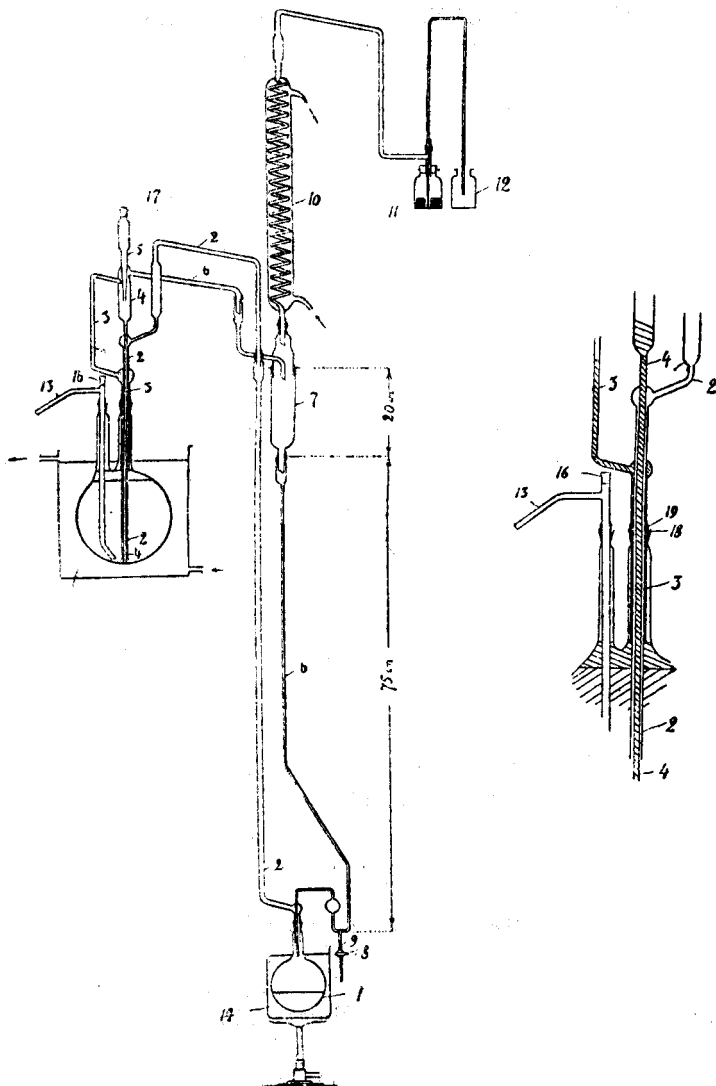
Soc., 1919, **115-116**, 1071) the author has employed the extraction apparatus here described (*Ber.*, 1893, **25**, 3652). The smaller flask shown in the diagram receives

the ether, and is heated in a water-bath ; the large two-necked flask contains the solution to be extracted ; it is filled through the opening (16) of the tube (13), which is also used for siphoning off the exhausted liquor. The capacities of both flasks may vary within wide limits. The two-necked flask is placed in a vessel through which cold water is run ; it is then filled nearly to the neck with the liquid to be extracted, the tubes (16 and 13) are closed, and ether is poured in through the opening (17) of of the tube (5). The ether flows through the tube (4) to the bottom of the flask, rises in the aqueous liquid and in the annular space between the tubes (3 and 2) (see enlarged inset), and descends through the tubes (6 and 7) into the small flask, filling the seal (9) ; a little mercury is poured through the condenser (10) to prevent any leakage of ether from the tap (8). On heating the water-bath the ether vapour raises the liquid ether in the seal to a certain height in the tube (6), and also passes through the tube (2) to the bottom of the two-necked flask, where it is condensed ; the liquid ether then returns through the tubes (3 and 6), and the seal into the small flask. Any aqueous liquid carried over with the ether returns through the tube (4) into the two-necked flask. By regulating the flow of water in the vessel (15), the temperature of the aqueous liquid can either be kept quite low or allowed to rise more or less. The joints are simple and efficient. As seen in the sketch (inset), the outer tube is very slightly conical (18), and the inner tube, which is little less in diameter, is provided with a short length of rubber tubing (19), which, on being pressed into the conical opening of the outer tube, makes a perfectly tight joint. The mercury tap (11 and 12) is connected with the apparatus after the air has been expelled by the vapour of ether ; it prevents losses of the solvent by diffusion. The apparatus may be used equally well for the extraction of solid substances by means of ether, chloroform, etc. In this case the two-necked flask may be comparatively small, and the tube (7) must be provided with a thimble or filter to arrest any particles of solid that may be carried over by the solvent. The cap of this tube is ground on.

H. F. E. H.

REPORT.

Analysis of Ammoniacal Liquor. Fifty-fifth Annual Report (1918) on Alkali, etc., Works, by the Chief Inspector, 53-74. (*J. Soc. Chem. Ind.*, 1919, **38**, 716 A.)— The quantitative estimation of the respective constituents of ammoniacal liquors has been re-investigated, more particularly with a view to testing the accuracy of the procedure recommended by Colman and Yeoman (ANALYST, 1919, 110). Feld's method for the estimation of cyanide by distillation with lead nitrate gives low results if free ammonia co-exists in the solution with thiosulphate. Moreover, the interaction of ammonium polysulphide and cyanide in the analysis of concentrated liquor is slow, and conversion of cyanide into thiocyanate apt to be incomplete unless a decided excess of polysulphide (or, conversely, of cyanide) be present. Investigations of the stability of solutions of ammonium ferrocyanide, cyanide, sulphide, and thiosulphate show that loss of ammonia and cyanogen accompanies the boiling of a ferrocyanide solution. A solution of sodium ferrocyanide suffers no decomposition on boiling. Sodium cyanide suffers little change on boiling in solution

in absence of free ammonia. No loss of cyanogen occurs on boiling a solution of ammonium thiocyanate *in vacuo* at 40° to 45° F. (4° to 7° C.). Ammonium thiocarbonate is unstable, and is readily converted into thiocyanate. Details are given of experiments to determine the amount of such conversion under various conditions. Thiocarbonate is not completely removed by treatment with lead carbonate in presence of strong ammonia. The conversion of ammonium thiocarbonate into ammonium thiocyanate at 80° to 90° C. is retarded by the presence of ammonium polysulphide, and is about 50 per cent. of that effected in the absence of polysulphide. An approximate measure of the amount of thiocarbonate present can be obtained by digesting the sample in absence of air and with addition of free ammonia, if necessary, at 80° to 90° C., with subsequent removal of sulphide by shaking with lead carbonate. Estimation of thiocyanate in concentrated ammonia liquor is subject to interference owing to the solubility of thiocarbonate on shaking with lead carbonate in the presence of free ammonia. With concentrated liquor it might be found possible to apply a colorimetric method for the estimation of thiocyanate, where thiocarbonate is present, based on the procedure of Spielmann and Wood (ANALYST, 1919, 143). The method of Colman and Yeoman (*loc. cit.*) for the estimation of cyanide in concentrated liquor yielded results which are invariable low when thiosulphate was present. This was due to the decomposition of lead thiosulphate on distillation, free sulphur being produced and reacting with cyanide and lead oxide to form non-volatile thiocyanate. The procedure has been modified to avoid such fixation of cyanide, and the modified method involves the use of aluminium chloride. When ferrocyanides are present, addition of sodium carbonate is necessary to remove excess of aluminium chloride prior to addition of lead nitrate and distillation with caustic soda. In the case of concentrated liquor it is desirable to expel the bulk of ammonia by boiling with caustic soda prior to addition of the aluminium salt. Details are given of the application of the modified procedure to the estimation of cyanogen compounds in ammoniacal liquors of ordinary and concentrated strengths respectively in the presence of free ammonia, and when sulphide or thiocarbonate is present in addition.

✢   ✢   ✢   ✢   ✣

REVIEWS.

CATALYSIS IN INDUSTRIAL CHEMISTRY. By Professor G. G. HENDERSON. Pp. 202.
Longmans, Green and Co., London, 1919. Price 9s.

Professor Henderson's contribution on "Catalysis in Industrial Chemistry"
forms a welcome addition to the interesting series of monographs on Industrial
Chemistry edited by Sir Edward Thorpe.

Since the time of Davy's observation in 1817 of the influence of a heated
platinum wire on the combination of hydrogen and oxygen, a large number of
substances have gradually been recognised as capable of increasing the velocity of
chemical reactions, or, in the words of Berzelius, of "arousing the slumbering
affinities" of the substances concerned. The magnitude of the results effected by
the minute quantities of added substances, and their apparently unchanged condition
after reaction—the outstanding characteristics of catalysts—have caused the
phenomenon to be regarded as one of increasing importance both in the study of
chemical reactions and in the preparation of both inorganic and organic compounds.
The former idea that catalytic actions are the exception rather than the rule must be
discarded in view of the wide range of reactions and substances that participate in
catalytic changes. With the progress of investigation it appears that catalysis must
now be recognised as one of the "small causes" that can probably influence all
reactions, and further that, under suitable conditions, all substances are capable of
exerting a catalytic effect. The "contact" process for the manufacture of sulphuric
acid has for many years been a typical example of catalysis in chemical industry.
The investigations of Sabatier and Senderens, together with those of Ipatiev, have
given a great impetus to the development of industrial catalysis, whilst the physico-
chemical investigations of others have led to the realisation of the important part
played by catalysts in many manufacturing processes which were not previously
recognised as dependent upon catalytic influence.

The aim of Professor Henderson's monograph is to indicate the number and
variety of the industrial applications of catalysis. The selection of the examples
from the large mass of material available is excellent, and the arrangement of the
subject matter, which is necessarily of a somewhat heterogeneous character, is well
and carefully planned. Considerable interest is added to the descriptions given by
short references to the technical use of the substances dealt with, and full references
to patent and other literature are a valuable help towards giving the subject its
proper environment.

In the opening chapter a sound and concise account is given of the generalities
concerning catalysis and catalysts. This includes descriptions of the inhibiting action

of negative catalysts, of auto-catalysis, of anti-catalysis, of the important part played by "promotors" in catalytic reactions, and a very good account of the methods employed in the preparation and application of catalysts, which is supplemented in the descriptions of specific processes in subsequent chapters. There is also a short summary of the rival theories of the mechanism of catalysis, in which the difficulty of reconciling the physical theory with the specific action of certain catalysts is rightly emphasised.

The succeeding chapters deal not only with industrial applications of recognised importance, such as the manufacture of hydrogen from steam and carbon monoxide, the Deacon chlorine process, the manufacture and oxidation of ammonia, the manufacture of sulphuric acid, the "hardening" of fats and the "cracking" of petroleum, but also with less well-known processes in which catalysis plays an important part, such as the hydrogenation and hydration of hydrocarbons and their derivatives, polymerisation and catalytic oxidations. The former are described with considerable detail, and give a comprehensive outline of the processes concerned, although more reliable authority than the patent specification would be welcome in many cases as an indication of the real technical value of the methods described. For instance, the statement (p. 24) that of the various proposals that have been made for the manufacture of hydrochloric acid from its elements "one, at least, claims the use of a catalyst, in this case charcoal," is not very informing.

In dealing with less well-known catalytic processes the descriptions are both helpful and suggestive, and their interest is much extended by the inclusion of a large number of reactions, especially amongst organic compounds, such as the preparation of halogen and nitro-compounds, diazotisation, and electrolytic reduction, the catalytic character of which is apt to be overlooked.

The book is so carefully compiled and so well written that it will be appreciated by all who desire to gain a knowledge of the part catalysis has played in the development of industrial chemistry; it will also serve as a stimulus to further research. It is by no means easy to realise these results in a book of 200 pages, and Professor Henderson is to be cordially congratulated on the successful and interesting manner in which he has recorded so much scientific and industrial achievement.

<div align="right">CHARLES A. KEANE.</div>

SIR WILLIAM RAMSAY, K.C.B., F.R.S.: MEMORIALS OF HIS LIFE AND WORK. By Sir WILLIAM A. TILDEN, F.R.S. London: Macmillan. 1919. Price 10s. net.

The life of Sir William Ramsay, by Sir William Tilden, is a work which should be welcomed by all chemists, and by all who concern themselves with the progress of knowledge.

To the writer, who many years later had the good fortune to spend some time in Tatlock's laboratory, where the tradition of Ramsay's early inventiveness lingered, Sir William Tilden's biography possesses much of interest.

Sir William Tilden makes effective use of the correspondence and reminiscences of Ramsay's numerous friends, thereby revealing his character from various points of view.

The inevitableness of his choice of a scientific career, his early University life and participation in annual meetings of societies, and his facility in acquiring languages, are all happily described and illustrated by quotation from his own and contemporaries' letters, while the important part he took in obtaining Government aid for University Colleges is recorded by our author, who himself shared in that movement.

It is of interest to read that in 1881 research did not necessarily come within the duties of a professor. With Ramsay, however, in spite of the administrative duties of his office and the time he devoted to lecturing, that spirit of "divine curiosity" led him to those physico-chemical studies on vapour pressures with Professor Young at Bristol, and later to the discovery of the argon series of elements and to the investigation of radium emanation.

The story of the rarer gases of the atmosphere, the discovery of argon and helium, and the prediction and isolation of neon and other allied elements, are dramatically told by the author, and the triumphs of manipulation on the minute scale attained in the work on radium emanation are well narrated.

On the other hand, the records of journeyings, while often fascinating, are perhaps in some cases set forth in unnecessary detail, and with insufficient bearing on the main subject of the book.

Sir William Tilden's final appreciation is full of a kindly insight into a life devoted to discovery, but at the same time full of human interest, and one which will be an inspiration to many generations of chemists. In a fine passage he ends: "The stream of time bears along to oblivion the vast majority of the sons of men, and though in this age of scientific activity there is an ever-increasing army of workers, most of them are engaged in supplying merely the bricks of which the edifice of scientific knowledge is built. They have their reward in their day and generation. The name of William Ramsay will always stand among those of the master builders."

R. ROBERTSON.

BEVERAGES AND THEIR ADULTERATION: ORIGIN, COMPOSITION, MANUFACTURE, NATURAL, ARTIFICIAL, FERMENTED, DISTILLED, ALKALOIDAL, AND FRUIT JUICES. By HARVEY W. WILEY, M.D. 1919. London: J. and A. Churchill. Price 21s. net.

As in the case of the companion volume entitled "Foods and their Adulterations," Dr. Wiley addresses this work, not to "the scientific investigator," but to "the average sober-minded, reasonably well-educated American citizen, who is daily taking a greater and deeper interest in what he eats and drinks."

A perusal of the work has had the effect of arousing in the mind of the writer a very high degree of respect for the intelligence of the average American citizen, and a feeling of regret that his own countrymen and countrywomen have, so far, declined to take the same intelligent interest in matters dietetic.

The volume deals, in the first place, with water, which is described as the "typical beverage," and one which, it is hoped, may come into more general use.

Then follow chapters dealing with mineral waters, the so-called "soft" drinks

so dear to the American heart, fruit-juices, coffee, tea, cocoa, and the various kinds of fermented beverages, including wines, beer, spirits, and liqueurs. Finally, some space is devoted to a consideration of products known as "alcoholic remedies" and beverages containing cocaine.

The author's disavowal of any intention to appeal to the scientific public tends, perhaps, to some extent to disarm criticism, but there are a good many statements which are so very involved and misleading that attention may be called to some of the more striking, in order that they may undergo revision when future editions are called for.

The sections dealing with the hardness of water and its treatment affords some examples of this want of clearness. Thus, it is stated (p. 5) that "the hardness (of water) is due to solution of excessive quantities of the salts of magnesia and other similar mineral substances," and that "these salts are found held in solution by the carbon dioxide which the water carries." The author then goes on to say that the form of hardness due to the solvent action of carbon dioxide "is caused chiefly by the sulphates of lime and magnesium, bodies which are more or less soluble in water not containing carbon dioxide." He adds a little later: "*According to some authors*" (the italics are the writer's), "the permanent hardness is caused chiefly by magnesium chloride and calcium sulphate."

The information that when a potash or soda soap "is added to the water containing calcium and magnesium salts the soap is decomposed, and the fatty acid is set free in an insoluble state," is more than likely to be misunderstood, and the implied recommendation of soap for the commercial softening of water will be read with interest by technical men. It is stated that the hardness of the water in question having been determined by titration with soap solution, "the required quantity of soap can be added to large quantities of water."

On p. 16 a paragraph is devoted to the scientific demonstration of the composition of water by its electrolytic decomposition. The author states that "if water containing an electrolyte . . . is subjected to the action of the electric current," oxygen is given off at the one pole and hydrogen at the other, and that if, as "*shown in the figure*," "the negative pole be placed in one arm of a bent tube and the positive pole in the other, the two gases may be collected separately." On reference to the illustration, it will be seen that both electrodes are actually in the same limb of the eudiometer. In explaining the phenomenon the author states it is necessary to add to the pure water an electrolyte which cannot be decomposed, and that "consequently nothing is decomposed except pure water."

The sections dealing with the interpretation of the results of the analysis of water contain a good many obscure statements, and some to which general assent would certainly not be given. The main reflection, however, produced by reading this portion of the work is that the American citizen must indeed be a very highly intelligent and educated person if he takes the trouble to provide himself with an analysis of the water he drinks, and, with the aid of a Manual of Chemistry, endeavours to interpret the results given therein. As evidence of a somewhat touching confidence in standards laid down by authority—a confidence which Dr. Wiley shares with many of his countrymen—it is suggested that "the law-makers, after consulting with

competent and unprejudiced experts on this matter " (*i.e.*, the number of bacteria in water), " could fix upon a maximum limit and regulate it by law."

The section dealing with mineral water contains some very interesting matter, and the author very properly calls attention to the undesirability of assigning to any natural water a geographical name calculated to mislead the public. It is interesting to note that our American cousins are not altogether free of offence in this matter, since three of the famous Saratoga springs are known respectively by the names of " Vichy," " Seltzer," and " Carlsbad."

Dr. Wiley deals incidentally with a very important point frequently overlooked—namely, the impossibility, even with the help of a very detailed chemical analysis, of insuring that an artificially prepared mineral water shall have precisely the same therapeutic properties as the natural supply. The discovery of radio-activity and the possibility of the existence of highly active elements in minute quantities may well give to the natural water properties which the artificial one does not possess.

The chapters on tea, coffee, and cocoa are well written, and contain much that cannot fail to prove of very great interest to the ordinary reader. From these, to which some further reference will be made, we pass to alcoholic drinks.

The impending advent of total prohibition in the States gives to the appearance of Dr. Wiley's work at this moment an added piquancy, and the reader will very naturally turn to see what the distinguished author has to say on this much-debated and important question. That Dr. Wiley appears to be in general sympathy with the movement is shown by the following and many other statements appearing in different parts of the work :

" The whole subject of alcoholic beverages is one difficult of treatment, because of the growing conviction that, even when continuously used in small quantities, alcohol will in the end prove injurious. . . . There is a marked tendency, in social entertainments, to diminish the supply of alcoholic beverages. Not only are the dangerous kinds, such as distilled liquors, cocktails, cordials, and other mixtures, more or less under ban, but even the serving of wine or beer is growing more and more infrequent. When these beverages are served, the quantities consumed are gradually becoming less. In fact, there are signs which are not without significance of the approach of a nation (*sic*), and perhaps a world-wide prohibition."

Although in his preface the author states that the object of his book " is not to discuss chiefly questions of health or hygiene, nor of ethics," it is impossible, having regard to the general character of the work, and to the obvious bias throughout in favour of teetotalism, for a reviewer to ignore entirely the above aspects of the matter. In this connection, one is naturally interested to glean some information in regard to the drinks which are to replace alcoholic beverages in the transatlantic Utopia, and to know what the author thinks of these.

Tea and coffee, owing to their tendency " to create caffein-dyspepsia or poisoning," are clearly more than suspect, and terrifying—but not, perhaps, greatly exaggerated —pictures are drawn of the dire effects of over-indulgence in these beverages.

Thus, under the heading "The Coffee Habit," an American writer, Lloyd, is quoted to the following effect:

"This stimulant that does not intoxicate may become man's enemy. A fair friend is it, but a dogmatic master. Fortunately, it does not inebriate. So long as it is used in judicious moderation, most persons find it a cheering, exhilarating companion, but when coffee obtains the upper hand of man or woman, it shatters the nerves and demoralises the victim's disposition. In our opinion, the soporific action of an alcoholic drink is to be preferred to the wakefulness of the person who tosses the night through, a victim to coffee dissipation. But it is not safe to suggest, even to a nerve-wrecked coffee slave, that he is to be classed with the man who abuses himself by means of alcohol: the indignation of such people is most pronounced. Nor is it discreet, with some people, to include coffee with the stimulants that enslave. But yet, when one views the condition of nervous America, the question arises as to why the pronounced prohibitionists who object to even the temperate use of malt or other alcoholic beverages that by their abuse are harmful, are overlooking the tyranny of coffee and tea. But this is a problem in itself, and somewhat foreign to this historical article."

Mr. Lloyd appears to have hit not one, but several nails squarely upon the head, for with the total prohibition of all alcoholic beverages there will be a natural tendency to turn to other forms of stimulant, of which there would appear to be no lack on the American market, and some of these may establish a "tyranny" even worse than that of alcohol. Many of the so-called "soft" drinks are, according to Dr. Wiley, not above suspicion, and the formidable list of alcoholic remedies—the mere names of which occupy no less than six and a half pages—would appear to indicate either that the American public is much more addicted, even than our own, to proprietary remedies, or, if one may dare to suggest it, that these are not always employed for purely medicinal purposes.

As showing Dr. Wiley's general standpoint, the following reference to the therapeutic effects of caffein may be quoted:

"A safe attitude to take, on a question of this kind, is that which should be taken on that of beverages and tobacco," that, "inasmuch as there is a difference of opinion among experts, the layman will do well to follow the rule of avoiding, in his diet, anything which is not necessary, and which *may possibly* produce injury." (The italics are the writer's.)

This, if carried far enough, would, it seems to the writer, rule out of the human dietary not only tea, coffee, cocoa, and all artificially flavoured or artificially coloured beverages and foodstuffs, but even meat itself, for are not many of the bases present in meat and in meat extracts well known to be possessed of very powerful physiological activity?

It might be suggested to the "expert" and to the prohibitionist that, after all, human experience and common sense are the safest and, indeed, the only trustworthy guides in matters of diet, as in most other of the affairs of life.

In the sections on alcoholic beverages a good many errors and obscurities have met the reviewer's eye. Thus, the statement is made that " during the sprouting " (of malt), " especially if it is a slow one, practically all the starch in the grain is converted into maltose "; and, a little lower, that, " on treating the ground malt with water, from 60 to 70 per cent. of it is dissolved ; the process of extracting the sugar with water is called ' mashing.' "

The description of dextrose as a " right-handed optical body " is not very illuminating, and the following statements in the section on beer will be read with some surprise by those who have any knowledge of brewing technology : " The term ' beer ' is applied to a product containing from 3 to 5 per cent. of alcohol, whilst the term ' ale ' is used when the liquor contains from 4 to 7 per cent. of alcohol "; and " the difference between ' bottom ' fermentation and ' top ' fermentation is that the yeast cells tend to sink in the consistency of a mash which produces ' beer,' whilst they would tend to come to the top of a denser mash, such as is used for the manufacture of ' ale.' " " The terms ' porter ' and ' stout ' are given to products similar to beer and ale made under slightly different ' conditions ' of fermentation." The American " near beer " is described as " light beer which to a degree tastes like the genuine article, but contains less than 2 per cent. of alcohol "; and the author continues : " If beer must be consumed, it is advisable to keep its content of alcohol as low as possible." Two analyses are given, showing respectively 0·26 and 0·34 per cent. of alcohol by volume, and the information is vouchsafed " that these beverages were hopped, carbonated, and looked like beer." What one would like to know is what they tasted like ; and here it may be mentioned, as a curious psychological fact, that teetotalers invariably show a marked preference for products which resemble in their appearance and outward characters, at least, the very beverages which they are supposed to abhor.

There are many other points to which the reviewer would like to have referred, but he feels that he has perhaps already exceeded reasonable limits of space.

In summing up, it may be said that Dr. Wiley, as might have been expected, has produced a book well conceived and full of very interesting matter. It must, however, be added that it would be greatly improved if he could find the time to give it the thorough revision of which it obviously stands in need.

Perhaps by the time the next edition is called for there will be some further light on the great American experiment in prohibition, and it will be interesting then to see how far the hopes of the prohibitionist have been justified by the event. Whilst any steps taken in the interests of increased sobriety cannot fail to secure the warm approval of every decent-minded person, there are many of us who feel very strongly that the total prohibition of alcohol is not by any means the best way of securing that end, and who fear that it will result only in subterfuge and evasion, and have the effect of substituting injurious for wholesome—or at least for less injurious—beverages. A telegram, reliably stated to have been received from America by a whisky firm in this country only a few days ago, to the effect that the senders could dispose of 20,000 to 25,000 cases " if they arrived by November "

is a significant commentary upon the prospective total "dryness" of the United States.

If one may venture to modify slightly the well-known lines of a poet who certainly would not have had any sympathy with Mr. Johnson and his friends, it may yet be found that :

> " The best-laid schemes o' mice an' ' pussyfeet '
> Gang aft a-gley."

<div align="right">A. CHASTON CHAPMAN.</div>

ERRATA.

(ANALYST, *September*, 1919, *issue.*)

Page 318, 8 lines from bottom, for "p. 311 " read "p. 345."

 ,,   , 17 ,,   ,,   ,,   for "ANALYST, 1891, **16**, 209," read "ANALYST, 1898, **23**, 169."