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# THE ANALYST

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

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Tuesday, May 18th, 1926, the President, Mr. E. Richards Bolton, F.I.C., being in the chair.

Certificates were read for the first time in favour of Messrs. Francis Harrold Bamfield, M.Sc., Ph.D., A.I.C., and Albert Lester Williams, A.I.C.

Certificates were read for the second time in favour of Messrs. Arthur Barraclough, B.Sc., A.I.C., George Gordon Elkington, Kenneth Massy Griffin, M.Sc., A.I.C., Herbert Firth, A.I.C., and Thomas Pickerill, B.Sc.

The following were elected Members of the Society:--Messrs. John Allan, Michael Thomas Casey, B.Sc., M.Sc., George Henry Davis, Julius Grant, M.Sc., A.I.C., and Miss Monica Mary Ruston, F.I.C.

The following papers were read and discussed:—"The Detection and Determination of Glycerin in Tobacco," by A. Chaston Chapman, F.R.S., F.I.C.; "Further Notes on the Crystalline Bromides of Linseed and other Oils," by Harold Toms, M.Sc. (under the Analytical Investigation Scheme); "The Polarimetric Determination of Sucrose in Condensed Milk," by A. Bakke and P. Henegger (summarised by E. B. Hughes, M.Sc., F.I.C.); "The Determination of very small Quantities of Iron," by Henry L. Smith, B.Sc., F.I.C., and J. H. Cooke, B.A., A.I.C.; "The Separation of Iridium from Iron," by W. R. Schoeller, Ph.D.; and "The Determination of Total Alkaloids, Sugar and Oily Substances in Opium," by Jitendra Nath Rakshit.

# ADDRESS OF THE SOCIETY TO THE ASSOCIAZIONE ITALIANA DI CHIMICA.

#### (Presented by Mr. A. H. Bennett, the Society's representative at the Congress.)

THE PRESIDENT, THE COUNCIL, AND THE MEMBERS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS, on the occasion of the II. National Congress of Pure and Applied Chemistry at Palermo, send hearty GREETINGS to the ASSOCIAZIONE ITALIANA DI CHIMICA and desire to add their tribute of admiration and respect to the memory of STANISLAO CANNIZZARO.

Chemists throughout the world owe a debt of gratitude to Stanislao Cannizzaro for his famous work upon the determination of Atomic Weights, and the general relation of Atomic Weight to Specific Heat among the solid elements, as well as his elucidation of problems connected with the co-ordination of Organic with Inorganic Compounds.

The Members of the Society of Public Analysts specially appreciate the masterly manner in which Cannizzaro applied the knowledge of science to the practical problems of Public Health at a time when Palermo was stricken with an epidemic of sickness, and, furthermore, that during a life devoted to so many branches of Chemical Science he found time to make valuable contributions to the Science of Analytical Chemistry, embracing the important subject of Food Control.

The name of Stanislao Cannizzaro will ever be revered by Chemists for the legacy of knowledge he has left to those who practice the Science. British Chemists will recall his association with British Scientific Societies and his marriage with an English lady as constituting a further link of fellowship with this country.

The Society of Public Analysts hopes that the Congress will be a great success and that the Associazione Italiana di Chimica may ever prosper in the advancement of Science in the future as it has done in the past.

On behalf of

THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

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(Signed) E. R. BOLTON, President.

E. HINKS, Honorary Treasurer.

F. W. F. ARNAUD, Honorary Secretary,

LONDON, May 1926.

# The Analysis of Acetic Anhydride.

### BY H. DROOP RICHMOND, F.I.C., AND J. A. EGGLESTON, B.Sc.

(Read at the Meeting, April 7, 1926.)

WHEN many samples of acetic anhydride have to be examined the labour and time involved by the Menschutkin and Wasiljew method, which is the most accurate, is very great (J. Russ. Chem. Soc., 21, 190; cf. Report of International Glycerol Commission, ANALYST, 1911, 26, 316; and Richmond, ANALYST, 1917, 42, 133). This method calls for close attention to detail and the greatest accuracy in titration; we may mention here a point which is not usually emphasised, viz. that, as the titrations are to phenolphthalein (about  $P_{\mu} = 8$ ), it is essential that the alkali solution used should be standardised against standard acid (free from carbon dioxide), phenolphthalein being used as indicator to the same  $P_{\mu}$  value; there is a difference of about 0.4 per cent. between this value and that obtained if methyl red is used as indicator. The direct titration method reduces both time and labour, but it lacks accuracy; the results depend on the assumption that only acetic anhydride and acetic acid are present, and when 1 grm. is taken the difference between 100 per cent. of anhydride and no anhydride at all is represented by 2.94 c.c. of N solution, which is about 15 per cent. of the amount for the total titration.

THERMOMETRIC METHOD.—One of us, in conjunction with the late J. E. Merreywether, had found that the strength of sulphuric acid can be determined in a simple apparatus by a thermometric method (ANALYST, 1917, 42, 273). Acetic anhydride and aniline react with a great evolution of heat, but it is necessary to keep the temperature down, since only at a comparatively low temperature is the equation

## $(CH_3CO)_2O + C_8H_5NH_2 = C_8H_5NHCO.CH_3 + CH_3COOH$

realised, for at higher temperatures the reaction proceeds further, and the acetic acid forms acetanilide. It was necessary, therefore, to find a diluent which would be inactive towards acetic anhydride, acetic acid, and aniline. Preliminary experiments showed that toluene, which can easily be obtained in a high degree of purity and is not expensive, fulfilled the requirements. We found that if to 200 c.c. of a mixture of 94 parts of toluene and 6 parts (by volume) of aniline 2 c.c. of acetic anhydride were added, a rise of temperature of approximately 5° C. was obtained, which in a vacuum-jacketed flask, as used by Richmond and Merreywether, was easily measurable to a few thousandths of a degree. With a well-graduated pipette a nearly constant weight of acetic anyhdride was delivered,

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which, though rather under 2 c.c., bore practically a constant ratio to the specific gravity, as the following results show:—

Weight of acetic anhydride delivered by 2 c.c. pipette.

Sp. Gr.	Weight delivered by 2 c.c. pipette.	Theoretical weight.
1.0880	$2 \cdot 1747 : 2 \cdot 1706$	2.176
$1.0825 \\ 1.0610$	$2 \cdot 1545 : 2 \cdot 1547$ $2 \cdot 1111 : 2 \cdot 1086$	$2 \cdot 165 \\ 2 \cdot 122$

The method adopted was as follows:—Two hundred c.c. of toluene mixture (94 per cent. of toluene, 6 per cent. of aniline by volume) were measured in a 200 c.c. graduated flask and poured into the vacuum flask. The thermometer was inserted and the neck plugged with cotton wool. The flask was shaken with a rotatory movement, and the temperature taken when constant. Two c.c. of acetic anhydride were then added by means of a pipette, the flask well shaken, and the final temperature read.

						Rise in	Rise in				
						temp.	temp.	Cor-			
					Rise	for	for	rected	Rise		
					in	acetic	acetic		imes 20.08	Total	(M and
		Dice i	n tempe	ratura	temp.	acid	acid	of	1.0889	rise	W's)
Comm 1			-		-				X		,
Sample		р	er 2 c.c	•	(mean).	present.	iormea.	temp.	Sp. Gr.		method.
No.	Sp. Gr.									$\mathbf{Per}$	Per
		°C.	°C.	°C.	°C.	°C.	°C.	°C.		Cent.	Cent.
1.	1.0888	5.092	5.113	$5 \cdot 107$	5.104		0.123	4.981	100.0	100.0	100.1
<b>2</b> .	1.0885	5.094	5.100	$5 \cdot 102$	5.099		0.123	4.976	99.9	99.9	99.9
3.	1.0883	5.057	5.045	5.044	5.049	0.002	0.122	4.925	98.9	99.0	<b>99</b> ·0
4.	1.0880	5.004			5.004	0.004	0.121	4.879	97.9	$98 \cdot 1$	$98 \cdot 1$
5.	1.0880	5.000			5.000	0.004	0.121	4.875	97.9	98.0	98.0
6.	1.0880	4.988	4.970	4.986	4.979	0.004	0.120	4.855	97.5	97.6	97.8
7.	1.0868	4.870	4.880	-	4.875	0.009	0.118	4.746	95.5	$95 \cdot 5$	$95 \cdot 8$
8.	1.0876	4.861			$4 \cdot 861$	0.010	0.117	4.734	$95 \cdot 1$	$95 \cdot 3$	$95 \cdot 2$
9.	1.0875	4.848	4.820	4.844	4.837	0.011	0.116	4.710	94.6	$94 \cdot 8$	94.5
10.	1.0869	4.661	4.646	4.650	4.652	0.019	0.112	4.521	90.9	91.2	90.9
11.	1.0865	4.668	4.672		4.670	0.020	0.111	4.539	91.2	91.5	90.5
12.	1.0865	4.610	4.620	4.615	4.615	0.020	0.111	4.484	90.1	90.5	90·4
13.	1.0865	4.625	4.610	4.620	4.617	0.020	0.111	4.486	90.2	90.5	90.4
14.	1.0825	4.112	4.090	4.092	4.098	0.042	0.098	3.958	79.9	80.3	79.9
15.	1.0752	3.108	3.129	3.092	3.104	0.083	0.074	2.947	$59 \cdot 9$	60.8	60.3
16.	1.0690	2.072	2.060	2.068	2.067	0.130	0.046	1.891	38.6	40.5	37.8
17.	1.0637	1.417	1.398	1.406	1.407	0.156	0.031	1.220	$25{\cdot}1$ .	27.6	$25 \cdot 1$
18.	1.0610	0.674	0.680	0.677	0.677	0.187	0.013	0.477	$9 \cdot 8$	$13 \cdot 3$	10.6
19.	1.0600	0.395	0.392	0.399	0.393	0.198	0.006	0.189	$3 \cdot 9$	$7 \cdot 7$	$5 \cdot 2$
Acetic										-	
acid.	1.0560	0.203	0.208	0.210	0.209	0.209	_				0.0

CORRECTION FOR ACETIC ACID.—It will be seen that acetic acid gives a small and constant rise of temperature, which we assume to be the heat of the reaction—

$$CH_3COOH + C_6H_5NH_2 = CH_3COONH_3C_6H_5-$$

and we have corrected the rise of temperature obtained for the calculated rise for the formation of aniline acetate from the acetic acid originally present, together with that formed in the reaction between the anhydride and aniline, and the close agreement of the results indicates that our assumptions are justified. We have pushed our experiments far beyond the strengths of acetic anhydride usually met with in commerce, for the purpose of testing the method. The correction for the heat of formation of aniline acetate has so little influence on the result with acetic anhydride of 90 per cent. strength and over, that practically as good results are obtained by multiplying the rise of temperature by a factor and ignoring the small corrections. Each determination takes about five minutes.

CALCULATION FACTORS.—The factors given are empirical, as we have made no cooling corrections (which are so small as to be negligible) and have not determined the heat capacity of our apparatus, taking this as a constant which affects the factor equally every time. It will be necessary, therefore, to work out a factor for each apparatus.

Our results for duplicate determinations on the same sample show that the maximum divergence between two experiments has been  $0.037^{\circ}$  C.; it is usually very much less, and we claim, therefore, that, when the factor has been determined, the thermometric method gives results comparable in accuracy to those given by Menschutkin and Wasiljew's method and better than the direct titration.

This work was carried out in the Analytical Laboratory of Boots Pure Drug Co., Ltd., to whom we express our thanks.

# The Analysis of Glacial Acetic Acid.

## BY H. DROOP RICHMOND, F.I.C., AND ERIC H. ENGLAND.

#### (Read at the Meeting, April 7, 1926.)

ACETIC acid is unique in that over the whole range of strength at which it solidifies above  $0^{\circ}$  C. the specific gravity decreases with increasing percentage; the freezing point is very definite, and the precautions to be taken for its accurate determination are not excessive. All likely impurities cause a lowering both of the freezing point and of the specific gravity, and, therefore, a comparison of these two physical properties forms a very sensitive test for the purity of glacial acetic acid.

RELATION BETWEEN SPECIFIC GRAVITY, FREEZING POINT AND PERCENTAGE.— We have constructed a table which shows the relation between percentage, specific gravity, and freezing point; the specific gravities are taken from the well known tables of Oudemans (Z. f. Chem., 1866, 2, 150), which are expressed on the basis of  $\frac{15^{\circ}}{4^{\circ}}$  C. or  $\frac{20^{\circ}}{4^{\circ}}$  C., and we have adjusted them to  $\frac{15 \cdot 5^{\circ}}{15 \cdot 5^{\circ}}$  C., as being the usual mode of expression; the freezing points are taken from the tables of Pickering (*Trans. Chem. Soc.*, 1893, 63, 998) and Rudorff (*Ber.*, 3, 390). The freezing point of 100 per cent. acid is taken as  $16 \cdot 63^{\circ}$  C., following Pickering, although Rudorff

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gives  $16.70^{\circ}$  C., and Bousfield and Lowry (*Trans. Chem. Soc.*, 1911, 99, 1432) and de Visser (*Rec. trav. Chem.*, 1893, 12, 101) give figures on specially purified acid as  $16.60^{\circ}$  C. The final tables were obtained by plotting out large scale curves and reading off the smoothed figures from these, and we have found that the results obtained with our most highly purified samples agree very closely with these tables.

FREEZING POINTS AND SPECIFIC GRAVITIES OF ACETIC ACID.

					-		*			
Acid		0.1	0.2	0.3	<b>ð</b> ∙4	0.2	0.6	0.7	0.8	0.9
$\operatorname{Per}$			· · · · · ·							
Cent	-									
99	14.74	14.92	$15 \cdot 10$	15.28	15.47	15.65	15.84	16.04	16.24	16.43
	1.0582	1.0580	1.0577	1.0574	1.0572	1.0569	1.0566	1.0564	1.0561	1.0558
98	13.12	13.27	13.43	13.58	13.74	13.90	14.06	14.23	14.40	14.57
	1.0606	1.0604	1.0602	1.0599	1.0596	1.0594	1.0592	1.0589	1.0587	1.0584
97	11.68	11.82	11.96	$12 \cdot 10$	12.24	12.38	12.52	12.67	12.82	12.97
	1.0627	1.0625	1.0623	1.0621	1.0619	1.0617	1.0615	1.0613	1.0611	1.0608
96	10.34	10.47	10.61	10.74	10.87	11.00	11.14	11.27	11.40	11.54
	1.0646	1.0644	1.0642	1.0641	1.0639	1.0637	1.0635	1.0633	1.0631	1.0629
95	9.08	9.20	9.32	9.45	9.57	9.70	9.82	9.95	10.08	10.21
	1.0663	1.0661	1.0660	1.0658	1.0657	1.0655	1.0653	1.0651	1.0650	1.0648
94	7.83	7.95	8.08	8.20	8.33	8.46	8.58	8.70	8.83	8.95
	1.0677	1.0676	1.0674	1.0673	1.0671	1.0670	1.0669	1.0667	1.0666	1.0664
93	6.67	6.78	6.89	7.01	7.13	7.24	7.36	7.48	7.59	7.71
	1.0689	1.0688	1.0687	1.0685	1.0684	1.0683	1.0682	1.0681	1.0679	1.0678
92	5.57	5.67	5.78	5.89	6.00	6.11	6.22	6.33	6.45	6.56
	1.0699	1.0698	1.0697	1.0696	1.0695	1.0694	1.0693	1.0692	1.0691	1.0690
91	4.52	4.62	4.72	4.83	4.93	5.04	5.14	5.25	5.35	5.46
	1.0708	1.0707	1.0706	1.0705	1.0704	1.0704	1.0703	1.0702	1.0701	1.0700
90	3.51	3.61	3.71	3.81	3.91	4.01	4.11	4.21	4.32	4.42
	1.0716	1.0715	1.0715	1.0714	1.0713	1.0712	1.0711	1.0710	1.0710	1.0709

Between 95 and 100 per cent. the following relation connects freezing points and specific gravities with an error not exceeding 0.1 and 0.0001 respectively.

 $(16.63 - F.P.) \times 0.00144 = Sp. Gr. - 1.0555.$ 

EFFECT OF PROPIONIC ACID.—The most common impurity in glacial acetic acid is propionic acid, which depresses both the specific gravity and freezing point. Mixtures were made of glacial acetic acid with propionic acid as follows:—

Propionic acid added. Per Cent.	Depression of specific gravity.	Depression of freezing point. °C.
3∙0 5∙0 6∙0	0.0019 0.0032 0.0040	$1.45 \\ 2.40 \\ 2.95$

These figures show, on the average, a depression of 0.00065 in the specific gravity for each one per cent. of propionic acid, and  $0.485^{\circ}$  C. in the freezing point. The percentage of propionic acid can be calculated by dividing the difference between the specific gravity calculated equivalent to the freezing point and that found, by 0.00135. This figure was determined by actual experiments, as well as by adding together the depression of specific gravity and that of the freezing point multiplied by 0.00144 (see formula above).

For convenience of calculation a table is appended, of specific gravities calculated equivalent to each  $0.1^{\circ}$  C. freezing point.

Freez											
point	-	0	0.1	$0 \cdot 2$	0.3	0.4	0.5	0.6	0.7	0.8	0.9
¹°C.						<u> </u>					
16	1.05	641	626	612	597	583	569	554		—	
15	1.05	785	770	756	742	727	713	698	684	670	655
14	1.05	927	912	897	883	868	854	840	826	813	799
13	1.06	075	061	046	031	016	$001 \ 1.05$	986	971	956	941
12	1.06	224	209	194	179	165	151	136	121	106	091
11	1.06	368	354	340	326	311	297	283	268	<b>254</b>	239
10	1.06	506	492	479	466	452	438	<b>424</b>	410	396	382
9	1.06	. 637	625	612	599	585	572	559	545	532	519
8	1.06	750	739	728	717	706	695	683	672	661	649
7	1.06	857	847	837	826	816	805	794	783	772	761
6	1.06	951	942	933	924	915	905	896	887	877	867
5	1.07	040	032	023	014	$005 \ 1.06$	996	987	978	969	960
-	1.07	121	113	105	097	089	081	073	065	057	049
3	1.07					_	160	152	145	137	129
9 8 7 6 5 4	$ \frac{1 \cdot 06}{1 \cdot 06} \\ \frac{1 \cdot 06}{1 \cdot 06} \\ \frac{1 \cdot 07}{1 \cdot 07} \\ $	637 750 857 951 040	625 739 847 942 032	612 728 837 933 023	$599 \\ 717 \\ 826 \\ 924 \\ 014$	585 706 816 915 005 1.06	572 695 805 905 996 081	559 683 794 896 987 073	$545 \\ 672 \\ 783 \\ 887 \\ 978 \\ 065$	532 661 772 877 969 057	

FREEZING POINTS OF ACETIC ACID.

PRECAUTIONS IN FREEZING POINT DETERMINATIONS.—The precautions to be observed in determining the freezing point are: first, not to supercool to too low a temperature, one degree below the freezing point being ample, and secondly, not to expose too much to moisture; it is best to take a fairly large volume, say 100 c.c., as the moisture absorption is then negligible. The thermometer must read easily to 0·1°C., and the zero point should be checked at frequent intervals.

CORRECTION FOR PROPIONIC ACID.—The percentage of propionic acid may be checked by fractional distillation of an aqueous solution by Duclaux's method. It is convenient to take one grm. of glacial acid and neutralise it to the extent of 75 per cent., and to distil the remainder; the distillate may then be distilled in fractions, and the percentage of propionic acid deduced; under these circumstances about 70 per cent. of the propionic acid distils, and the results require correcting for this proportion. For example, a mixture of 5 per cent. of propionic acid with very carefully purified acetic acid gave a distillate, on 75 per cent. neutralisation, which distilled as a mixture containing 12.4 molecular proportions of propionic acid to 87.6 molecular proportions of acetic acid, equivalent to 3.43 per cent. of propionic acid in the original mixture, or, dividing by 70/100, 4.9 per cent. in the original.

When examining glacial acetic acid, it is essential that the whole of the acid should be melted completely before drawing a sample, as it is acetic acid which separates out, leaving the propionic acid concentrated in the liquid; we have found, for instance, that a well mixed sample of glacial acid which had a specific gravity of 1.0530 and a freezing point of  $14.95^{\circ}$  C., equivalent to 3.6 per cent. of propionic acid, yielded, on partial solidification, a liquid portion which had a specific gravity of 1.0498 and a freezing point of  $9.35^{\circ}$  C., equivalent to 12 per cent. of propionic acid, and a solid portion with a freezing point of  $15.95^{\circ}$  C.

ALDEHYDES AND KETONES AS IMPURITIES.—Glacial acetic acid is liable to contain as impurities small quantities of aldehydes and ketones, usually to so

small an amount as to have no appreciable influence on the specific gravity or freezing point; the aldehyde is detected by Schiff's reagent, and the ketones by Deniges's mercuric chloride test. The two may be determined together by means of the iodine absorption in alkaline solution. When calculated as acetone the iodine absorption does not usually reach much over 0.01 per cent., though we have had samples which have been over 0.3 per cent.; such samples proved quite unsuitable for making Wijs's solution. From such an acid a fraction was obtained boiling at about  $80^{\circ}$  C. upwards, which was probably largely propionaldehyde and its homologues.

ADDENDUM.—In a recent note (ANALYST, 1926, 238), C. O. Harvey has noted that the direct titration method almost invariably gives higher figures than those given by the freezing-point method, and attributes this to the presence of traces of formic acid and the difficulty frequently experienced in obtaining a definite "end-point." In our experience the amount of formic acid present is insufficient to have any appreciable effect, and, if the titration is done with alkali standardised to phenolphthalein, there is no difficulty about the "end-point." We think that Mr. Harvey has been, like ourselves, handling samples containing propionic acid. It may be mentioned that the tables in Fresenius's *Chemical Analysis* are those of Rudorff, which are not in the most convenient form, and we think that our table (above) will be far more convenient either than Rudorff's or Mr. Harvey's approximation formula.

### DISCUSSION.

The PRESIDENT remarked that the authors' methods of analysis were of general interest. He had had great difficulty in deciding whether the glacial acetic acid at his disposal was suitable for the Valenta test.

Dr. H. E. Cox said that it was quite evident that the quality of acetic anhydride had much improved in the last few years. During the war it had been almost impossible to obtain it of more than about 90 per cent. purity, whereas recently he had had a sample of 99 per cent., and some of the author's figures were even better. He had found in determining the saponification value of an acetylated product a blank of about 0.2 of N caustic soda on 7.5 c.c. of anhydride, whereas a very much lower figure was now obtainable—a point of some value in acetin determinations.

He asked how the ketone was determined, and was informed that this had been done by iodine absorption in alkaline solution.

Mr. C. A. MITCHELL said that, in his experience, the strength of commercial 80 per cent. acetic acid, as determined by titration, frequently did not correspond with the strength as calculated from the specific gravity, whereas when the same acid was diluted to strengths of 25 to 35 per cent. there was not this discrepancy. He asked the author whether this was also in accordance with his experience, and, if so, what was the explanation.

Mr. RICHMOND, replying to Dr. Cox, said that he was now getting acetic anhydride giving practically no saponification value. The strength was certainly greatly improved; 98 per cent. was quite usual, and he did not use anything of lower strength than 95 per cent.

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He confirmed Mr. Mitchell's experience; the explanation appeared to be that the density of acetic acid was anomalous, decreasing with increasing strength at high percentages, whilst propionic acid did not show this abnormality; at high percentages there was a marked difference between the specific gravities of the two acids, which was near its maximum at 80 per cent., whereas when the strength was reduced to 33 per cent. the difference in the specific gravities was small.

# A Modification of the Gillespie Approximate Method of Determining Hydrogen Ion Concentration.

By J. McCRAE, Ph.D., F.I.C.

THE Gillespie method of determining the  $P_{\rm H}$  value of a water or solution by the drop-ratio method (described on p. 130 of W. Mansfield Clark's *The Determination of Hydrogen Ions*, 2nd edn.) has proved exceedingly useful in practice, and is now extensively employed.

To prepare the standard colours for comparison involves for each indicator 18 tubes into which a measured volume of water and a definite number of drops of indicator-solution must be introduced. This procedure involves no less than 36 separate measurements, without allowing for the further measurements required in alkalising one half of the solutions and acidifying the other half.

The range of colours corresponding with the series of drop-ratios can also be made with single buffered solutions, and these are now supplied in sealed tubes by various dealers. Experience with such sealed tubes has not been uniformly satisfactory, and the chemist will naturally prefer to make his own standards when this can be easily accomplished.

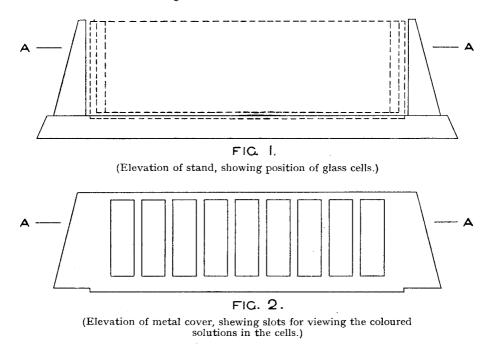
The apparatus described here was designed to avoid the inconvenience of having to make a large number of volume and drop measurements, and, provided that a quantity of water of not less than 300 ml. is available, no volume or other measurement need be undertaken.

The apparatus consists of two right-angled, triangular, glass cells which are placed together to form a divided rectangular cell, over which is fitted a metal cover provided with lateral slots. A sliding holder, carrying a small, rectangular, glass cell, sits on the top of the metal cover, and can be moved along this for the colour comparison.

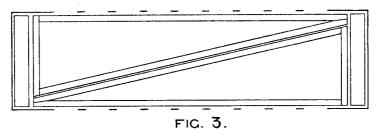
The accompanying figures show the construction of the apparatus. The drawings are half-size.

Fig. 1 is the elevation of a wooden stand. The two triangular glass cells (shown by dotted lines) fit into a depression in the base of the stand,

Fig. 2 is an elevation of the metal cover, and it shows the slots, nine of which are provided to correspond with the nine drop-ratio colours of Gillespie's method; these slots are cut in both long sides of the cover, and the slots in the two sides must



register exactly. The cover provides spaces 12 mm. wide and 40 mm. high, through which the coloured solutions in the cells can be viewed. The bands between the slots are 4 mm. wide. The slightly extended piece of the cover along the major portion of the bottom fits into a groove on the base of the wooden stand.

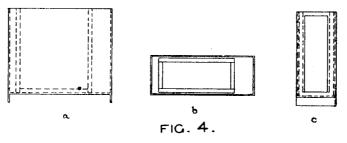


(Horizontal section of apparatus with metal cover in place.)

Fig. 3 shows a horizontal section of the apparatus, with the metal cover in place, through the line A.

The triangular glass cells have an internal dimension of 150 mm. along the long side forming the right angle, and 35 mm. along the short side forming the right angle

(hypotenuse about 154 mm.). The depth of the cell is 47 mm. The capacity of each cell is about 125 ml. There is no particular virtue in these special dimensions, but they have been found to be convenient in practice, and do not give too abrupt colour change, and the colour viewed through any one slot is sufficiently uniform to make comparison easy, and yet sufficiently different from the colours seen through the slots on either side.



(Sliding carrier and glass cell for solution under examination.)

Fig. 4 shows the sliding carrier and the oblong glass cell for the solution under examination. The carrier consists of a metal box, and on the narrow sides slots are cut of the same dimensions as those on the large cover. At the narrow ends a downward overlap is made, and these overlaps serve to keep the box steady on the metal cover over the triangular cells, and, at the same time, permit the box to be moved along the cover. The box carries the rectangular glass cell, the internal dimensions of which are 35 mm. (corresponding with the length of liquid column across the divided rectangular cell) by about 14 mm., and the cell is 47 mm. deep. The capacity of this cell is about 24 ml. A top view of the box with the glass cell is shown in (b); (a) is an elevation of the wide, closed side, and (c) is an elevation of the narrow, slotted side.

To determine the  $P_{\rm H}$  value of a water, trial is made to ascertain what indicator is suitable for use. To about 300 ml. of the water sufficient of the solution of appropriate indicator is added to impart a good strong colour. The two triangular cells and the small rectangular cell are filled with the coloured water. A few drops of acid are added to the water in one of the triangular cells to ensure the full acid colour of the indicator, and a few drops of sodium hydroxide solution are added to the water in the other triangular cell to ensure the full development of the alkaline colour of the indicator. After addition of acid or alkali the solution is well stirred to ensure uniformity of colour throughout the body of the liquid in each cell. The cover is placed over the triangular cells, and the metal carrier with the small rectangular cell is placed on top of the cover. The carrier is moved along the cover until the tint of the water in the small cell, as viewed against a white background, matches the colour seen immediately below through one of the slots in the cover.

#### 290 MCCRAE: A MODIFICATION OF THE GILLESPIE APPROXIMATE METHOD, ETC.

If it is arranged that the thick column of indicator solution in the acid phase is always to the left, and if the slots are marked 1 to 9 from left to right, then the colour tints viewed through the slots correspond with the following  $P_{\rm H}$  values in accordance with Gillespie's determinations:—

Slot No.	Bromo- phenol blue.	Methyl red.	Bromo- cresol purple.	Bromo- thymol blue.	Phenol red.	Cresol red.	Thymol blue.
1	$3 \cdot 1$	4.1	$5 \cdot 3$	$6 \cdot 2$	6.8	$7 \cdot 2$	7.9
2	3.5	4.4	5.7	6.5	$7 \cdot 1$	7.5	$8 \cdot 2$
3	3.7	4.6	5.9	6.7	$7 \cdot 3$	7.7	8.4
4	3.9	4.8	$6 \cdot 1$	6.9	7.5	7.9	8.6
5	4.1	$5 \cdot 0$	6.3	7.1	7.7	8.1	8.8
6	4.3	$5 \cdot 2$	6.5	7.3	7.9	8.3	9.0
7	4.5	$5 \cdot 4$	6.7	7.5	8.1	8.5	$9 \cdot 2$
8	4.7	$5 \cdot 6$	6.9	7.7	$8 \cdot 3$	8.7	9.4
9	$5 \cdot 0$	$5 \cdot 9$	$7 \cdot 2$	8.0	8.6	9.0	9.7

It frequently happens that the tint of the solution in the small cell does not *exactly* match one of the tints as seen through the slots of the cover over the triangular cells, but an intermediate position can be found which allows a  $P_{\rm H}$  value between those quoted in the above table to be determined.

If the quantity of water or solution the  $P_{\rm H}$  value of which is to be determined is insufficient for the above procedure it is easy, by measuring the quantity of indicator, to carry out the determination with 25 ml., or even less. In this case, 250 ml. of water are measured out, and the quantity of indicator solution required to establish a good strong colour is measured. This coloured water is distributed between the two triangular cells; one portion is acidified and the other is alkalised. To 25 ml. of the water or solution the  $P_{\rm H}$  value of which is to be determined is added one-tenth of the quantity of indicator solution used for the larger quantity of water. This coloured solution is introduced into the small rectangular cell, and the colour comparison is made as before.

My thanks are due to Mr. C. E. Mason, Chief Engineer to the Rand Water Board, for assistance in constructing the apparatus and for the drawing.

GOVERNMENT CHEMICAL LABORATORIES, JOHANNESBURG.

# The Examination of Canadian Sprayed Apples for Arsenic.

## By FRANK T. SHUTT, D.Sc., F.I.C. (Dominion Chemist.)

IMMEDIATELY on the appearance in the daily press of cablegrams stating that cases of arsenical poisoning had occurred in England from eating imported apples, steps were taken to procure for analysis, samples of Canadian apples from sprayed orchards in various parts of the Dominion. The work of collection was undertaken by the Dominion Entomologist, who through his provincial officers secured authenticated sprayed apples from the chief apple-exporting districts.

Forty-three samples, in all, were subjected to analysis; eight from Nova Scotia, eight from Quebec, seventeen from Ontario, and ten from irrigated orchards in British Columbia.

Each sample, consisting of from six to twelve apples, was divided, and each portion was separately analysed. The examination was confined to skin, calyx and stalk, as it is agreed generally that the flesh of the apple is practically free from arsenic, even though "ponderable amounts" of this poison may be present on the skin.

The results of this examination are presented in the accompanying table. Following the particulars as to province, variety and spraying, the arsenic content is expressed in fractions of a grain per pound and parts per million, the results obtained for each portion being separately reported. The spraying particulars comprise the number of sprayings, date of last arsenical spraying and the nature of the compound.

For the consideration of the results obtained in this enquiry it may be stated:

(1) That the limit of arsenic  $(As_2O_3)$  suggested by the Royal Commission on Arsenical Poisoning (1903) is 1/100 grain per pound; and

(2) That the medicinal dose of arsenic  $(As_2O_3)$  given in the British Pharma-copeia, 1914, is from 1/64 to 1/16 of a grain.

Summarising the tabulated data, it will be seen that approximately one-half the samples were entirely free from arsenic; that, roughly, one-sixth showed traces of arsenic in amounts less than 1/10000 of a grain per pound (a negligible quantity), and that one-third contained arsenic in quantities ranging from 1/10000 to 1/190 of a grain per pound.

With the heaviest amount of arsenic found, viz. 1/190 of a grain per pound, it would require three pounds or one dozen apples of average size to supply the minimum medicinal dose of arsenic, and twelve pounds or four dozen apples of average size to supply the maximum medicinal dose.

The results of this enquiry furnish satisfactory evidence to the effect that a very large proportion of Canadian sprayed apples is entirely free from arsenic, and that in those cases in which the presence of arsenic has been detected the quantities are negligible.

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### SHUTT: EXAMINATION OF CANADIAN SPRAYED APPLES FOR ARSENIC

### RESULTS OF THE EXAMINATION OF CANADIAN APPLES FOR ARSENIC.

											Arsenic as Ar Oxide $(As_2$	
Lab. No.	Province.	Variety.		$\mathbf{S}_{\mathbf{F}}$	orayin	g pa	rticu	lars	*		Grains per pounds.	Parts per million.
82672	Ontario	Northern Spy	4 s	prays	June	1-7	, arse	nate	e of	lead	1/2000 - 1/650	0.07 - 0.2
82726	,,	Delicious	4	,,	- ,,	22,		,,	, <b>,</b>	,,	free-trace	
82727	,,	McIntosh Red	4	,,	,,	23,		,,	,,	,,	1/830	0.17
82744	,,	N. W. Greenings	4	,,	end c	of Ju:	ne,	,,	,,	,,	trace(?) - 1/10000	0.014
82745	,,	Stark	4	,,	June	5,		,,	<b>,,</b>	<i>,,</i>	trace - 1/740	0.19
82746	,,	Baldwin	4	,,	early	Jun	e,	,,	,,	,,		
82747	,,	Golden Russet	3	,,	•			,,	,,	,,	trace-1/2630	0.054
82748	,,	Greening	4		June	24,		,,	,,	,,	free-trace	
82749		,,	4	,,	· ,,		calciu	ım a	arse	nate		
82750	,,	Northern Spy	4	,,	,,	24,	arse	nate	e of	lead	1/5000	0.03
82756	, ,,	,, ,,	7	,,	July	15,		,,	,,	,,	free-1/650	0.22
82778	,,	Winter Rose	4	,,	June	25-3	30, ca				te —	
82779	,,	McIntosh Red	4	,,	· ,,	,,		,		,,		
82780	,,	Stone	4	,,		,,	,			,,	<pre>free-trace(?)</pre>	
82783	,,	Baldwin	5	,,	Aug.	10,	,			,,	1/740-1/715	0.19 - 0.20
82800		Northern Spy	6	,,			7, lea				· _ ·	
82801		Greenings	6	,,	.,	,,	· ,	,		,,		
82856	Quebec	McIntosh Red	5	,,	Aug.				arsei	nate		
82867	~ ,,	Fameuse	5	,,	,,	,,	,			,,	+	
82858		McIntosh Red	8			20,	,			,,	trace-1/2000	0.075
82859	,	Fameuse	8		,,	,,	,			,,	free-trace	
82860	,,	Fameuse	5		July		,	,		,,	trace	
82861	,,	Fameuse	<b>5</b>	,,	,, ,,	,,	· · ·	,		,,		
82862		McIntosh Red	6	,,	Aug.		,	,		,,	1	
82863		Fameuse	6.	,,	,,	,,	,			,,	A constant	
82925	Nova Scotia	Wagner	4	,,	June		,			••	free-trace	
82926	,,	Stark	7	,,	Aug.	7,	lead			,,	free	
82927	,,	Baldwin & Stark	5	,,	July	3,	,,			,,	free-1/1250	0.11
82928	,,	** **	4	,,		2,	calc	ium	L	,,	free-1/2630	0.054
82929		Wagner & Russet				20.						
83102	,,	Wagner & Russer	4	,,	,,	20, 30,	lead	,,		,,	free-trace	
	,,			"		JU,	leau			,,	nee-trace	
83103			4	,,	**	"	,,			,,		
83104	,,		7	,,	**	"	,,			**		
83093	British Columbia		4	,,	,,	15,	,,			,,		
83183	,,	McIntosh Red			-	•	4 ti				free-1/190	0.76
83184	,,	Spitzenberg		W	ith ar	seni	cal sp	ray	s		free-1/190	0.76
83185	,,	Northern Spy									1/2130 - 1/220	0.06 - 0.64
83186	·	Newton			•						free-1/209	0.68
83187	,,	Jonathan	$\operatorname{spr}$	ayed	4 time	s wit	h ars	enic	cal s	prays		
83188	• •	Snow		,,		:	,,	,	,	,,	free-1/6250	0.02
83189	,,	Salome			twice	:	,,	,	,	,,	10.00 mg mm	
83190	,,	Newton			once		,,	,	,	,,	Baad-1	
83191	,,	Winesap		<b>,</b> ,	twice		,,	,	,	,,		
	4 37		• •									

\* Number of sprayings, date of last arsenical spraying, and nature of arsenicals.

† A dash indicates that no arsenic was detected.

CHEMICAL LABORATORIES,

EXPERIMENTAL FARM, OTTAWA.

#### NOTES

## 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.

### ANALYSIS OF RED MERCURIC IODIDE OINTMENT.

IN an addendum to the reply to the discussion on his paper on the determination of mercury (ANALYST, 1926, 234) Dr. B. S. Evans said that the method would probably be found applicable to the analysis of the mercuric iodide ointment of the British Pharmacopoeia.

Experiments have now been made on the lines suggested, and these have shown that the method affords a rapid and accurate means of analysing this drug.

A sample of the ointment (B.D.H.) was shaken in a separating funnel with two successive portions of the boiling acid mixture (nitric acid, 1; hydrochloric acid, 1; water, 2). The aqueous layer was run off through a wet filter, and the fat rinsed on to the filter and washed with hot water. From this point onward the procedure previously indicated by Dr. Evans (*loc. cit.*) was followed.

The following results were obtained with this ointment (B.P. requirement = 4 per cent. of mercuric iodide):—

Weight of ointment taken.	Mercury found.	Mercuric iodide corresponding to mercury found.
Grms.	Grms.	Per Cent.
10.0000	0.1758	3.98
5.0026	0.0868	3.93
		EDITOR.

#### DATA USED IN GRAPH FOR BEESWAX.

In the April issue of the ANALYST (p. 181) there was published a communication from Mr. A. Weir, giving the data which he used to construct his beeswax graph, which was published last year (ANALYST, 1925, 50, 445).

Among the limits which he gives for pure beeswax are those for the ester value (65.9 to 85), and it would be interesting to know what evidence he had for believing that the beeswaxes which gave him these extreme ester values were, in fact, pure.

I may say that, in the course of the last 10 years, I have examined almost every known variety of beeswax, and I have never yet seen a sample of *yellow* beeswax of unquestioned purity which had an ester value lower than 70 or higher than 78.5.

M. S. SALAMON.

# INVERT SUGAR AS A REAGENT FOR BORIC ACID DETERMINATIONS.

IN a former issue of THE ANALYST (1924, 49, 576) Mr. G. van B. Gilmour claimed that he was the first to show the effectiveness and cheapness of invert sugar as a reagent in the titration of boric acid (ANALYST, 1921, 46, 3).

It may be mentioned that the use of invert sugar for this purpose had already been suggested by M. Boeseken (*Proc. Roy. Acad. Amsterdam*, 1917, 26, 3) and that the method was worked out by me (*Rec. trav. chim.*, 1920, 39, 350).

J. A. M. VAN LIEMPT.

EINDHOVEN, HOLLAND.

## Notes from the Reports of Public Analysts.

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

#### CITY OF BIRMINGHAM.

#### ANNUAL REPORT OF THE CITY ANALYST FOR 1925.

DURING the year, 5421 samples were analysed, of which 4736 were taken under the Sale of Food and Drugs Acts, 18 under the Fertilisers and Feeding Stuffs Act, 6 were samples of medicine for the Birmingham Health Insurance Committee, 36 were samples from soot gauges, and 625 were from various Corporation departments.

Of the samples under the Food and Drugs Acts, 4466 were informal, and 270 were formal. The number of samples purchased was at the rate of 498 per 100,000 inhabitants. Of the 218 samples found to be adulterated, 200 were food and 17 drugs (percentage of adulteration = 4.6); there were also 35 samples incorrectly labelled.

MILK.—The total number of samples examined was 2601, and of these, 181 were adulterated.

On January 20 informal samples from a shop were found to be adulterated with 20 per cent. of water and artificially coloured. On January 22nd and 28th (after the vendor had warned the wholesaler) samples taken from the shop were genuine. On February 9th and 11th about 3 per cent. of added water was present, and on February 20th this amount had increased to 11 per cent., which was the same as that found in two samples purchased directly from the wholesaler. The last five samples were also coloured. Proceedings were taken and the vendor was fined  $\pounds 5$  for adulteration and  $\pounds 5$  for selling coloured milk, contrary to Section 4 of the Milk and Dairies (Amendment) Act, 1922.

CHICORY.—One of the 5 samples examined was adulterated, the ash being 8.3 per cent., which included 3.7 per cent. of sandy matter.

ALE, BEER.—One sample of ale contained 6 grains of boric acid per gallon, but a second sample from the same vendor was free from this preservative.

DRUGS.—Seventeen of the 219 samples (8 per cent.) were unsatisfactory.

BORIC ACID OINTMENT.—The B.P. requires this ointment to contain 10 per cent. of boric acid. Four samples contained from 9.9 to 10.2 per cent. Another, though marked "Prepared according to B.P.," contained 12.3 per cent., and the vendor was cautioned.

ZINC OINTMENT.—The B.P. requirement is 15 per cent of zinc oxide. Five of the 6 samples contained from 14.6 to 15.6 per cent., but one was too strong, containing 17.5 per cent.

ALMOND OIL.—Eleven informal samples were genuine, but 2 samples from one vendor were peach-kernel oil. In each case the bottle was labelled "almond oil." The vendor was prosecuted under Section 6 of the Sale of Food and Drugs Acts, and fined  $\pounds 1$ . He was also fined  $\pounds 2$  under Section 27 for wilfully giving a label which falsely described the article sold. This is the first time a prosecution has been taken under this section.

For particulars of other foods and drugs examined during the year see the Quarterly Reports (ANALYST, 1925, 50, 446, 502, 606; 1926, 182).

J. F. LIVERSEEGE.

#### GREGORY'S POWDER.

FURTHER investigation of the question of the action of calcined magnesia in preventing the solution of the soluble matter in rhubarb has been made (cf. ANALYST, 1925, 50, 502). Five samples of light magnesia-bought from retail shops, were tested with a sample of rhubarb, and, in the conditions of the experiment, the amounts of soluble matter, expressed on the rhubarb, varied from 24 to 39 per cent. Six other samples, obtained directly from a wholesale dealer, yielded, with another sample of rhubarb, from 29 to 40 per cent. of soluble matter. At first it was thought that these differences were due to impurities in the light magnesia, but in a series of experiments the addition of various impurities to the magnesia had little effect on the aqueous extract of the rhubarb, and the different action appears to be due to the varying physical condition of the magnesia, and not to its chemical composition. It was also discovered that the amount of soluble matter in Gregory's powder increases with time. For instance, a sample which gave 8.9 per cent. of soluble matter, yielded, after 6 weeks, 10.3 per cent. It seems probable that this increase may be due, to some extent, to the activity of the magnesia having altered by its taking moisture from the rhubarb and ginger with which it was mixed.

Samples of the magnesia from which the Gregory's powders giving low results had been made were obtained, and were found to be active with regard to rhubarb and ginger. A modification of the analytical method to prevent this varying action of the magnesia has been devised. The low results obtained with two samples of Gregory's powder from one manufacturer may have been intensified by the fact that the powdered rhubarb and ginger had been dried before mixing with the magnesia. The powder had, therefore, not been made in accordance with the directions of the B.P., which orders powered drugs to be used without drying

J. F. LIVERSEEGE.

#### THE COMPOSITION OF MILK IN "APPEAL TO THE COW" CASES.

ALTHOUGH the breed of the cows and circumstances of taking the samples were different, interesting comparisons may be made between the milks given by individual Scotch cows in Dr. Tocher's report (ANALYST, 1926, 146), and those from cows supplying Birmingham.

During 21 years 216 farms have been visited by inspectors and 434 samples obtained from normal milkings. The farms were in 8 different counties, mostly within 50 miles of Birmingham, but as only those farms which had been sending milk of low quality were visited, the samples cannot be considered as representative of Birmingham milk, and further, more than one quarter of them were taken during war time, when many cows were badly fed. When more than one churn of milk was sampled at a farm, the average composition of the whole meal has been used in the calculations.

The following table shows the average composition of the samples taken at the farms; the average of all Birmingham samples for 26 years (8.8 per cent. adulterated); and Dr. Tocher's average for all the individual Scotch cows.

Samples of Milk.	Total solids. Per Cent.	Solids- not-fat. Per Cent.	Fat. Per Cent.
314 Normal meals from farms	12.51	8.67	3.84
36,407 Birmingham samples	12.31	8.70	3.61
676 Individual Scotch cows	12.75	8.80	3.95

The lower values given by the cows in the farms supplying Birmingham than by the Scotch cows is probably due partly to difference in breed and partly to the farms being selected for poor quality. The fact that the percentage of solidsnot-fat of the farm samples (8.67 per cent.) is distinctly above the presumptive limit (8.5 per cent.), shows that most of the visits to the farms were necessitated by the addition of water by farmers, and not by the natural poorness of the milk of the cows. From each farm, milk had previously been sent which had given results below one or both of the limits.

The percentage distribution of the milks from the farms for solids-not-fat and for fat was as follows:—

Perc	entage of	Solids-not-	Fat.	Percentage of Fat.				
Under 8.3	8.3-8.4	8.5 - 8.9	9 and over	Under 3.0	3-3-4	3.5-3.9	4.0 and over	
·6	<b>14</b>	<b>68</b>	12	3	<b>23</b>	<b>32</b>	<b>42</b>	

The worst sample was one which contained  $8\cdot 1$  per cent. of solids-not-fat and  $2\cdot 9$  per cent. of fat. It was taken from the milk of 3 poorly-fed cows, the total yield of which at one milking was only 1 gallon. Only 5 per cent. of the Birming-ham supply farms numbered as few as 3 or 4 cows. The next worst samples came from a farm where the evening milking gave  $8\cdot 2$  per cent. of solids-not-fat, and the morning milking  $2\cdot 8$  per cent. of fat; the other figures were not below the limits. The herd was in poor condition and contained some old cows; the intervals of milking were  $13\frac{1}{2}$  and  $10\frac{1}{2}$  hours. These were the only two farms from which samples low, both in solids-not-fat and fat, were obtained.

Morning samples from 6 other farms were below the limit for fat. In each case the evening milk was of good quality, and the mixture of the morning and evening milk was above the limit. The chief cause of the low fat was the long interval from the previous milking. In 5 of the farms from 14 to  $15\frac{1}{2}$  hours had elapsed since the evening milking. At one of the farms there were only 3 cows, and in two cases the cows were in poor condition.

In 12 other farms the solids-not-fat were below 8.3 per cent. This is to be attributed to improper feeding of the cows, in some cases almost to starvation point during war time.

Classification of the farm cows according to condition gave the following average results for the mixed morning and evening milk from each farm:—

Condition of Cows.	Solids-not- fat.	Fat.	Total Solids.	Daily yield.
	Per Cent.	Per Cent.	Per Cent.	Gallons.
Poor	8.52	3.47	11.99	1.77
Fair	8.59	3.64	12.23	1.72
Good	8.80	3.77	12.57	$2 \cdot 13$

These results support the view that insufficient feeding of the cows will affect the quantity of the milk more than the quality, and also that the condition of the cows will suffer. The average yield was 1.93 gallons per day (2 meals), which compares rather unfavourably with that from Dr. Tocher's Scotch cows, which yielded on the average 1.35 gallons per meal.

A comparison between the number of gallons of milk obtained in a day and its composition showed that the quality is not much affected by the amount yielded. The larger meals contained about 0.2 per cent. more of solids-not-fat than the smaller meals, and about 0.2 per cent. of fat less. Dr. Tocher also found that an increased yield was accompanied by a decrease of fat, but he observed a *decrease* of solids-not-fat as well.

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The farm samples gave results which agreed with Dr. Tocher's observation that there is a uniform rise in the percentage of solids-not-fat with ascending values of butter fat. On the average, samples containing less than 8.5 per cent. of solidsnot-fat were accompanied by an average of 3.51 per cent. of fat; those with 8.5to 8.8 per cent. of solids-not-fat with 3.67 per cent. of fat; and those with 8.9per cent. of solids-not-fat had, on the average, 3.97 per cent. of fat.

The following table gives the results for farms which were visited morning and evening, and where in each case the same number of cows were milked for each meal, so that the figures for morning and evening are strictly comparable:—

					Hours from previous milking.									
					A	<u>B</u>	С	D	E	F				
	Avera	ge comp	osition		9-	10	11-12	12-	13-	14-15				
			•		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.				
Solids-:	not-fat	••			8.62	8.59	8.69	8.74	8.73	8.74				
Fat	• •	••	••	••	$4 \cdot 16$	4.07	3.71	$3 \cdot 48$	3.51	3.39				
Total s	solids	••	••	• •	12.78	12.66	12.40	12.22	12.24	12.13				
Diffe	rences.				F-A	E <b>−</b> B	DC	CD	B-E	A-F				
Solids-1	not-fat	••	••		0.12	0.14	0.05							
Fat ·	••	••	• •	••		—		0.23	0.56	0.77				

The morning milk for the solids-not-fat was about 0.1 per cent. higher than the evening milk, and for fat it was about 0.5 per cent. lower than the evening milk. The Scotch cows of Dr. Tocher's report showed less difference.

The quarterly variations in the composition of the milk from 100 farms, and the quarterly averages of the Birmingham samples were as follows:—

			100 Fai	ms.	36,407 Samples.			
Quarters.			ids-not-fat.	Fat.	Solids-not-Fat.	Fat.		
		1	Per Cent.	Per Cent.	Per Cent.	Per Cent.		
First	••	••	8.62	3.60	8.64	3.56		
Second	••		8.68	3.50	8.73	3.44		
Third	••		8.69	3.75	8.68	3.62		
Fourth	••		8.79	4.17	8.74	3.81		
First (sev	vere co	ld)	8.60	3.80				

Dr. Tocher found that the solids-not-fats of his samples fell slightly from the first to the third quarters, and rose to the fourth. The fat, on the other hand, was lowest in the first quarter of the year and highest in the third. The seasonal distribution of quality for Scotch cows is, therefore, somewhat different from that for cows in the Birmingham district.

The last line of the table shows the average composition of milk from some farms visited in first quarters, when the inspectors reported the weather as being unusually cold. The solids-not-fat were similar to the average of all the first quarter farm samples, and the fat was 0.20 per cent. higher. These figures do not support the claim, sometimes made, that a low quality of milk is due to cold weather.

The general conclusion drawn from this experience of 21 years is that, in the comparatively few cases in which the cows yielded poor milk, the cause was to be found in defective feeding, particularly in war time, in some cases combined with abnormal intervals between the times of milking.

J. F. LIVERSEEGE,

# Legal Notes.

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

#### SALE OF IMPORTED EGGS AS NEW-LAID EGGS.

ON April 7, a dairy company, having 779 branches, was summoned at Salford on two charges: (1) For selling by retail as new-laid eggs, at their premises in Salford, eggs which had been imported into the United Kingdom on March 1; and (2) for having unlawfully, by means of an advertisement in a newspaper, offered for sale by retail, as new-laid eggs, eggs which had been imported.

The Deputy Town Clerk stated that the proceedings were taken under the Sale of Food Order, 1921, made by the Board of Trade under the Ministry of Food (Continuance) Act, 1920, and he said that both the Act and the Order would remain in force until December 31, 1926.

According to Section 8 of the Order: "A person shall not sell or offer or expose for sale, whether by wholesale or retail, as fresh eggs or new-laid eggs, or under any description of which the words 'fresh' or 'new-laid' form part, any eggs which have been imported into the United Kingdom, unless the description also includes the word 'Imported,' or a word or words disclosing the country of origin."

Evidence was given that an advertisement of the defendant company in a Manchester newspaper on February 25, contained the words: "Fine, large, new-laid eggs,  $1_4^3$ d. each," and there was no suggestion that the eggs were anything but what the public believed to be English new-laid eggs. Two days later the inspector visited the defendants' shop and ascertained from an assistant that all the eggs sold by them were either Danish or Belgian.

On March 1, an agent of the inspector purchased "four new-laid eggs," and nothing as to their origin was said to him by the assistant who sold the eggs. The assistant and manager admitted to the inspector that the eggs had been sold as new-laid and that they were of foreign origin.

On March 5, there was another advertisement in the paper, with the word "Imported" underneath the word "eggs," but this did not appear until after the firm had been told that the charges had been made.

In cross-examination, the inspector admitted that there was a bill in the window, which said "Danish eggs," and that on the eggs in the window was a label which said "New-laid eggs" in fairly large letters, with "Danish" in smaller letters; also, that on the window itself was a large placard with the words "New-laid Eggs," and in white underneath "Imported."

The eggs were sold from a basket labelled with a card "New-laid Eggs: Imported," but the prosecution contended that the notice on the basket was of no use, since if a purchaser asked for new-laid eggs he was entitled to receive newlaid eggs and must not be sold imported eggs. A new-laid or fresh egg must be an English egg.

The Magistrates took the view that, as regards the selling, the defendants had complied with Section 8, though they might not have acted as the Bench would have liked them to act. This summons would be dismissed.

Referring to the second summons, concerning the advertisement, the solicitor for the defence said that the advertisement was really a part of the transaction. It was an invitation for anyone to go to the defendant's shop to see what these new-laid eggs were. It was an offer of new-laid eggs for sale, but the material LEGAL NOTES

part of the transaction took place when the offer was exercised. When the inspector had asked if the defendants had English new-laid eggs, he was told at once that they had none. So it was not a case of anyone suffering from a misapprehension. He submitted that, at most, there had only been a technical breach of the Order. Although the firm had altered the wording of their advertisement, they did not, at the time, think it necessary, because at the shop they made it clear what was being sold.

The Bench intimated that they had decided to convict. A fine of  $\pounds 25$  was imposed.

#### EGG POWDER.

A COMPANY owning a number of shops was summoned at Tower Bridge Court on April 15, for selling, at their Southwark branch, egg powder not of the nature, substance and quality demanded. Evidence was given by the inspector that he had bought two ounces of egg powder for  $2\frac{1}{2}d$ . Upon analysis the powder was found to consist of the following ingredients:—Maize flour, 63.0; sodium bicarbonate, 20.6; tartaric acid and a trace of colouring 16.4 part. There was no trace of egg in the mixture, which should have been labelled "Egg Substitute."

The Solicitor for the defence said that all the firm's branches were supplied with a rubber stamp bearing the word "substitute," but that in this case they had neglected to use it. In future the word would be printed on the packet.

The Magistrate (Mr. Sandbach) convicted the defendants, and imposed a fine of 20s. with 21s. costs.

#### BORIC ACID IN POTTED MEAT.

ON April 16, a co-operative society was summoned at East Dereham, Norfolk, for having sold at their local branch potted meat containing 0.372 per cent. of boric acid.

The inspector who bought the sample admitted, in cross-examination, that there was no authoritative standard as to the amount of boric acid which might be used. He was not aware that, in 1901, a Departmental Committee had suggested 0.5 per cent. as a suitable standard. In re-examination, he said that under the Public Health (Preservatives in Food) Regulations, 1925, which would come into force shortly, the use of boric acid in foods was entirely prohibited.

The County Analyst (Mr. W. Lincolne Sutton) said that the quantity of boric acid in the sample was equivalent to 26 grains per lb., and was liable to render the article injurious to health. Of recent samples of potted meat examined, more than half were free from boric acid, and the remainder contained, on an average, 5 grains per lb. This sample was in a state of putrefaction, when received, and owing to the nature of boric acid and the chemical process that went on, the amount of preservative originally present in the sample must have been larger than the quantity he had found. The amount of boric acid in this case was so excessive as to take the potted meat completely out of the description of article demanded by the purchaser. In his opinion, this large amount of preservative had been used because of the questionable state of the meat, but it was of no avail, for the sample had come to him in a very bad state of putrefaction.

For the defence it was stated that the potted meat came from the same source as that which had been found satisfactory to the society and its customers for the last six years.

After hearing legal arguments as to the absence of a standard, the Bench dismissed the case.

## Parliamentary Notes.

MEDICATED WINES.—On April 19, Mr. Scrymgeour (Dundee) asked the Minister of health whether he was aware that many meat and tonic wines, which were widely advertised as containing no drugs, contained from 15 to 20 per cent. of alcohol, and whether he would consider the advisability of having compulsory notification of such particulars on the bottles.

Sir Kingsley Wood (Parliamentary Secretary) said that this question had been considered by the Select Committee on Patent Medicines (1914), and that their recommendation was in accordance with the hon. member's suggestion. It would be considered in connection with any legislation for the purpose of regulating the sale of secret or patent medicines.

# Government of Palestine.

# ANNUAL REPORT OF THE DEPARTMENT OF HEALTH FOR THE YEAR 1924.

In the Chemical Division of the Laboratory Section of the Report, the Government Analyst, Mr. G. W. Baker, gives an account of the chemical work undertaken for the different Government departments during the year 1924. The total number of samples examined was 4132.

#### Department of Health.

MILK.—The standard adopted is a minimum of 3 per cent. of fat and 8 per cent. of solids-not-fat, and is based on the results of the analysis of samples of known origin. The total number of samples examined was 3103, and 244 prosecutions were instituted for the sale of watered or skimmed milk. There have been a few cases, especially among imported Dutch cattle, where an appeal to the cow has shown a genuine milk containing less than 3 per cent. of fat. Matters are complicated by the fact that a great deal of the milk sold is a mixture of cow's milk with goat's milk and sometimes sheep's milk.

BUTTER AND SEMNI.—The new ordinance mentioned in the last report (ANALYST, 1925, 50, 22) has not come into operation. Hence, in dealing with the adulteration of food, it has been necessary to fall back upon the powers conferred by the Ottoman Penal Code and by municipal regulations. In municipal areas public establishments are licensed by the Department of Health, and new conditions have been drawn up for application to factories manufacturing butter and artificial butter. These conditions define butter and prohibit the manufacture of the two articles in the same factory.

Some of the semni (pure rendered butter fat) is made in Palestine, but large quantities are also imported from Syria and Egypt. Of 32 samples recently examined, 12 were adulterated, vegetable fats and artificial colouring matters being the usual adulterants.

COFFEE.—Ground coffee is widely adulterated, usually with roasted peas and roasted wheat, and it is not uncommon to find a sample containing 60 to 70 per cent. of these adulterants. Of 184 samples examined, 74 were adulterated. Although the vendors often plead the excuse that the adulterated coffee is only sold to those who want a very cheap article, it has been proved that, as often as not, it is sold at the price of pure coffee. ALCOHOL AND ALCOHOLIC LIQUORS.—On August 15, 1924, new customs regulations came into force, whereby potable spirits and all alcohol, other than that rendered unfit for consumption, are subject to an import duty of 60 piastres per gallon (irrespective of alcoholic strength). As a temporary measure paraffin oil and commercial cresol have been adopted as denaturants, but it has been recommended that crude pyridine should be used in the place of cresol as soon as supplies are available. Owing to the large stocks of undenatured alcohol already in the country, it will be some considerable time before the denaturing of alcohol has any appreciable effect in reducing the manufacture of spurious liquors. The results of the prosecutions instituted in 1923 (cf. ANALYST, 1925, 50, 23) are of little value in controlling the abuse, as the accused were convicted of using improper labels, but not of selling articles, which were "imitated and adulterated," as is required to be proved under Article 194 of the Ottoman Penal Code.

Fresh cases, however, were instituted in Jaffa, the issue being that spirit not made from grapes is not brandy or cognac, and spirit not made from a mash of cereal grains saccharified by the diastase of malt is not whiskey. Convictions were obtained.

SILICATE DEPOSITS IN AERATED WATERS.—Towards the end of the summer manufacturers of mineral waters in Jerusalem experienced much trouble and loss of trade through the formation of a flocculent sediment in their lemonade and ginger beer. The cause of this was traced to the main reservoir of the Jerusalem water supply at Ain Arub. The water from this reservoir was found to contain a colloidal silicate, which coagulated on the addition of the tartaric acid used in the manufacture of mineral waters, and thereby occluded the ginger and any other suspended matter. As a temporary remedy, treatment of the water with alum and filtration in the factory was recommended. The water in Solomon's pool has now been taken into use; this gives no sediment on acidification.

PROTECTION OF CANVAS FROM FUNGUS.—All tentage in Palestine is liable to rapid destruction by the "diamond spot" fungus, unless specially protected. It was found that treatment of the canvas with a weak solution of sodium or potassium dichromate inhibited the growth of the fungus, and that staining the tents with cutch (with dichromate as mordant) was an effective means of prevention.

LEGAL AND CRIMINAL INVESTIGATION.—Arsenic was detected in 4 cases of human poisoning and mercury in 4 cases. Two cases of gorging with cheese were also investigated. Two children aged three and fifteen years, had died in a few hours, and from the stomach of each a solid mass of goat's cheese weighing about 300 grms. was recovered.

There was also a case of fatal poisoning by hydrogen sulphide, which occurred while a cesspit was being cleaned. The sludge at the bottom of the pit was saturated with hydrogen sulphide. The only place connected with this pit was a photographer's shop, and the gas was probably developed from the chemicals used in the photographic work. A similar non-fatal accident occurred previously, and in that case, also, a cesspit was connected with a photographic establishment.

Arsenic was found in three cases, and strychnine in one case of cattle-poisoning.

Forgery Cases.—Examination of the exhibits in a forgery case showed that a stamp bearing a signature had been removed from a genuine receipt and affixed to a spurious one.

In another case, which concerned the age of two documents supposed to have been written at the same time, it was possible to show, by examination of the ink, that one was written at a later date than the other.

# Mines Department.

## SAFETY IN MINES RESEARCH BOARD.

### THE IGNITION OF FIREDAMP.\*

THE composition of the most easily ignitable mixture of methane and air depends on the means of ignition, that is, the source of heat available during a definite period of time. When the period is long, *e.g.* when the gas in enclosed in a heated vessel, mixtures containing 5–7 per cent. methane are ignitable at the lowest temperatures, the lag on ignition being shorter the smaller the proportion of methane. When heat is applied by sudden compression the proportion of methane for ignition at the lowest temperature is about 6.5 to 8 per cent.; with a heated wire there is little difference for all ignitable mixtures; with electric sparks 8–9 per cent.; with a gas flame of short duration, 10 per cent.; with some explosives 9 per cent.; whilst there is at present no information for frictional sparks.

"Bursting into flame" occurs when a sufficient volume of a suitable mixture of firedamp and air is maintained at a sufficient temperature during a sufficient time, and with any sustained flame and an ignitable mixture these conditions will occur. Unless the temperature of a heated surface is unusually high, such surface is less dangerous than a lamp flame, but the larger the surface the greater the danger, so that a wire is more dangerous than a frictional spark. Capacity sparks are more dangerous than inductance sparks of equal energy.

#### THE LIMITS OF INFLAMMABILITY OF FIREDAMP AND AIR.<sup>†</sup>

The values of the limits of inflammability of mixtures of firedamp and air are affected by the direction of flame propagation, due to convection currents, and are widest with upward propagation, narrowest with downward, and intermediate for horizontal propagation. If the mixture is free to expand, the lower limit is least with upward propagation, and with total enclosure the upper limit is greatest, but with horizontal propagation confinement of the gas mixture makes little difference.

The limits of inflammability are not appreciably affected by the changes in temperature and pressure ordinarily occurring in coal mines. The lower limit of inflammability is not appreciably affected by the presence of water vapour, but the reduction of oxygen in the atmosphere narrows the limits, the upper limit being the more affected, until, with 13 per cent. oxygen, they coincide, and only that mixture containing 6 per cent. of methane is inflammable. Reduction of oxygen obtained by addition of carbon dioxide hastens the narrowing, owing to the specific heat of carbon dioxide being higher than that of nitrogen.

The effect of the presence of another combustible gas can be calculated from the known limits of its inflammability with air alone. Limits were found to be as follows (the lower limit of percentage of methane preceding the upper) for quiescent mixtures. Upward propagation and mixture enclosed,  $5\cdot4$ ,  $14\cdot8$ ; free to expand,  $5\cdot25$ ,  $14\cdot0$ ; horizontal propagation, enclosed or free,  $5\cdot4$ ,  $14\cdot3$ ; downward propagation,  $6\cdot0$ ,  $13\cdot4$ ; for turbulent mixtures, lower limit,  $5\cdot0$ ; upper limit not yet determined; for mixtures travelling as currents at a speed between 69 and 128 ft. per minute, lower limit,  $5\cdot05$ ; upper limit not determined.

D. G. H.

\* Paper No. 8. By H. F. Coward and R. V. Wheeler. H.M. Stationery Office. Price 6d. net.

+ Paper No. 15. By M. J. Burgess and R. V. Wheeler. H.M. Stationery Office. Price 6d. net.

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

# Food and Drugs Analysis.

The Iron Content of Meats. E. B. Forbes and R. W. Swift. (J. Biol. Chem., 1926, 67, 517-521.)—Experiments have been made to find how nearly iron varies in meats directly as the protein. Samples of meat for iron determinations were ignited to a white ash in silica dishes, care being taken that all spirting was avoided, and dissolved in hydrochloric acid. The iron was determined by titration with approximately 0.005 N potassium permanganate solution. In all cases triplicate determinations were made, and all three agreed within 0.0001 per cent. The results are tabulated. There is a marked similarity of the iron content of muscle meat from different parts of the carcass. The factor of Sherman (Chemistry of Food and Nutrition, 1918) of 15 mgrms. of iron per 100 grms. of protein seems to be a little high for beef and veal, and much too high for lamb and pork, and it does not apply at all closely in relation to heart, brain, liver, spleen, kidney, and blood. The organ meats are much richer in iron than carcass meat, and should be used more as human food. When compared with analyses compiled by Sherman, beef spleen, liver, kidney and blood contain more iron than do any foods of vegetable origin. Beef and veal contain two-thirds more iron than pork and lamb, and ten times as much as milk. Beef heart and brain contain about twice as much as beef and veal; beef liver twice as much as beef heart, and beef spleen half as much again as beef liver. Beef contains twice as much iron as do potatoes; two and a half times as much as white flour and corn-meal; and eight times as much as do apples. More iron is contained in peas, beans, lentils, Graham flour, oatmeal, shredded wheat, and spinach than in beef. P. H. P.

Effect of Short Periods of Cold Storage on Beef and Mutton, W. M. Clifford. (Biochem. J., 1925, 19, 998-1003.)-Butchers have stated that meat is " spoilt " by being placed in a cold room for any period of time, however short, and that carcasses must be taken straight from slaughter to the butchers' shops. Experiments were carried out to show the effect, if any, on beef and mutton kept in cold storage for periods up to 13 days, and duplicate determinations of the total nitrogen, soluble nitrogen, amino nitrogen, carnosine, and creatine were made at intervals of approximately 3 days. The weather at the time was exceptionally hot and sultry. Beef or mutton kept at  $25^{\circ}$  F. and  $35^{\circ}$  F. appear identical in appearance with freshly killed meat up to the third day of storage. Beef and mutton kept at 25° F. show ice spicules, and the red colour characteristic of frozen meat on the sixth day of storage. In hot English weather beef and mutton will not keep for 6 days in a room at  $35^{\circ}$  F. The changes in frozen meat appear to be physical. since there is no change in total nitrogen, amino nitrogen, soluble nitrogen, carnosine or creatine in meat kept at 35° F. for 3 days, or at 25° F. for 13 days. The "drip" of frozen meat is probably due to the rupture of the muscle cells by ice spicules. P. H. P.

Formaldehyde in Certain Marine Products. D. B. Dill and P. B. Clark. (J. Assoc. Off. Agric. Chem., 1926, 9, 117-122.)—Certain crustacea and also so-called red rock cod, when canned and sterilised and kept for some time, respond to tests for the presence of formaldehyde. This development of formaldehyde, which occurs in absence of oxygen, is independent of the nature of the container, of processes of corrosion of the can, and of the blackening of the products owing to the formation of iron sulphide. The proportion of formaldehyde found in the canned goods is sometimes as high as 1 in 30,000, and, as it is found impossible by acidification and steam distillation to recover more than one-third of a quantity of the aldehyde added to salmon, the true proportion may be as high as 1 in 10,000.

T. H. P.

Preparation of Laevulose. Analysis of Jerusalem Artichokes and Dahlia Tubers. R. F. Jackson, C. G. Silsbee, and M. J. Proffitt. (Scientific Papers of Bureau of Standards, Washington, 1926, 20, 587–617.)—Laevulose may be prepared at a moderate cost from Jerusalem artichokes, which contain from 8.5 to 23.8 per cent. of the sugar as soluble polysaccharides, or from dahlia tubers, which contain from 9.3 to 14 per cent., mainly as the insoluble inulin. Under suitable conditions, the sugar may be obtained crystalline from aqueous syrups. For analysis, the tubers are cleaned with a dry brush and passed through a mincer, 55.8 grms. being then digested on a steam-bath in a 250 c.c. dish with 20 c.c. of water, and afterwards pressed in a small meat-juice press lined with a circular piece of canvas. The extract is pressed into a 100 c.c. flask, two 10 c.c. portions of boiling water being added to wash the beaker and pulp and pressed into the flask.

The weight of flask and extract is determined, and the dry matter found by removing a drop on a glass rod and examining it refractometrically, use being made of Schönrock's tables for sucrose. The subsequent analytical data are corrected for the weight of the drop removed.

The extract, amounting to 85 to 90 c.c., is heated for 35 minutes at 70° C. with 2.5 c.c. of 8.12 N hydrochloric acid, cooled to room temperature, treated with 4 to 6 c.c. of saturated normal lead acetate solution, made up to volume and filtered. The filtrate, usually colourless, is polarised at room temperature, and also at about  $60^{\circ}$  C., the latter reading being corrected for expansion by means of the coefficient of expansion 0.0003.

The total reducing sugars may be determined by removing 7.168 c.c. of the above filtrate by a special pipette to a 100 c.c. flask, neutralising its acidity, adding sufficient sodium sulphate to precipitate the lead, making up to the mark and filtering. Use may then be made of Eynon and Lane's method.

Typical results (percentages) obtained for Jerusalem artichokes are given below: Total solids Total reducing

	Lotal solids		lotal reducing
Year.	in juice.	Laevulose.	Sugars.
1923	18.66	12.22	15.40
1924	18.92	11.73	14.70
1924	17.87	10.67	14.45
1924 (mean	a) $18.24$	11.18	14.89

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The most advantageous period for extraction appears to be during November and December, but an increased crop seems to be obtained if the artichokes are allowed to winter in the ground.

For dahlia tubers the analytical results obtained, calculated as percentages on the original weight of the tubers, are as follows:—Total solids extracted, 12.9 to 18.25 (average 15.9); laevulose, 9.32 to 14.05 (average 11.6).

Determinations of the solubility of pure laevulose give, for the percentages of the sugar in saturated solutions (and for grms. of laevulose per 100 grms. of water), the following figures :—At 20° C., 78.94 (375); 25° C., 80.29 (407); 30° C., 81.64 (445); 35° C., 82.98 (488); 40° C., 84.34 (539); 45° C., 85.64 (596); 50° C., 86.90 (663); 55° C., 88.10 (740). T. H. P.

New Distinguishing Value for Milk Fat. J. Kuhlmann and J. Grossfeld. (Z. Unters. Lebensm., 1926, 51, 31-42.)-A method has been devised to extend the differentiation of the volatile fatty acids of butter fat effected by Gilmour (ANALYST, 1925, 50, 276), by eliminating the influence of the caprylic acid. For this purpose the distillate obtained as in the Reichert-Meissl determination is "salted out" with sodium sulphate and sufficient potassum caprylate (coconut soap solution) to form a saturated solution. Five grs. of the fat are saponified with 2 c.c. of potassium hydroxide solution (750 grms. KOH per litre) and 10 c.c. of glycerin, and the soap solution cooled below 100° C., and diluted with 100 c.c. of water. The liquid is then cooled to 20° C., treated with 50 c.c. of dilute sulphuric acid (25 c.c. H<sub>2</sub>SO<sub>4</sub> per litre), 15 grms. of powdered anhydrous sodium sulphate, 10 c.c. of coconut soap solution (prepared as described below), and a pinch (about 0.1 grm.) of purified kieselguhr. The flask is then repeatedly shaken, allowed to stand for 10 minutes or longer, its contents filtered through a dry filter, and 125 c.c. of the clear filtrate distilled (after addition of a little pumice stone), until 110 c.c. of distillate have been obtained in a period of 20 minutes. This distillate is titrated (without filtration) with 0.1 N sodium hydroxide solution, phenolphthalein being used as indicator. A blank determination, without the fat, but with 10 c.c. of the coconut soap solution, is made, and the difference between the number of c.c. of alkali in the two determinations calculated on 5 grms. of the fat, and expressed in terms of 0.1 N solution, is termed the "butyric acid value."

The coconut soap solution is prepared as follows :---Pure coconut oil (100 grms.) is saponified by heating it with 100 grms. of glycerin and 40 grms. of potassium hydroxide solution (750 grms. per litre), and the solution, when cold, is made up to a litre.

It has been proved that by this process 96 per cent. of the butyric acid present in a fat will be found in the final distillate. Samples of pure butter of different origin gave butyric acid values ranging from 18.6 to 23.0 (average 20.3), whilst coconut oil gave values of 0.8 to 1.0 (average 0.9), probably due to a volatile acid other than caprylic acid (? caproic acid). The butyric acid value stands in a definite relationship to the Reichert-Meissl value. If the former is divided by the latter the average quotient is 0.745. The influence of coconut oil is practically

#### ABSTRACTS OF CHEMICAL PAPERS

proportional to its quantity, but each 20 per cent. of that fat causes a deviation of only 0.1 per cent. in the butyric acid value. For an accurate determination of the amount of butter fat in an unknown fat the butyric acid value and saponification value are determined, and from these values the amount of coconut oil present can be calculated, whilst the residual amount of the butyric acid value corresponds to the butter fat. In this way it is possible to determine the proportion of butter fat to within about 1 per cent. The following table enables the percentage of butter fat in a fat to be obtained directly from the butyric acid value and saponification value :—

	Sapon- ification value	200 and under	205	210	215	220	225	230	235	240	245	250	255	260 and over
	$\left\{\begin{array}{c} 0 \\ 0 \cdot 1 \\ 0 \cdot 2 \\ 0 \cdot 3 \\ 0 \cdot 4 \\ 0 \cdot 5 \\ 0 \cdot 6 \\ 0 \cdot 7 \\ 0 \cdot 8 \\ 0 \cdot 9 \end{array}\right.$	$0 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.1 \\ 2.6 \\ 3.1 \\ 3.6 \\ 4.1 \\ 4.6 $	$0 \\ 1 \cdot 0 \\ 0 \cdot 2 \\ 1 \cdot 1 \\ 1 \cdot 7 \\ 2 \cdot 2 \\ 2 \cdot 7 \\ 3 \cdot 2 \\ 3 \cdot 7 \\ 4 \cdot 2$	$0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 7 \\ 1 \\ 3 \\ 1 \\ 8 \\ 2 \\ 3 \\ 2 \\ 8 \\ 3 \\ 3 \\ 8 \\ 8$	$0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 3 \\ 0 \\ 4 \\ 1 \\ 4 \\ 1 \\ 9 \\ 2 \\ 4 \\ 2 \\ 9 \\ 3 \\ 4$	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 4 \\ 1 \\ 9 \\ 2 \\ 4 \\ 2 \\ 9 \\ 9 \\ 9 \\ 9 \\ 9 \\ 9 \\ 9 \\ 9 \\ 9 \\ 9$	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 5 \\ 2 \\ 0 \\ 2 \\ 5 \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ -$	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 5 \\ 2 \\ 0 \\ \end{array} $	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 1 \\ 6 \end{array} $	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	0 0 0 0 0 0 0 0 0 0 0 0 0 3	0 0 0 0 0 0 0 0 0 0 0 0	0 0 0 0 0 0 0 0 0 0 0 0 0
Butyric Acid Values.	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 and over	$5 \cdot 1 \\ 10 \cdot 2 \\ 15 \cdot 3 \\ 20 \cdot 5 \\ 25 \cdot 6 \\ 30 \cdot 7 \\ 35 \cdot 8 \\ 40 \cdot 9 \\ 46 \cdot 0 \\ 51 \cdot 1 \\ 56 \cdot 2 \\ 61 \cdot 3 \\ 61 \cdot 3 \\ 61 \cdot 6 \\ 71 \cdot 6 \\ 76 \cdot 7 \\ 81 \cdot 8 \\ 86 \cdot 9 \\ 92 \cdot 0 \\ 97 \cdot 1 \\ 100$	$\begin{array}{c} 4\cdot7\\9\cdot8\\14\cdot9\\20\cdot1\\25\cdot2\\30\cdot3\\35\cdot4\\40\cdot5\\6\\50\cdot7\\55\cdot8\\59\cdot9\\66\cdot0\\71\cdot2\\76\cdot3\\81\cdot4\\86\cdot5\\91\cdot6\\96\cdot7\\100\end{array}$	$\begin{array}{c} 4\cdot 3\\ 9\cdot 4\\ 14\cdot 5\\ 29\cdot 9\\ 35\cdot 0\\ 40\cdot 1\\ 45\cdot 2\\ 50\cdot 3\\ 55\cdot 4\\ 59\cdot 5\\ 65\cdot 5\\ 70\cdot 8\\ 75\cdot 9\\ 81\cdot 0\\ 86\cdot 1\\ 91\cdot 2\\ 96\cdot 3\\ 100\\ \end{array}$	$3 \cdot 9$ $9 \cdot 0$ $14 \cdot 1$ $24 \cdot 2$ $29 \cdot 5$ $34 \cdot 6$ $39 \cdot 7$ $44 \cdot 8$ $49 \cdot 9$ $55 \cdot 0$ $60 \cdot 1$ $65 \cdot 2$ $70 \cdot 4$ $75 \cdot 5$ $80 \cdot 6$ $85 \cdot 7$ $90 \cdot 8$ $95 \cdot 9$ 100 mediate	$\begin{array}{c} 3\cdot 4\\ 8\cdot 5\\ 13\cdot 6\\ 23\cdot 9\\ 29\cdot 0\\ 34\cdot 1\\ 39\cdot 2\\ 44\cdot 5\\ 49\cdot 4\\ 54\cdot 5\\ 59\cdot 6\\ 64\cdot 7\\ 69\cdot 9\\ 75\cdot 0\\ 80\cdot 1\\ 85\cdot 2\\ 90\cdot 3\\ 95\cdot 4\\ 100\\ \end{array}$	3.0 8.0 13.2 18.4 23.5 28.6 33.7 38.8 49.0 54.0 59.2 64.3 79.7 84.8 89.8 95.0 100 s (for $6$	$2 \cdot 5$ $7 \cdot 6$ $12 \cdot 7$ $17 \cdot 9$ $23 \cdot 0$ $28 \cdot 1$ $33 \cdot 2$ $33 \cdot 2$ $33 \cdot 3$ $43 \cdot 4$ $48 \cdot 5$ $53 \cdot 6$ $58 \cdot 7$ $63 \cdot 8$ $69 \cdot 0$ $74 \cdot 1$ $79 \cdot 2$ $84 \cdot 3$ $89 \cdot 4$ $94 \cdot 5$ $99 \cdot 7$ but vric	$\begin{array}{c} 2 \cdot 1 \\ 7 \cdot 2 \\ 12 \cdot 3 \\ 17 \cdot 5 \\ 22 \cdot 6 \\ 27 \cdot 7 \\ 32 \cdot 8 \\ 37 \cdot 9 \\ 43 \cdot 9 \\ 43 \cdot 1 \\ 53 \cdot 2 \\ 58 \cdot 3 \\ 63 \cdot 6 \\ 73 \cdot 7 \\ 78 \cdot 8 \\ 83 \cdot 9 \\ 89 \cdot 9 \\ 89 \cdot 9 \\ 89 \cdot 9 \\ 99 \cdot 3 \\ acid viewer and the set of the set $	1.7 6.8 11.9 17.1 22.2 27.3 32.4 42.6 47.7 52.8 57.9 63.2 73.3 78.4 83.5 88.6 93.7 98.9 <i>clusted</i>	$\begin{array}{c} 1\cdot 3\\ 6\cdot 4\\ 11\cdot 5\\ 16\cdot 7\\ 21\cdot 8\\ 26\cdot 9\\ 32\cdot 0\\ 37\cdot 1\\ 42\cdot 2\\ 47\cdot 3\\ 52\cdot 4\\ 57\cdot 5\\ 62\cdot 6\\ 67\cdot 8\\ 72\cdot 9\\ 78\cdot 0\\ 83\cdot 1\\ 88\cdot 2\\ 93\cdot 3\\ 98\cdot 5\\ \cdot 0-20). \end{array}$	$\begin{array}{c} 0.8\\ 5.9\\ 11.0\\ 21.3\\ 26.4\\ 31.5\\ 36.6\\ 41.5\\ 51.9\\ 57.0\\ 62.1\\ 72.4\\ 77.5\\ 82.6\\ 87.7\\ 92.8\\ 98.0\\ \end{array}$	$\begin{array}{c} 0\cdot 4\\ 5\cdot 5\\ 10\cdot 6\\ 20\cdot 9\\ 26\cdot 0\\ 31\cdot 1\\ 36\cdot 2\\ 41\cdot 3\\ 46\cdot 4\\ 51\cdot 5\\ 56\cdot 6\\ 61\cdot 7\\ 66\cdot 9\\ 72\cdot 0\\ 77\cdot 1\\ 82\cdot 2\\ 87\cdot 3\\ 92\cdot 4\\ 97\cdot 6\end{array}$	$\begin{array}{c} 0\\ 5\cdot 1\\ 10\cdot 2\\ 15\cdot 4\\ 20\cdot 5\\ 25\cdot 6\\ 30\cdot 7\\ 35\cdot 8\\ 40\cdot 9\\ 46\cdot 0\\ 51\cdot 1\\ 56\cdot 2\\ 61\cdot 3\\ 66\cdot 5\\ 71\cdot 6\\ 76\cdot 7\\ 81\cdot 8\\ 86\cdot 9\\ 92\cdot 0\\ 97\cdot 2\end{array}$
				d value Per cent	e 0.05		$0.2 \\ 1.0$	$0.3 \\ 1.5$	$0.4 \\ 2.1$	${0 \cdot 5 \over 2 \cdot 6}$	0·6 3·1	0·7 3·6	$0.8 \\ 4.1$	0·9 4·6

Determination of Unsaponifiable Matter in Wheat Flour, Alimentary Pastes and Eggs. R. Hertwig and L. H. Bailey. (J. Assoc. Off. Agric. Chem., 1926, 9, 122–124.)—The direct ethereal extract of flour and eggs does not contain all the unsaponifiable matter of these materials, and the hydrolysis of the sample with strong acid in the acid hydrolysis method for extraction of fat apparently has some chemical action on the unsaponifiable matter, which causes low results. The neutral

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method for the lipoid extraction of flour, alimentary paste, and eggs gives the highest results and appears to be the most accurate (cf. ANALYST, 1924, 49, 37). The lipoids are extracted from 5 grms. of wheat flour or alimentary paste, 10 grms. of liquid eggs, or 2 grms. of powdered dried egg. Either the dried crude lipoids or the final purified and weighed lipoids are then treated with 30 c.c. of alcohol and 3 c.c. of concentrated potassium hydroxide solution (1:1), as in the method for determining unsaponifiable matter (J. Assoc. Off. Agric. Chem., 1925, 8, 441); this is preferably weighed in a light 100 c.c. flask. T. H. P.

**Determination of Pectin.** C. F. Ahmann and H. D. Hooker. (Ind. Eng. Chem., 1926, 18, 412–414.)—A volumetric method is described : To 200 c.c. of a solution containing about 1 grm. of pectin is added a known amount of sodium hydroxide solution, so that the concentration of the alkali shall be about 0.1 N. The mixture is kept in a close flask for twelve hours at  $55^{\circ}$  C., and the excess of alkali is then titrated with standard hydrochloric acid. Each c.c. of N sodium hydroxide solution is equivalent to 0.2089 grm. of pectin. The results obtained agree with those given by the gravimetric method described by Carré and Haynes (cf. ANALYST, 1922, 47, 263), but, when dealing with plant juices containing salts, the volumetric method is more trustworthy. W. P. S.

Modification of the Calcium Pectate Method for the Determination of Pectin. A. M. Emmett and M. H. Carré. (Biochem. J., 1926, 20, 6-12.)-Experiments are described which show that precipitation of pectin by neutral 95 per cent. alcohol is an exceedingly untrustworthy method of determining pectin, owing to the failure of alcohol to effect the precipitation from a dilute solution, and they thus confirm the results of Carré and Haynes (Biochem. J., 1922, 15, 60). The calcium pectate method of Carré and Haynes is not applicable if the solution to be examined contains a substance which gives with calcium a compound insoluble in dilute acetic acid. Acidified alcohol precipitates pectin completely at practically all dilutions. This precipitate does not give directly a measure of the pectin content of the solution, owing to the difficulty of washing the precipitate free from hydrochloric acid without dissolving pectin. The acid alcohol method devised is as follows :--- A solution containing about 0.02 grm. of pectin is treated with 4 times its volume of alcohol containing the amount of hydrochloric acid required to make the resulting mixture 0.1 N. After standing overnight, the precipitate is filtered off, washed once with acidified alcohol and dissolved in hot water. It is then hydrolysed with sodium hydroxide and determined as calcium pectate. The precipitate is washed free from chlorides and re-boiled with water 3 times, then filtered into a Gooch crucible and dried at 100° C. The results cited show good agreement between the calcium pectate and acid alcohol methods for pectin solutions as dilute as 0.05 per cent. The acid alcohol method is shown to be satisfactory in the case of pectin solutions which contain substances precipitable by calcium, such as oxalates. P. H. P.

**Freshly-ground Coffee and "Blown" Tins. T. B. Shaw and R. C. Frederick.** (*J. Roy. Nav. Med. Service*, 1926, 12, 152.)—Freshly-ground coffee was packed by a firm of merchants in tins designed to be completely air-tight. Within a few days very many of the tins were "blown"; this also occurred with subsequent consignments. On piercing a 1 lb. tin about 100 c.c. of gas were discharged; this had the following composition:—Carbon dioxide, 45.6; oxygen, 6.1; nitrogen and argon, 48.3 per cent. The coffee itself was quite sound. It thus appears that the production of gases on contact of freshly-ground coffee with air is a normal reaction comparable with that occurring with damp vegetable matter, such as tobacco, hay, potatoes, etc. (Frederick , *J. Hyg.*, 1920, 19, 203), but with this difference, that it will occur with coffee containing only 1 per cent. of moisture.

Determination of Essential Oil of Mustard in Mustard Flour. L. Colombier. (Ann. Falsificat., 1926, 19, 160–169.)—The author confirms the results of Luce and Doucet (ANALYST, 1922, 47, 353). It is essential that the time during which the mustard flour is macerated with water should be reduced to one hour, but if it is found more convenient to prolong the maceration, loss of the mustard oil may be avoided by adding either 25 c.c. of alcohol or a little sodium fluoride. The results are rendered more exact if the volume of liquid collected during distillation is increased to 90 instead of 65 c.c., and if the titration with thiocyanate is carried out with 100 c.c. of the filtrate from the silver sulphide. Under these conditions most mustard seeds are found to contain more than 0.7, and some more than 1.0 per cent. of mustard oil, but in certain Roumanian seeds only about 0.4 per cent. is present.

The above method determines all products capable of precipitating silver nitrate, and when an exact determination is required or when doubt exists as to the origin of the mustard flour, Jörgensen's method (*Ann. Falsificat.*, 1909, 372), in which the mustard oil is collected in ammonia and the thiosinamine formed is weighed, is to be preferred. Further, this method admits of the determination of the nitrogen (18 to 24 per cent.) in the thiosinamine by Kjeldahl's method in presence of mercury, but the latter must be added only after the sulphur is converted completely into sulphuric acid, since, otherwise, troublesome bumping occurs. Jörgensen's method gives results in agreement with those furnished by the modified French Codex method described above. T. H. P.

**Determination of Aldehyde in Ether. E. P. Phelps and A. W. Rowe.** (J. Amer. Chem. Soc., 1926, **48**, 1049–1053. See ANALYST, 1924, **49**, 593.)—The colorations produced by Schiff's reagent are compared either in a Duboscq colorimeter with 10 cm. cups or, if the colorations are faint, in narrow, flat-bottomed tubes of the standard Nessler type. Into each of two of the containers are introduced 10 c.c. of aldehyde-free alcohol, followed, in one case, by 1 c.c. of a 0.1 per cent. solution of aldehyde in ether and 4 c.c. of pure ether, and in the other by 5 c.c. of ether; 5 c.c. of Schiff's reagent are now added to each. After the lapse of 15 minutes the colours are compared. If the colours in the two containers differ appreciably in intensity, the procedure must be repeated with more or less of a suitable ethereal aldehyde solution, since the depth of the coloration is not proportional to the concentration of the aldehyde. The determination of proportions of aldehyde of the order of 0.003 per cent. in ether is possible by this method.

T. H. P.

# Biochemical, Bacteriological, etc.

Determination of Iron in Blood, Tissues and Urine. F. S. Fowweather. (Biochem. J., 1926, 20, 93–98.)—Methods are described in detail for the determination of the amount of iron present in blood, tissues and urine by means of the colorimetric method dependent on the formation of ferric thiocyanate in the presence of acetone. The procedure of Wong (J. Biol. Chem., 1923, 55, 421) is largely followed, but "perhydrol" (100-volume hydrogen peroxide) is used in place of chlorate, and the acetone modification of Berman (J. Biol. Chem., 1918, 35, 231) is utilised. "Perhydrol" has two advantages over chlorate; it leaves no residue and the steady evolution of oxygen which results from its addition ensures steady ebullition, thus avoiding the possibility of loss by spirting, which is a danger in Wong's method. It is shown that these methods are capable of a high degree of accuracy and are simpler and less tedious than the methods at present in use. The new methods are being employed in a quantitative study of certain aspects of iron metabolism.

P. H. P.

Analysis of Proteins. VII. Direct Determination of Arginine. R. H. A. Plimmer and J. L. Rosedale. (Biochem. J., 1925, 19, 1020–1021.)—Arginine, determined directly in solutions of hydrolysed proteins by boiling with sodium hydroxide, has a higher value than if determined in the di-amino fraction precipitated by phosphotungstic acid. On treating the mono-amino filtrate from the phosphotungstate precipitation in the same way, ammonia is yielded, and a value is obtained which represents the difference. The presence of arginine, assuming the absence of an unknown amino-acid, in the mono-amino fraction is further evidence of incomplete precipitation by phosphotungstic acid in the Van Slyke method. The arginine value of a protein is the sum of the figures obtained from the di-amino and mono-amino fractions, or the figure obtained directly, assuming that no other amino-acid behaving like arginine is present in proteins. P. H. P.

Determination of Sugar in Blood and in Normal Urine. O. Folin. (J. Biol. Chem., 1926, 67, 357-370.)—The author criticises Benedict's technique (J. Biol. Chem., 1925, 64, 207), but agrees with him that the Folin-Wu sugar values are too high—if by blood sugar is meant blood glucose—and that the sugar method which gives the lowest sugar values when applied to urine, if it is at the same time dependable for glucose, will give blood sugar values which correspond most nearly to the glucose content of blood. Whilst a part of the high sugar values obtained in nephritic blood may be represented by reducing products which are not sugar or sugar derivatives, it is highly probable that a large fraction of these unknown

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reducing materials is of the same nature as the non-glucose carbohydrate materials which occur in normal urines. Since they are eliminated by normal kidneys, they would accumulate in the blood when the kidneys fail to work. Normal kidneys may possibly excrete these foreign carbohydrate derivatives in response to a floating supply of these products in the blood. One cannot definitely deny that the blood sugar may contain some maltose. This does not imply that the various reducing substances sustain the same quantitative ratio to one another in the blood as in the urine. The abnormally high non-glucose reducing materials in diabetic blood would seem to require a different explanation, and may, in part, represent some form of intermediary carbohydrate metabolism. A new alkaline copper tartrate solution is described in detail, and a new acid molybdate reagent for the determination of cuprous copper. P. H. P.

Identification and Determination of Cholesterol and Certain other [Identification of Hydrogenated Oils.] Compounds. J. V. Steinle and L. Kahlenberg. (J. Biol. Chem., 1926, 67, 425-467.)-With a dilute solution of cholesterol a chloroform solution of antimony pentachloride forms a muddy brown precipitate which, upon solution in more chloroform, yields a clear, purple liquid, upon exposure to light, changing to a cobalt-blue colour, fairly stable upon heating and very stable at low temperatures in the dark, but fading on long exposure to light. The compound which forms the blue coloration in chloroform may be obtained in pure form, as a black powder, by first preparing the muddy brown precipitate and then washing it free from the excess of both cholesterol and antimony pentachloride by means of carbon tetrachloride. From the results obtained upon analysis for antimony, chlorine and carbon, and a molecular weight determination, the pure compound is concluded to be a simple addition product of the formula  $C_{27}H_{46}O.SbCl_5$ . Since the blue compound is quite definite in composition, the colour reaction between cholesterol and antimony pentachloride is perfectly quantitative, and may be used in the colorimetric determination of cholesterol. Phytosterol may also be determined colorimetrically by this method, as it reacts in a similar manner. A slight modification of the method of Henz (Z. anorg. Chem., 1903, 37, 18) was used for the determination of antimony as trisulphide; it is as follows :---A weighed amount of the material is dissolved in chloroform. Hydrogen sulphide is passed into the cold solution for half-an-hour; then, without stopping the gas current, the solution is heated by placing the flask in a bath of water ( $50^{\circ}-60^{\circ}$  C.), and hydrogen sulphide is allowed to pass through for another half hour, after which more warm chloroform is added, and the flask placed in boiling water for 5 minutes. The precipitate is allowed to settle and filtered off in a Gooch crucible, previously heated at 280°-300° C. The precipitate is washed 4 or 5 times with chloroform, and the pentasulphide is converted to the black modification of the trisulphide by heating in an atmosphere of carbon dioxide in a special Henz apparatus. The oven temperature is kept at  $100^{\circ}-130^{\circ}$ C. for 2 hours and then raised to  $280^{\circ}-300^{\circ}$ C. for 2 hours longer. The crucible is cooled in the stream of carbon dioxide and weighed. The

colour reaction with antimony pentachloride may be used to differentiate between hydrogenated and unhydrogenated oils. A modified structural formula for cholesterol is suggested. P. H. P.

Vitamin A in "Oleo Oil" and Oleostearine. R. Hoagland and G. G. Snider (J. Agric. Res., 1926, 32, 397-416.)-Oleo oil (expressed from premier jus at about 90° F.) is usually graded as No. 1, No. 2, No. 3, and yellow oil, the last of which is prepared from fats derived from grass-fed cattle. The results are reported of a study of the vitamin A content of 24 samples of oleo oil and 8 samples of oleostearine, collected from various commercial meat-packing plants. The vitamin A content of each sample was determined by feeding tests with young albino rats, the oil or stearine being the only known source of this vitamin in an otherwise adequate ration. In general, the yellow oleo oil was much the richest in vitamin A; No. 2, No. 3 and mutton oleo oil had approximately the same value; and No. 1 oleo oil was the poorest in vitamin A. Similarly, each sample of yellow "stearine" was richer in this vitamin than any sample of the other grades of oleostearine. Although the yellow oleo oil was richer in vitamin A than the other lighter coloured grades, there appeared to be no constant relation between the colour of an oil and its vitamin content. Thus, the mutton oleo oil, dead white in colour, was richer in vitamin A than the light yellow No. 1 oleo oil, and approximately as rich in it as the medium-yellow No. 2 and No. 3 oils. "Oleo oil" ranks below butter, but ahead of lard and the vegetable fats and oils, as a source of vitamin A. P. H. P.

Colour Reactions Associated with Vitamin A. W. R. Fearon. (Biochem. J., 1925, 19, 888-895.)—The familiar observation that liver oils give a transient purple colour on treatment with sulphuric acid acquired a new significance when Drummond and Watson (ANALYST, 1922, 47, 314) demonstrated the close relationship between the occurrence of this reaction and the distribution of vitamin A. Experiments are described which were undertaken to ascertain the connection between the vitamin and the pigment; to see if the test would help in the isolation of the vitamin; and to devise a colorimetric method for the determination of the quantitative distribution of the vitamin. Phosphorus pentoxide forms a deep violet colour on addition to oils containing vitamin A and adsorbs the pigment. A method is described, based on this fact, for the complete separation of the pigment from the oil. A residue is left which is deficient in growth-promoting properties. The vitamin enters into the formation of the pigment, probably by condensation with a sterol. It was not found possible to recover the vitamin from the products of hydrolysis of the pigment. With the use of a 12 per cent. solution of trichloroacetic acid in dry petroleum spirit as a condensing agent, pyrogallol and other phenols interact with oils containing vitamin A to give stable pigments suitable for colorimetry. In distribution and intensity the pyrogallol test closely follows the test of Drummond and the phosphorus pentoxide test. Since no biologically active preparation was obtained from the pigment separated by the phosphorus pentoxide method, no effort was made to isolate the pigment formed in the pyrogallol test. P. H. P.

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Studies on the Chemical Nature of Vitamin A. J. C. Drummond, H. J. Channon and K. H. Coward. (Biochem. J., 1925, 19, 1047-1067.)-Vitamin A may be concentrated without loss in the unsaponifiable fraction of cod-liver oil, provided that the preparation is carried through with precautions against oxidation. The authors have attempted the isolation of this vitamin, without much success, for the last 5 years, and publish their results because much larger quantities of raw material (unsaponifiable matter) are necessary to carry their researches further; also they criticise claims, especially those of Takahashi, to have isolated vitamin A. Takahashi claims to have identified it as an unsaturated alcohol  $C_{27}H_{46}O_8$  ("bios-The concentrate contains no detectable traces of iodine or nitrogen. terin''). Approximately 50 per cent. of the unsaponifiable matter from cod-liver oil is cholesterol, which may be quantitatively removed without loss of vitamin activity. The vitamin is volatile in superheated steam. Distillation of the cholesterol-free residue, in a high vacuum did not satisfactorily separate the components. Vitamin A distils mainly between  $180^{\circ}-200^{\circ}$  C. at 2-3 mm. The active distillates appeared to contain a saturated solid alcohol, the unsaturated hydrocarbon spinacene and one or more unsaturated alcohols boiling at about 200° C. at 2-3 mm. Spinacene and the solid alcohol are without vitamin A action. Possibly vitamin A is identifiable with one of the unsaturated alcohols, but evidence presented rules out oleyl alcohol ( $C_{18}H_{36}O$ ), phytol ( $C_{20}H_{40}O$ ), and selachyl alcohol ( $C_{20}H_{40}O_3$ ). Brief reference is made to the possible relation between the lipochrome pigment of codliver oil and the vitamin activity of the oil. P. H. P.

Effect of Chemical Preservation of Eggs upon the Stability of their Vitamin Contents. E. Tso. (Biochem. J., 1926, 20, 17-22.)--" Pidan" is prepared by preserving Chinese raw ducks' eggs as follows :--For 100 fresh, selected and washed ducks' eggs 5 ounces of pure soda, 25 ounces of straw ash, and a little less than 4 ounces of table salt are mixed uniformly with about 20 ounces of boiling water. Gradually 40 ounces of slaked lime are added to make a thick paste, with stirring and application of heat, if necessary, until the ingredients are thoroughly mixed. A layer of this mixture, a quarter of an inch thick, is wrapped round each egg and covered with rice husks to prevent sticking. The eggs are then placed in earthenware jars, which are sealed with wet clay when full, and in a month they acquire the desired flavour and degree of coagulation and are ready for table. "Pidan" is used as much in China as is cheese in Western countries. The coagulated white appears dark brown and translucent, and the coagulated yolk looks deep green or greenish grey with concentric rings of different shades of grey, brown or dark green. The egg has a piquant lime taste and an ammoniacal odour. A study of the stability of the vitamins in these preserved eggs has shown that the originally rich vitamin B content is practically completely destroyed, but that the potency of vitamin A and the anti-rachitic food-factor is little, if at all, affected. Tables and charts show the results of experiments which were carried out on young P. H. P. rats.

# Toxicological and Forensic.

Fluorides and Fluosilicates as Scheduled Poisons. (Z. Unters. Lebensm., 1926, 51 (Gesetze), 13-15.)—In the new Prussian regulations, which came into force on March 1st, hydrofluosilicic acid and its salts, acid fluorides, and soluble neutral fluorides are added to the schedule of poisons. Since, hitherto, only hydrofluoric acid has been included in the list, it has been assumed that the fluorides and fluosilicates are harmless, and the use of these salts in the preparation of vermin killers has been steadily increasing. These preparations, consisting mainly of sodium silicofluoride, are sold under such names as Orwin, Kabalin, kattentod, Schwabex, Rotsalz, Radarsan, etc., and some of them are even labelled as being harmless to human beings and domestic animals. In consequence, there have been many fatal accidents due to their being taken in mistake for sodium bicarbonate or medicinal bromides (cf. ANALYST, 1926, 99). The Prussian official circular accompanying the Regulation also refers to the use of hydrofluosilicic acid as a sterilising agent for pipes, etc., in breweries, the principal product thus employed being "Montanin," which contains about 30 per cent. of the acid.

Proposed Regulations for the Manufacture and Use of Lead Tetraethyl. (*Ind. Eng. Chem.*, 1926, 18, 432–433.)—Following the report of the United States Public Health Service (*cf.* ANALYST, 1926, 210) regulations have been formulated for the control of the manufacture, etc., of lead tetraethyl. Strict rules are made for the supervision of the health of the workers, ventilation of the plant, etc., special containers must be used, and the lead tetraethyl must contain a dye in sufficient quantity to render it plainly distinguishable from ordinary petrol. The maximum quantity of lead tetraethyl in petrol or other motor fuel shall be in the proportion of 1: 1260 by volume for commercial lead tetraethyl, or 1: 1300 for pure lead tetraethyl. Numerous rules govern the ethylising process (mixing the lead tetraethyl with the motor fuel), distribution of the product, service stations and garages. W. P. S.

Quantitative Toxicological Investigations on Mandibulate Insects. F. L. Campbell. (J. Agric. Res., 1926, 32, 359-365.)—Drops of a standard solution of the poison from a weighing burette were placed on the leaves of the experimental plants on which weighed specimens of the tent caterpillar (Malacosoma americanum), and the yellow-necked caterpillar (Dalana ministra) were feeding. Every caterpillar whose mouth touched a drop drank it completely, and the survival periods were determined with a probable accuracy of about 5 minutes. The results were expressed as the weight of poison consumed per grm. weight of insect. The results showed that trivalent arsenic is more toxic than pentavalent arsenic, and that the yellow-necked caterpillar is more susceptible than the tent caterpillar. The minimum lethal dose, however, of both trivalent and pentavalent arsenic for the two species is about 0.02 mgrm. of arsenic per grm. of insect.

# Agricultural Analysis, etc.

Effectiveness of Aliphatic Compounds in Attracting Flies. W. C. Cook. (J. Agric. Res., 1926, 32, 347-358.)---Experiments were made at a time when flies were abundant, and, in all, 50,000 were captured in small wire balloon-type traps, which were arranged in series in circles and kept in the same position throughout the summer. The standard bait was 25 c.c. of a 10 per cent. solution of molasses, and to this was added a sufficient quantity of the chemical to give the desired concentration. The bait solution was then absorbed by sufficient bran to make a wet mash. In determining the relative attractiveness of two substances differing in boiling point the time factor was taken into consideration, and finally a uniform exposure period of 24 hours was given. The results indicated that there is a definite optimum concentration for each of the compounds studied. This concentration is related to the boiling point of the compound, and becomes smaller as the boiling point rises. For instance, the following dilutions of alcohols were found most attractive to flies :--Ethyl alcohol (b.pt., 78° C.), 7 per cent.; iso-propyl alcohol (b.pt., 80°-81° C.), 1 per cent. ; *n*-butyl alcohol (b.pt., 106°-108° C.), 0.25 per cent. ; iso- amyl alcohol (b.pt., 130°-132° C.), 0.06 per cent. The relative attractiveness of aliphatic alcohols and esters is related to the boiling points of the compounds, the attractiveness decreasing as the boiling point rises. This relationship is somewhat obscured by two other factors : (a) The addition of a CH<sub>2</sub> group to the acid radical reduces the attractiveness much more than the addition of a similar group to the alcohol radical. (b) This is a corollary of a. Of a given set of isomeric compounds, that one is generally most attractive which has the lowest acid radical. Iso- or branched-chain compounds are relatively more attractive than their normal isomers. The difference in attractiveness increases as the boiling point increases.

# Organic Analysis.

Refractometric Determination of Alcohols and Esters in Aqueous and in Cottonseed Oil Solutions. J. C. Munch. (J. Amer. Chem. Soc., 1926, 48, 994–1003.)—Results are given of measurements of the change of refractivity of water and of cottonseed oil caused by solution of 1 per cent. of each of a number of aliphatic alcohols and alkyl esters. Knowledge of such refractive increments serves for the accurate and rapid determination of the concentration of an alcohol or ester in aqueous or cottonseed oil solution. If only one alcohol or ester is present, distillates from medicines, beverages, perfumes, and essences may be tested directly. When several such compounds are present in the distillate, information in addition to the refractive index will be required. The refractive increments of the aqueous and oil solutions are so correlated that it is possible to calculate the increment for either solution from that for the other. T. H. P.

Method for the Direct Identification of Rapeseed Oil by Isolation of Erucic Acid. A. W. Thomas and M. Mattikow. (J. Amer. Chem. Soc., 1926, 48, 968-981.)-Under certain conditions it is possible to precipitate magnesium erucate quantitatively from rapeseed oil and hence to separate and examine the erucic acid. About 10 grms. of the oil, accurately weighed into an Erlenmeyer flask, are saponified by heating under a reflux condenser for 30 minutes with 50 c.c. of alcoholic potassium hydroxide (50 grms. of the hydroxide in 1 litre of alcohol) and 50 c.c. of 95 per cent. alcohol. While still warm, the soap solution is neutralised to phenolphthalein by means of a solution of 20 c.c. of glacial acid in 80 c.c. of 95 per cent. alcohol, a permanent pink colour being restored by addition of just sufficient alcoholic potassium hydroxide. The liquid is then treated with 25 c.c. of a reagent prepared by dissolving 50 grms. of magnesium acetate in 100 c.c. of boiling water, filtering the solution, and adding three volumes of 95 per cent. alcohol to each 1 volume of the cold filtrate. The liquid is heated to boiling, cooled, and left overnight in a cold chamber at  $10^{\circ}$  C., the insoluble soaps being then filtered off, washed with 50 c.c. of 90 per cent. alcohol, and restored to the Erlenmeyer flask by puncturing the filter-paper and spraying with hot 5Mhydrochloric acid. The soaps are decomposed by boiling for about 10 minutes, the clear oily layer formed being cooled to solidify the fatty acids, which are filtered off, washed free from chloride and magnesium, and transferred to a 150 c.c. beaker; the filter-paper is washed with 60 c.c. of 90 per cent. alcohol to dissolve any adhering fatty acid. The covered beaker is kept overnight at 10° C., the crystals of saturated acids then formed being filtered off and the filtrate caught in a weighed 150 c.c. beaker. These crystals are washed first with 50 c.c. of 90 per cent., and then with 50 c.c. of 70 per cent. alcohol, the washings being collected in the weighed beaker. The absence of an oily stain on the filter paper after this has been dried at about 35° C. indicates complete removal of the erucic acid. The solvent is evaporated slowly at about 70° C., and drying to constant weight completed in a vacuum oven at 60° C. If the product thus obtained represents about 44 per cent. of the weight of the oil, melts at about 27° C., and has iodine value about 73, and molecular weight about 336, the oil may be regarded as genuine, pure, refined rapeseed oil.

Confirmation of the result may be obtained by hydrogenating the erucic acid to behenic acid. The erucic acid is dissolved in 80 to 100 c.c. of 90 per cent. alcohol in a bottle fitted with a two-holed rubber stopper, 2 c.c. of 1 per cent. palladious chloride solution and 0.5 c.c. of 1 per cent. gum arabic solution being added, and hydrogen passed through the solution as long as a white precipitate continues to form. The bottle is then left overnight in a thermostat at  $25^{\circ}$  C., and the precipitate filtered off, washed with cold 90 per cent. alcohol, and dissolved in hot 95 per cent. alcohol in a weighed 150 c.c. beaker. The solvent is slowly evaporated and the behenic acid dried at 80° C. to constant weight, which should represent about 35 per cent. of the weight of oil taken ; after two fractional crystallisations the behenic acid should melt at  $77^{\circ}$ - $79^{\circ}$  C. The method may be applied to determine approximately the compositions of mixtures of rapeseed and olive oils. With 26.5 per cent. of the latter the erucic acid product has m.pt. 28° C. and with 100 per cent. 48° C. Similarly, for rapeseed and cottonseed oil mixtures, the m.pts. are respectively 28° C. and 55° C. for 24.8 and 100 per cent. of the cotton-seed oil. In both cases the variation of the melting point is virtually linear. The iodine values also vary progressively. The method does not distinguish rapeseed oil from mustard seed oil, since the latter also yields a large proportion of erucic acid. T. H. P.

Determination of Unsaturated, Aromatic, Naphthene, and Paraffin Hydrocarbons in Motor Fuels. G. Egloff and J. C. Morell. (Ind. Eng. Chem., 1926, 18, 354-356.)-A method is described for the determination of the four series of hydrocarbons in the presence of each other; unsaturated hydrocarbons are determined by sulphuric acid absorption and polymerisation, aromatic hydrocarbons by nitration, naphthenes by means of the aniline index, and the paraffins by difference. Unsaturated hydrocarbons.-Five hundred c.c. of the mixture (e.g. motor fuel) are distilled through a fractionating column until the temperature of the vapour at the top of the column is 210° C.; the residue is discarded. The distillate is shaken for fifteen minutes with twice its volume of 80 per cent. sulphuric acid, and the decrease in the volume of the oil layer, calculated as a percentage of the 210° C. fraction, gives percentage of unsaturated hydrocarbons that have dissolved in the acid. The oil is separated, washed with water, neutralised with sodium hydroxide solution, and re-distilled until the temperature reaches 210° C. The volume of the residue, calculated as a percentage of the first 210° C. fraction, gives the amount of the unsaturated hydrocarbons which have been polymerised ; this amount added to that of the dissolved hydrocarbons gives the total quantity of unsaturated hydrocarbons. Aromatic hydrocarbons.—Twenty c.c. of the second 210° C. fraction obtained above are nitrated slowly with a mixture of nitric acid, 25 per cent., sulphuric acid, 58 per cent., and water, 17 per cent.; at the end of this operation three layers are usually obtained. The volume of the middle layer of nitro derivatives is measured; the number of c.c., multiplied by 4.3, gives the percentage of aromatic hydrocarbons in the second 210° C. fraction. Naphthenes.—The upper layer of oils from the nitration treatment is washed with water and dried over calcium chloride, and the naphthenes are then determined by the method described by Tizard and Marshall (ANALYST, 1921, 46, 155). Paraffins. These are determined by difference. W. P. S.

Indicators for Alkaloidal Titrations. H. Wales. (Ind. Eng. Chem., 1926, 18, 390–392.)—The following indicators are recommended for the titration of different alkaloids :—Methyl red for aconitine, arecoline, atropine, brucine, cephaeline, codeine, cocaine, diacetyl morphine, emetine, ethyl morphine, homatropine, hyoscyamine, morphine, nicotine, physostigmine, strychnine, thebaine, and yohimbine. Bromocresol purple for cinchonine, cinchonidine, cotarnine, ethyl hydrocupreine, quinine, and quinidine; Bromophenol blue for delcosine, narceine, narcotine, and pilocarpine. Hydrastine does not give any definite endpoint with either methyl red or bromophenol blue, and papaverine cannot be titrated. W. P. S.

## Inorganic Analysis.

Buffer Mixture for the Alkaline Range of Hydrogen Ion Concentration Determinations. W. R. G. Atkins and C. F. A. Pantin. (Biochem. 1., 1926, 20, 102–104.)—When sodium carbonate is used instead of sodium hydroxide the preparation of fresh solutions is facilitated and the error due to absorption of carbon dioxide, which reduces alkalinity, is lessened. The following solutions are recommended for use from  $P_{H}$  7.8–10.8, though they cover a slightly more extended range : (a) 0.2 M boric acid, made 0.2 M with respect to potassium chloride also, as recommended by Clark (Determination of Hydrogen Ions, 1922). One litre should contain 12.4048 grms. boric acid (atomic wt. of boron = 11.0) and 14.912 grms. of potassium chloride. (b) 0.2 M sodium carbonate 21.2000 grms. per litre, prepared anhydrous from the bicarbonate as is usual in alkalimetry. A table shows the quantities of (a) and (b) to be mixed for use and diluted in 100 c.c. of water. These buffer solutions keep well if stored in tightly-stoppered waxed bottles. Below  $P_{\mu}$  9.6 thymol blue and xylenol blue are satisfactory and stable indicators. Phenolphthalein may be used up to  $P_{\rm H}$  10.5 and alizarine yellow G (B.D.H.) from  $P_{\rm H}$  10.1 P. H. P. to 12.1. Full details for the determinations are given.

Colour Reaction for Disulphides. E. Walker. (Biochem. J., 1925, 19, 1082-1084.)—A colour reaction for the detection of the disulphide grouping is described which is a modification of the nitroprusside reaction for the sulphydryl group. Potassium (or sodium) cyanide is used instead of ammonia. A few drops of 5 per cent. aqueous sodium nitroprusside are added to a solution containing a disulphide, followed by 3 to 5 drops of 10 per cent. aqueous potassium cyanide solution. The final reaction of the solution must be alkaline. If the disulphide is present in high concentration, the colour (a deep magenta) is formed immediately; if present in low concentration, there is a delay of a few minutes. The reaction, which was discovered in the course of work upon the sulphur constituents of tissue, is sensitive for a concentration of 1: 10,000. A few illustrations of its applicability are briefly described. The suggestion of Harris (Proc. Roy. Soc., 1923, B, 94, 426), viz. that the precursor of the sulphydryl group formed on denaturation of ovalbumin is not a disulphide linkage, is confirmed. It is also shown that blood serum in the native state gives no disulphide reaction, but gives a vivid reaction after coagulation. It is difficult to say what is the precursor of the disulphide group, but the disposition of the cystine component in serum albumin is not simple. P. H. P.

Use of Hydrazine Sulphate for the Standardisation of Iodine Solutions. E. Cattelain. (Ann. Falsificat., 1926, 19, 145–148.)—Owing to the ease with which it is purified, to its stability in the solid state and in aqueous solution, and to the readiness with which it is oxidized by iodine in accordance with the equation:  $N_2H_4 + 2I_2 = 4HI + N_2$ , commercial hydrazine sulphate forms an excellent substance for standardising iodine solution. T. H. P.

Phenylarsonic Acid as a Precipitant for Zirconium and Thorium. A. C. Rice, H. C. Fogg and C. James. (J. Amer. Chem. Soc., 1926, 48, 895–902.) --The precipitate produced by phenylarsonic acid,  $C_8H_5AsO(OH)_2$ , in zirconium solutions is extremely insoluble. The acid is readily prepared from cheap reagents (J. Amer. Chem. Soc., 1922, 44, 1361). The acidified chloride solution is precipitated with a 10 per cent. solution of phenylarsonic acid, boiled one minute, and filtered hot; the precipitate is collected, washed with one per cent. hydrochloric acid, dried, and gently ignited till the carbon is burned off, then heated in a hydrogen current, and finally ignited over a blast burner. In presence of thorium, uranium, and iron, the precipitate produced by phenylarsonic acid in 10 per cent. hydrochloric acid solution is returned to the beaker and dissolved by warming with 15 c.c. of sulphuric acid (1:1); strong hydrochloric acid (50 c.c.) is added, and the solution (500 c.c.) boiled and re-precipitated with 30 c.c. of the reagent. The separation of zirconium from aluminium, the rare earths, manganese, nickel, cobalt, zinc, beryllium, and potassium is successfully accomplished by single precipitation from 500 c.c. of 10 per cent. hydrochloric acid solution. The precipitation of titanium is prevented by suitable addition of 3 per cent. hydrogen peroxide, followed by the precipitant; it is safest to dissolve the precipitate in sulphuric acid, as in the case of iron, and add 20 c.c. of hydrogen peroxide, 50 of hydrochloric acid, water to 500, and re-precipitate the zirconium with 20 c.c. of the reagent.

Thorium is precipitated by phenylarsonic acid in presence of ammonium acetate and acetic acid, and can be separated from the rare earths by this means. For the determination of thoria in monazite sand the latter is decomposed by sulphuric acid, and the phosphoric acid removed by double oxalate precipitation of the thoria and rare earths. The oxalate precipitate is decomposed with strong nitric acid, the excess evaporated, and the residue dissolved in 300 c.c. of hot water. The cerium is reduced by cautious addition of sulphur dioxide, and the boiling solution treated with 30 c.c. of the reagent and 75 of acetic acid. A decided excess of ammonium acetate is then added, and the liquid digested hot for 10 minutes. The precipitate is collected, washed, dissolved in 30 c.c. of hydrochloric acid (1:1), and the solution diluted to 300 c.c. and treated with a little sulphur dioxide. This is followed by a few c.c. of phenylarsonic acid solution, 75 of acetic acid, and ammonium acetate as before. The precipitate is again dissolved in 30 c.c. of hydrochloric acid (1:1), 5 grms. of oxalic acid are added, and the solution diluted to 200 c.c. After standing overnight, the precipitate is collected and washed as usual, and ignited to ThO<sub>2</sub>. W. R. S.

## Physical Methods, Apparatus, etc.

A Foam Meter. H. E. Williams. (Ind. Eng. Chem., 1926, 18, 361-362.)— The liquid to be tested is placed in a cylindrical vessel provided with water-jacket; a tube at the bottom of the vessel is fitted with a tap or valve and this tube discharges into a weighed flask when the valve is opened. The liquid is stirred for three minutes by means of an ordinary egg-beater operated at constant speed by an electric motor, the tap is then opened, and the liquid (foam or liquid or both) allowed to fill the flask. The weight of liquid collected in the flask enables the volume to be calculated, the total volume of the flask being taken as the "foam meter volume." The foaming tendency of the liquid may therefore be expressed numerically on the basis of the ratio of the weight of the liquid placed in the stirring vessel to the weight of the "foam meter volume" of the liquid after stirring. W. P. S.

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  - to the Royal Microscopical Society. J. Roy. Microsc. Soc., March, 1926. Classification of Mycomycetes—Fungi Imperfecti—Effects of Torulæ in Industry— Mycoderma Species—"Mineral yeast" as food—Need of Institute for Industrial Research—for training specialists—preparation of pure cultures—as Centre for British Micro-biological Science.
- AN ADDRESS ON THE MEDICAL ASPECTS OF TOBACCO. By Sir H. Rolleston. Lancet, 1926, 210, 961 (May 22).

History of Tobacco Smoking—Comparative Effects of Pipes, Cigars and Cigarettes— Therapeutic Uses—Effects on Nervous System—Heart—Blood Pressure—Alimentary Canal—Bibliography.

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THE DANGEROUS DRUGS ACTS. By Sir W. Willcox. Lancet, 1926, 210, 1071 (May 29).

History of Movement to restrict use of Dangerous Drugs—Recent Developments in Great Britain—What are Dangerous Drugs—Proposed inclusion of Codeine and Heroin—Illegal Trafficking—The Regulations—Application of the Acts to the Pharmacist—and to the Physician.

- THE GROWTH OF CRYSTALS. By Prof. C. H. Desch. Nature, 1926, 117, 694. The Space Lattice in Crystallography—The process of Crystal Growth—Periodic Crystallisation.
- THE ORGANISATION AND WORK OF THE UNITED STATES BUREAU OF STANDARDS. By G. K. Burgess. J. Chem. Education, 1926, 3, 7.

General Description of the Bureau—Bureau's relation to the Government and the Public—Detailed description of the various Divisions of the Bureau.

FORGOTTEN CHEMISTS. By Edgar F. Smith. J. Chem. Education, 1926, 3, 29. Short accounts and portraits of Geoffroy, Marggraf, Wallerius, de Luc, Ingenhouz, Wiegleb, Kirwan, Bergmann, von Diemann, Gmelin, Achard, Hermbstaedt, von Jacquin, Trommsdorff, and Godfrey.

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# **Reviews.**

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Fifth edition. Vol. IV. Entirely rewritten. Edited by S. A. SADTLER, S.B., E. C. LATHROP, A.B., Ph.D., and C. A. MITCHELL, M.A., F.I.C. 8vo. Pp. x.+648. London: J. & A. Churchill, 1926. Price 30s. net.

This volume, as in the previous edition, deals with Resins, Indiarubber, and Essential Oils and their Constituents, rather more than two-thirds of its pages being devoted to the subject of Essential Oils. The number of contributors has on this occasion been reduced to four, Mr. E. J. Parry being responsible for sections on Resins, and on the Constitution and Analysis of Essential Oils, Messrs. E. K. Nelson and G. A. Russell for one on the Special Characters of Essential Oils, whilst the subject of Indiarubber is dealt with by Mr. J. B. Tuttle. It is difficult to see what reason there can be for the arrangement of the book adopted, the first section, on the special characters of essential oils, being separated from the other portions of the book dealing with essential oils by those on Resins and Indiarubber.

The first section consists chiefly of more or less complete monographs on some seventy essential oils, those of cassia, cinnamon, wintergreen and bitter almond being now included for the first time. The allocation of space to the different oils appears rather out of proportion, 42 pages being given to turpentine oil, as compared with only 21 pages to the various geranium oils, and not quite 4 pages, of which one is almost entirely taken up with a table, to citronella oils. Most of the errors in this section pointed out by the reviewer of the previous edition have now disappeared, but under Sandalwood oil one still finds the work of Potlivet attributed to Potoliet, and European pennyroyal oil (Mentha pulegium) again appears under *Hedeoma*, though the two genera are quite distinct. No reference is made to the great improvement in character which has taken place in recent years in West Australian sandalwood oil, and the figures given do not in the least represent present-day oil, which contains 90-95 per cent of total alcohols (calculated as santalol), and has a laevo-rotation up to  $-15^{\circ} 30'$ . The practice now usually adopted in this country of referring to the oil from Mentha arvensis as Japanese Mint oil, rather than peppermint oil, has not been followed, and no figure is given for the pulegone-content of pennyroyal oil. Shiu oil, which has recently been renamed "Ho oil," deserves more notice than the bare mention of the fact that it is sometimes used as an adulterant of linaloe cil. In the description, under eucalyptus oil, of Schimmel's resorcinol method for the determination of cineol it is stated that 100 c.c. of oil should be taken, whereas this should be 10 c.c.

This section closes with a short reference of  $l\frac{1}{2}$  pages to terpeneless oils, a tabular list of source, characters, and known constituents of the better-known oils, and a solubility table of the most used odoriferous substances, in alcohol, glycerol, olive oil, and paraffin oil. Many of the limits given for genuine oils would

not find universal acceptance, and some calling for special criticism are a minimum gravity at  $30^{\circ}$ C. for otto of rose of 0.848 instead of 0.850, and a range of specific gravity for spike lavender oil of 0.905–0.920, instead of 0.900–0.915. It is rather unfortunate that the whole of these tables appear under the page heading of Terpeneless Oils.

The section on Resins is extremely good, and embraces the more important resins, gum resins, oleo-resins and balsams, together with certain "resinous substances," such as ambergris, civet, and castor, which, though one would hardly expect to find them here, are very conveniently included in a book so largely concerned with perfumery materials. The treatment of each substance is, in general, the same, the points dealt with comprising occurrence, chemical composition, uses and adulterants, and general properties, together with special information in the more important cases, such as colophony, copal, shellac, copaiba, and asafoetida. Following the monograph on colophony, nine pages are devoted to a full account of rosin oil, but it is rather surprising to find no figures given for the heated or "run" resins used in varnish-making. No reference at all is made to the important Indian gum oleo-resin obtained from Boswellia serrata, and under colophony hardly sufficient prominence seems to have been given to the more recent work, such as that of Tschirch and Studer, Fahrion, and Seidel, on the constitution of abietic acid. This section overlaps at certain points Vols. II and III; e.g. methods for the separation of fatty and resin acids in soaps and varnishes, and the examination of benzoin, storax and the balsams of Peru and Tolu. With regard to the former the long description of a combination of Twitchell and Gladding's methods appears somewhat unnecessary, but in the case of benzoin, etc., this seems the proper place to have included a more complete account of their evaluation, and under Tolu balsam it is regrettable to find no reference to the work of Cocking and Kettle. The resin esters or ester gums hardly receive adequate treatment in view of their considerable technical importance, and to class these under "Hardened Rosin" is liable to lead to confusion.

In the following section, on Indiarubber, are considered not only indiarubber, but also gutta percha, balata, chicle, reclaimed rubber, and rubber substitutes. This section has been somewhat extended, but even now only covers 62 pages. Some obsolete and little used methods of analysis have been eliminated, and the section brought well up to date. The great development in the use of "accelerators" is referred to, and a number of the substances used are mentioned, but the author points out the difficulty of identifying these owing to the very small quantities employed, and deplores the lack of analytical work published on the subject.

Of the remaining sections, that on the Constituents of Essential Oils gives a useful summary of the occurrence, constitution, and properties of the different constituents, classified as hydrocarbons, alcohols, phenols, aldehydes, ketones, esters, and nitrogen compounds. Here, also, is included information regarding many of the more important commercial synthetic perfumes, among them the artificial musks, which are not strictly constituents of any essential oils. This is

a great improvement on the last edition, where in place of this section there were two separate articles dealing with the hydrocarbons and ketones only.

The last section, on the Analysis of Essential Oils, deals with a subject which has for some time past engaged the attention of a Sub-committee of our Society, whose labours are still far from complete. Most of the usual methods for the determination of constituents and detection of adulterants are clearly described, but no method is given for the determination of thymol when admixed with carvacrol, and the recommendation, in the acetylation process for determination of alcohols, to dry the acetylated oil with *potassium* sulphate is most unusual. The author's criticism of the formylation process for the determination of citronellol appears rather too severe, especially in view of the prominence given to the process in Section I, and the reproduction *verbatim*, at the end of this section, of all the monographs on the essential oils of the British Pharmacopoeia, 1914 is redundant, as in most cases these figures are already given in the first section of the book. Probably where two parts of a book on the same subject are dealt with by different authors, a certain amount of overlapping and lack of cohesion is inevitable, but quite a considerable amount of matter given in Section I is again repeated in Sections III and IV.

The book positively bristles with misprints, some of which make rather amusing reading, and its index is so incomplete as to be practically useless, even the table of contents being more helpful. In spite of these blemishes, however, the book should prove a most valuable work of reference to all interested in the analysis of the materials dealt with. W. H. SIMMONS.

THE CHEMISTS' YEAR-BOOK, 1926. Eleventh Edition. Edited by F. W. ATACK, D.Sc. Pp. 1180 and Index. Manchester: Sherratt & Hughes. Price 21s.

This book has now been reviewed so often and is so well-known that any detailed account of its contents is unnecessary. The volume under review, which is the eleventh edition, marks a further increase in size, and includes a new chapter dealing with "Lubricants," which gives a good general account of the subject, when allowance is made for the fact that it occupies only six pages, and it includes an extremely useful conversion table for Redwood, Saybolt and Engler viscometers. The value of this section would be much enhanced if it included a bibliography, and the same criticism applies to certain of the other sections.

The chapter on Oils and Fats includes a section on Adulteration, which requires drastic revision, because many of the statements made are only partly true, and some of the others are not very informative. It is stated, for instance, that turpentine may be detected by its dextro rotation, but no mention is made that castor oil is often as strongly rotatory as is turpentine, nor that much of the turpentine sold nowadays is either laevo-rotatory or optically inactive. The property of fish oils to yield ether-insoluble bromides is suggested as a means for their detection, but no caution is given regarding the behaviour of some of the vegetable oils in this respect. Arachis oil is to be detected by the separation of arachidic acid (m.pt.  $75^{\circ}$  C.), but, as no references are given, nor any precise details

as to how this separation is to be attained, the information is not very helpful. The paragraph under Soap Analysis dealing with the determination of rosin acids gives only one method, with no reference to any of the newer methods, and the whole of the section dealing with oils and fats lacks both references and a bibliography.

In the section dealing with Agricultural Chemistry, there is a useful chapter on methods used in American practice, but under the Analysis of Feeding Stuffs no details are given of the American method for the determination of fibre, and, as this differs somewhat from the English procedure, outlined on page 823, a reference to it seems desirable. In the section on Dairy Products, one is surprised to see no reference to the findings of the recent Committee on Preservatives, particularly as the recommendations of the previous Departmental Committee are mentioned.

The chapter dealing with the Volumetric Determination of Sugars should contain some reference to Eynon and Lane's methylene blue method which has recently come into extensive use, and a reference to the various iodimetric methods would also be useful. The word "commercial" appears so frequently in the carbohydrate section that one is disappointed that some of the common expressions used in commercial sugar analyses, such as "Net Sugars," receive no mention.

The book, as a whole, is remarkably free from misprints, and the information contained in it is fairly up-to-date, but on page 662, there is a reference to Vol. I.; in the index the Weights and Measures conversion tables are referred to as being on page 1124 instead of 1138; and on page 581 a table of Limits of Impurities allowed in the Drugs of the United States Pharmacopoeia 9th revision is given, but no mention is made of the 10th revision, copies of which were available in the autumn of 1925, and which came into force on January 1st of this year.

In a work of reference such as this volume, which deals with a variety of subjects, one can scarcely expect all the sections to be of equal merit, and while some of them may be a little disappointing, others are extremely good, and there are very few books on technical subjects which contain, in such a concise and easily available form, the variety of information that this volume does. The more one consults this book, the more is one impressed with its value, and, despite certain imperfections, it is, in the opinion of the reviewer, one of the few books that should find a place in every technical library.

M. S. SALAMON.

INTRODUCTION À L'ÉTUDE DES COLLOIDES (ÉTAT COLLOIDAL ET SES APPLICATIONS). Par W. KOPACZEWSKI, M.D., D.Sc. Avec 36 figures dans le texte, et 2 portraits hors-texte. Pp. vii. +226. Paris: Gauthier-Villars et Cie. 1926.

Professor Kopaczewski has written several volumes dealing with colloid chemistry, the present being intended as an elementary introduction to the science. His aim is "to facilitate the spread of knowledge concerning the colloidal state of matter, not only for academic teaching, but for application in technical practice."

Seventeen pages are devoted to a historical survey, forty-seven pages to general properties of colloids, seventy-one pages to industrial applications, and seventy-seven pages to the colloid state in relation to biology and medicine, and to colloids in therapeutics.

Professor Kopaczewski writes clearly and vigorously, and covers a very wide field. As a medical man, he devotes most attention to the biological side; indeed, he enjoys a considerable reputation as a colloid investigator in this connection.

The book covers too many points to deal with any really deeply. But little of it is useful to the general scientific student, whereas the medical student interested in the relations between physical chemistry and his own studies will find considerable food for thought. To the colloid chemist, the book is interesting, in reviewing the many applications of modern colloid chemistry, but the treatment is essentially elementary and brief. WILLIAM CLAYTON.

MITTEILUNGEN DES CHEMIKER-FACHAUSSCHÜSSES DER GESELLSCHAFT DEUTSCHER METALLHÜTTEN- UND BERGLEUTE, e.V., BERLIN. AUSGEWÄHLTE METHO-DEN FÜR SCHIEDSANALYSEN UND KONTRADIKTORISCHES ARBEITEN BEI DER UNTERSUCHUNG VON ERZEN, METALLEN, UND SONSTIGEN HÜTTENPRO-DUKTEN. In two Volumes. Vol. I. (1924): Pp. xii. +155. Vol. II. (1926): Pp. x. +146. Berlin: Selbstverlag der Gesellschaft Deutscher Metallhüttenund Bergleute, e.V.

As the sub-title indicates, these volumes contain the methods recommended for reference and contradictory analyses of non-ferrous metals, their ores, alloys, salts, and important metallurgical products. The methods have been tested and selected by a Committee of chemists appointed by the G.D.M.B., and each important metal has been dealt with by a sub-committee of specialists. Volume I. contains a chapter on the routine to be followed in sampling, and the analytical methods for lead, copper, tin, antimony, arsenic, aluminium, noble metals, and metals for alloy steels (tungsten, vanadium, molybdenum, chromium, but not manganese); Volume II. gives the methods for zinc, cadmium, nickel, cobalt, bismuth, magnesium, corundum, and carborundum. Analytical methods for impurities and constituents other than the principal metal are described in the great majority of cases.

The reviewer's task has been a pleasant one, as the book is the result of collaboration between a number of prominent authorities on metallurgical analysis, who have enriched the literature on the subject with a typical product of German thoroughness and efficiency.

There is one subject, however, the treatment of which proved disappointing to the writer: the brief chapter on arsenic consists merely of the description of Pearce and Low's method, preceded by the bare remark that it is uniformly suitable (gleichmässig brauchbar) for all ores containing appreciable (nennenswerte) quantities of arsenic. This statement requires qualification, as the accuracy of the method is conditional upon the absence of other acid-forming elements giving insoluble

silver salts under the conditions of the assay. In fact, the reviewer has known it to give erroneous results due to the above cause, and has discontinued its use.

In the chapter on lead, Alexander's molybdate titration, with tannin as external indicator, is described as equal in accuracy to the gravimetric method. The writer is not prepared to contradict this statement, which is made as the result of a series of careful tests; but he would advise those not thoroughly familiar with Alexander's method to use a gravimetric process for reference work.

The chapter on antimony having been compiled in 1924, the stoichiometric calculations are based on the old atomic weight  $120 \cdot 2$ ; at the same time the principle is laid down that the volumetric solutions should be standardised against metallic antimony of known purity. It is satisfactory to note that the permanganate titration for antimony is declared to be as accurate as the bromate method, and to possess distinct advantages over the latter process.

In the volumetric zinc assay the iron is eliminated by a single precipitation with ammonia, and an approximately equal amount of iron (which has to be determined) is added to the standard; the latter is treated in exactly the same manner as the assay.

The volumetric determination of nickel has not been included; the reason given is, that, though the process gives perfectly accurate results in many cases, it is not always applicable. (This criticism might have been extended to Pearce and Low's method for arsenic.) However, it is added that the nickel titration will be included in a future volume devoted to Rapid Methods. Those acquainted with the two books under review will look forward with interest to the publication of the next volume. W. R. SCHOELLER.

THREE CENTURIES OF CHEMISTRY. PHASES IN THE GROWTH OF A SCIENCE. By IRVINE MASSON, M.B.E., D.Sc., F.I.C., Professor of Chemistry, University of Durham. Pp. vi.+191. London: Ernest Benn, Ltd. 1925. Price 10s. 6d. net.

Not only knowledge but also sympathy is required from a historian, and there is no other summary of the phlogiston theory in which knowledge is so well tempered with sympathy as the one presented by Professor Masson. Many writers have tried to give an unbiassed view of this much-despised chapter of chemistry, but it seems nowhere to have been done with so much success as in the book under review. However, not only the phlogiston theory, but also the development of chemistry as a whole from Bacon to Lavoisier has been dealt with in the same manner, and the frequently obscure concepts of the English, German and French schools of chemical philosophy until 1800 are developed on lines which command admiration.

Professor Masson as a historian is naturally more attracted by the chemistry of the past than of the present. This is evident from the part of the book which summarises our knowledge from Lavoisier onwards and which is, at best, very

sketchy, perhaps due to lack of space. We must, however, look forward to Professor Masson's further publications on early chemistry, which, to judge from the book under review, are sure to be valuable additions to the history of science in general and of chemistry in particular. M. NIERENSTEIN.

 PHOTOSYNTHESIS. THE ASSIMILATION OF CARBON BY GREEN PLANTS. By WALTER STILES, Sc.D., Professor of Botany in University College, Reading. Pp. vi. + 268. London: Longmans, Green & Co. 1925. Price 16s. net.

Photosynthesis has been much in prominence lately, and one must therefore welcome a summary of our present knowledge of the subject, as given by Prof. Stiles in his perfectly unbiassed digest of 870 chemical and botanical papers on the assimilation of carbon by the green plant.

The study of this book makes it clear that we have no definite chemical knowledge how this very simple reaction, which is generally written:—

$$6CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2$$

takes place in the living plant. Two main hypotheses have been put forward:-(1) The acid theory of Liebig, which assumes the intermediate formation of oxalic acid-like substances from carbon dioxide, by which means the carbon atoms are joined and subsequently formed into  $C_6H_{12}O_6$ . (2) The formaldehyde theory of Baever, according to which CO<sub>2</sub> is at first reduced to CH<sub>2</sub>O and then polymerised The latter theory is the more favoured one, but, to quote from to  $C_6H_{12}O_6$ . p. 199 of the book under review, "though alluring on account of its simplicity, [it] is by no means as well established as many writers of the subject would have us believe." Whereas the conversion of formaldehyde into carbohydrates was established beyond doubt so far back as 1861, there is no evidence that CO<sub>2</sub> is reduced to CH<sub>2</sub>O by the living plant. Even the presence of formaldehyde in aqueous suspension of chlorophyll which has interacted with carbon dioxide in sunlight is no proof of the formation of formaldehyde from carbon dioxide, since chlorophyll itself may be disintegrated under these conditions into formaldehyde, as is evident from the classical researches of Willstätter on chlorophyll.

Whereas the chemical methods of attack have so far been more or less abortive, many valuable data have been accumulated by the botanists, and the summary of their researches, as given by Prof. Stiles, should be most valuable reading to chemists who venture into the field of photosynthetical research. Blackman's investigations, which are exceptionally well summarised in pp. 44–161, are most suggestive, and many a chemist would be well advised to study these pages with care. It is for this part of the book that chemists to whom botanical literature is not easily accessible have particularly to be thankful to Prof. Stiles.

Photosynthesis affects humanity in general, and there is no branch of science which is not directly or indirectly concerned with this problem. Much gratitude is therefore due to Prof. Stiles for collecting such a vast amount of material and presenting it in such an unbiassed form. M. NIERENSTEIN.