

# THE ANALYST

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

### The Differential Halogen Absorptions of Oils and Fats.

By J. W. CROXFORD.

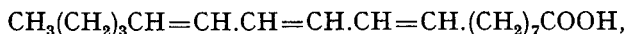
(Work done under the Analytical Investigation Scheme.)

(Read at the Meeting, May 1st, 1929.)

It was considered that an investigation into the differential halogen absorptions of some of the more common oils and fats would be of theoretical interest, and possibly of some analytical value, in helping to determine the position of the unsaturated linkings in the various fatty acid molecules contained therein.

**EXPERIMENTAL.**—The iodine, bromine and chlorine values of a series of oils and fats, etc., were determined, the usual Wijs method being used for the iodine values, whilst the bromine values were determined volumetrically by using an approximately  $N/5$  solution of pure bromine in glacial acetic acid, with subsequent addition of 10 per cent. potassium iodide solution, and titration with a standard solution of sodium thiosulphate (as in the Wijs iodine method), and gravimetrically by the method of Toms (ANALYST, 1928, 53, 69). The chlorine values were determined by a modification of the gravimetric bromine vapour method. Attempts were also made to effect direct combination with iodine, by using iodine vapour, but, owing to the condensation of the iodine on the oil on the one hand, and the removal of any excess being prevented by the instability of the iodine compound to heat, and even in the vacuum desiccator, on the other, these attempts were unsuccessful. The pure unsaturated organic acids used only absorbed traces of iodine after some hours' exposure.

**TUNG OIL AND ELAEOSTEARIC ACID.**—Toms (*loc. cit.*) showed that tung oil gives results by his bromine method in a short time (although the figures obtained are much higher, which was accounted for in his paper), whilst days are required by the Wijs method. Elaeostearic acid



was prepared from tung oil by the method of Böesenken (*cf.* ANALYST, 1928, 53, 54), but the  $\beta$ -modification (m.p.  $71^\circ\text{C}$ .) was obtained, probably owing to exposure to light during recrystallisation. This acid behaved similarly to tung oil, giving rapid absorptions with bromine and chlorine vapours, and being very slow with Wijs method.

Substance.	Iodine value.		Bromine solution.			Bromine vapour.		Chlorine vapour.		
	Theory.	Wijs.	Br.	Br.	Iodine	Br.	Iodine	Chlorine	Cl.	Iodine
			value.	value.	value.	value.	value.	value.	value.	value.
			Theory.		Calcd.		Calcd.	Theory.	Observed.	Calcd.
Tung oil ..	—	4 hrs. 152.3	—	4 hrs. 95.5	151.6	40 mins. 140.3	222.7	—	80 mins. 61.8	221.1
$\beta$ -Elaeostearic acid (m.pt. 71° C.)	181.4	18 hrs. 177.5	114.2	18 hrs. 106.5	169.0	2 hrs. 165.9	263.4	50.7	2 hrs. 74.1	265.1

COMPARATIVE RESULTS WITH UNOXIDISED OILS.—A series of ordinary unoxidised oils gave fairly concordant results with three of the four methods, but the chlorine vapour method gave in some cases high results, owing to substitution by the more active element. This substitution apparently reaches a maximum. In the case of coconut oil, larger films were used in the vapour absorptions, owing to the large proportion of saturated glycerides present.

Oil.	Iodine value. Wijs.	Iodine value.		Iodine value.		Iodine value.	
		Br. solution.	Calcd.	Br. vapour.	Calcd.	Chlorine value.	Calcd.
Linseed ..	4 hrs. 173.6	4 hrs. 107.6	170.8	30 mins. 109.7	174.1	1 hr. 48.8	174.6
Rubber seed ..	4 hrs. 140.8	4 hrs. 84.2	133.7	40 mins. 88.7	140.9	1 hr. 39.6	141.7
Soya bean ..	4 hrs. 132.5	4 hrs. 79.3	126.0	40 mins. 84.2	133.6	30 mins. 36.6 1 hr. 40.8 7 hrs. 49.35 maximum	131.0 145.9 176.5
Coconut ..	1 hr. 7.8	1 hr. 4.8	7.6	30 mins. 5.0	7.9	40 mins. 2.3	8.2
Maize (?) ..	2 hrs. 101.3	2 hrs. 63.2	100.3	30 mins. 63.0	100.0	15 mins. 29.0	103.7
Olive ..	2 hrs. 85.0	2 hrs. 52.1	82.75	30 mins. 54.5	85.3	15 mins. 24.5 30 mins. 29.5 1 hr. 30.0 7 hrs. 49.5 maximum	87.6 105.6 107.3 177.0
Almond ..	2 hrs. 100.7	2 hrs. 59.35	94.2	30 mins. 64.0	101.6	30 mins. 29.3	104.8
Whale ..	3 hrs. 114.5	3 hrs. 70.05	111.2	40 mins. 73.4	116.5	45 mins. 32.9	117.7
Cod liver ..	4 hrs. 170.1	4 hrs. 101.0	160.3	1 hr. 108.6	172.4	1 hr. 45.8 1½ hrs. 52.5 2 hrs. 53.3 maximum	163.8 187.8 190.7

In the above and subsequent tables where a maximum is stated, no further absorption occurred on additional exposure for 1 hour.

CASTOR OILS AND RICINOLEIC ACID.—Ricinoleic acid,  $C_{17}H_{32}(OH)COOH$ , or  $CH_3.(CH_2)_5.CH(OH).CH_2.C_{10}H_9H(CH_2)_7.COOH$ , was prepared from pure castor oil by repeated crystallisation (ten times) of the barium salt from alcohol, but the acid was still impure.

Substance.	Iodine value. Wijs.	Bromine value. Solution.		Iodine value. Calcd.	Br. value. Vapour.		Iodine value. Calcd.	Chlorine value.		
		2 hrs.	2 hrs.		5 mins.	15 "		5 mins.	15 "	24.3
Castor oil, A.	2 hrs.	2 hrs.		82.7	5 mins.	51.0	81.0	5 mins.	24.3	86.9
	83.7	52.1			15 "	56.2	89.2	15 "	25.0	89.4
					30 "	65.3	103.6	30 "	31.3	112.0
					4 hrs.	68.8	109.2	1 hr.	37.1	132.7
					maximum			7 hrs.	73.0	261.0
								maximum		
Castor oil, B.	2 hrs.	2 hrs.		79.6	5 mins.	48.8	77.5	5 mins.	24.2	86.6
	84.8	50.1			15 "	56.5	89.7	15 "	27.1	97.0
					30 "	58.2	92.6	30 "	33.6	120.2
					4 hrs.	68.4	108.6	7 hrs.	72.4	259.0
								maximum		
								maximum		
Ricinoleic acid	(Theory 85.2)	(Theory 53.7)			5 mins.	56.8	90.0	5 mins.	20.1	71.9
	2 hrs.	2 hrs.		82.4	15 "	57.6	91.4	15 "	24.6	88.0
	82.7	51.9			30 "	61.6	97.8	30 "	28.0	100.2
	No increase for 18 hrs.	No increase for 18 hrs.			maximum			7 hrs.	48.8	174.6
								maximum		

The above results show that the halogen vapour absorptions are not comparable with the absorption obtained by Wijs method. The high results obtained are due, no doubt, to substitution which is probably accelerated by the presence of the hydroxyl grouping in the molecule.

**RICINOLEIC ACID.**—Two large films were brominated for 7 hours, and the resulting compound was dissolved in alcohol and reduced with dry hydrogen chloride gas and zinc dust for one hour. The mixture obtained was filtered and washed, and the hydrochloric acid and alcohol were evaporated. The resulting ester was hydrolysed with excess of potassium hydroxide in alcohol, and the fatty acid liberated in the usual manner. The final substance obtained had an iodine value (Wijs) of 80.0, and was probably the original ricinoleic acid used.

**ARACHIS OILS.**—It was found that the chlorine vapour method gave remarkably high results with arachis oil. The difference may prove to be of analytical value.

#### Arachis Oils and Fatty Acid.

Substance.	Iodine value. Wijs.	Br. value. Solution.		Iodine value. Calcd.	Br. value. Vapour.		Iodine value. Calcd.	Chlorine value.		
		2 hrs.	2 hrs.		30 mins.	1 hr.		15 mins.	30 "	24.9
Arachis oil, A.	2 hrs.	2 hrs.		90.4	30 mins.		94.0	15 mins.	24.9	89.1
	94.9	57.0			59.2			40 "	30.8	104.0
								1 hr.	36.2	110.2
								7 "	48.1	129.5
								maximum		172.0
								maximum		
Arachis oil, B.	2 hrs.	2 hrs.		82.0	30 mins.		86.2	15 mins.	28.2	100.9
	86.2	51.7			54.3			30 "	28.7	102.7
								40 "	30.7	109.8
								1 hr.	34.9	124.9
								7 hrs.	44.5	159.2
								maximum		
								maximum		
Fatty acid from B.	2 hrs.	2 hrs.		82.75	1 hr.		85.7	30 mins.	27.5	98.4
	87.6	52.1			54.0			2 hrs.	29.3	104.9
								7 "	46.5	166.3
								maximum		
								maximum		
								maximum		
Arachis oil, C. (extracted in the laboratory)	2 hrs.	2 hrs.		89.05	30 mins.		95.2	15 mins.	27.3	98.0
	93.3	56.1			60.0			30 "	28.3	101.2
								40 "	31.1	111.3
								1 hr.	33.1	118.2
								7 hrs.	49.0	175.3
								maximum		

It should be mentioned that, as the fatty acids were of a somewhat solid consistence, a higher temperature than usual was necessary for the vapour methods, to keep the film liquid and allow the absorption to take place.

EXPERIMENTS WITH DRY CHLORINE.—As there was a possibility that the high chlorine results obtained in the foregoing experiments might have been due to excessive substitution through the gas being wet (having been prepared from calcium hypochlorite, water and hydrochloric acid), the following three experiments were carried out, with the use of chlorine thoroughly dried through a large tower of freshly fused calcium chloride in small granules, sulphuric acid having been found unsatisfactory as a drying medium for such an active element.

		Chlorine value.	Iodine value.
Castor oil, A.	7 hrs. in dry chlorine,	72.5 =	259.4 (maximum).
Castor oil, B.	„ „ „ „ „	72.0 =	257.6 „
Arachis oil, A.	„ „ „ „ „	48.3 =	172.8 „

As can readily be seen, these results are almost identical with those previously obtained with "wet" chlorine, and the substitution is therefore due to the great chemical activity of the element, and not to the promoting action of moisture.

DIFFERENTIAL ABSORPTION AS A CRITERION OF CONSTITUTION.—Ponzo and Gastaldi (*Gazz. Chem. Ital.*, 1912, 42, 92; *ANALYST*, 1912, 37, 463) showed that when the double bond in an unsaturated fatty acid of the oleic series occurs next to the carboxyl group, absorption with Hübl, Wijs or Hanus solution is exceedingly slow, even taking two or three days. Experiments were therefore carried out with the following unsaturated acids of this and other groups:

Oleic acid (ordinary 9.10-oleic acid, B.D.H., redistilled),  $\text{CH}_3(\text{CH}_2)_7, \text{C}_{10}\text{H}=\text{C}_9\text{H}(\text{CH}_2)_7.\text{COOH}$ .

Parsley seed oil fatty acids free from essential oil, and unsaponifiable matter (mainly petroselinic acid, *viz.* isomeric 6.7-oleic acid) extracted from seeds in the laboratory.

Petroselinic acid,  $\text{CH}_3(\text{CH}_2)_{10}\text{C}_7\text{H} = \text{C}_6\text{H}(\text{CH}_2)_4.\text{COOH}$ .

Crotonic acid (B.D.H.),  $\text{CH}_3\text{CH} = \text{CH}.\text{COOH}$ , M.P. of sample 72° C.

Tiglic acid (B.D.H.),  $\text{CH}_3\text{CH} = \text{C}(\text{CH}_3)\text{COOH}$ , M.P. of sample 65° C.

Maleic acid (B.D.H.)  $\begin{array}{c} \text{HC}.\text{COOH} \\ || \\ \text{HC}.\text{COOH} \end{array}$ , M.P. of sample 140° C.

Fumaric acid (B.D.H.)  $\begin{array}{c} \text{COOH}.\text{CH} \\ || \\ \text{H}.\text{C}.\text{COOH} \end{array}$ , sublimed at 200° C.

Cinnamic acid (synthetic),  $\text{C}_6\text{H}_5\text{CH} = \text{CH}.\text{COOH}$ , M.P. of sample 133° C.

Cinnamyl alcohol (B.D.H.)  $\text{C}_6\text{H}_5\text{CH} = \text{CH}.\text{CH}_2\text{OH}$ , B.P. of sample 241° C.

Croton oil, A & B (A from B.D.H. with iodine value of 108.5).

Croton oil, B, fatty acids (*i.e.*, containing tiglic acid).

The pure organic acids were placed in small porcelain boats for the vapour absorptions.

Substance.	Iodine value.	Bromine value.		Iodine value.	Bromine value.		Iodine value.	Chlorine value.	
	Wijs.	Solution.	Calcd.	Vapour.	Calcd.	Calcd.	Calcd.	Calcd.	
Oleic acid	Theory 90.0 2 hrs. 85.1	Theory 56.7 2 hrs. 51.6	82.0	53.3	84.6	Theory 25.2 23.9	85.5		
Parsley seed oil fatty acids	2 hrs. 102.3	2 hrs. 63.1	100.2	30 mins. 65.6	104.1	1 hr. 28.45	101.8		
Crotonic acid †	Theory 295.4 18 hrs. 86.7 6 days 188.9 14 „ 190.3	Theory 186.0 18 hrs. 40.9	65.0	(M.P. 85° C.) 1 hr. 86.6*	296.2	Theory 82.6 2 hrs. 79.25 † liquid	283.5		
Tiglic acid	Theory 254 18 hrs. 47.0 3 days 96.6 No acid left for further expts.	Theory 160 18 hrs. 141.8	225.1	(M.P. 81.5° C.) 1 hr. 157.2*	249.7	Theory 71.0 2 hrs. 69.7 † liquid	249.3		
Maleic acid †	Theory 218.9 18 hrs. 2.2	Theory 137.9 18 hrs. 5.6	8.9	2 hrs. 9.0	14.3	Theory 61.2 6.5	24.4		
Fumaric acid †	Theory 218.9 18 hrs. 15.6	Theory 137.9 18 hrs. 16.0	25.4	4 hrs. No absorption	—	4 hrs. No absorption	—		
Cinnamic acid †	Theory 171.6 18 hrs. 25.4 14 days 54.9 28 „ 65.5	Theory 108.1 18 hrs. 89.3 3 days 107.4	141.8 170.5	(M.P. 195° C.) 2 hrs. 107.2	170.2	Theory 48.0 2 hrs. 47.2 liquid	168.8		
Cinnamyl alcohol	Theory 189.5 18 hrs. 135.6 No substance left.	Theory 119.4 18 hrs. 115.6	183.5	2 hrs. 107.2* liquid	170.2	Theory 52.9 2 hrs. 46.5 † liquid	166.4		
Croton oil, A.	2 hrs. 109.1 14 days 123.4 28 „ 123.7	2 hrs. 66.4	105.4	15 mins. 61.9 30 „ 71.2 1 hr. 73.8 7 „ 79.6 maximum	98.2 113.0 117.1 126.4	15 mins. 32.5 30 „ 38.0 1 hr. 41.0 7 „ 68.2 maximum	116.3 136.0 146.7 244.0		
Croton oil, B.	2 hrs. 106.6 14 days 122.3 28 „ 122.8	2 hrs. 66.0	104.8	15 mins. 62.9 30 „ 70.5 1 hr. 70.8 7 „ 74.5 maximum	99.8 111.9 112.4 118.3	15 mins. 36.3 30 „ 36.5 1 hr. 37.3 7 „ 71.65 maximum	129.9 130.6 133.4 256.3		
Croton oil, B.	2 hrs. 116.9 14 days 128.4	2 hrs. 69.6	110.5	30 mins. 73.5 1 hr. 74.1	116.7 117.6	30 mins. 31.7 1 hr. 34.0	113.4 121.6		
Fatty acids	28 „ 128.9			7 „ 78.5 maximum	124.5	7 „ 70.5 maximum	251.9		

\* These results were obtained by heating the bromine derivative at 60° C., to remove excess bromine, the compound being volatile at higher temperatures.

† These results were obtained by removing the excess chlorine in a vacuum desiccator. The crotonic and tiglic acid derivatives were volatile even under these conditions; hence the lower results.

‡ The iodine values (Wijs) obtained for these substances are similar to those obtained by Lewkowitsch (5th edition, Vol. I, 400), although the above figures are higher. It is worthy of note that the starch iodide end-points with this and the bromine solution method were very fugitive.

CROTON OIL.—The sample marked A was kindly supplied by British Drug Houses, who also gave its analysis as follows:—Sp. gr., at 15.5° C., 0.951; rotation, +10.6°;  $n_D^{40}$ , 1.4735; acid value, 22.4; saponification value, 209.4; and iodine value, 108.5.

The value obtained by me after 2 hours' absorption by the Wijs method was 109.1, and a similar result (106.6) was obtained with another sample.

It has been shown by Margosches (*Die Iodzahl-Schnellmethode und die Ueberiodzahl der Fette*, 1927, p. 12, 20) that by using a very large excess of halogen and continuing the absorption for a long period much higher iodine values are obtained with croton oil (e.g. 117.1 and 117.7). By continuing the absorption with the Wijs solution for 14 days and using 100 per cent. excess of the reagent, an iodine value of 123.4 was obtained with croton oil A, and a value of 122.3 with croton oil B. These results are thus in accordance with the theory of Ponzio and Gastaldi (*loc. cit.*), and may be explained by the presence of tiglic acid in the oil. On the other hand, the bromine vapour method gave results after 7 hours' absorption approximating those of Margosches.

As croton oil is an important drug in the British Pharmacopoeia, this anomaly in the iodine value is a point that should be recorded.

MALEIC AND FUMARIC ACIDS.—A 5 per cent. solution of each of these acids in pure glycerin was prepared, in an attempt to obtain higher bromine and chlorine vapour results, but the maleic acid solution gave the same result as the glycerin blank, and the fumaric solution precipitated on standing. No other suitable non-volatile solvent was found.

HYDROGENATED OILS AND THEIR FATTY ACIDS.—These are said to contain iso-oleic acids. According to Bauer (*Oil and Fat Ind.*, 1928, 5, 266) that of hydrogenated arachis oil is 12.13-oleic acid,  $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_{10}\text{COOH}$ . The following results were obtained with various hydrogenated oils and fatty acids:

Oil.	Iodine value. Wijs.	Bromine		Iodine		Chlorine	
		value. Solution.	value. Calcd.	value. Vapour.	value. Calcd.	value.	value. Calcd.
Hydrogenated palm	2 hrs.	2 hrs.		30 mins.		30 mins.	
	22.5	13.85	22.0	15.3	24.3	7.9	28.3
Do. Fatty acids	2 hrs.	2 hrs.		30 mins.		15 mins.	
	24.4	18.1	28.7	16.8	26.6	8.0	28.7
Hydrogenated whale	2 hrs.	2 hrs.		30 mins.		30 mins.	
	15.6	9.8	15.6	8.75	13.9	4.0	14.3
Do. Fatty acids	2 hrs.	2 hrs.		30 mins.		30 mins.	
	15.9	10.1	16.0	11.0	17.5	4.6	16.4
Hydrogenated maize	2 hrs.	2 hrs.		30 mins.		45 mins.	
	38.5	24.2	38.4	23.8	37.8	11.5	41.1
Do. Fatty acids	2 hrs.	2 hrs.		1 hr.		45 mins.	
	39.5	24.25	38.7	23.7	37.6	11.4	40.8

For the bromine vapour and chlorine absorptions in the above series, the substances were used in a finely divided solid condition in small porcelain boats,

the melting points being high compared with previous oils and fats used. In these absorptions also, slightly variable results were obtained, due to substitution, which appears to occur somewhat readily with hydrogenated oils.

The fairly close agreement between the Wijs results and the bromine vapour results suggest that the iso-oleic acids present in these hydrogenated oils are not 2-3 oleic acids.

**SUMMARY AND CONCLUSIONS.**—From the foregoing experiments it can be claimed that the bromine vapour method for determining the degree of unsaturation of an oil or fat compares very favourably with the method of Wijs, usually being much more rapid (particularly with croton oil), and in many cases more nearly complete. The exceptions are castor oil and its predominant acid (ricinoleic acid), which readily undergo substitution with bromine vapour, such substitution presumably being caused by the presence of a hydroxy grouping in the molecule. The differences obtained for one hour's absorption with the two reagents (Wijs and bromine vapour) probably enable a judgment to be formed as to the position of the unsaturated bond in the fatty acids of the oleic series. The bromine vapour method also has a great advantage over others used, as it can be successfully employed when only small quantities of material are available. (Not more than 0.025 grm. of substance was used in any of the above gravimetric experiments.)

The chlorine vapour method, when applied to oils and fats, in most cases gives results which are too high, owing to the substitution caused by the greater chemical activity of this element, as previously stated. Such substitution, however, appears to reach a limit.

Although primarily concerned with oils and fats, this work was extended to other unsaturated organic substances, and the experiments made, both with bromine and chlorine vapours, show that results agreeing closely with theory can be obtained, except with maleic and fumaric acids, which are evidently very inert under this treatment. This method could, therefore, be successfully used to determine the amount of unsaturated compounds present in admixture with saturated substances.

The results obtained for oils and fats with bromine in acetic acid solution are not satisfactory, the figures usually being lower than those obtained with Wijs solution, probably owing to the formation of bromhydrins during the absorption. This method, however, shows promise with the other organic substances used, but is not to be compared with the vapour absorption results obtained.

In conclusion, I should like to thank Dr. Toms for his help and interest in these experiments, Dr. Mitchell for his helpful suggestions throughout the experimental period, and the Directors of Messrs. Loders and Nucoline, Ltd., for the use of their laboratory for practically the whole of the work.

#### DISCUSSION.

Mr. E. R. BOLTON referred to the many methods which had been used or proposed in past years to determine the iodine value. He expressed the opinion that the Wijs method had been clearly established as giving a definite measure of

the unsaturated oils of a simple type, but no method was absolutely satisfactory in the case of highly unsaturated or complex bodies. It now seemed that the application of the bromine method was likely to supply a better differentiation than had been possible hitherto. If the figures given in the paper were plotted out and carefully studied, they might lead to a new way of arriving at the nature of the unsaturated acids present. It was impossible to criticise or discuss the wonderful mass of figures put before the Society, but he was very much impressed with the way they had fitted into theory.

Mr. C. A. MITCHELL thought that the paper was very valuable from the point of view of developing a new aspect of halogen absorption. Many years ago Lewkowitsch had said that he was thankful he had not added another method to the methods of iodine absorption—he rather implied that the Wijs method was the last word in iodine absorption, and that nothing further could be done. However, even Wijs himself had recently admitted that his method did not hold good for such acids as mentioned in this paper, although if continued long enough it would be possible to get better results; but even then there was a risk of decomposition of the reagent. He was not sure whether Mr. Croxford had taken precautions to eliminate moisture from the chlorine.

Mr. E. J. LUSH remarked that in all these halogen absorptions there was a certain risk of substitution. One element which had not been mentioned was hydrogen, and the determination of the hydrogen number might add a confirmatory method free from the danger of substitution.

Mr. K. A. WILLIAMS demonstrated by means of curves the progress of the iodine absorption with reference to time, and showed it to occur in two stages, the first being rapid and the second very slow. For most oils the beginning of the second stage was well defined and corresponded to the Wijs iodine value of the oil. In the case of tung oil, however, the change from the first to the second stage was gradual, and the apparent iodine value was consequently somewhat indefinite. He suggested that the real iodine value would be given by the point of intersection of the lines representing the two stages of absorption.

Dr. H. TOMS, replying on behalf of the author, referred to the question of bromhydrin formation during the determination of unsaturation by means of bromine solution, and said that this was very unlikely to occur, since water (as a solvent for potassium iodide) was added only at the end of the absorption period in order to titrate the excess of bromine. Of course, when bromine vapour was used the possibility of bromhydrin formation did not occur, since water was not present.

In the case of chlorine the corresponding possibility had occurred to Mr. Croxford in the later stages of the work, for the chlorine used was obtained from bleaching powder and was necessarily damp. This might account for the fact that some of the values obtained by chlorine absorption were not so satisfactory as those obtained by the use of dry bromine vapour. Throughout the whole of the work Mr. Croxford and he had had in mind the possibility of substitution occurring simultaneously with the direct addition, but unfortunately no satisfactory means of settling this point had, as yet, suggested itself. In most cases it appeared that bromine vapour gave complete saturation in a few minutes.

In reply to Mr. Williams, Dr. Toms assumed that the phrase "true iodine value" meant the maximum theoretical absorption obtainable for the complete saturation of the double bonds and not the maximum value obtainable under the specified conditions of some standard method, such as that of Wijs or Hübl, which, as was now known, did not necessarily give figures representing complete saturation.



One important point had emerged from Mr. Croxford's work, namely, that the position of the double bond in the fatty acid molecule exerted a pronounced influence on the absorption of iodine as determined by the Wijs method. Thus one could not say when a Wijs test was finished, *i.e.* when the oil was completely saturated with iodine chloride. He (Dr. Toms) had entirely overlooked this position effect, although he had shown that the combination of double bonds present in a molecule exerted a profound influence on halogen absorption. This was pre-eminently so in the case of tung oils, for which, for many years, figures representing only about two-thirds of the real unsaturation value of these oils had been accepted as correct, although it had now been proved that the older values did not represent complete absorption.

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## Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates.

### XV. A New Method for the Separation of Tantalum and Niobium from Titanium and Zirconium (1 : Qualitative).

By W. R. SCHOELLER, Ph.D.

THE separation of tantalum, niobium, titanium, and zirconium (with hafnium) is, no doubt, the central and most difficult problem of earth-acid analysis. Its solution is of practical importance to the mineralogist, as a number of rarer earth-acid minerals contain titania and zirconia in substantial proportions; many of the published analyses of such minerals can only be regarded as rough approximations. Other tantaloniobate minerals contain small to minute amounts of the dioxides.

The complexity of the problem will be better understood when it is borne in mind that the quantitative separation of the three binary mixtures,  $(\text{Ta}_2\text{O}_5:\text{Nb}_2\text{O}_5)$ ,  $(\text{M}_2\text{O}_5:\text{ZrO}_2)$ , and  $(\text{M}_2\text{O}_5:\text{TiO}_2)$ , in any proportions, has only recently been made reasonably accurate (Sections IV, V, ANALYST, 1925, 50, 485, 494; IX, *id.*, 1927, 52, 633; XIII, *id.*, 1928, 53, 515; and XIV, *id.*, 1929, 320). The resolution of the ternary mixture  $(\text{M}_2\text{O}_5:\text{TiO}_2:\text{ZrO}_2)$  into its constituents is accounted difficult enough even as a proposition of qualitative analysis. It involves a preliminary splitting up into simpler groups, such as (a)  $(\text{M}_2\text{O}_5+\text{TiO}_2):\text{ZrO}_2$ ; (b)  $(\text{M}_2\text{O}_5+\text{ZrO}_2):\text{TiO}_2$ ; or (c)  $\text{M}_2\text{O}_5:(\text{TiO}_2+\text{ZrO}_2)$ . *Grouping* (a) was wrongly held to be the result of bisulphate fusion followed by boiling of the solution of the melt (XII, ANALYST, 1928, 53, 472). *Grouping* (b) is what Noyes and Bray (*A System of Qualitative Analysis for the Rare Elements*; New York, 1927; Procedure 41, p. 98) claim to be able to accomplish by extraction of the precipitated hydroxides with sodium salicylate and salicylic acid. This method, which I have come to regard as ineffective, will be criticised at greater length in the concluding paragraph of this paper. *Grouping* (c) was believed by the earlier mineralogists to take place when

the bisulphate melt of the oxides is extracted with cold water or dilute acid. The procedure is now known to be utterly unreliable (*cf.* Sect. XII, *loc. cit.*).

**AUTHOR'S INVESTIGATION.**—The object of the present investigation was to work out a reliable qualitative method before attempting the quantitative separation under discussion. After experimenting with several schemes I had the good fortune to discover a method which not only makes the identification of the elements in question a surprisingly simple operation, but is also expected to provide the basis for their quantitative separation. This Section contains the directions for the qualitative separation method and a preliminary notice of its application for quantitative purposes.

**CHEMISTRY OF THE PROCESS.**—The new process is an application of certain principles of colloid chemistry. The dioxides  $\text{TiO}_2$  and  $\text{ZrO}_2$  are capable of forming definite sulphates relatively stable in aqueous solution, whilst the pentoxides  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  do not form salts. As mentioned above under *Grouping (c)*, the earliest attempts at a separation, *i.e.* extraction of the bisulphate melt with cold water, were based on this fundamental difference in chemical deportment. What makes the separation ineffective is the pronounced tendency of the reacting elements to form complexes with each other, the result of association being a profound alteration of the specific properties of the pure compounds. This constitutes "loss of individuality" (Crookes). Hence, when the bisulphate melt is extracted with cold water or dilute acid no separation takes place, the titania and earth acids distributing themselves more or less evenly over the solution and the residue; zirconia accentuates the solvent effect of titania upon the earth acids.

Now it occurred to me to attempt to treat the bisulphate melt with a reagent that would prevent complex-formation. Tannin having been used in the course of these investigations as an effective precipitant of the earth acids, it was surmised that they would remain insoluble upon treatment of the melt with a tannin solution containing sufficient sulphuric acid to act as a solvent for the sulphates of titanium and zirconium. In the light of colloid theory, when the bisulphate melt is in contact with a tannin dispersion, the small particles of the molecularly-dispersed sulphates of potassium, titanium, and zirconium would be able to diffuse through the mesh-like structure of the liquid phase, whereas the larger aggregates of tantalic and niobic acid would be entangled and coagulated by the tannin sol as soon as they were formed during the disintegration of the melt.

These deductions were verified experimentally and fully confirmed. Extraction of the bisulphate melt with 5 per cent. sulphuric acid containing 1 per cent. of tannin yields a solution of titanium and zirconium sulphates and a residue consisting of the brightly-coloured tannin adsorption-complexes of the earth acids. To use Crookes's terminology, the addition of tannin restores the individuality of the elements.

The new method will hereafter be termed the "pyrosulphate and tannin method."

**THE SEPARATION.**—The mixed oxides (0.1 to 0.2 gm.) are fused with 2 to 3 grms. of bisulphate in a silica crucible. The melt is made to solidify in a thin layer around the sides of the crucible. The hot reagent (1 gm. tannin dissolved in 90 c.c. of water and 10 of 1:1 sulphuric acid) is poured into the crucible, which is gently heated with a moving bare flame, the melt disintegrating into small detached fragments. The contents of the crucible are transferred to a 400 c.c. beaker, and the crucible rinsed with the rest of the reagent. The liquid is heated to boiling, and then left on a hot plate or water-bath until it is clear and the precipitate has coagulated (roughly, 15 minutes). The precipitate, *TP*, is filtered off, and the filtrate collected in a conical flask.

*Identification of Titanium and Zirconium.*—The filtrate is boiled down rapidly with 5 c.c. of strong sulphuric acid until it darkens and foams. It is then treated with small portions of strong nitric acid till it becomes clear and colourless. The tannin is very readily oxidised, the operation taking only a few minutes. The liquid is then heated over a bare flame until copious white fumes are given off, another drop or two of nitric acid being added, if necessary, to bring about complete decolorisation. After cooling, 50 c.c. of cold water are added, and the titanium and zirconium identified by known methods: the solution is treated with an excess of hydrogen peroxide, the familiar yellow to orange colour proving the presence of titania. Zirconia is next detected by addition of a large excess of ammonium phosphate, which precipitates flocculent colourless zirconium phosphate.

*Identification of Tantalum and Niobium.*—The precipitate *TP* has a buff to bright scarlet colour, according to the composition of the oxide mixture. Its formation proves the presence of the earth acids; the subsequent procedure here given serves for their separate identification. It may be added that *TP* is quite different from the flocculent, extremely voluminous tannin complexes obtained by precipitation: it is remarkably compact, and in part retains the shape of the fragments of the melt if the mixed oxides contain much earth acid.

Even if the joint detection of the earth acids is sufficient for the purpose of the qualitative analysis, I would advise operators not too familiar with the subject to proceed with the next stage, as it provides an unmistakable confirmatory test.

The precipitate *TP* is well washed with 2 per cent. sulphuric acid containing a little tannin, ignited, fused with bisulphate, and the melt dissolved in a hot, strong solution of tartaric acid. The liquid is suitably diluted (20 c.c. for 0.01 gm. of pentoxides), and treated while boiling with one-fifth of its bulk of strong nitric acid; a white, flocculent precipitate *HP*, forming either at once or after short boiling, is a certain proof of the identity of the earth acids. This procedure is the tartaric hydrolysis method fully described in Section XIV (ANALYST, 1929, 321).

For the separate identification of tantalum and niobium, the precipitate *HP* is collected, ignited, fused with bisulphate, the product dissolved in ammonium oxalate solution, and the latter submitted to Powell and Schoeller's tannin method described in Section V (ANALYST, 1925, 50, 495).

If the titania content of the oxide mixture is found to be low, the procedure for identifying tantalum and niobium may be shortened: the tannin precipitate *TP* is ignited and treated by Powell and Schoeller's process without having to pass through the *HP* stage. If, on the other hand, the mixed oxides are rich in titania, the tartaric hydrolysis is advisable, as it frees *TP* from a slight contamination with titania, which might otherwise discolour the yellow tantalum precipitate (Section XI, ANALYST, 1928, 53, 265).

RESULTS OF TEST SEPARATIONS.—In order to demonstrate the efficacy of the method, I analysed 13 oxide mixtures, the composition of which was not disclosed to me till after the conclusion of the work. The composition of the mixtures was varied in such a manner as to present the greatest diversity, from the total absence of each constituent to its forming the bulk of the mixture. Let *M* and *m* represent large and small amounts of  $M_2O_5$ , respectively; *T* and *t*, large and small amounts of  $TiO_2$ ; *Z* and *z*, large and small amounts of  $ZrO_2$ . These values were permuted in the following manner:

Binary mixtures:  $mT$ ;  $Tz$ ;  $mZ$ ;  $tZ$ ;  $Mt$ ;  $Mz$ .

Ternary mixtures:  $mTz$ ;  $mtZ$ ;  $Mtz$ .

$mTZ$ ;  $MTz$ ;  $MtZ$ .  $MTZ$ .

The cases *MT*; *MZ*; and *TZ* were disregarded as superfluous. The mixtures were not analysed in the order given, but chosen at random (*vide infra*, Quantitative Separation). In all cases the composition was ascertained correctly without any difficulty within two hours. The time taken does not include the separate identification of tantalum and niobium; this part of the process having been exhaustively treated in Section V (*loc. cit.*), I felt justified in saving myself the time and labour it would have entailed.

TARTARIC HYDROLYSIS AS AN IMPORTANT EARTH-ACID TEST.—While the detection of the earth acids is under consideration, I must call attention to the great practical value of tartaric hydrolysis as a distinctive reaction of tantalum and niobium. It need hardly be pointed out that precipitation of a hydrated oxide by a mineral acid from a tartrate solution is a novel and peculiar reaction. On theoretical grounds we may say that it cannot take place with metals that form soluble nitrates or chlorides; it must be confined to those more electro-negative elements the hydroxides of which are insoluble in the mineral acid used: the reaction might possibly be given also by antimony, tin, germanium, and tungsten. This deduction was verified by experiment, with the following results:

	Nitric acid.	Hydrochloric acid.
Antimony (1).	No ppt.	No ppt.
Tin (2).	White flocculent ppt.	No ppt.
Germanium (3).	No ppt.	No ppt.
Tungsten (4).	Yellow ppt.	Yellow ppt. (5).

(1)  $NaSbO_3$  (1 grm.) dissolved in tartaric and a little sulphuric acid; boiled with 30 c.c. mineral acid in 200 c.c. bulk. (2)  $Na_2SnO_3$ , as (1). (3)  $GeO_2$  (0.03 grm.) dissolved in  $NaOH$ ; a few drops  $H_2SO_4$ ; 0.25 grm.  $C_4H_6O_6$ ; boiled with 5 c.c. mineral acid. (4)  $WO_3$  fused with  $KHSO_4$ ; dissolved melt in  $C_4H_6O_6$ . (5) No ppt. in dilute solution.

*Specificity.*—It appears, then, that stannic acid is the only other substance giving the same reaction as the earth acids when nitric acid is used; hydrochloric acid gives no precipitate, stannic chloride being soluble. Now, as stannic oxide is hardly soluble in bisulphate, and the dissolved part removable from the tartrate solution by hydrogen sulphide (Sect. I, ANALYST, 1922, 47, 93), we may conclude that the formation of a white precipitate under the above conditions is a specific reaction of tantalum and niobium.

*Sensitiveness.*—Quantitative tests demonstrating the sensitiveness of the reaction and the recovery of small amounts of earth acid, both in presence and absence of titania, are given on p. 321 of Section XIV (ANALYST, 1929). A conservative estimate, based on those tests, gives a sensitiveness of the order of 0.03 mgrm.  $M_2O_5$  per c.c., the test being unaffected by five times that amount of titania; zirconia, if present in such proportions, should be previously removed by the pyrosulphate and tannin method (this Section).

*Mineralogical Application.*—The test should prove a valuable adjunct in determinative mineralogy. The powder is fused with bisulphate, and the product dissolved by boiling with strong tartaric acid solution. The (filtered) liquid, boiled with one-fifth its bulk of strong hydrochloric acid, furnishes a white flocculent precipitate of tantalic and niobic acids. Betafite, euxenite, and stibiotantalite (0.02 grm. each), tested in this manner, readily gave a positive reaction.

**IMPORTANT EARTH-ACID TESTS.**—It is concluded that tartaric hydrolysis is a specific, as well as a sensitive and convenient, test for the joint detection of tantalum and niobium, applicable in presence of the more electropositive, or salt-forming, elements. It will be useful here to append a list of the most important reliable earth-acid reactions, as this subject continues to receive but scant attention in analytical text-books.

(a) *Reactions for their Joint Detection.*—(1) Tartaric hydrolysis (this Section); (2) precipitation of the crystalline sodium salts (VI, ANALYST, 1926, 51, 615); and (3) precipitation of the earth acids from solutions of 4:3 potassium tantalate and niobate by acetic or mineral acids.

(b) *Reactions for their Separate Identification.*—

	Tantalum.	Niobium.
(4) Tannin in oxalate solution.	Sulphur-yellow ppt.	Red ppt.
(5) Zinc dust in phosphoric acid solution.	No coloration.	Dark to black coloration.
(6) KF in fluoride solution.	Crystalline ppt.	No ppt.

(4) Section V, *loc. cit.* (5) Giles, *Chem. News*, 1907, 95, 1. (6) Marignac's method.

Finally, it may be pointed out that Rose (*Traité Complet*, 1859) correctly describes the tantalum-tannin precipitate as being light yellow (*jaune clair*); whereas most modern text-books give yellow-brown or light brown. Such a precipitate, however, indicates that the tantalic acid contains titania (XI, *loc. cit.*).

QUANTITATIVE SEPARATION OF THE EARTH ACIDS FROM TITANIA AND ZIRCONIA (PRELIMINARY NOTICE).—The quantitative possibilities of the pyrophosphate and tannin method were investigated, simultaneously with its qualitative application, by means of the 13 test separations described above.

All the pentoxide precipitates *TP* were washed, ignited, and weighed. Titania and zirconia, if subordinate, were actually determined, the former colorimetrically, the latter gravimetrically as pyrophosphate (Lundell and Knowles, *ANALYST*, 1920, 45, 28); if present in large amount, they were taken by difference, the total weight of mixed oxides taken, and that only, being known to me: quantities computed by difference are shown in *italics*. The numbering of the experiments indicates the order in which the "unknown" mixtures were received. The pentoxide preparation used contained 61.4 per cent.  $Ta_2O_5$  and 38.6 per cent.  $Nb_2O_5$ :

Type.	Exp.	$M_2O_5$ .		$TiO_2$ .		$ZrO_2$ .	
		Taken. Grm.	Found. Grm.	Taken. Grm.	Found. Grm.	Taken. Grm.	Found. Grm.
<i>mT</i>	7	0.0058	0.0077	0.0922	0.0903	nil	nil
<i>Tz</i>	4	nil	nil	0.0946	0.0937	0.0058	0.0067
<i>mZ</i>	12	0.0072	0.0070	nil	nil	0.1054	0.1056
<i>tZ</i>	11	nil	nil	0.0052	0.0056	0.0965	0.0961
<i>Mt</i>	8	0.0900	0.0900	0.0033	0.0055	nil	nil
<i>Mz</i>	9	0.0925	0.0894	nil	nil	0.0050	0.0060
<i>mTz</i>	10	0.0050	0.0046	0.0950	0.0946	0.0092	0.0100
<i>mtZ</i>	2	0.0054	0.0042	0.0056	0.0055	0.0936	0.0949
<i>Mtz</i>	13	0.0908	0.0900	0.0030	0.0020	0.0044	0.0043
<i>mTZ</i>	1	0.0054	0.0046	0.0709	0.0686	0.0708	0.0739
<i>MTz</i>	3	0.0723	0.0757	0.0716	0.0673	0.0050	0.0059
<i>MtZ</i>	6	0.0704	0.0720	0.0054	0.0044	0.0736	0.0730
<i>MTZ</i>	5	0.0620	0.0625	0.0643	0.0603	0.0628	0.0663

It must be understood that no attempt has been made at introducing any analytical refinements, the idea being merely to ascertain the qualitative composition of the oxide mixture, supplemented by a rapid exploratory quantitative analysis for purposes of orientation. Under these circumstances it will, I think, be conceded that the results are, on the whole, very gratifying, and justify my confidence in the ultimate success of the method as a strictly quantitative process.

A few supplementary remarks may here be added. The zirconium phosphate precipitate was mixed with a large proportion of filter pulp, so as to expedite filtration and washing with dilute ammonium nitrate solution; except in two cases, the ignited zirconium pyrophosphate was dark grey to black, and the error positive: "black residues of excessive weight," to quote Lundell and Knowles (*loc. cit.*). The approximate factor 0.46 was used for the conversion  $ZrP_2O_7:ZrO_2$  (Lundell and Knowles' factor is 0.4632). As the constant association of zirconium and hafnium has now been proved, the mixed oxides  $(Zr,Hf)O_2$  should be determined as such. For this, if for no other reason, I intend confining the use of the phosphate method to the qualitative and preliminary quantitative analyses as outlined in this Section.

A THIRD METHOD FOR THE SEPARATION OF TITANIA FROM THE EARTH ACIDS.—The particulars here given make it fairly clear that the utility of the pyrosulphate and tannin method is not necessarily confined to the separation to which it was first applied. In particular, the procedure may yet prove a valuable adjunct for the separation of titania from the earth acids, along with the tartaric hydrolysis and oxalate salicylate methods (IX and XIV, *loc. cit.*). The question will be investigated at an early date.

OBSERVATIONS ON THE SALICYLATE PROCESS.—Noyes and Bray (*op. cit.*, pp. 76–81, 98–99) separate titanium from tantalum, niobium and zirconium by boiling the mixed hydroxides with 5 grms. of sodium carbonate and 15 grms. of salicylic acid in a total bulk of 400 c.c. for two hours, replacing the water lost by evaporation. They express themselves as follows (p. 77): “We have found that, by applying this process to the precipitated hydroxides . . ., all the titanium passes into solution, and that all the tantalum, columbium, and zirconium remain undissolved, whether the elements are present in large or small quantity, and whether they are alone or mixed.” The salicylate process would thus afford a means not only for the qualitative, but even for the quantitative separation of titania from the other oxides in one operation. My own experience being quite at variance with that of Noyes and Bray, it is necessary here to record my observations.

(1) Prior to the publication of Noyes and Bray’s work, Schoeller and Deering (IX, Table III, p. 630, *loc. cit.*) had conducted a series of experiments with an almost identical process in an endeavour to separate titania from the earth acids. They were unable to extract more than 80 per cent. of the titania in one operation; “even a third treatment failed to effect its complete removal. Moreover, niobic acid did not remain altogether insoluble.” With low  $\text{TiO}_2:\text{M}_2\text{O}_5$  ratios, the titanium extraction was poorer still (about 50 per cent.).

(2) During the initial stages of the present investigation, the appearance of Noyes and Bray’s book caused me to re-investigate the subject of salicylate extraction. This time I experimented with mixtures of titania and zirconia. Nine tests were carried out:

Exp.	TiO <sub>2</sub> . taken. Grm.	ZrO <sub>2</sub> . added. Grm.	TiO <sub>2</sub> in		Remarks: See below.
			1st extract. Grm.	2nd extract. Grm.	
1	0.1020	0.1018	0.0390	—	} (a)
2	0.1035	0.1048	0.0376	—	
3	0.1130	0.1450	a few mgrms.	—	} (b)
4	0.1364	0.1037	do.	—	
5	0.1560	0.1348	0.0280	0.0235	} (c)
6	0.1252	0.1585	0.0197	0.0183	
7	0.1027	0.1026	0.0288	—	} (d)
8	0.1068	0.1040	0.0319	—	
9	0.1000	0.1203	0.0385	—	(e)

The mixed oxides were fused with bisulphate, the acid solution of the melt precipitated with ammonia, the precipitate collected and washed with dilute ammonium nitrate solution. Various modifications of the procedure were then tried: (a) The precipitate was treated in strict accordance with Noyes and Bray's above directions. (b) The precipitate was dissolved in 2 c.c. of strong nitric acid, and the solution slowly poured into a boiling solution of 5 grms. of sodium salicylate in 500 c.c. of water. (c) The ignited residue from the extraction of the precipitate with sodium salicylate (5 grms.) and salicylic acid (2 grms.) was re-treated. (d) Sodium salicylate was used in Exps. 7, the ammonium salt in 8: 5 grms. of salicylate, 2 of salicylic acid, bulk 400 c.c.; boiled one hour. (e) The solution of the bisulphate melt was neutralised with sodium bicarbonate and slowly poured into a boiling solution of 5 grms. of sodium salicylate in 40 c.c. water; final bulk, 200 c.c.

These brief notes suffice to show, not only that Noyes and Bray's results could not be reproduced, but also that the extraction was almost uniformly poor and much lower still than in Schoeller and Deering's experiments with titania and the earth acids. I have become convinced that a molecularly-admixed constituent of a complex precipitate cannot be extracted quantitatively by a process of selective solution: the history of analytical chemistry, particularly that of the earth acids and the platinum metals, teems with instances of faulty methods based on that principle.

SUMMARY.—A new process (the "pyrosulphate and tannin method") is described for the qualitative separation of tantalum and niobium from titanium and zirconium. It consists in fusing the mixed oxides with bisulphate and extracting the fusion product with 5 per cent. sulphuric acid containing one per cent. of tannin. The earth acids remain insoluble as coloured tannin adsorption complexes, whilst the sulphates of titanium and zirconium dissolve. The addition of the tannin prevents the formation of complexes, which render the separation ineffective when the bisulphate melt is leached with cold water or dilute acid.

The most reliable tests for tantalum and niobium are discussed: it is shown that the precipitation of the earth acids from boiling tartrate solutions by excess of mineral acid is a specific, sensitive, and convenient earth-acid reaction applicable in presence of other metals. A preliminary notice is given of the quantitative application of the pyrosulphate and tannin method. The salicylate process for the separation of titanium from tantalum, niobium, and zirconium is adversely criticised.

I have much pleasure in acknowledging my indebtedness to Dr. Ludwig Moser, Professor of Analytical Chemistry in the Polytechnic University of Vienna, for courteously placing at my disposal the preparation of pure germanium dioxide used in this investigation.

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## Experiments on Quantitative Oxidation with Ceric Sulphate.

By A. J. BERRY, M.A.

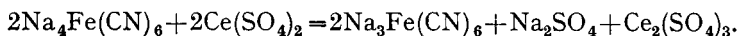
ALTHOUGH the powerful oxidising properties of ceric sulphate have long been known, little use appears to have been made of them for analytical work until quite recently. Benrath and Ruland (*Z. anorg. Chem.*, 1920, 114, 267) have described some experiments on the oxidation of various compounds by ceric sulphate, and detailed investigations on the use of this oxidising agent in potentiometric titration analysis have been published by Furman (*J. Amer. Chem. Soc.*, 1928, 50, 755, 1675, and 51, 1128, by Willard and Young (*ibid.*, 1928, 50, 1322, 1334, 1368, 1372, 1379, and 1929, 51, 139), and by Atanasiu and Stefanescu (*Ber.*, 1928, 61, 1343). Very few experiments have been described with ceric sulphate as a volumetric oxidising agent, apart from potentiometric methods for determining the end-point, but mention should be made of the titration of ferrous salts in conjunction with diphenylamine as an internal indicator (Willard and Young). The observations of previous investigators as regards the stability and highly oxidising properties of solutions of ceric sulphate have been verified by the experiments of the writer, so far as the work has overlapped; in particular, reference may be made to the quantitative oxidation of vanadyl salts, nitrites and ferrocyanides.

PREPARATION AND STANDARDISATION OF SOLUTIONS OF CERIC SULPHATE.—Meyer and Aufrecht (*Ber.*, 1904, 37, 140) have shown that ceric oxide, when treated with concentrated sulphuric acid, is converted quantitatively into ceric sulphate without passing into solution. The product is, however, readily soluble in water, the liquid having a deep orange colour. In my experiments the solutions were prepared from ceric nitrate, the salt being heated with excess of concentrated sulphuric acid in an evaporating dish, with frequent stirring, until qualitative tests showed the complete elimination of nitric acid. The resulting product, containing free sulphuric acid, was then diluted with water, and, after attaining a steady temperature, standardised with reference to its available oxygen. It was found that solutions of ceric sulphate of the order of  $N/10$  concentration could be readily prepared by treating 25 grms. of ceric nitrate with concentrated sulphuric acid in this way, and diluting the resulting aqueous solution to 500 c.c.

The available oxygen in such a solution may be standardised by reaction with various suitable reducing agents, such as ferrous ammonium sulphate. If this salt is used, the end-point of the reaction can be determined in the usual way with potassium ferricyanide as an external indicator, or, more conveniently, with a few drops of a 1 per cent. solution of diphenylamine in concentrated sulphuric acid as an internal indicator. In any case, as in all volumetric work,

it is very desirable to standardise the reagent under conditions as similar as possible to those in which it is to be employed.

OXIDATION OF FERROCYANIDES.—This reaction takes place readily at the ordinary temperature, the end-point of the reaction being determined accurately by means of diphenylamine sulphate:



The following results may be quoted by way of illustration.

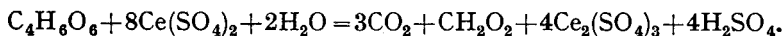
The concentration of a solution of sodium ferrocyanide was determined in the first instance by a standard solution of potassium permanganate containing 0.769 grm. of available oxygen per litre.

Fifty c.c. of the ferrocyanide solution required 33.75 c.c. of the potassium permanganate solution, and hence contained 19.6 grms. of sodium ferrocyanide (calculated as anhydrous salt) per litre.

Fifty c.c. of the ferrocyanide solution, diluted to about 300 c.c. and containing a few drops of a 1 per cent. solution of diphenylamine in concentrated sulphuric acid, required 28.55 c.c. of a solution of ceric sulphate. Thus the ceric sulphate solution contained 0.909 grm. of available oxygen per litre, and the sodium ferrocyanide solution contained 19.7 grms. of the salt (anhydrous) per litre.

In another experiment, in which a solution of ceric sulphate containing 0.844 grm. of available oxygen per litre was used, 50 c.c. of the sodium ferrocyanide solution required 30.75 c.c. of ceric sulphate. The calculated value of the concentration was identical with that of the previous experiment, *viz.* 19.7 grms. of sodium ferrocyanide per litre.

OXIDATION OF TARTRATES.—Benrath and Ruland (*loc. cit.*) studied the oxidation of tartaric acid by ceric sulphate in hot aqueous solution, and concluded that the reaction, which proceeds somewhat slowly, takes place as follows:—



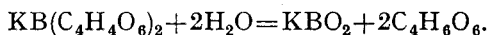
One molecule of tartaric acid requires, therefore, four atoms of available oxygen for conversion into carbon dioxide and formic acid, the latter resisting further oxidation. In my experiments the reaction was found to proceed somewhat differently, two molecules of tartaric acid requiring seven atoms of available oxygen, thus:



A solution of tartaric acid, containing 2.31 grms. of the acid per litre, as determined by titration with standard sodium hydroxide (phenolphthalein as indicator), was titrated with a solution of ceric sulphate containing 0.956 grm. of available oxygen per litre, 25 c.c. of the tartaric acid solution reacting with 22.6 c.c. of the ceric sulphate solution. From these numbers it follows that one molecular proportion of tartaric acid requires 3.51 atomic proportions of available oxygen.

This reaction was applied to determine the reacting weight of a potassium borotartrate,  $\text{KB}(\text{C}_4\text{H}_4\text{O}_6)_2$ , recently prepared by Professor Lowry (unpublished

observation). The calculated molecular weight of the compound is 346, and the aqueous solution is acid in consequence of hydrolysis:



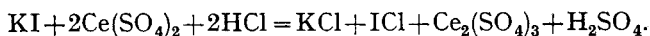
When titrated with *N*/10 sodium hydroxide solution, with phenolphthalein as indicator in presence of mannitol, an equivalent weight of 88.4 was found. With methyl red as indicator without mannitol, a value of 122 was determined for the equivalent weight.

A solution containing 8.842 grms. of the salt per litre was titrated with a solution of ceric sulphate corresponding to 0.956 gm. of available oxygen per litre. Twenty c.c. of the potassium borotartrate solution reacted with 62.5 c.c. of ceric sulphate. Assuming that one molecular proportion of the salt requires seven atomic proportions of available oxygen for oxidation by ceric sulphate, the value found for the molecular weight was 332.

ANALYSIS OF THALLOUS SALTS.—Under ordinary conditions ceric sulphate is without action upon dilute aqueous solutions of thalious salts. In the presence of a very high concentration of hydrochloric acid, however, the ceric salt acts like potassium iodate (Berry, *ANALYST*, 1926, 51, 137), and quantitative oxidation to the thallic condition can be realised.

In order to apply this reaction to the determination of thalious salts, a solution of iodine in chloroform is converted quantitatively into iodine monochloride to furnish a means for determining the end-point. A few c.c. of a dilute solution of iodine in chloroform are placed in a stoppered bottle, about 50 c.c. of concentrated hydrochloric acid (free from traces of chlorine) are added, and the solution of ceric sulphate delivered cautiously from a burette, with frequent shaking, until the violet colour of the chloroform just vanishes. A measured volume of the solution of the thalious salt is then added to the liquid, and the standard solution of ceric sulphate run in, again with frequent shaking, until the chloroform is once more rendered colourless.

A solution of ceric sulphate for determining thalious salts must be standardised in the way in which it is to be used, and not as, for example, in the titration of ferrocyanides with diphenylamine as indicator, as otherwise errors of the order of two or three per cent. may be involved. Standardisation can, however, be readily effected by oxidising a solution of potassium iodide of known concentration to iodine monochloride, thus:



Twenty c.c. of a solution of potassium iodide, containing 7.042 grms. of the salt per litre, required 18.7 c.c. of a solution of ceric sulphate. The concentration of the solution of ceric sulphate, in terms of available oxygen, was 0.819 gm. of available oxygen per litre.

A solution of thalious sulphate containing 30 grms. of the salt per litre, as determined by direct titration with potassium iodate, was titrated with ceric sulphate in the manner described, 10 c.c. of the thalious sulphate solution requiring

23.3 c.c. of ceric sulphate for complete oxidation. From this experiment it follows that the concentration of the solution was 30.05 grms. of thallos sulphate per litre.

THALLIUM TRI-IODIDE (compare Berry and Lowry, *J. Chem. Soc.*, 1928, p. 1748.)—When 0.342 gm. of the compound was titrated with ceric sulphate, as described above, the calculated weight was 0.349 gm. With the use of potassium iodate, 0.261 gm. of the compound gave a titration value of 0.264 gm.

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(GOLDSMITHS' METALLURGICAL DEPARTMENT),  
UNIVERSITY OF CAMBRIDGE.

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## Notes.

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

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### THE DETERMINATION OF COBALT IN DRIERS, JAPANS, ALLOYS, ETC.

THE following method is generally useful and time-saving where cobalt is to be determined in the presence of a large number of other metals, as is often the case with the inorganic constituents of varnishes and japans, especially those which have been extracted by organic solvents from the pigment.\* The results obtained by the nitroso-beta-naphthol method are as unsatisfactory as those given by Carnot's method (precipitation by means of ammonium molybdate as ammonium cobaltic molybdate). In order to isolate cobalt quantitatively the author succeeded in making the well-known qualitative cobalt test devised by Vogel, quantitative. A solution containing cobalt, nickel, iron, aluminium, chromium, manganese, zinc, tin, lead, copper, titanium, and vanadium was used.

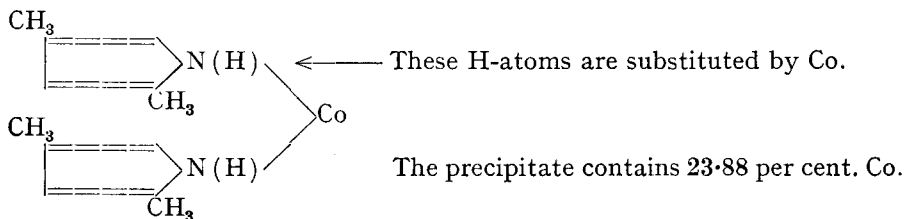
PROCEDURE.—The weak hydrochloric acid solution of the metals is made by treating the ash of the japan, etc., with hydrochloric acid, or, better, by oxidising 10 grms. of the material in a tall beaker or an Erlenmeyer flask by means of about 40 c.c. of sulphuric acid and 20 c.c. of hydrogen peroxide (30 per cent.). After the violent reaction has ceased the excess of water is driven off by boiling until white fumes of sulphuric acid begin to develop. After cooling somewhat, 20 c.c. of hydrogen peroxide are again added, and the mixture treated as before. When the dark liquid has finally become light in colour, indicating the absence of organic matter, the bulk of the sulphuric acid is driven off. After cooling and diluting, ammonia solution and then hydrochloric acid, each in slight excess, are added. If the other metals are also to be determined, the solution is made up in a volumetric flask. To the weak hydrochloric acid solution pure zinc oxide is added at 50° C. in very small quantities until only a visible trace of zinc oxide remains undissolved.† (Even a small excess of zinc oxide will precipitate a little cobalt.) The precipitate is filtered off, and washed with warm water. (It may contain

\* In this case there are sometimes quite appreciable amounts of metals (which originally belong to the pigment) extracted in the form of their soaps.

iron aluminium, chromium, copper, vanadium, titanium (and lead, partly.) If properly treated with zinc oxide the precipitate should give a negative "Vogel" reaction for cobalt, which is sensitive to 0.00002 grm. The filtrate may contain cobalt, nickel, manganese, and some of the lead. It is concentrated to a volume of about 20 c.c. and transferred, with several portions of water, quantitatively, to a separating funnel, so that the total volume is not more than 50 c.c. About 30 grms. of ammonium thiocyanate are added and dissolved.

The solution is shaken out with a mixture of ether and amyl alcohol (9:1) until exhausted.† (A Rothe extractor serves better.) The ethereal solution is shaken with 15 to 20 c.c. of dilute (10 per cent.) sulphuric acid and washed several times with water. The excess of water is evaporated from the aqueous solution, and the remainder is neutralised with ammonia and then electrolysed. Or the solution is made alkaline, while hot, with sodium hydroxide, and the precipitate is filtered off, washed very thoroughly with boiling water, ashed and weighed as cobalt oxide.

It is also possible to determine the cobalt, since it is the only metal in solution, by means of its 3, 5-dimethyl-pyrazol compound, as shown recently in the Siemens Laboratory in Berlin. A 2 per cent. solution of this specific cobalt reagent is poured (cold) into the cobalt solution which has previously been rendered nearly neutral with sodium hydroxide. It should still be faintly acid. Then about 5 c.c. of 0.5 N sodium hydroxide solution are added, whereupon all the cobalt settles out as a beautiful purple precipitate, which is analogous to nickel dimethyl-glyoxime. It is filtered off, washed with cold water, and dried in a Gooch crucible at as low a temperature as possible.



NEW YORK.

OSCAR HEIM.

† If no Fe is present, add a few drops of 10 per cent. FeCl<sub>3</sub> solution.

‡ This is indicated by the disappearance of the blue colour of the ammonium cobaltous thiocyanate.

## Notes from the Reports of Public Analysts.

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

### COUNTY OF LANCASTER.

ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1928.

DURING the year the total number of samples examined was 5395, of which 4933 were Food and Drugs samples (146, or 3.0 per cent. adulterated).

**INFORMAL SAMPLES.**—There appears to be an idea in the minds of some that “Informal” samples need less care and trouble bestowed upon their analyses than “Formal” samples. Indeed, a memorandum sent out by the Local Government Board in 1914 contained the following words: “The Board understands that, with a view to preliminary investigation ‘Informal’ samples have been collected in some districts for examination, by rough sorting methods only, by the Public Analyst or by some other person.” It is difficult to see how “the use of rough sorting methods . . . by some other person” can have the slightest advantage to anyone. The days have long gone by when the application of rough sorting methods is sufficient to detect adulteration. Even if the use of rough sorting methods is sometimes permissible in the hands of experienced persons, it is obviously highly improper for there to be the slightest possibility of their being undertaken by persons without knowledge, ability or experience.

**MILK.**—Of the 2771 samples examined, 95 (3·4 per cent.) were returned as adulterated. This figure is much less than that for the whole of England and Wales, which was 6·9 per cent. in 1927, and is very good as compared with the majority of other areas. It should be pointed out, however, that the public analysts for some areas describe as adulterated any sample of milk of which the percentage of solids-not-fat falls below 8·5 per cent. or the percentage of fat below 3·0 per cent., no matter how small the deficiency may be. Other public analysts ignore deficiencies of less than 0·1 per cent., whilst others do not report against a sample unless it is at least 0·2 per cent. below the limit laid down.

Sound arguments can be brought forward for all these methods of treatment; in fact, it does not seem possible to lay down any hard and fast rule, as special circumstances may affect any one particular sample.

**“APPEAL TO COW” SAMPLES.**—As was pointed out in the Report for 1927, the figures as to the percentage adulteration of milk will not agree with those given in the Annual Report of the Ministry of Health, owing to the fact that the Ministry include “Appeal to cow” samples whose composition is below the minimum limits, whilst they are not included here. In their own Memorandum the Ministry have asked that “Appeal to cow” samples should be excluded from the main tabular statement, and that only such “Appeal to cow” samples as are taken under the provisions of the Milk and Dairies (Consolidation) Act, 1915, should be so included.

It is difficult to see, however, how any “Appeal to cow” sample, if properly taken and properly supervised, can be classed as adulterated. No matter how improper many think it to be, it is undoubtedly quite legal to sell milk below the limits laid down by the Sale of Milk Regulations, 1901, provided that the milk is in exactly the same condition as it was when it came from the cow. If, therefore, it is permissible to describe as adulterated an “Appeal to cow” sample which is below the limits, we are forced into the anomalous position that it is legal to sell an adulterated article.

It is surely better on all grounds to continue along the lines originally suggested by the Ministry.

**AVERAGE COMPOSITION OF MILK.**—The average fat content of the whole of the milks examined, including “Appeal to the cow” samples, was 3·74 per cent., whilst the solids-not-fat showed 8·90 per cent. The average composition of the milks examined from 1916 to 1928 was: Fat, 3·68 per cent.; solids-not-fat, 8·93 per cent.

The following table shows the average composition of all milk samples in some other districts:

District.	Years.	No. of samples.	Fat per cent.	Solids-not-fat per cent.
Birmingham City	1923-1926	10,215	3.64	8.74
Bolton C.B. ..	1920-1926	1,483	3.61	8.87
Durham County	1917-1926	4,078	3.61	8.64
Hull City ..	1923-1927	2,461	3.70	8.78
Lancaster County	1913-1928	45,370	3.67	8.91
Liverpool City ..	1923-1926	15,375	3.60	8.83
Salford City ..	1915-1925	8,437	3.62	8.85
Stepney Borough	1924-1927	3,400	3.67	8.70
*Somerset ..	1924-1927	36,985	3.72	8.87
*Dorset .. ..	1924-1927	51,623	3.74	8.88

\* These figures have been obtained from the Laboratory of the West Surrey Central Dairy Co. Ltd., and have been supplied by the courtesy of their chief chemist, Mr. J. Tavroges.

Taking the whole of the samples in the above table, which amount to 179,427, the total average is 3.69 per cent. of fat and 8.86 per cent. of solids-not-fat.

Although the average amount of fat in these samples is thus well above the 3.0 per cent. limit, it has been claimed on many occasions that the percentage of fat is seriously diminished during the season when the cows are first put out to grass, diminished so seriously, in fact, that a considerable number, if not the majority of herds, will be giving milk containing less than 3 per cent. of fat.

This is not borne out by a consideration of the average composition of milks for each month from 1913 to 1928 in the County of Lancaster. These figures show that whilst the average percentage of fat for the whole period is 3.67, the total monthly variation ranges from 3.55 to 3.86 per cent. These figures are very similar to those obtained in Somerset, Dorset, Durham, and Salford, and to Richmond's figures.

It may be argued that natural milks of poor quality are very common, and that average figures therefore mean very little, but those who have any experience of milk statistics know that the percentage of herds giving mixed milk below the limits of the milk regulations is quite small.

An analysis of the figures of the milks supplied by 25,000 herds in the County of Lancaster over a period of 9 years has shown that less than 1 per cent. have given milks of lower quality than 3.0 per cent. of fat, and 8.5 per cent. of solids-not-fat. Even those "Appeal to cow" samples which were actually deficient were, as a general rule, only slightly deficient, in many cases so slightly deficient that no Public Analyst would dream of issuing a certificate for prosecution.

In view of these figures and these facts, it is difficult to fix at its true value the following sentence which has lately appeared in a Scottish journal: ". . . we have an unending succession of scandalous milk prosecutions." It is difficult, if not impossible, to put into official form in a report of this kind the impression that one gets of the methods of those who use this kind of language, but it should be remembered that miscarriages of justice are not always on the side of convictions.

The evidence is available for all those who wish to come to an unbiased conclusion on the whole matter. In view, however, of the repeated publicity of such statements, it may be desirable to indicate the methods which are adopted by the County Council of Lancaster, to avoid, as far as is humanly possible, any miscarriage of justice. When a sample of milk is found to be deficient either in fat or in solids-not-fat, an "Appeal to cow" sample is immediately taken. Every effort is made to take this within 48 hours, although sometimes, on account of distance,

this time has to be somewhat exceeded, but in all cases every reasonable effort is made to have the sample taken as soon as possible. When the results of the "Appeal to cow" sample have been obtained, they are carefully compared with those of the original sample. Where the "Appeal to cow" sample is of approximately the same composition as the original sample, no prosecution is instituted.

In order that a genuine milk considerably below the limits of 3.0 per cent. for fat or 8.5 per cent. for solids-not-fat shall be unjustly accused of being tampered with, two unlikely things must happen at the same time. These two improbabilities are, firstly, that a genuine milk shall have a composition below the legal limits; and, secondly, that having this composition it shall improve so considerably in two days as to suggest that it is not the same milk. It must also be remembered that for a realisation of these unlikely happenings to be a means of embarrassment to the defence they must take place on the very days that the samples are being taken for the prosecution. The possibility of two unlikely happenings occurring in the correct order on two particular days is somewhat remote.

Proceedings may be instituted on any sample the composition of which is below that of the Sale of Milk Regulations, but in practice such proceedings are only commenced when there is certainly a very strong case to answer. Even in these circumstances, however, the defence have their opportunity, and magistrates are quite rightly inclined to the side of the defendant until they are assured that he is guilty.

**PEARL BARLEY.**—A sample was coated with 0.2 per cent. of mineral facing. Whatever opinions may be held as to the desirability of treating rice in this way, it must be held to be objectionable in the case of pearl barley, which is used in considerable quantities in the preparation of barley water for invalids. The vendor was cautioned.

**CREAM CAKES.**—Eleven samples contained "cream" composed of an emulsion of margarine and sugar, but no legal proceedings were instituted, as it is desired to arrive at some conclusion as to the nature of the article which a purchaser of a "cream cake" is entitled to expect. In my opinion the expression is not a generic term synonymous with "fancy cake," but is a descriptive term showing that cream enters into the composition of the article.

**MAGNESIA.**—A sample of magnesia was found to consist of magnesium carbonate. In the British Pharmacopoeia the term "Magnesia" is applied to magnesium oxide, but there is some evidence that the term is popularly applied to the carbonate. Thus the B.P. Codex states: "It was the practice to refer to the carbonates as magnesia and the oxides as calcined magnesia. The practice when 'magnesia' is asked for is not uniform. In the majority of cases what is intended and supplied is the light carbonate." In these circumstances the sample was passed as genuine, but a state of affairs in which either of two substances may be supplied under the same name is obviously most undesirable, and some definite official ruling is required.

G. D. ELSDON.

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## Legal Notes.

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

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### CAFFEINE-FREE COFFEE.

On April 24, a trading company was summoned at Bow Street Police Court for applying to coffee a false trade description, and a retail tradesman was summoned for selling the coffee. The label on the tin stated: "P.R. Coffee. Practically caffeine-free, 100 ounces (representing 100 parts of liquid) containing 1-100th part of an ounce of caffeine."

According to the prosecution the P.R. ("physical regeneration") coffee contained 3.37 to 3.7 grains of caffeine per ounce, or more than one hundred times that given on the label.

Mr. J. K. Colwell, Public Analyst for Holborn, said that the amount of caffeine in the coffee, viz. 1.02 per cent., was rather below the average (1.2 per cent.), but there was nothing to suggest that it was not pure coffee, except the statement on the label.

Counsel for the second defendant (the retailer) argued that his client had no reason to suspect that there was anything wrong with "P.R." coffee, and he relied on the warranty of the first defendant.

To this, counsel for the prosecution (Mr. Wishart) replied that a warranty was no protection under the Merchandise Marks Act. The retailer should have procured a certificate of analysis from the wholesaler or have had the coffee analysed himself; otherwise he should not sell goods under a trade description. However, he did not press the case against the retailer, and would be satisfied if the summons were dismissed on payment of costs.

At the adjourned hearing, on May 8, the Magistrate (Mr. Graham Campbell) dismissed the summons against the retailer, without costs, and agreed to an adjournment for the completion of analysis for the defence in the case of the other defendant.

On June 12, evidence was given by Mr. J. B. Coppock that free caffeine might have been found in the coffee, but that the analyst would have to obtain it from caffeine chlorogenate, the properties of which were entirely different from those of ordinary caffeine salts.

The Magistrate said that he was not satisfied that the prosecution had made out their case. The statement on the tins was that the coffee was pale roasted, and was shown by analysis to be practically caffeine-free. The defence contended that this meant that the word "caffeine" must be taken to mean "free caffeine," and not caffeine in combination with other substances. The evidence of the analysts for the prosecution showed that in order to obtain free caffeine they had had to break down the compound. There was always more free caffeine in dark roasted coffee than in pale roasted coffee, so that it was correct to say that there was less caffeine in the coffee in question than in most other kinds. The summons would be dismissed, but without costs, since the nature of the defence was not disclosed until after several adjournments.

## OBLITERATING ORIGIN MARKS FROM EGGS.

ON May 16 three tradesmen were summoned at Brighton for removing or obliterating an indication of origin on certain eggs, contrary to the Merchandise Marks Act, 1906.

Evidence was given by an inspector that, on visiting the warehouse of one of the defendants, he saw a crate containing several hundreds of imported eggs bearing the importation mark of Belgium printed in blue. Near the crate were two pails, one containing water and the other water to which commercial sulphuric acid had been added. One of the defendants was taking eggs from the crate of marked eggs and washing them in the pail containing sulphuric acid, from which they were transferred to the bucket of clean water, near which another of the defendants was standing, so that he could take the washed eggs out and dry them. At the back was a crate containing unmarked English eggs, and another box containing eggs similar to those which had just been washed.

The solicitor for the defence submitted that his clients were fairly entitled to the presumption that the marks on the eggs were washed off accidentally and would have been replaced.

The Magistrates found that there was insufficient evidence against one of the defendants, and dismissed the case against him. The other defendants were fined £5 and £2 respectively.

## TINCTURE OF IODINE AND SOLUTION OF IODINE.

ON June 13, a trading company was summoned at Ealing Petty Sessions for having sold at their Uxbridge branch a compounded drug, tincture of iodine, not composed of ingredients in accordance with the demand of the purchaser.

Mr. R. A. Robinson, chief officer, Public Control Department, Middlesex County Council, stated that the defendants had exhibited on the counter of their shop cartons labelled "Tincture of Iodine, B.P." and also a full half-bottle similarly labelled. An inspector pointed to the cartons, and asked for tincture of iodine. What should have been supplied was weak tincture of iodine, B.P., containing 2.5 per cent. of free iodine and 2.5 per cent. of potassium iodide, with a trace of water, in 90 per cent. rectified spirit. What was sold was a solution containing only 0.66 per cent. of free iodine in isopropyl alcohol, and no potassium iodide—a cheap substitute for the official tincture. The cartons and bottles containing this article were of the same size and appearance as those containing the genuine tincture, except that the label bore the word "iodine" in large letters and the word "solution" in small letters, instead of the words "tincture of iodine, B.P."

There were several High Court cases establishing the authority of the B.P.; here it gave not only the formula, but also an official test for the amount of iodine. The cost of the genuine tincture was about 8s. per pint, and that of the substituted article between 2s. 6d. and 3s. 3d., according to the percentage strength of the iso-propyl alcohol. This alcohol was regarded as not fit to drink, and was therefore non-excisable. The manager of the shop had told the inspector that he did not know that there was any difference between the two articles, and did not know why the labels were dissimilar. An official drug should not be of one strength one day, and a quarter of that strength on another day, or on the same day.

Mr. F. J. Dyer, B.Sc., A.I.C., said that a pharmacist would always sell Tinct. Iodi. Mit., B.P., when asked for tincture of iodine, or even for a "bottle of iodine." There was no official recognition of such a preparation in any official pharmacopoeia

—nor of any tincture weaker than Tr. Iodi. Mit., B.P. Free iodine was the most important constituent. Potassium iodide was also necessary to keep the iodine in a free state. Combined iodine would not be efficacious.

In cross-examination, the witness agreed that "Martindale's Extra Pharmacopoeia" recommended a solution of iodine in isopropyl alcohol; also that the use of such a solution containing 1.25 per cent. of iodine was recommended in *The Lancet* (1928, Sept. 1, p. 443) as "an external antiseptic for hospital use." Re-examined, he said that "Martindale's Extra Pharmacopoeia" was in no sense an official book, nor had it statutory authority. The *Lancet* article only recommended the solution for external skin asepsis.

Mr. G. Beyfus, for the defence, said that his clients had by accident committed a technical offence. Last year they had sold the B.P. tincture, but in August the Customs and Excise Department raised the question that the tincture should not be sold without a spirit licence. In consequence, they had substituted a 1.25 per cent. solution of iodine in isopropyl alcohol, as recommended in the *Lancet* article. In February communications were received from the Birmingham Health Department, by whom it had been found that the preparation lost strength on keeping. To prevent this, potassium iodide was added. The isopropyl alcohol used was of 90 per cent., instead of 70 per cent. strength as recommended in the *Lancet*. His clients made virtually no extra profit—only one-twelfth of a penny per bottle. It was an unfortunate accident that all of the original bottles had not been disposed of before April.

A representative of the manufacturers said that he had advised the defendants to use the isopropyl solution, owing to the objection of the Excise authorities to their selling the tincture. The defendants had been charged 3s. 6d. per dozen half-ounce bottles of the tincture, and 3s. 5d. for the same quantity of the solution.

Dr. H. E. Cox, F.I.C., said that he had analysed part of the official sample, and had found it to contain 0.67 per cent. of free iodine and also 0.53 per cent. of combined iodine. The compounds formed would include a small percentage of hydriodic acid, and probably some di-iodo-isopropyl compound.

The Bench said that they considered that the defendants had been negligent, but not deliberately fraudulent. They imposed a fine of 40s., with 10 guineas costs.

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## Department of Scientific and Industrial Research.

### FUEL RESEARCH. Technical Paper No. 22.

#### THE REACTIVITY OF COKE (2).\*

THE method used for determining the reactivity of the cokes is based on the reaction  $\text{CO}_2 + \text{C} = 2\text{CO}$ , the value recorded being the volume of carbon monoxide obtained from 100 ml. of carbon dioxide under standard conditions. The standard volume of coke is heated to 950° C. during 1 hour in a stream of nitrogen passing at the rate of 1 litre per hour. Conditions are then kept constant for one hour, and then 100 ml. of carbon dioxide are passed over the coke at a prescribed rate. The actual determination is then begun by passing another 100 ml. of carbon

\* *Examination of a Number of Metallurgical Cokes*, by J. H. Jones, J. G. King and F. S. Sinnatt. Obtainable at Adastral House, Kingsway, W.C.2. Price 1s. 0d. net.

dioxide over the coke and collecting the gases over a solution of potassium hydroxide. The volume in ml. of insoluble gases collected is Reactivity I, and is the closest approximation to the primary reactivity value of the coke that can be obtained under experimental conditions. When carbon dioxide is passed over coke kept at 950° C. the volume of carbon monoxide obtained from 100 ml. alters until such a condition is established that the volume obtained in successive determinations is practically constant. This is Reactivity III. Results were obtained for 78 cokes prepared from a variety of coals in different types of ovens, and these show that the cokes may be broadly classified by their reactivities according to the fields whence they were obtained. Shatter\* indices obtained for 50 of the cokes show that there is a rough agreement between these and the reactivity values, in that the higher the reactivity value the lower the resistance to shatter, but the relationship breaks down when extended to particular cases. So far there is little accurate information as to comparative behaviour of cokes in the blast furnace, so that at present it can only be said that the results of the investigation indicate that low reactivity is desirable, but that regularity of behaviour may be of greater importance. The effect of the ash on the reactivity of metallurgical cokes is being investigated, and the removal of certain inorganic constituents has already been found to influence the Reactivity I value. For example, the gradual removal of iron caused a gradual fall in Reactivity I.

D. G. H.

\* The Shatter indices were determined at the Fuel Research Station or at the laboratories of the Coke Research Committees, or were given by private companies. In all cases the index was recorded as the percentage of coke remaining on a 2-in. sieve after the test.

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## Ministry of Agriculture and Fisheries.

### “VARIATIONS IN THE COMPOSITION OF MILK.”

The Committee of Public Analysts of the Society of Public Analysis has sent the following letter to the Ministry:—

SIR,

The Committee of Public Analysts of the above Society has had under consideration Miscellaneous Publication No. 65, recently issued by the Ministry of Agriculture and Fisheries, and entitled “Variations in the Composition of Milk.”

The Committee is of opinion that the publication has the effect of giving a wrong impression of the composition of milk as produced in this country. Although the object of the publication may not be to undermine the Sale of Milk Regulations, 1901, and to question the validity of the principle of the “appeal to cow,” it cannot but tend to have this effect.

We make the following criticism of the data included in the publication and of the conclusions which might be drawn from them:—

We consider that although milk as drawn from the cow does at times fall below the limits contained in the Sale of Milk Regulations, the frequency of this occurrence is exaggerated. For instance, the table contained on page 4 would tend to indicate that 10 per cent. of the samples obtained from herds of cows in

this country would fall below 8·5 per cent. of solids-not-fat, and about 7 per cent. below 3 per cent. of fat. The statement at the foot of page 4 that this impression is not intended loses weight in view of the data quoted on page 5.

During last year, out of 63,000 samples of milk taken under the provisions of the Sale of Foods and Drugs Acts only 6·9 per cent. were returned as being not genuine, but these include not only samples watered or separated, but also those containing preservatives, dirt or added colouring matter. It is obvious that the proportion of naturally deficient samples must fall well below 6·9 per cent. In this connection the results published by Liverseege (*ANALYST*, 1926, 51, p. 295) may be considered. They show that during 21 years 216 farms were visited, all of which had been sending deficient milk to Birmingham. Of the 434 samples taken at these farms 20 per cent. were found to be deficient in solids-not-fat, and 3 per cent. to be deficient in fat. This suggests that only about one-fifth of the samples originally found to be deficient were so naturally, and about four-fifths either deliberately adulterated or deficient owing to improper milking or subsequent careless handling, etc. If this proportion were to hold with regard to the 63,000 samples quoted above, the percentage of samples deficient in one respect or the other from natural causes would only amount to 1·4 per cent. This figure is confirmed by results obtained elsewhere.

Allowance must also be made in public analysts' returns for the fact that the apparent percentage of adulteration is increased through the taking of more than one sample from the same source when milk has been found to be unsatisfactory.

There is nothing to warrant the assumption that between 7 and 8 per cent. of the milk churns delivered to Dairies A and B (see page 5) and found to be deficient in fat, or 5 per cent. low in solids-not-fat, were in fact naturally poor, and had not been adulterated. We are, therefore, of opinion that it would not be right to put forward the high proportion of deficient milks generally quoted in the report as truly representing the produce of herds in this country.

Prominence is given in the publication to milk of individual cows. On page 6, extreme examples are given, and the publication proceeds to say that "it is clear that the presence in mixed milk of any considerable proportion of milk of cows, such as this, will affect the quality of the mixed milk." It is unlikely that a considerable proportion of *extreme* cases would occur in one herd. The quality of milk given by an individual cow, especially when it represents an extreme example, so frequently quoted in the publication, is of no use when judging the average quality of milk yielded by a herd.

In the publication, as a rule, milks are classed as deficient, no matter how small the deficiency may have been. Very small deficiencies have but a slight bearing upon the validity of the Sale of Milk Regulations, as no prosecution would probably be instituted in such cases, though the Annual Report of the Local Government Board, 1911-12, contains the following instruction:—"Whether it is considered that legal proceedings should or should not be instituted in the case of apparently slight adulteration, it remains the duty of the analyst to class as "adulterated or not up to standard" all milk samples failing to reach the minimum limits fixed by the Regulations."

The publication invariably mentions solids-not-fat as an entity, and gives no indication that the composition of the solids-not-fat has received attention. We are confident that a more complete analysis of the solids-not-fat, at any rate in the more highly deficient milks, would have disclosed such abnormality that the presence of added water would not have been indicated.

The matter of day-to-day variation in the composition of milk becomes of great importance in connection with "appeal to cow" samples. On this question the publication is unsatisfying in the extreme. Two graphs are given showing

the variation in the case of single cows; for practical purposes these may be neglected. One graph showing the daily variation of the milk of one herd is quoted, but as all the figures given for solids-not-fat are above 8.5 per cent., with the exception of one (*viz.* 8.46), and all the figures are above 3 per cent. for fat, this graph has no bearing on the issue for which "appeal to cow" samples are taken. Yet, on page 18, the very wide conclusion is drawn that ordinary market milk may be expected to show even larger variations than 0.87 per cent. of solids-not-fat between one milking and the next, without any mention of the fact that all the results on which the conclusion is based were, as already stated, higher than the minimal limits. The publication may be held to record the conclusion of the Ministry that the measure which enables a vendor to have samples taken from the cow is of no utility, and with this we do not agree.

We feel that the efforts of the Ministry should be directed to encouraging farmers to produce a high quality of milk, rather than to render the position of the producer of good milk more difficult, and the more so because we realise the danger of developing strains of cows giving quantity of milk without any regard to quality.

The Committee considers the publication of Miscellaneous Publication No. 65 as unfortunate and inopportune. It gives prominence to the composition of exceptionally poor milk and thereby not merely throws doubt upon the adequacy of the present standards adopted for genuine milk, but may even encourage the production of milk of low quality. As the publication will, no doubt, be made use of in courts of law, the punishment of adulteration will be rendered more uncertain. The fact has not been considered that a public analyst does not merely determine the amounts of solids-not-fat in a low or doubtful milk, but he also determines the composition of the solids-not-fat, and this analysis weighs with him before reporting as to the genuineness or otherwise of a sample.

Though we are not, at the moment, in a position to challenge the accuracy of the published results, or the conditions under which the samples were taken, we think that in a document, such as this, bearing an inferred endorsement by the Ministry, the analytical results should in all cases have been conducted and vouched for by analysts of repute.

We are, sir, your obedient servants,

(Signed) E. HINKS (Chairman).

F. W. F. ARNAUD (Hon. Sec.)

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## United Provinces of Agra and Oudh and Central Provinces.

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR  
THE YEAR 1928.

THE Chemical Examiner (Mr. D. N. Chatterji) reports that 1797 cases were investigated during the year, as compared with 1573 in 1927. Of these, 1597 were medico-legal cases (1402 in 1927). Inspected human poisoning cases showed an increase from 468 to 509; cattle poisoning cases increased from 33 to 53; and stain cases from 881 to 1014.

POISONING CASES.—Poison was detected in 311 of the 1114 articles examined. The favourite poisons were arsenic (133 articles), opium (35), datura (74), copper sulphate (10); strychnine (7), potassium cyanide (4); mercury (7).

In the cattle poisoning cases arsenic was found in 29 cases, opium in 2, bhang (Indian hemp), yellow sulphide of arsenic, and mercury in 1 case each.

GHEE.—Forty-three samples were examined, as against 12 in the previous year. All except 9 were adulterated with animal or vegetable fats or with sesame oil.

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## Siam.

### REPORT OF THE GOVERNMENT LABORATORY.

THE Director of the Government Laboratory of Siam (Mr. A. Marcan, F.I.C.), in his 4th Report to the Ministry of Commerce and Communications, covers the period from April 1st, 1926, to March 31st, 1928.

The analysis of opium dross is the only branch of the work which may be designated as repetition work, and even here it is of interest to note that some adulterated drosses defy the usual methods of morphine determination, owing to the addition of a protective colloid.

Reports on materials of interest included the following:—

HYDNOCARPUS ILICIFOLIA OIL.—The trees grow extensively in Siam. A sample of the dried kernels yielded 36.1 per cent. of crude oil on extraction with ether. Two samples of cold-pressed oil gave the following values: Acidity (as oleic acid), 21.0 and 0.6 per cent.; sp. gr. at 30°/4° C., 0.944 and 0.947; saponification value, 203.6 and 213.1; iodine value (Wijs), 89.7 and 89.7; specific rotation,  $[\alpha]_D^{20}$ , 52.7 and 51.2;  $n_D^{20}$ , 1.4739 and 1.4763; m.pt. 25.8° to 32.6° C., and 23.0° to 28.2° C. The oils and the esters prepared from them were very similar to those from *Hydnocarpus anthelmintica*. Clinical tests are in progress in the Leprosy Research Laboratory, Calcutta.

KRATOM EATING.—Kratom leaves from *Mitragyne speciosa* are much used for chewing in Peninsular Siam and, to a small extent, in Bangkok. Investigations of the physiological action of the alkaloid, mitragynine, are still in progress. According to the reports of the officials of the Revenue Department the chewing of kratom leaves is habit-forming. Addicts appear to be able to endure great fatigue and exposure to heat. The habit has not a bad reputation, like opium smoking, nor does there seem to be any progressive change in the condition of the addict or in his character. On the other hand, educated people avoid the habit. Habitual eaters are thin, having unhealthy complexions and dark lips. No immunity from malaria is conferred. A fresh leaf weighs on the average 1.7 grms., and 0.43 gm. when dry, and contains about 0.2 per cent. of mitragynine; other alkaloids appear to be present. When an excess of the leaves is eaten vomiting and dizziness are produced; numbness of the body, twitching of the hands and feet, and an effect on the heart have also been reported. From 10 to 30 leaves are usually taken from 3 to 10 times a day, and water is drunk after chewing.

CURCAS OIL.—Oil extracted from the seeds of *Jatropha curcas*, which is grown as a hedge plant in Siam, gave the following values: Sp. gr. at 15.5° C., 0.923;  $n_D^{20}$ , 1.4623; saponification value, 202.9; iodine value (Wijs), 98.2; and acidity

(as oleic acid), 12.4 per cent. The oil is thus similar to the commercial oil from other countries, except that it has a high acidity.

**TOXICOLOGICAL EXAMINATIONS.**—Fifty-four exhibits (representing 33 cases) were examined for poisons, and 26 of these were found to contain them (16 cases). Arsenic was found in 16 articles, apomorphine in 1 viscera, atropine in 1 drug, calomel in 1 horse dope, copper in 1 viscera, morphine in 1 drug, and strychnine in 1 drug and 1 viscera.

A poisonous fish, identified as a species of *Tetraodon* (globe fish) was a new-comer in the list of poisons. In one case a soldier died 3 hours after eating the fish. In another case the gall bladder of the fish was mixed with the juice of *Excoecaria agallocha*, and a *Croton tiglium* seed, and added to water. Two children died, and two adults recovered. It is reported that in Kelantan the gall bladder of a species of *Tetraodon* is used as a poison, and is frequently mixed with Upas Sap or intestinal irritants.

Some of the above cases may well make the toxicologist in the tropics ponder as to how far and how often the criminal is ahead of him. A glance at such a work as Gimlette's "Malay Poisons and Charm Cures" will show that many poisons are in use which find no place in systematic toxicology. In the East the criminal has all the resources of the jungle at his disposal, including many plants of which the active principles have not been investigated. In the West, the poisoner, as a rule, has to depend on what refined active drugs he can purchase, which limits his powers for evil to a great extent. The situation is worthy of consideration by those with time and facilities at their disposal for toxicological research.

**DEPARTMENT OF PUBLIC HEALTH.**—Pickled shellfish (apparently mussels) submitted as causing illness, were examined for arsenic, as mussels in Europe have been found to contain up to 119 parts of arsenious oxide per million. This exhibit only contained 0.5 part of arsenic ( $As_2O_3$ ) per million.

*Chenopodium Oil.*—A sample of mixed chenopodium oil (2 vols.) and carbon tetrachloride (3 vols.) for hookworm treatment, stored for one year, was submitted for examination for toxicity. The separated carbon tetrachloride was found to conform to the stringent standards of purity for internal use. No hydrolysis of the carbon tetrachloride had taken place, but, as ascaridole decomposes at low temperatures when diluted with volatile indifferent solvents (Henry and Paget, *J. Chem. Soc.*, 119, 1722), it appears preferable to store the two drugs unmixed. Any decomposition of the ascaridole would probably reduce the toxicity of the chenopodium oil, and also its value as an anthelmintic.

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## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

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### Food and Drugs Analysis.

**Detection of Apple and other Fruit Juices in Wine.** J. Werder. (*Ann. Falsif.*, 1929, 22, 260-261.)—Sorbitol is present in Sorb fruits and in nearly all *Rosaceae* fruits, but not in grapes. It combines with 2 volumes of benzaldehyde to form the insoluble amorphous white compound, dibenzal-sorbitol. In order



to detect it, 7 grms. of pure animal charcoal are added to 100 c.c. of the liquor, fermented as completely as possible, and the boiled liquid is filtered hot, placed in a 300 c.c. distilling flask, carrying a capillary tube through its cork, reaching to the bottom of the flask, and closed by rubber tubing and a pinch cock. The side-arm is connected with a vacuum pump, and the solution is concentrated on a water-bath under reduced pressure until it becomes strongly viscous. The vacuum is maintained until room temperature is reached, when 4 drops of benzaldehyde and 1 c.c. of 1:1 sulphuric acid are added, and, after shaking, the flask is left overnight. If 10 per cent. or more of fruit juice are present, the mass will be solid, but with pure wine it will be liquid. Water (100 c.c.) is added, little by little, and with constant shaking, when the insoluble dibenzal-sorbitol will be precipitated as white flakes. The product of pure wine is soluble, although a slight precipitate is sometimes present. If the results are doubtful, the test is repeated with 200–300 c.c. of wine, and the nature of the precipitate determined by Foch's method, whereby the dibenzal sorbitol is transformed into the easily crystallisable hex-acetylated sorbitol. A blank test should be made with a pure wine of the same district, and also a test made with the wine to which 10 per cent. of cider has been added. (Cf. ANALYST, 1929, 422.)

D. G. H.

**Palm Oil from the Belgian Congo.** G. S. Jamieson and R. S. McKinney. (*Oil and Fat Ind.*, 1929, 6, 15–17.)—This oil, from Port Maladi, gave the following values: Sp. gr. at 25°/25°, 0.9146;  $n_D^{40}$ , 1.4578; acid value, 20.6; saponification value, 197.9; unsaponifiable matter, 0.39 per cent.; iodine value (Hanus), 53.7; acetyl value (Andrè-Cook), 15.3; Reichert-Meissl value, 0.10; Polenske value, 0.29; saturated acids (corrected), 44.3 per cent.; unsaturated acids (corrected), 50.6 per cent.; iodine number of unsaturated acids, 99.9. The percentages of the different glycerides present were: Oleic, 47.2; linolic, 5.6; myristic, 0.5; palmitic, 40.8; stearic, 5.2; lignoceric, 0.1. This is the first indication of the presence of lignoceric acid in palm oil.

T. H. P.

**Composition of Gum Arabic.** C. L. Butler and L. H. Cretcher. (*J. Amer. Chem. Soc.*, 1929, 51, 1519–1525.)—A botanically authentic sample of gum arabic Cordofan from *Acacia Senegal* (L.) Willd. was hydrolysed for 20 hours with 2 per cent. sulphuric acid, and the salt obtained by treatment with calcium carbonate was purified by precipitation with methyl alcohol. Analysis indicated 28.3 per cent. of an aldobionic acid,  $C_{12}H_{20}O_{12}$ , identical with O'Sullivan's  $\lambda$ -arabinosic acid. This was confirmed by the percentage of carbon dioxide liberated on boiling with 12 per cent. hydrochloric acid, from the calcium content, and from the iodine required for oxidation. By removal of the calcium as oxalate a mixture of aldobionic acid and its lactone was obtained. The sugar constituent of the acid had the rotation of *d*-galactose, and yielded mucic acid on oxidation. Since simultaneous oxidation and hydrolysis of the acid by boiling with hydrobromic acid in the presence of bromine (Goebel, *J. Biol. Chem.*, 1927, 74, 619) produced saccharic acid, it is concluded that the acid is a galactoso-glucuronic acid which retains its uronic acid residue intact after oxidation, the linkage being between

the aldehyde group of the glucuronic acid and a hydroxyl group of the galactose. Such types of compound have hitherto been found only in products of bacterial metabolism. The sugar fraction of the hydrolysis product was shown to contain *d*-galactose (29.5 per cent. of the ash-free arabic acid), *l*-arabinose (34.4 per cent.) and methyl pentose (14.2 per cent. as rhamnose hydrate). Titration of arabic acid in hot and cold solution showed it to exist as lactone to the extent of about 22 per cent., and indicated an equivalent weight of 1030. J. G.

**Method of Identification and Determination of the Value of Rhubarbs, based on Fluorescence. Maheu.** (*Ann. Chim. Anal.*, 1929, 11, 165-168.)—

For some time a new variety of rhubarb from Asia has been in the market, sometimes under the name of "Indian rhubarb." It has been examined under ultra-violet rays to see if it has the properties of true rhubarb or of rhapontic (bastard monk's rhubarb); it gave the rhapontic reactions in most cases. The author has now made a systematic study of the action of ultra-violet rays from a mercury vapour lamp on rhapontics and on rhubarbs, on the drugs themselves, their powders, and on pharmaceutical preparations (tinctures, extracts) which are derived from them. The results show that all true officinal rhubarbs give a velvety brown red fluorescence under ultra-violet light. European rhubarbs are produced by three or four species of *Rheum*: *R. rhaponticum*, *R. undulatum*, *R. emodi*, *R. compactum*. All these species are Asiatic, imported into Europe and cultivated in England, Austria, Russia and France. Of these, *R. emodi* gives a velvety brown red fluorescence, identical with that given by the officinal types; Austrian rhubarb (from *R. undulatum*) gives a deep violet fluorescence, and French rhubarb (from *R. rhaponticum*) gives a very clear violet fluorescence. The powders which correspond to these rhizomes show the same macroscopic signs of fluorescence. Mixtures of powders of rhapontic and of rhubarb show a violet fluorescence, which gets darker as the proportion of rhapontic is decreased; in a mixture which only contains 10 per cent. of rhapontic the colour is still violet. A microscopic fluorescence method is described for the determination of the percentage of rhapontic powder added to a rhubarb powder. The mixture to be analysed is compared with mixtures of known percentages. By this means 1 per cent. of powder of rhizome of rhapontic can be determined in rhubarb powder. The parenchyme cells of false rhubarb appear bright violet under the microscope. Tinctures give the same fluorescence colours as the powders. An alcoholic extract of rhapontic gives a white milky fluorescence, and that of rhubarb gives an orange brown. Rhizomes of rhubarbs tested with ultra-violet rays, can be divided into:— (1) True rhubarbs: *R. officinale* H. BN.; *R. tanguticum* Wall.; and *R. emodi* Wall., which give a brown fluorescence and can be considered as officinal, and (2) rhubarbs produced by *Rheum compactum* L., *R. undulatum* L., *R. ribes* L., *R. rhaponticum* L., which produce Austrian, English and French rhubarbs which give a violet fluorescence, and must be considered as non-official. In conclusion, all rhubarbs, rhubarb powders, and tinctures which under ultra-violet rays give a violet fluorescence should be rejected. P. H. P.

**Reaction for the Ergot of Rye Alkaloids, Ergotamine, Ergotoxine and Ergotinine. Examination and Colorimetric Determination of Rye Alkaloid Preparations.** H. W. Van Urk. (*Pharm. Weekblad*, 1929, 66, 473-481).—The author's *p*-dimethyl amino benzaldehyde reagent (*id.*, 1929, 66, 101) is preferable to the (Dutch) Pharmacopoeia test (Tanret's test) or to the nitrobenzaldehyde reagent (ANALYST, 1929, 424) for these alkaloids. A one per cent. alcoholic solution is added to the alkaloid in the presence of 2 per cent. of sulphuric acid in the form of a ring test, or preferably, the violet to red colour may be produced by evaporation on the water-bath of the reaction mixture. Coloured samples, such as tinctures and extracts, are shaken with five times their volume of ammoniacal ether and the ethereal extract used for the test. In this case it is preferable to add directly an ethereal solution of the reagent rather than to use the residue after evaporation. The Pharmacopoeia method is rendered more sensitive by the addition of a trace of oxidising agent, *e.g.* ferric chloride. The method may be adapted to the colorimetric determination of 0.01 c.c. of a 1 per cent. solution of ergotinine, 0.025 c.c. of a 0.1 per cent. solution of ergotoxine, 0.05 c.c. of a 0.005 per cent. solution of ergotamine, 0.125 c.c. of 0.01 per cent. tincture or 0.25 c.c. of 0.05 per cent. extract.

J. G.

## Biochemical.

**Biochemical Determination of Allantoin in the presence of Urea.** R. Fosse, A. Brunil and P. de Graeve. (*Comptes rend.*, 1929, 188, 1418-1420).—Allantoin is totally transformed into allantoinic acid by the enzymes of *Soja hispida* seeds in the presence of ammonium carbonate. A solution of allantoin containing 1 grm. or less per litre is mixed with 1 per cent. of recently crushed soya bean, 1 per cent. of ammonium carbonate solution, and chloroform, and kept at 60° C. for 5-6 hours, or at 40° C. for 10 hours. Five c.c. of the filtered liquids are neutralised in the presence of methyl orange, and hydrochloric acid is added until the solution is 0.05 *N*. This is warmed for 30 minutes at 60° C., made alkaline with sodium hydroxide, and cleared with mercuric iodide in acetic acid. To the filtrate and washings are added twice the volume of acetic acid and one-twentieth of the total volume of methyl xanthidrol. The condensation takes 4 hours. If urea is substituted for the ammonium carbonate the transformation of the allantoin is still complete.

D. G. H.

**Biochemical Determination of Allantoin in Urine.** R. Fosse, A. Brunil and P. De Graeve. (*Comptes rend.*, 1929, 188, 1632-1634).—Allantoin may be determined in the presence of urea by the simultaneous action of the enzymes of soya bean followed by hydrochloric acid. Allantoin is first transformed in alkaline reaction into allantoinic acid by allantoinase, and urea is destroyed by urease. Hydrochloric acid is then used to destroy the urease and liberate urea (which is weighed as the xanthylated base), and glyoxylic acid. No other substance must be present capable of forming urea under the given conditions,

and uric acid must, therefore, be eliminated by means of Denigès' reagent (acid mercuric sulphate), which is without action on allantoin, but precipitates urea in solutions containing over 1 part of 100,000. The allantoin found per litre in the urine of a rabbit was 1 grm.; and in that of a dog (1) 1.92 and (2) 2.60 grms.

D. G. H.

**New Method for the Determination of Urea.** F. W. Allen and J. M. Luck. (*J. Biol. Chem.*, 1929, **82**, 693-701.)—The authors have sought to improve the following three features of the method of Luck (*J. Biol. Chem.*, 1928, **79**, 211; *ANALYST*, 1928, **53**, 607) for the determination of urea, which consisted in principle in the oxidation of its xanthydril derivative with potassium permanganate:—(1) The end-point of the titration (yellow to colourless) is not sufficiently sharp, (2) the sample to be titrated may not exceed 2 mgrms. of the derivative, and (3) the relationship between the permanganate and material oxidised is merely empirical. These undesirable features have now been overcome. A micro method is described for the precipitation of urea as dixanthydril urea from urine, blood and animal tissues. The derivative is determined by oxidation with potassium dichromate and sulphuric acid in place of potassium permanganate. The excess of the oxidising agent is determined iodometrically. For the determination of urea in muscle and other tissues the use of copper sulphate and baryta is recommended for clarification of the tungstic acid extract. No loss of urea results from this procedure, since added urea is quantitatively recovered, urea values are independent of the amount of copper sulphate employed per unit weight of tissue, and the values obtained are identical with those yielded by extracts from two other methods of precipitation and clarification, namely, Tanret's and the phospho-tungstic acid method.

P. H. P.

**Relations between Constitution and Taste of Pungent Principles.** N. A. Lange, H. L. Ebert and L. K. Youse. (*J. Amer. Chem. Soc.*, 1929, **51**, 1911-1914.)—Capsaicin, the pungent principle of cayenne pepper, and piperin or chavicin, the pungent principle of black pepper, are both acid amides; therefore it was thought that a relation might exist between pungency and the amide structure. The synthesis of a number of closely related amides has shown this relation to exist, and has led to conclusions as to the effect on pungency which accompanies changes in the molecular structure. In compounds similar to capsaicin, a free phenolic group (preferably in the para position to the side chain) in the amine portion is necessary to produce pungency, the methoxy group in the meta position exerts a favourable influence toward pungency, the pungency is a maximum when the acid portion consists of nine to ten carbon atoms, and the pungency is not influenced by the position of the double bond in the acid portion. Capsaicin and closely related substances, apart from the pungent taste, are practically devoid of odour or flavour; dulcin, the carbamic amide of phenetidine, is very sweet. It seemed of interest to prepare a series of compounds which would have a close similarity to capsaicin and dulcin. The following six different substituted ureas and thioureas, which are the carbamic or thiocarbamic amides

of vanillylamine, and analogues of capsaicin (a carboxylic amide of the same amine), were therefore prepared and are described:—Vanillylurea, vanillylthiourea, phenylvanillylurea, phenylvanillylthiourea, *p*-tolylvanillylthiourea and *o*-tolylvanillylthiourea. They were tested particularly for their taste. The last three have the property of pungency, but to a lesser degree than capsaicin. None of the compounds has a sweet taste, for the effect of the phenyl and tolyl groups, which are known to repress the sweetness of compounds, predominates over the favourable effect of the methoxy group. The slightly bitter taste which is characteristic of many thioureas was observed in several of these compounds.

P. H. P.

### Test for Vitamin A in Margarine, Butter and Other Fatty Foods.

**A. Andersen and E. Nightingale.** (*J. Soc. Chem. Ind.*, 1929, **48**, 139–140 T.)—The vitamin A content of cod-liver oils can be determined by direct colorations with antimonious chloride, but with butters or margarines reliable direct colorations cannot be obtained; cod-liver oil is 30 to 100 times as potent in vitamin A as butter, and with it there is little or no interference from natural pigments or artificial colouring matter. With butters the vitamin A must be concentrated, and the influence of pigments and colouring matters eliminated before the antimonious chloride test can be applied. The authors have devised a comparative test on butters, oils and fats, margarines, etc., which contain vitamin A, which takes advantage of the fact that the vitamin fraction is associated with the extractable unsaponifiable matter. The test, which furnishes a fairly rapid method of analytical control to ascertain the degree to which vitamin A is present, is as follows:—Ten grms. of the sample under examination are weighed into a 300 c.c. flat-bottomed flask, and 4 c.c. of 56 per cent. aqueous potassium hydroxide solution, and 10 c.c. of alcohol are added from pipettes. The flask and contents are heated at 40–50° C. until clarification results, and gently shaken for 5 minutes. The resulting soap solution is cooled to room temperature, and made up to 100 c.c., and 25 c.c. of this soap solution (=2.5 grms. of margarine or butter) are transferred to a separating funnel together with 50 c.c. of methylated ether (sp. gr. 0.720). The funnel is stoppered, the contents thoroughly shaken and allowed to separate, and the soap liquor is run off. The ethereal layer is run into a porcelain beaker (used to exclude transmitted light as far as possible) and the soap liquor is successively extracted in the funnel with 30 c.c., 20 c.c., and two 10 c.c. portions of ether, and all the fractions are collected in the beaker. The combined ethereal extracts, together with a little ether used to rinse the beaker, are poured into a clean separating funnel containing 30 c.c. of cold distilled water, and the aqueous layer is run off without shaking, in order to remove most of the soap contained in the ethereal extract without risk of emulsification. The ethereal solution is then shaken and washed with 4 successive 20 c.c. portions of distilled water, and then left for 5 minutes in contact with 5 to 10 grms. of anhydrous sodium sulphate, with frequent vigorous shaking, after which 0.1 gm. of good alkali-washed decolorising charcoal, such as "norit," is added, and after further shakings the ether is filtered off (funnel and filter paper being washed with ether) into a porcelain

beaker. After distillation, or evaporation on a water-bath, of the ether, the residual unsaponifiable matter is dissolved in 2.5, 5 or 10 c.c. of chloroform, according to the expected strength of the reaction. If still coloured, which is unlikely, 0.1 grm. of charcoal must again be added and the solution filtered. One c.c. of the chloroform solution is mixed with 1 c.c. of antimonious chloride (24 per cent.  $\text{SbCl}_3$  in chloroform by weight, dissolved by shaking and not by heating), and the coloration noted; the final test must then be made as soon as possible. A "dilution test" is used for the measurement, *i.e.* the unsaponifiable matter is diluted in chloroform until the blue colour with antimonious chloride is just visible, or on the point of vanishing. If the total unsaponifiable matter from 10 grms. of butter or vitaminised margarine could be made up to 430 c.c. (=1 grm. to 43 c.c.) with chloroform, and 1 c.c. of the resultant solution still gave a just perceptible blue colour with 1 c.c. of reagent, the dilution strength would be 43. An aliquot portion only of the unsaponifiable matter is measured. The following are some characteristic figures obtained:—

Substance.	Dilution figure.
Unsaponifiable matter from cod-liver oil	Up to 1 million.
Medicinal cod-liver oil. Average of 100 market samples (direct dilution of oil) .. .. .	1950
Butter .. .. .	25-60
Ordinary vegetable margarine .. .. .	Nil
Ordinary oleo-margarine .. .. .	Trace
Viking margarine (vitaminised) .. .. .	52-65

The accuracy and reliability of the test have been confirmed by duplicate tests by independent laboratories and by biological tests. The method has been applied to "oleo oils," and extended to food products, such as, cakes, bread, eggs, etc. An extension of the method to the assay of milk and certain milk products is in progress.

P. H. P.

**Vitamin B Terminology.** (*Pharm. J.*, 1929, 122, 451.)—A Committee of the American Society of Biological Chemists has reported as follows:—(1) That the term "Bios" should be used to designate the factor or factors encouraging the rapid growth of yeast cells; (2) That the term "B" should be restricted to the more heat-labile (anti-neuritic) factor; (3) that the term "G" should be used, for the more heat-stable, water-soluble dietary factor, called the "P-P" (pellagra-preventive) factor by Goldberger and his associates. (4) That the naming of newly discovered dietary factors by other than descriptive terms should be discouraged until their identity has been established beyond doubt. It is suggested that American, British and Continental Committees should co-operate in settling questions of vitamin terminology.

**Further Progress towards the Isolation of the Antineuritic Vitamin (Vitamin B) from Brewers' Yeast.** A. Seidell. (*J. Biol. Chem.*, 1929, 82, 633-640.)—The antineuritic concentrate previously prepared by Seidell (*J. Biol.*

*Chem.*, 1926, 67, 593) has now been further purified by benzoylation in alkaline solution and extraction with chloroform. The aqueous solution thus formed was found to contain only about one-fourth of the nitrogen originally present in the concentrate, and also the major part of the antineuritic vitamin. This highly active aqueous solution, when poured into 10 volumes of acetone, yields a nearly white precipitate of salts which contains less than one-half of the remaining nitrogen (about 0.25 per cent.), and again most of the antineuritic vitamin. The final nitrogenous product protects pigeons from loss in weight on a diet of polished rice in doses of about 60 mgrms., *i.e.* doses which contain 0.15 mgrm. of nitrogen. The quantity of each sample required to protect varied inversely with the percentage of nitrogen which it contained. Therefore it appears most probable that the activity lies in the nitrogenous compound present, but there is as yet no indisputable proof of this point. Judged on the basis of nitrogen activity, the final product represents a purification of antineuritic material more than 100 times that of dried brewers' yeast. A very careful study will be necessary to develop a method for the final separation of the active from the inactive components of the mixture.

P. H. P.

**Effect of Drying and of Sulphur Dioxide upon the Antiscorbutic Property of Fruits.** A. F. Morgan and A. Field. (*J. Biol. Chem.*, 1929, 82, 579-586.)—

The effect of various methods of preservation upon the vitamin C content of foods is of great importance. Inconsistent results by previous workers are discussed. The more acid foods, such as citrus fruits and tomatoes, contain more of the antiscorbutic vitamin than others, and are also better able to resist destruction by drying or processing. Experiments are now described in which peaches of known origin, namely, fresh, sun-dried and dehydrated, both sulphured and unsulphured, have been tested on guinea pigs for vitamin C content. The sulphured peach products retained the full antiscorbutic vitamin content of the fresh fruit, but the unsulphured sun-dried and dehydrated peaches retained no detectable amount of this property. In view of the long-disputed question as to the possibly deleterious effects of sulphurous acid in dried fruits, these results are somewhat surprising. The objection to excessive sulphuring seems to be on the score of the possible marketing of excessively watery dried fruits, rather than based on the danger of physiological injury resulting from their ingestion. Data already obtained upon prunes and apricots, which substantiate these conclusions, will be published later. The suggested possible relation of vitamin C protection to a minimum sulphur dioxide content or acidity is now under investigation. The sulphured dried peach preparations were found to rank with orange juice, raw tomatoes, and other highly potent antiscorbutic foods; 1 grm. daily of the sulphured dried peaches protected standard guinea-pigs from scurvy over a period of at least 90 days; for similar protection 1.5 to 3 grms. of oranges or lemon juice, or fresh tomato, 3 times as much banana, 6 times as much raw apple or pear or cooked potato, and nearly twice as much pineapple are required. The minimum protective dose of fresh peaches is given as 8 grms. daily.

P. H. P.

## Bacteriological.

**Penetration of Ultra-violet Rays through Fabrics.** A. Latzke. (*Amer. J. Hyg.*, 1929, 9, 629-645).—Measurements of the protective action of various black and white fabrics on bacteria (*B. coli*) when light rays are allowed to penetrate the fabrics and when the rays exert their action on fabrics inoculated with the organisms, indicate that bacteria are held in a fabric by some physical force which renders difficult the removal of a large proportion by the mechanical process of washing. Exposure for 10 minutes to ultra-violet rays is more effective in its germicidal action to organisms on white cotton, linen and silk than to those on a woollen fabric of similar percentage interspace, and the action is less with black than with white material.

When the fabric is used merely as a screen for light rays, and the time of exposure is uniform, black offers greater protection to bacteria than white material. Light seems to be more effective in destroying bacteria through silk and linen than through cotton and wool. When the duration of the exposure was varied according to ratios established with sensitised paper, and the bacteria screened by black fabric were given an exposure three times as protracted as with white fabrics, the light passing the black fabrics proved the more highly bactericidal. Hence the size of interspace appears more important in the transmission of ultra-violet rays of germicidal properties than the colour of the fabric. T. H. P.

**The Eijkman Fermentation Test as an Aid in the Detection of Faecal Organisms in Water.** L. W. Leiter. (*Amer. J. Hygiene*, 1929, 9, 705-724).—Eijkman's test, consisting in the introduction of samples of water into dextrose-peptone broth and incubation at 46°, was carried out with a solution consisting of dextrose, 10; peptone, 10; sodium chloride, 5; and water, 75 per cent. The medium is sterilised at 10 lbs. pressure for 10 minutes at 110° C., and 1 part of medium is diluted with 7 parts of the water. For small quantities (10 c.c.) ordinary fish-hook fermentation tubes are used, and for large quantities a 250 c.c. flask fitted through the stopper with two U tubes, one reaching to the bottom of the flask and the other just through the stopper. The outer ends are drawn out and sealed. After sterilisation the sealed top of the shorter tube is broken, the flask filled with medium and sample, and the stopper replaced with pressure enough to expel all air. The tube is re-sealed, and the sealed end of the longer one broken. The whole is placed in the incubator with the end of the open tube over a beaker, to receive fluid expelled by formation of gas in the top of the flask. In testing the power of growth of pure cultures in the medium the concentration corresponding to above is given by using dextrose, 12.5; peptone, 12.5; sodium chloride, 6.25 grms.; and water, 1000 c.c. Eijkman's test was found to be selective for *Bacillus coli* and to inhibit or destroy other organisms ordinarily present in water. Strains obtained in pure culture from warm-blooded animal faeces produce typical gas, acid and growth reaction in the medium as a fairly constant characteristic,



but at 46° C. certain organisms, apparently *Bacillus coli*, isolated from cold-blooded animals do not produce a typical reaction under the same conditions. The fermentation in Eijkman's medium is correlated with the production of indol, the non-utilisation of sodium citrate and of the nitrogen in uric acid by strains of *Bacillus coli* isolated from warm-blooded animal fæces. The test is usually complete in 16–24 hours, and in 92·75 per cent. of positive Eijkman fermentation tests the presence of *Bacillus coli* can be confirmed, and positive tests yield members of the aerogenes-cloacae group infrequently, in marked contrast to the frequency of isolation by standard methods. Waters freely inhabited by cold-blooded animals, but not contaminated by warm-blooded animal fæces, may be passed by the Eijkman test and condemned by standard methods. D. G. H.

## Agricultural.

**Application of the Strychno-molybdc Method to the Determination of Phosphoric Acid in Soil.** C. Antoniani and S. Bonetti. (*Giorn. Chim. Ind. Appl.*, 1929, 11, 154–155.)—To determine the total phosphoric acid in soil by the strychno-molybdc method (ANALYST, 1928, 53, 405, 605), 20 grms. of the soil are heated to boiling for an hour in a 500 c.c. measuring flask with 30 c.c. of hydrochloric acid (1·18), 20 c.c. of nitric acid (1·40) and 50 c.c. of water. The liquid is then cooled, made up to volume with water, mixed, and filtered through a pleated filter. Of the filtrate, 50 c.c. are made neutral to phenolphthalein by addition of 10 per cent. sodium hydroxide solution, the slight precipitate of basic salts being redissolved by adding a few drops of 10 per cent. nitric acid. The resulting clear solution is mixed with 45 c.c. of the strychno-molybdc reagent and, after standing for about an hour, the precipitate is collected on a dried and weighed Gooch crucible, washed with 100 c.c. of dilute nitric acid (10 c.c. of 1·40 acid made up to 100 c.c.), and dried to constant weight in a water-oven. Multiplication of the weight of the precipitate by 0·0257 gives the weight of  $P_2O_5$ , and further multiplication by 0·983 corrects for the volume occupied by the soil in the 500 c.c. flask.

To determine the  $P_2O_5$  soluble in 1 per cent. citric acid solution, 100 grms. of the soil are shaken for 5 hours in a 1000 c.c. flask with 750 c.c. of the citric acid solution and left for 12 hours to settle. The liquid is filtered, if necessary, and 250 c.c. are evaporated to dryness, the residue being gently calcined with a few crystals of ammonium nitrate until all organic matter is oxidised. The residue is then dissolved in a little water containing a few drops of nitric acid, and the liquid heated on a water-bath for some minutes and filtered. The neutralised filtrate is then treated as described above. T. H. P.

## Organic Analysis.

**Menthone as a Reagent for Aldehydes.** D. Vörländer. (*Z. anal. Chem.*, 1929, 77, 241–268.)—Menthone is prepared by heating a solution of 23 grms. of sodium in 400 c.c. of absolute alcohol with 170 grms. of malonic acid ester and

100 grms. of freshly distilled mesityl oxide (b.pt. 126 to 131° C.) for 2 hours under a reflux condenser, and for a further 6 hours after the addition of 700 grms. of 18 per cent. potassium hydroxide solution. After neutralisation of the solution to litmus with dilute hydrochloric acid the alcohol is distilled off, the solution decolorised with charcoal, and the menthone (130 grms.) is precipitated from the pale-yellow, neutral solution by boiling it for 1 minute with sufficient dilute hydrochloric acid to render the reaction acid to methyl orange. It is filtered off and washed in the cold, treated with charcoal and recrystallised from acetone-water as pale yellow monoclinic crystals, soluble in petroleum spirit. When heated it reddens if freshly prepared, and decomposes at the m.pt. (148 to 150° C.). A saturated aqueous solution contains 0.4 gm. per 100 c.c. at 20° C. and deposits white crystals, m.pt. 200° C. (with decomposition), on standing, and is eventually converted into dimethyl glutaric acid. Warm saturated solutions of menthone, but not its esters or anhydride, give characteristic crystalline precipitates of the type (aldehyde+2 menthone-H<sub>2</sub>O) with aldehydes. These are enolic di- or triphenyl methanes which, on treatment with alcohol, glacial acetic acid or concentrated sulphuric acid, lose another molecule of water and form characteristic, non-acidic anhydrides (xanthone compounds) which do not give a brown colour with ferric chloride solution. Methods of preparation and properties of numerous aldehyde-menthones and their anhydrides and derivatives are fully described. The following are included, figures in brackets representing the corr. m.pt. of the menthone compound and its anhydride, respectively:—*Formaldehyde* (189° C., 171° C.). 0.00005 per cent. solutions yield a haze after 6 hours in contact with warm, saturated solutions of menthone. *Acetaldehyde* (139° C., 174° C.) reacts at room temperature, and the method may be used for the detection and determination of it in wood distillation products. *Propionic aldehyde* (155° C., 143° C.) is also precipitated quantitatively. *Isovaleraldehyde* (80 to 90° C., 172° C.). *Oenanthaldehyde* (103° C., 112° C.). *Acrolein* (186 to 192° C., 163° C.). *Crotonaldehyde* (183° C., 166° C.). *Citronellal* (78° C., 173° C.). *Citral* gives a very indefinite reaction. *Glycolaldehyde* (237.5° C.) gives the same condensation product with menthone (C<sub>18</sub>H<sub>24</sub>O<sub>4</sub>) as is obtained by reaction with *monochloroacetaldehyde*, one molecule each of water and hydrochloric acid being removed in the latter case. It forms a characteristic acetyl derivative, m.pt. 206° C. *Glycer-aldehyde* (197.5° C., 172° C.). A 0.001 per cent. solution is detectable. *Glyoxaldehyde* (186° C., 224° C.). *Methylglyoxaldehyde* (164° C.). *Lactic aldehyde* gave no reaction. *Malonaldehyde* (237° C.). *Benzaldehyde* (see *Ann. der Chem.*, 1899, 309, 379). *Cinnamaldehyde* gives (1) white prisms, m.pt. 213° C. (turning yellow) in hot alcoholic solutions, and (2) fine crystalline yellow plates, m.pt. 161° C., with the same formula (C<sub>25</sub>H<sub>28</sub>O<sub>3</sub>) in cold solution. Acetic anhydride converts both into the same anhydride, m.pt. 175° C. *Coumaraldehyde* (171° C., 173° C.). *p-Hydroxybenzaldehyde* (190° C., 246° C.). *p-Anisaldehyde* (145° C., 243° C.). *Salicylaldehyde* (208° C., 191° C.). *o-Chlorbenzaldehyde* (205° C., 225° C.). *Vanillaldehyde* (197° C., 228° C.). *Piperonaldehyde* (178° C., 220° C.). *Furfuraldehyde* (160° C., 164° C.). *Isatin* (284° C.).

J. G.

**Determination of Ethylene by Absorption in a Solution of Silver Nitrate.** V. N. Morris. (*J. Amer. Chem. Soc.*, 1929, **51**, 1460–1462.)—By means of the author's absorption apparatus (*id.*, 1927, **49**, 979) 12 c.c. of a 40 per cent. solution of silver nitrate will remove 35 c.c. of ethylene from 50 c.c. of a mixture of ethylene and nitrogen in 1 minute. Larger quantities of more dilute solutions (up to 80 c.c. of a 5 per cent. solution) give slower absorptions, but in all cases the results agree with those obtained with other absorbents less convenient to handle. The ethylene may be recovered by evacuation, and if acetylene is present it may be determined by titration of the nitric acid liberated. J. G.

**Identification of Ortho-, Meta- and Para-Hydroxybenzoic Acids.** F. F. Blicke and F. D. Smith. (*J. Amer. Chem. Soc.*, 1929, **51**, 1947–1949.)—During the course of some recent work in which it was necessary to isolate, purify and identify small amounts of *o*-, *m*- and *p*-hydroxybenzoic acids, unsatisfactory results were obtained by the use of the method of Lyman and Reid (*J. Amer. Chem. Soc.*, 1917, **39**, 704) for the identification of these acids. In this method the acids are converted into their sodium salts, and these, dissolved in a mixture of water and alcohol, are heated with *p*-nitrobenzyl bromide to give the *p*-nitrobenzyl esters. The authors have found that the esters, as soon as they are formed, react to some extent with *p*-nitrobenzyl bromide to form the *p*-nitrobenzyl ethers, that is, the dinitrobenzyl derivatives of the hydroxy acids. The substance described by Lyman and Reid as the *p*-nitrobenzyl ester of *p*-hydroxybenzoic acid, is now shown to be the dinitrobenzyl compound. The esters, or mononitrobenzyl compounds, are very soluble in organic solvents, but the dinitrobenzyl derivatives are much less soluble, and can be recrystallised readily from acetone. The method has therefore been modified in such a way that the formation of the dinitrobenzyl products is favoured. Compounds have been formed which can be recrystallised with less loss of material, and since the dinitrobenzyl derivative has a higher molecular weight than the mononitrobenzyl compound, a larger amount of material, in the case of the former substance, can be obtained from a given weight of the hydroxy acid. Furthermore, by the use of the dinitrobenzyl derivatives, it is possible to separate a mixture of two isomeric hydroxybenzoic acids; the derivative of the *p*-hydroxy acid is quite insoluble in acetone, that of the meta acid more soluble, whilst the ortho isomer is fairly soluble. Details are given of the preparations, melting points and analyses of the di-*p*-nitrobenzyl derivatives, the *p*-nitrobenzyl esters and the *p*-nitrobenzyl ethers of hydroxybenzoic acids.

P. H. P.

**Studies on the Combination between certain Basic Dyes and Proteins.** L. M. C. Rawlins and C. L. A. Schmidt. (*J. Biol. Chem.*, 1929, **82**, 709–716.)—In a previous communication by Chapman, Greenberg and Schmidt (*J. Biol. Chem.*, 1927, **72**, 707) studies were reported on the nature of the combination which takes place between certain acid dyes and proteins. Gortner (*J. Biol. Chem.*, 1927, **74**, 409) took exception to the interpretation given to the data presented, and considered that they confirmed his own conclusions. A reply to his criticism

would necessitate the opening of the question as to the exact definition of adsorption, so the authors prefer to let the matter rest, and believe that they and others have found sufficient evidence to place the reaction between proteins and acids or bases (*i.e.* acid or basic dyes) in the category of true chemical reactions. The present investigation is a continuation of that previously reported by Chapman, Greenberg and Schmidt. Casein, fibrin and gelatin were each titrated with methylene blue, safranin Y, and induline scarlet. Edestin was titrated with methylene blue and safranin Y, but not with induline scarlet, as its manufacture was discontinued after the work was begun. Titration curves show that in the region of  $P_H 11$ , gelatin binds  $70 \times 10^{-5}$  equivalents of dye, casein  $210 \times 10^{-5}$ , edestin  $70 \times 10^{-5}$ , and fibrin  $168 \times 10^{-5}$  equivalents. Within limits of error and taking into account the possibility of modification of the protein taking place at high alkalinities, a correlation between certain groups in the proteins studied and their capacity for binding base can be made. This correlation suggests that the union between protein and basic dye, under the experimental conditions observed, takes place in stoichiometric proportions.

P. H. P.

**Determination of Insoluble Matter in Tanning Extracts.** C. Riess. (*J. Inter. Soc. Leather Trades Chem.*, 1929, 13, 246.)—The disadvantages involved in the ordinary methods for determining the insoluble matter in extracts, namely, the trouble of thoroughly cleaning the filter candle, and the time required for and uncertainty of obtaining clear filtrates with filter paper, would appear to be largely overcome by the adoption of the following apparatus:—A Büchner funnel is fitted with an adapter which is attached to a piece of thick-walled glass tubing, 120 cm. long and 2 mm. internal diameter. A suspension of 1 gm. of kaolin clay in 75 c.c. of the tannin solution is poured on to the filter paper in small portions at intervals. The funnel is then filled with fresh solution. As soon as the filtrate becomes optically clear (25 to 50 c.c.) the requisite amount is rejected, and 50 c.c. of the next 60 c.c. are taken for the evaporation. The 120 cm. column of solution causes a partial vacuum to form, thus accelerating filtration, and the apparatus is easily prepared for subsequent analyses.

R. F. J.

## Inorganic Analysis.

**Detection and Determination of Carbon Disulphide in Air.** E. Selivounoff. (*Ann. Chim. anal.*, 1929, 11, 133.)—Carbon disulphide may be determined in the atmosphere by aspirating air at the rate of 10 litres an hour through two flasks containing 10 per cent. potassium or sodium hydroxide solution, then through 2–5 per cent. sulphuric acid, and lastly through two wash-bottles containing 5 per cent. alcoholic potassium hydroxide solution. Hydrogen sulphide, sulphur dioxide, carbon dioxide and hydrocyanic acid are thus eliminated. The carbon disulphide is held by the alcoholic potash, and potassium xanthate is produced. This solution is reduced to half its volume at  $80^\circ C.$ , neutralised with 5–10 per cent. acetic acid, with 1 drop of phenolphthalein, 0.5 to 1 c.c. of an alcoholic solution of guaiacum resin added, and the liquid titrated, drop by drop,

with 0.0002 *N* copper sulphate solution in a test tube without shaking. When the blue colour spreads through the whole liquid the titration is finished. One c.c. of the copper solution equals 0.011 mgrm. of carbon disulphide; the method is suitable for 0.001 to 0.002 mgrm. of carbon disulphide. D. G. H.

**Reaction for Primary Arsines. S. S. Nametkin and W. Nekrassow.** (*Z. anal. Chem.*, 1929, 77, 285–289.)—If 3 drops of clear saturated hydrogen sulphide water are added to 1 c.c. of an aqueous solution of a primary arsine a white opalescence is produced (easily visible against a white ground), which may be extracted with ether. The reaction, which has been used to detect 0.05 mgrm. of methyl-, ethyl-,  $\beta$ -chlorvinyl-, and phenyl-dichlorarsines, follows the equation (Baeyer, 1858)  $\text{RAsCl}_2 + \text{H}_2\text{S} = 2\text{HCl} + \text{RAsS}$ . The reagent, which in alcoholic solution is less sensitive and produces crystalline deposits, will remain clear for a month if it is filtered after addition of 1 drop of sulphuric acid. Ferrous, copper, cadmium, nickel and zinc sulphates, potassium chromate, lead cobalt and bismuth nitrates, and ferric, stannous and mercuric chlorides do not influence the test appreciably, but mercurous nitrate solution gives white, grey or black precipitates of calomel or reduced mercury, or both, with aqueous solutions of these arsines. This reagent, though less sensitive, may be adapted to distinguish different arsines. J. G.

**Use of Cresol Red in Acid Solutions. F. R. McCrumb and W. R. Kenny.** (*J. Amer. Chem. Soc.*, 1929, 51, 1458–1459.)—Cresol red has an acid range from  $\text{P}_H$  0.2 to 1.8 (red to yellow) with a half transformation point at  $\text{P}_H$  1.0. Its solutions are more stable than those of methyl violet and are useful to test for free mineral acids or acidic salts in the presence of weak acids, and in qualitative analysis for the separation of the sulphides of the third and fourth groups. J. G.

**Determination of Sulphur in Galena and Lead. H. Leysaht.** (*Z. anal. Chem.*, 1929, 77, 209–213.)—This evolution method is based on solution of the material in hydrobromic acid (sp. gr. 1.49) containing a little stannous chloride to bind any free bromine. The liberated hydrogen sulphide is conducted into a receiver containing a cadmium solution (25 grms. of cadmium acetate and 200 c.c. of glacial acetic acid per litre). The cadmium sulphide precipitate is decomposed by 0.1 *N* iodine solution, the excess of free iodine being measured with thiosulphate. W. R. S.

**Sensitive Test for Magnesium. W. L. Ruigh.** (*J. Amer. Chem. Soc.*, 1929, 51, 1456–1457.)—Suitsu and Okuma's *o,p*-dihydroxy-azo-*p*-nitrobenzene reagent (*J. Soc. Chem. Ind. Japan*, 1926, 29, 132) is prepared by coupling diazotised *p*-nitraniline with a solution in dilute sodium hydroxide solution of the theoretical quantity of resorcinol. The dye is precipitated by acid, filtered off, and recrystallised from methyl alcohol (m.pt. 199 to 200° C.). The solution to be tested, containing at least 0.002 mgrm. of magnesium, is made just acid with hydrochloric acid, and one drop of a 0.5 per cent. solution of dye in 1 per cent. sodium hydroxide solution added; a sky-blue precipitate settles out when the mixture is made

alkaline or shaken. Excess of ammonium salts, which destroy the sensitiveness of the test, and nickel and cobalt (which give similar lakes) should be removed.

J. G.

**Ceric Sulphate in Volumetric Analysis. VI. Oxidation of Hydrogen Peroxide by Ceric Sulphate. Indirect Determination of Lead.** N. H. Furman and J. H. Wallace. (*J. Amer. Chem. Soc.*, 1929, 51, 1449-1453.)—Furman's potentiometric method (*cf.* ANALYST, 1929, 371) has been applied to the titration of ceric sulphate with hydrogen peroxide according to the equation  $2\text{Ce}(\text{SO}_4)_2 + \text{H}_2\text{O}_2 = \text{Ce}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 + \text{O}_2$ . Results with a mean error of  $\pm 0.02$  c.c. were obtained in the presence of 1.5 *N* nitric acid, or, for the reverse titration, of 1.0 to 3.0 *N* hydrochloric, sulphuric or acetic acid. The rise in voltage at the end-point is sharper for hydrochloric or acetic acid, but the visual end-point, which is usually 0.05 c.c. higher than that obtained potentiometrically, is obscured in the former case by the presence of iron. Lead peroxide may be determined by titrating the excess of hydrogen peroxide in a solution of 0.2 gm. of sample in 25 c.c. of standardised 0.1 *N* hydrogen peroxide and 25 c.c. of nitric acid (sp. gr. 1.42) free from oxides of nitrogen.

J. G.

**Rapid Test for Tungsten in Ores.** A. Petrovsky. (*Z. anal. Chem.*, 1929, 77, 268-269.)—A powdered ore containing 0.5 per cent. or more of tungsten yields a blue colour when 0.2 gm. is reduced by the action of a piece of lead and 2 c.c. of hot concentrated hydrochloric acid for 2 minutes. On the addition of 15 c.c. of water a blue precipitate of the pentoxide forms, which may appear green or brown with small amounts of tungsten. Similar reduction of niobium gives a similar but duller colour, which disappears on dilution; titanium gives a green colour which disappears on standing or turns pale violet, whilst vanadium is distinguished by the fact that reduction to a blue compound may be effected by tartaric acid. Molybdenum gives no reaction.

J. G.

**Separation of Tungsten from Vanadium.** A. Jilek and J. Lukas. (*Czechoslovak Chem. Communications*, 1929, 1, 263-274.)—The method is based on the precipitation of quinine arsenotungstate in presence of vanadyl salt. The neutral solution (100 c.c.), containing less than 0.2 gm. of  $\text{WO}_3$  and 0.1 gm.  $\text{V}_2\text{O}_5$ , is acidified with 1 c.c. of hydrochloric acid and boiled with 0.5 gm. of hydroxylamine hydrochloride for the reduction of the vanadate; it is then treated with 10 c.c. of 2 per cent. arsenic acid and another c.c. of hydrochloric acid, diluted to 200 c.c., boiled, stirred, and precipitated with 20 c.c. of 2 per cent. quinine hydrochloride solution. Next day, the precipitate is collected and washed with water containing a little arsenic and hydrochloric acids and quinine hydrochloride, and finally with acidulated water containing a little of the precipitant, and ignited in platinum. The oxide is evaporated with nitric acid and ignited to constant weight. With large amounts re-precipitation is advisable. For the determination of the vanadium, the organic matter in the filtrate is destroyed with sulphuric acid and copper oxide; copper and arsenic are precipitated as sulphides; the filtrate is made alkaline and oxidised with hydrogen peroxide, neutralised, and precipitated with mercurous nitrate.

W. R. S.

**Zirconium. IV. Precipitation of Zirconium by Phosphates. R. D. Reed and J. R. Withrow.** (*J. Amer. Chem. Soc.*, 1929, 51, 1311–1315.)—Phosphoric acid, ammonium phosphate or microcosmic salt in five-fold excess are equally efficient for the quantitative precipitation of zirconium as phosphate, and more efficient than sodium phosphate, a forty-fold excess of which will, however, remove practically all the zirconium after a long period of standing and does not interfere with subsequent tests for potassium. The best results were obtained in the presence of 0.35 to 0.65 *N* sulphuric acid, 0.27 *N* nitric acid or 0.2 *N* hydrochloric acid being less suitable, whilst removal was incomplete in the absence of acid. The procedure was to allow the precipitated solution to stand over-night, and then to filter on a fine paper, and to test the warm, concentrated filtrates and washings for zirconium by neutralisation with ammonia (*cf.* ANALYST, 1929, 370).  
J. G.

**Volumetric Determination of Vanadium by Means of Potassium Iodate. E. H. Swift and R. W. Hoeppe.** (*J. Amer. Chem. Soc.*, 1929, 51, 1366–1371.)—The vanadate solution (25 c.c.) is well shaken in a flask, and carbon dioxide blown rapidly over the liquid to remove oxygen. It is then rendered 6 to 8 *N* with respect to hydrochloric acid by addition of oxygen-free 12 *N* acid. Carbon tetrachloride (5 c.c.) and a measured excess of standardised iodate-free potassium iodide solution are added, the flask stoppered, and the mixture titrated rapidly after a few minutes with a standard 0.025 *M* solution of potassium iodate until no more colour is visible in the solvent. Acid is added during titration to keep the concentration above 6 *N*. Under these conditions quadrivalent vanadium is not oxidised by the iodine monochloride formed by interaction of the hydrochloric acid, iodate, and iodine liberated according to the equation  $H_3VO_4 + HI + 2HCl = VOCl_2 + \frac{1}{2}I_2 + 3H_2O$ . The method may be used in the presence of tungstic acid, phosphates, arsenates or ferric iron, but tungstic acid must be held in solution by addition of phosphoric acid.  
J. G.

**Chlorate Method for determining Nitrate Nitrogen, Total Nitrogen, and other Elements in Soils and Plant Tissues. E. M. Emmert.** (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 240–247.)—The chlorate method allows of the rapid and accurate determination of nitrate and total nitrogen in plant tissues and soils, and gives a residue in which other inorganic elements may be determined. Sufficient of the dry sample—ground to pass a 50-mesh sieve and leave the green tissue intact—to yield 0.5–1 mgrm. of nitrate nitrogen is placed in a 500 c.c. Kjeldahl flask and washed down with 25 c.c. of 50 per cent. (vol.) sulphuric acid. The flask is joined to a condenser, the free end of which leads through a two-holed rubber stopper into an absorption tower containing 150 c.c. of freshly prepared, yellowish-green chlorine dioxide solution, made by dropping concentrated hydrochloric acid on to sodium chlorate and passing the gas into water. The exit from the tower is fitted with a trap into which part of the liquid is forced during the action. The flask is heated to expel the gases rapidly but not violently into

the tower. Distillation is carried out quickly as soon as water vapour condenses, foaming ceases, and little gas is evolved, and the distillation is continued until white fumes appear. The flask is disconnected before the flame is extinguished, and the residue is saved for the determination of reduced nitrogen.

The condenser, trap and tubes are washed out with water, and fresh chlorine dioxide solution is added, if necessary, to make the solution in the tower yellow. The solution is at once boiled until colourless and made up to a definite volume. An aliquot part containing at least 0.25 mgrm. of nitrate nitrogen is treated, while hot, with 0.05–0.1 gm. of silver sulphate, and shaken now and then during five minutes, 0.5–1 gm. of lime being then added. After being again shaken occasionally for a few minutes, the liquid is filtered bright and an aliquot part containing at least 0.2 mgrm. of nitrate nitrogen evaporated to dryness. The residue is covered with 2–3 c.c. of phenoldisulphonic acid, left for 5–10 mins., and treated with 20–30 c.c. of water until most of the salts dissolve. A few c.c. more 25 per cent. sodium hydroxide are added than is necessary to give a yellow colour, the liquid being made up to 100 c.c., shaken with 0.5 gm. of calcium hydroxide, and filtered. A standard containing 0.0025 mgrm. of nitrogen per c.c. is used for comparison, the volume of the unknown being suitably adjusted. The method gives consistent results and determines added nitrate nitrogen accurately, but much lower results were obtained with certain soils than were found by the official method.

To determine reduced nitrogen, either the cold residue in the Kjeldahl flask, together with 10 c.c. of water, or a smaller amount of fresh sample is boiled for about 5 mins. with 20 c.c. of 50 per cent. (vol.) sulphuric acid until it is charred and all nitrate nitrogen is expelled. The cooled mass is treated with 10 c.c. of water, again cooled, shaken with 1 gm. of sodium chlorate for each 0.1 gm. of dry tissue or 0.5 gm. of green tissue or soil, and heated rapidly until the green chlorine peroxide fumes are decomposed and only white fumes remain; if the green fumes are excessive, special care is taken, as explosion may occur at about 100° C. The liquid is placed in the apparatus described above and, when violent action ceases, is distilled into water in the absorption tower. The Kjeldahl flask is disconnected when the solution remains colourless and white fumes form. The procedure is then as described for nitrate nitrogen.

To determine total nitrogen, a still smaller sample is placed in a Kjeldahl flask, with sodium chlorate at the same rate as for reduced nitrogen, and 25 c.c. of the 50 per cent. sulphuric acid. The heating and distillation are effected similarly, collection of masses of chlorate over the flame being prevented. The nitrate nitrogen is determined as described above.

The residue in the flask, when freed from sulphuric acid by distillation, serves for the determination of any non-volatile element except sodium and sulphur; sodium may be determined if potassium instead of sodium chlorate is used. The carbon appears to be evolved as carbon dioxide during the distillation, and preliminary experiments indicate that it may be determined by absorbing the gas in soda-lime.

T. H. P.



**A more Stable Alcoholic Potash Reagent for Saponification.** D. T. Englis and V. C. Mills. (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 248-251.)—To 2 litres of alcoholic potash reagent, prepared according to the official method, 10 grms. of sodium hydrosulphite were added, the solution being mixed and left undisturbed, except for an occasional shaking, for about a year in a stoppered flask. Determinations of the saponification values of several oils, then made with the clear, almost colourless supernatant liquid, gave results in close agreement with those obtained by the official reagent. It has not been found possible to discover a general inhibitor of the development of colour during the saponification process.

T. H. P.

**Volumetric Determinations by Iodate.** A. Schwicker. (*Z. anal. Chem.*, 1929, 77, 161-169.)—Sulphurous acid reacts with acidified iodate solution in two stages: (1)  $2\text{HIO}_3 + 5\text{H}_2\text{SO}_3 = 5\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{I}_2$ ; and (2)  $\text{H}_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HI}$ . The sulphite solution is run from a burette into a measured excess of 0.1 *N* iodate solution acidified with hydrochloric or sulphuric acid. The liquid is then treated with excess of potassium iodide and the liberated iodine titrated with thiosulphate as usual. Hydrazine, ferrocyanide, thiocyanate, arsenious and antimonious oxides, can be determined volumetrically by means of the same technique, for details of which reference is invited to the original paper.

W. R. S.

**Iodimetric Determination of Thiocyanates.** A. Schwicker. (*Z. anal. Chem.*, 1929, 77, 278-280.)—A measured quantity of a solution of the sample is made alkaline with 5 to 10 c.c. of *N* ammonium borate solution (170 grms. of 10 per cent. ammonia and 20 grms. of boric acid per litre) and allowed to react with a measured excess of 0.1 *N* iodine solution for 2 minutes. It is then acidified with 10 c.c. of 2 *N* acid, and the residual iodine titrated with 0.1 *N* sodium thiosulphate solution in the presence of starch. The borate solution increases the velocity of the reaction— $\text{CNS}' + 3\text{I}_2 + 4\text{H}_2\text{O} \rightarrow \text{SO}''_4 + 6\text{I}' + 8\text{H}' + \text{CN}'$ , and is preferable to ammonia or ammonium chloride for this purpose. An accuracy of 0.02 c.c. of iodine solution is obtainable.

J. G.

## Physical Methods, Apparatus, etc.

**Zinc Sulphide Method of Measuring Ultra-violet Radiation, and the Results of a Year's Observations on Baltimore Sunshine.** J. H. Clark. (*Amer. J. Hyg.*, 1929, 9, 646-662.)—The author's method for measuring the intensity of ultra-violet radiation by the rate of darkening of lithopone is modified, use being made of zinc sulphide, moistened with saturated lead acetate solution. Chemically pure zinc sulphide, when prepared by different methods, varies in its sensitiveness towards ultra-violet radiation. A standard grade, known as "ZnS ignited," has been developed by the J. T. Baker Chemical Company, and is highly satisfactory for this determination. A spatula-full of the zinc sulphide powder is moistened in a small mortar with a few drops of saturated lead acetate

solution and ground to a soft paste, which is placed on a piece of glass and pressed flat under a plate of transparent quartz. The glass and quartz are held together by elastic bands, and the paste is exposed normally to the radiation through the quartz. As the paste darkens somewhat on exposure to air, fresh material should be used for each observation.

Before exposure the paste has a reflexion factor of 76–78 per cent. It darkens rapidly and irreversibly on exposure to ultra-violet radiation. After exposure of 1, 2, 3, etc., minutes, the reflexion factor is determined with a Macbeth illuminometer, or, failing this, with a set of standard grey papers. The curve of darkening thus obtained gives the time required to produce darkening to a 50 per cent. reflexion factor, which is taken as that giving one ZnS unit of ultra-violet radiation; the intensity of the radiation is inversely proportional to the time required to give one unit. In practice, a set of typical darkening curves will indicate the time to give one unit from a single observation.

With sunlight and with mercury arc-light filtered through a Corning G 986 A filter, one ZnS unit equals one lithopone unit, but with the bare mercury arc one ZnS unit equals 1.33 lithopone unit. For zinc sulphide the temperature coefficient of darkening,

$$Q_{10} = \frac{\text{velocity at } (T+10) \text{ } ^\circ\text{C.}}{\text{velocity at } T \text{ } ^\circ\text{C.}}, \text{ has the value about } 1.2,$$

If this method is used to measure the intensity of a quartz mercury arc, wave-lengths not greater than  $313\mu\mu$  are alone effective. With solar radiation the method is less satisfactory, as the darkening is then due to a band  $290\text{--}350\mu\mu$ , with the maximum effect at  $320\mu\mu$ . Marked therapeutic effect is produced only by waves of  $290\text{--}310\mu\mu$ , and only about one-sixth of the energy measured lies in this region, although the value of this fraction varies greatly throughout the year.

Measurements of solar ultra-violet radiation made in Baltimore during 15 months by the zinc sulphide method gave results comparing favourably with those of other methods and show that there is maximum intensity in August and minimum in January, the ratio between the two being 8:1. T. H. P.

**New Method of Mounting Vegetable Powders for Microscopical Examination.** W. O. Howarth. (*Pharm. J.*, 1929, 122, 522–523.)—A little of the powder (stained according to the type of material) is mixed with a drop of a mounting medium composed of: carbolic acid, 20; lactic acid, 20; glycerin, 40; and water, 20 parts. The slide is covered and allowed to stand for a few minutes, or it may be warmed. All details of cell structure are brought out perfectly. For permanent preparations as much as possible of the liquid is drained off, glycerin jelly added, and the cover slip ringed round with gold size. Sections may also be mounted in the same medium. For staining powders containing leaves, fruits, seeds and soft tissues generally, aniline blue may be used; for lignified tissues, cotton red stain (a form of safranin).

## References to Scientific Articles not Abstracted.

COMPOSITION OF WATER AND MOSQUITO BREEDING. By W. RUDOLFS and J. B. LACKEY. *Amer. J. Hyg.*, 1929, 9, 179.

Attempts to correlate chemical composition of water, and biological growth therein, with the breeding of larvae of *C. pipiens*—Gradual change of the reaction of water did not affect growth—Breeding absent when protozoa, fungi, etc., were low in amount—Breeding not affected by ratios of carbon to nitrogen in the water—Specific substances formed by decomposition of vegetable matter may be a promoting cause.

THE PROPERTIES AND APPLICATIONS OF "VITA" GLASS. By F. E. LAMPLOUGH. *J. Roy. Soc. Arts*, 1929, 77, 799 (June 28th).

"Vita" glass transmits rays between 3000 and 3200 Å.U.—Tests of permeability—Use of fluorescent substances in testing—Therapeutic effects—Initial deterioration—Stability reached in about a month—Approximate efficiency figure (for 2 mm. thickness) is then about 65 per cent. at 3130 Å.U.—Loss due to reflection at the two glass surfaces (about 8 per cent.) and to absorption—Glass for window purposes must be resistant to atmospheric influences.

THE ACTION OF THALLIUM. *Brit. Med. J.*, 1929, 962 (May 25, 1929).

A summary of the literature on the physiological action of thallium—Use as a depilatory has become popular—Fuld (*Muench. med. Woch.*, 1928, 75, 1124) describes mild and fatal cases of poisoning—Dixon (*Proc. Roy. Soc. Med.*, 1927, 20, 1197) demonstrated that the action is not locally upon the hair follicles but upon the cells—Case of acute poisoning by thallium rat paste described by Greving and Gagel (*Klin. Woch.*, 1928, 7, 1323)—Histological effects described by Buschke (*Klin. Woch.*, 1928, 7, 1515)—Effects of chronic industrial poisoning studied by Buschke (*Med. Klin.*, 1928, 24, 1042), and by Teleky (*Wien. med. Woch.*, 1928, 78, 505)—Lutz (*Zeit. Gewerbehyg. u. Unfallverhütung*, 1928, 15, 172) found that thallium acetate (5 per cent.) ointment, when applied to rabbits and guinea-pigs, caused death in 4 days—Cumulative action with small doses—Use of gloves advisable when handling thallium salts.

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## Reviews.

BAYLEY'S CHEMISTS' POCKET BOOK. Edited by ROBERT ENSOLL. Ninth Edition. Pp. xvi+460. Price 8s. 6d. net.

The ninth edition of this useful book of reference has been revised throughout. Certain sections, including those on mathematical conversions, chemical analysis and hydrogen ion concentration have been considerably amplified.

While the book is a mine of useful information, both chemical and general, it provides several examples of the folly of striving to include too much in a book of this character, with the attendant results of over-compression. When a compilation of this character attempts to invade the province of the text-book it necessarily fails. Thus, while it is obviously necessary that, when certain tables of analytical constants, such as those used in sugar analysis, are published, the methods of analysis should be plainly indicated, it is not clear what purpose is

served by the inclusion of some of the condensed descriptions of methods of analysis. The treatment of the whole subject of oil and fat analysis in a page and a half can hardly be adequate for the needs of any variety of chemist.

The section on hydrogen ion concentration is a further example. The table on pp. 350-351 includes a number of indicators, the colour changes of which are not given. It also includes several mixed indicators without any indication that they are anything but simple, or of what their special uses may be. The table on p. 353 is out of date and should be revised so as to be more in accordance with modern practice. A more extended table of acids and bases giving the  $P_H$  of the end-points of titrations and the most suitable indicators should replace this table with great advantage.

Unfortunately, it is noticeable throughout the book that there has been a certain carelessness in the proof reading. There is frequent mis-spelling of proper names, *e.g.* Keppler, Schlipp, Devardos, and Ilosvoy, besides numerous misprints. One hopes that the figures are more reliable. Judging by the small proportion that one can check in a short time, they appear to be so.

In spite of these deficiencies, the amount of information published at so reasonable a price is remarkable, ranging from the Greek alphabet and the sizes of photographic plates to the calculation of compound interest, in addition to a large amount of matter of more direct concern to chemists. Indeed, the book abounds in useful hints and unusual information, not to be found elsewhere.

NORMAN EVERS

STANDARD METHODS OF TESTING PETROLEUM AND ITS PRODUCTS. Second edition. Pp. xiv+137. Published by the Institution of Petroleum Technologists. London: W. Speaight & Sons, Ltd. 1929. Price 7s. 6d. net.

In the testing of complex commercial products, such as crude petroleum and the products derived from it, many of the tests used for which purpose are purely empirical and need strict uniformity of conditions in order to obtain concordant results, standard methods are essential, not only to prevent disputes between buyer and seller, but also to enable the properties of the products as determined by the tests to be strictly comparable with the results obtained in practice by the use of the products. Provided the standard tests and methods are drawn up and agreed upon by technical experts, scientifically qualified and thoroughly representative of all the interests involved, and are revised and amended from time to time in accordance with the growth of knowledge and experience, they are no hindrance but a help to progress. Such a series of test methods is contained in the book under review.

The book contains methods for the determination of specific gravity, colour, sulphur in various forms, calorific value, viscosity, aromatic content, acidity, flash-point and fire-point, volatility, burning properties (illuminating oil), carbon

residue, cloud-point and setting-point, hard and soft asphalt, demulsifying properties, sludging value, dielectric strength, paraffin wax content, softening point, ductility and penetrability (asphaltic bitumen), &c., &c., as applied to Gasoline, White Spirit, Benzol Mixtures, Kerosine, Long-Time Burning Oil for signal lamps, Gas Oil, Mineral Lubricating Oils, Transformer and Switch Oils, Fuel Oils, Asphaltic Bitumen and Asphaltites, Commercial Paraffin Scale and Refined Paraffin Wax, and Crude Petroleum.

The "Standardisation Committee" appointed by the I.P.T., and its co-opted members, under whose auspices the methods have been formulated and are revised from time to time, is composed of technologists of the highest standing and attainments in the petroleum industry, and includes representatives of Government Departments, the National Physical Laboratory, the leading petroleum companies and individual specialists and consultants, and is divided into sub-committees, each having charge of one of the six classes into which the products dealt with are divided. Not only methods, but also apparatus, are standardised. Grave variations in what been have regarded as standard instruments, such as the Redwood viscometer, have been dealt with, the dimensions and tolerances of the essential parts are now laid down, and provision has been made for their calibration and certification by the National Physical Laboratory.

Weight has been given to the valuable work done by the American Society for Testing Materials and the American Bureau of Standards, and many of the American methods of testing have been adopted. The British Engineering Standards Association have also co-operated with the Committee, to prevent overlapping, and have agreed to adopt the standard methods of the I.P.T. for the purposes of their specifications, so far as petroleum products are concerned. Assistance has also been afforded to the Committee by the principal firms of instrument makers and by the British Lampblown Scientific Glassware Manufacturers' Association. Standard methods of sampling are also laid down. The tests are very conveniently arranged, a reference letter being given to each of the products dealt with and the same reference number to the same test as applied to each particular product. Thus, the method for determining the viscosity of Gasoline (G) has the Serial Designation G8, and of Lubricating Oil (LO) the serial designation L.O.8. The book is interleaved throughout, for the purpose of making notes.

The volume, produced under the general editorship of Prof. J. S. S. Brame, assisted by Mr. Geo. Sell, the Secretary of the Committee, is of handy size, well bound and printed, and contains thirty dimensioned figures of apparatus described in the text. It is indispensable to every analyst whose practice includes the testing of the products with which it deals, and reflects credit on all concerned in its production.

L. ARCHBUTT.

VOLUMETRIC GLASSWARE. By VERNEY STOTT. Pp. 232. London: H. F. & G. Witherby. 1928. Price 20s.

The book under review deserves a place on the shelves of every laboratory in

which volumetric glass apparatus is used, especially where investigations requiring a high degree of volumetric accuracy are involved, for it contains much food for thought for the careful worker. It gives the history of the connection between the litre and the kilogramme and explains the reasons for the adoption of the units of volume, times of delivery and drainage of measuring vessels, and other standard conditions required by the National Physical Laboratory in the Tests for Volumetric Glassware. If there be any chemists who use glassware which has not been calibrated, as is alleged in the preface to the book, or who use pipettes or burettes capable of quick delivery, data are given in the book to show the risks they run when doing work of a high degree of accuracy.

After dealing with the distinctions between the millilitre and the cubic centimetre, and between the litre, the cubic decimetre and Mohr's litre, in a form familiar to those who have seen Report No. I on Units of Volume by the Joint Committee for the Standardisation of Scientific Glassware, the author works out the relationship between the volume in ml. and the weight in grms. in air, of water at different temperatures and barometric pressures.

Two tables are given by which an observer who possesses accurate gramme weights, knowing the weight of water in a litre vessel, and noting the temperatures of the water and air and barometric pressure, can find the correction to the nearest milligramme to be applied to the weight in order to find the numerical measure of the volume, in ml., at 15° C., of the vessel. These tables and similar tables in the last chapter, covering volumes ranging from 1 ml. to 2000 ml., enable one almost at a glance, and without elaborate calculations from the density of water, to calibrate quickly any vessel at temperatures ranging from 5.0° C. to 30.9° C., and barometric pressures from 730 to 790 mm. Another labour-saving table gives the factors, for the same temperature range, to connect weight of mercury with volume in ml. at 15° C.

Tables showing the actual amount of water, and of four common volumetric reagents, required to fill a graduated vessel at different temperatures give data for calculating the errors arising through use of standard liquids at temperatures different from that at which they were prepared. For instance, normal sulphuric acid prepared at 15° C. will be incorrect to the extent of 0.07 per cent. if used at 10° C., or of 0.2 per cent. if used at 23° C.

The methods used at the National Physical Laboratory for testing and marking flasks, burettes and other vessels are described and give useful information to users and manufacturers of these goods.

The data and curves showing the volume of water delivered and drained from pipettes and burettes in different times show the necessity for the slow-delivery tolerances adopted by the National Physical Laboratory. They should be carefully studied by every user of these vessels. Errors due to the use of quick-delivery milk-testing pipettes and of pipettes calibrated for water and used for solutions or for other liquids are shown in tables. Curves showing volumes delivered and drained from quick-delivery burettes show that appreciable errors may arise by

use at different rates of delivery, and, also that drainage for several minutes does not compensate for the differences in delivered volumes.

Consideration is given to the possible cumulative errors which may arise in various operations using National Physical Laboratory Class A vessels without corrections, but allowing the maximum tolerances in error.

Calibration of gas burettes by means of mercury, and for use with mercury is described, but no comment is made on meniscus errors due to different heights of mercury meniscus, nor on the calibration of closed gas-measuring tubes and the meniscus errors involved in their calibration and use.

Several typographical errors occur, two of which should be noted, namely:—"0·0000026" on page 27 should be "0·000026" and "one fifth" on page 123, line 5, should be "one fiftieth."

As a book of reference, its value is much reduced by the absence of an index, which may have been considered to be unnecessary in a book of this size, but would have been of great value in assisting a person who knows what is in the book to refer quickly to tables, tolerances allowed by the National Physical Laboratory, or other subject-matter. Then, again, the tables are as mysterious as they can be. Table I, page 24, gives a series of numbers corresponding with each tenth of a degree from 5·0° C. to 30·9° C., and Table II, on the following page, gives another series of numbers correlating degrees Centigrade with "pressures in millimetres of mercury at 0° C.," but there is no information on the table pages to indicate the significance of the temperatures or the units in which the corrections are expressed, and the reader has to search through several pages of letterpress for the information. If Table I had been headed "Table I, 1000 ml. correction in milligrammes to be added to observed weight in grammes, using brass weights, for various temperatures of water," it would have added greatly to the usefulness of the table. Similar headings on Table II, and on the thirty-two amplifications of these two tables at the end of the book would have been useful. Also, if one wants to find the connection between barometric pressure, as read, with that at 0° C., there is no hint until the last chapter is reached that there is a table on the last page of the book.

A. MORE.

ARTIFICIAL SILK. By Dr. O. FAUST. Translated from the German by E. FYLEMAN. Pp. v+184. Isaac Pitman & Sons. 1929. Price 10s. 6d. net.

A number of books dealing with artificial silk have appeared in the last few years. The majority of them were written by experts in the manufacture of artificial silk, so that the technical side was adequately treated. The authors, however, felt it necessary, in most cases, to include an account of the scientific basis of the industry. The treatment of this, in general, was far from satisfactory, and might, with advantage, have been omitted.

In the case of the little work now under review the author himself has obviously been trained on the scientific-research side of cellulose and artificial silk.

His book is based on the thesis that further progress in the manufacture of artificial fibres is dependent on an understanding and control of the basis—chemical, physical, colloidal—on which the industry is built. He therefore devotes about half the volume to the structure of cellulose and of artificial fibres as revealed by X-ray analysis and other methods, to the study of swelling power, the nature of the spinning process—particularly the stretch spinning process—and the ripening of viscose solutions.

The general section, Part I, covers 68 pages, and includes an account of the properties of cellulose, especially in relation to the size of the complex and its influence on the degree of solubility and viscosity of the cellulose and its derivative, the spinning solution, and the spinning process. In this chapter he refers briefly to his own investigations on the X-ray structure and double refraction of artificial silk threads. Another chapter deals with the lustre and colour of the threads, and a full chapter is devoted to swelling power and the determination of the degree of swelling of cellulose fibres in sodium hydroxide solutions in which he describes the methods of Weltzien and his own applications of them.

The technical section, Part II, deals briefly with raw materials, machinery, and spinning apparatus. Some account is given of Ost's experiments on the stretch spinning process, illustrated by a number of photographs showing the withdrawal of the thread at different speeds through nozzles of various dimensions. A few typical illustrations of German machinery are given. The chapters that follow deal with the individual methods of production, nitrate, acetate, viscose, and other silks. Each is considered under (*a*) theoretical, and (*b*) practical, the general chemistry and theory of the process being described first, followed by an account of the technical methods involved. The final chapter gives a brief survey of the economics of artificial silk, and a useful bibliography is included.

The feature of the book is its scientific treatment which, however, is useful not so much in regard to the definite facts it includes, as in the way it suggests to the reader problems for future research. The author's enthusiasm leads him, perhaps, to over-estimate the application of science. He refers particularly, for example, to the investigations of Karrer on the degradation of cellulose by the enzymes from the edible snail. These enzymes apparently enable silks from different German factories to be differentiated when all other tests fail. It is a little difficult to see the utility of such differentiation, except possibly in a criminal case. The book is quite well translated, though examples of involved sentences and German idiom are common. The following is an example—"this is less influenced by the distance traversed in the precipitating bath, although this also has some influence, because the concentration and temperature of the adhering precipitating bath which is carried along by the fibre, are constantly altering on account of the continued reaction." Some parts of the book also read like a collection of scraps taken from a note-book, *e.g.* the chapter on cellulose acetate, pp. 134–135.

The work is a useful contribution to the literature on artificial silk.

C. DORÉE.



QUESTIONED DOCUMENTS. By A. S. OSBORN. 2nd Edition. Pp. xxiv+1028. Albany, N.Y.: The Boyd Printing Co. London: Sweete & Maxwell. 1929. Price 55s. net.

Mr. Osborn's book, which has long been recognised as a standard work on the examination of documents, has, for some years, been out of print, and this new and enlarged edition should therefore meet with a wide welcome. The main features of the original edition have been retained. As before, the book opens with instructive chapters on the preliminary examination of documents and on standards of comparison. Then come chapters on photography and photographic methods, the microscope and its most suitable forms for examining documents, and on special measuring instruments, which include a "curve meter," a useful device of the author's for measuring and recording the shapes of curves.

The following chapters deal with handwriting and its variations, and the methods used in its examination, including the detection of traced and other forgeries. Paper and its water marks, the evidence of folds in paper, inks, pencil writing, and type-writing, are all discussed in detail, although, as the author makes no claim to chemical knowledge, his methods are mainly based on physical and optical measurements.

The way in which scientific evidence should be presented in Court is dealt with shrewdly and with humour, and stress is rightly laid upon the point that such evidence should be based on observed facts which can be demonstrated, and should not be allowed to degenerate into a "counting of heads," as it too often does when opinion is countered by opinion. These chapters will repay careful study by all who have to bring scientific reasoning before a judge or jury.

A new feature of this edition is a very full classified summary of legal citations of discussions on the facts and law relating to questioned documents, with references to the several judgments. Although this section of the book is mainly concerned with American law, yet much of what the author has so skilfully collated and indexed should be of use to lawyers and scientific witnesses in this country.

The bibliography, which was a valuable section of the first edition, has been retained and expanded, and, with its interesting accompanying commentaries now forms a fairly complete guide to the literature on handwriting and disputed documents. The subjects discussed in the 36 chapters are effectively illustrated with photographs and photographic enlargements, many of them relating to actual cases, and the book concludes with a good index.

This review gives only a slight indication of the immense amount of labour and thought which have contributed to the making of this book; and although we must differ from the author's conclusions on some of the technical questions, it is difficult to over-praise the work as a whole.

EDITOR.

## Publications Received.

- THE ANALYSIS OF DRUGS AND CHEMICALS. By N. EVERS and G. D. ELSDON. London: Chas. Griffin & Co., Ltd. Price 25s. net.
- AN INTRODUCTION TO THE CHEMISTRY OF PLANT PRODUCTS. Vol. II. METABOLIC PROCESSES. By P. HAAS and T. G. HILL. 2nd Edition. London: Longmans, Green & Co. Price 10s. 6d. net.
- AN INTRODUCTION TO MODERN ORGANIC CHEMISTRY. By L. A. COLES. London: Longmans, Green & Co. Price 7s. 6d.
- THE PYROLYSIS OF CARBON COMPOUNDS. By C. D. HURD. New York: The Chemical Catalog Co., Inc. Price \$12.50.
- INDUSTRIAL CARBON. By C. L. MANTELL. London: Chapman & Hall. Price 21s. net.
- CRYSTAL STRUCTURE AND CHEMICAL CONSTITUTION. A General Discussion held by the Faraday Society. Price 8s. 6d.
- CHEMISTRY OF PULP AND PAPER MAKING. By E. SUTERMEISTER. New York: John Wiley; London: Chapman & Hall. Price 32s. 6d. net.
- ENZYME ACTIONS AND PROPERTIES. By E. WALDSCHMIDT-LEITZ. Translated and Extended by R. P. WALTON. New York: John Wiley; London: Chapman & Hall. Price 20s. net.
- INORGANIC QUANTITATIVE ANALYSIS. H. A. FALES. London: G. Bell & Sons. Price 12s. 6d. net.
- THE THEORY AND TECHNIQUE OF QUANTITATIVE ANALYSIS. By M. FARNSWORTH. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. Price 12s. 6d. net.
- CHEMISTRY IN THE HOME. By J. B. FIRTH. London: Constable & Co. Price 5s. net.
- ANNUAL REPORTS OF THE SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY FOR 1928. Vol. XIII. Price, 12s. 6d. to non-members; 7s. 6d. to members.
- ANLEITUNG ZUR ORGANISCHEN QUALITATIVEN ANALYSE. By H. STAUDINGER. 2nd Edition. Berlin: Julius Springer. Price 6.60 Marks.
- PRACTICAL PLANT BIOCHEMISTRY. By M. W. ONSLOW. 3rd Edition. Cambridge: The University Press. Price 12s. 6d. net.
- DIZIONARIO DI MERCEOLOGIA E DI CHIMICA APPLICATA. 5th Edition. Vol. I. (ABELMOSCO-CUSCUTA). By G. VITTORIO VILLAVECCHIA. Milan: U. Hoepli. Price L.60.