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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 in the Chemical Society's Rooms, Burlington House, on Wednesday, April 4th, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of: Arthur Duncan Gay, John Gordon Mayne, Reginald Arthur McNicol, M.Sc., A.I.C., William Ramsden Orrell, B.Sc., A.I.C., Laurence Frederick Smith, M.Sc., A.R.C.S., D.I.C., A.I.C., Charles Frederick Turner, F.I.C.

Certificates were read for the second time in favour of: Frank Rowland Hill, B.Sc., A.I.C., Edward Thomas Illing, B.Sc., F.I.C., Farid Iskander, Harry Bulmer Marston, B.Sc., A.I.C., Reginald James Munro, B.Sc., A.I.C., John Ralph Nicholls, B.Sc., F.I.C., H. Gordon Reeves, D.Sc., Ph.D., F.I.C., George Walsh, B.Sc., A.I.C., Ronald George Warren, B.Sc., William Arthur Waygood, B.Sc., A.R.C.S., A.I.C.

The following were elected Members of the Society:—John Edmund Aps, Edward Eric Billington, M.Sc., Ralph C. Chirnside, Ralph David Owen, A.I.C., A.M.I.Chem.E.

The following papers were read and discussed:—"Coffee Parchment as an Adulterant of Bran and Sharps," by John Evans, F.I.C., and T. E. Wallis, B.Sc., F.I.C.; "Determination of the Colour-producing Constituents of the Cacao Bean," by W. B. Adam, M.A., A.I.C.; "The Determination of Vanadium in Steel," by A. T. Etheridge, Ph.D., F.I.C.; "Colorimetric Determination of Antimony and its Separation from Tin," by S. G. Clarke, B.Sc., A.I.C.; and "The Determination of Carbon Dioxide in Soils," by A. Riad, B.Sc., Ph.D.

Ordinary Members of Council.—The names of Messrs. M. Salamon and J. Wood were accidently omitted from the list of the new Council given on p. 189.

Composition of the Fatty Acids Present as Glycerides in Elasmobranch Oils.

By THOMAS PERCY HILDITCH, D.Sc., F.I.C., and ALBERT HOULBROOKE, M.Sc., A.I.C.

(*Read at the Meeting, March* 7, 1928.)

The work described in the present communication was undertaken in order to obtain quantitative data on the composition of the fatty acids present as glycerides in the fatty portion of shark and other fish liver oils which stand apart in their high content of non-saponifiable matter (mainly squalene). It has proved of considerable interest, from a biochemical standpoint, to compare the general composition of these acids with those from other fish and marine animal oils which are not characterised by the presence of abnormal amounts of non-saponifiable matter, and from which, in particular, squalene is absent.

We were fortunate in having access to a quantity of fish-liver oil residues from which the squalene had been removed by distillation in a vacuum by Heilbron, Kamm and Owens for the purpose of their studies of this hydrocarbon (*J. Chem. Soc.*, **1926**, 1630). This was converted into sodium soaps and extracted with acetone in order to remove as much residual unsaponifiable matter as possible. The extracted soaps were reconverted into fatty acids and then separated into acids, the lead salts of which were respectively insoluble or soluble in cold alcohol; each group of acids was then converted into methyl esters, which were submitted to an exhaustive process of fractionation and re-fractionation in a vacuum. Our methods of applying the lead-salt separation and methyl ester fractionation processes were identical, broadly speaking, with those which have recently been described, for example, by one of us with Riley and Vidyarthi in the case of the *Brassica* seed-fats (*J. Soc. Chem. Ind.*, 1927, **46**, 457 T).

Before describing our present quantitative results, it may be stated that qualitative information on the fatty compounds of these oils has been given by some of the Japanese chemists who have made a study of squalene-containing oils. Thus Tsujimoto (*Z. Deuts. Oel. Fett Ind.*, 1926, **46**, 385) has isolated selachoceric acid, $C_{24}H_{48}O_2$ (m.pt. 78°), and selacholeic acid, $C_{24}H_{46}O_2$ (m.pt. 42·5–43°) from the liver oil of two species of the red shark, and Toyama and Tsuchiya (*J. Soc. Chem. Ind. Japan*, 1927, **30**, 63, 116, 207) have recently stated that the liver oils of yamato-torpedo, *Chimaera barbouri* and *Squalus wakiyae* contain the following fatty acids:

Saturated (10–15 per cent.): Palmitic, with less myristic and stearic; traces of arachidic and behenic; selachoceric.

Monoethylenic (considerable amounts, frequently nearly all the remainder): Palmitoleic, oleic, gadoleic, cetoleic and selacholeic.

Multiethylenic (smaller amounts): $C_{18}H_{32}O_2$, $C_{18}H_{30}O_2$, $C_{18}H_{28}O_2$ (traces); $C_{20}H_{32}O_2$ and $C_{22}H_{34}O_2$ (main components); $C_{20}H_{30}O_2$ and $C_{22}H_{36}O_2$ (smaller amounts).

In a recent examination of the oil of *Centrophorus granulosus* by Chapman (ANALYST, 1927, **52**, 622), the fatty acids present were observed to consist of stearic, palmitic, and oleic, and possibly smaller proportions of other saturated and unsaturated fatty acids, including a small amount of an acid with a molecular weight of about 340.

In the course of the present investigation we employed two sources of raw material: (i) Mixed residual oils from the livers of various species, including *Scymnorhinus lichia, Centrophorus granulosus, Lepidorhinus squamosus* and *Etmopterus spinax*; and (ii) a residual liver oil from a single species, *Scymnorhinus lichia*. In the case of the first-named oil residue, which was available in relatively large amount, we also made an analysis of the fatty acids after they had been completely hydrogenated, to serve as a check on the main results. We propose to describe in some detail the data which we obtained from one of these analyses, and to refer only briefly to the final results for the composition of the fatty acids present in the *Scymnorhinus lichia* oil, since full details of all the analyses would occupy considerable space.

INVESTIGATION OF THE MIXED FISH-LIVER OIL RESIDUES FROM *Scymnorhinus lichia, Centrophorus granulosus, Lepidorhinus squamosus* AND *Etmopterus spinax*.

This was a brown, fairly limpid oil which still contained 36·2 per cent. of non-saponifiable matter (apparent saponification equivalent 458·8, iodine value 117·7).

The material (1500 grms.) was saponified in batches of 250 grms. by refluxing with alcohol (1500 c.c.) containing anhydrous sodium hydroxide (150 grms.) for several hours. The alcoholic soap solution was evaporated and mixed with pure sand (1000 grms.), when a friable mass of dried soap and sand was obtained; this was placed with glass beads in a large Soxhlet apparatus and extracted thoroughly with acetone. The acetone extract was evaporated, taken up in ether, and then extracted repeatedly with water to remove small quantities of soap dissolved by the acetone. The aqueous extracts and the residual soap in the extractor were treated with dilute mineral acid, and the mixed fatty acids liberated, washed and dried. There were thus obtained 473 grms. of unsaponifiable matter (iodine value 173·5) and 922 grms. of mixed fatty acids (mean equivalent 297·4, iodine value 78·7). The acids were divided into two parts, one of which was analysed as such, whilst the other was converted at once into methyl esters and hydrogenated (*cf.* p. 253).

For the direct analysis the mixed acids (590 grms.) were dissolved in boiling 95 per cent. alcohol (1160 c.c.), and mixed with a hot solution of lead acetate

(413 grms.) in 95 per cent. alcohol (1160 c.c.); after boiling for a short time the solution was set aside at room temperature for 24 hours, when the deposited lead salts were filtered and washed with a little cold alcohol. Each portion of lead salts was then converted back into fatty acids, when there were obtained 361·5 grms. of solid acids (S) from the insoluble lead salts and 229·1 grms. of liquid acids (L) from the lead salts soluble in alcohol.

These acids were converted into methyl esters by refluxing them with twice their weight of methyl alcohol in presence of 3 per cent. of sulphuric acid:

	Neutral esters.			Unesterified acids.
From.	Grms.	Sap. equiv.	Iod. val.	Grms.
Solid acids S	357·1	306·2	65·3	12·9
Liquid acids L	226·6	318·7	87·4	4·3

The esters were then distilled from Willstätter bulbs of 500 c.c. or 250 c.c. capacity, the lower bulb on the stem of the flask being packed with small hollow metallic cylinders, thus providing a fractionating column about 8 cm. in height. The distillation flask was connected with a Perkin triangle, coupled in turn to a good pump which maintained a vacuum of 1 mm. of mercury or less. Finely broken porous tile (about 2 grms.) was employed to maintain steady ebullition, the flask was heated in an oil-bath and distillation was conducted as far as possible at a steady rate not exceeding about 30 drops of condensate per minute.

Most of the primary fractions were re-distilled in the same way, until eventually each fraction, so far as could be judged from its analytical constants and qualitative identification tests, consisted of an individual ester or a simple mixture of esters.

The data obtained in this way are recorded in the tables below.

METHYL ESTERS OF SOLID ACIDS S.

PRIMARY FRACTIONATION.

No.	Wt. (grm.).	B.P./1 mm.	Sap. equiv.	Iod. value.
S1	114·8	89–140° C.	280·4	36·4
S2	79·2	140–154° C.	297·7	68·3
S3	33·0	154–170° C.	318·5	74·4
S4	66·0	170–198° C.	344·4	78·6
S5	22·4	198–207° C.	361·1	79·6
S6	35·5	Residue	370·9	96·3
	350·9			

REFRACTIONATION OF S1.

S11	4·7	74–120° C.	257·4	22·1
S12	7·1	120° C.	260·8	19·7
S13	7·8	120–123° C.	268·1	20·8
S14	9·1	120–127° C.*	274·2	22·6
S15	48·3	127–128° C.	276·7	26·8
S16	11·4	128–137° C.	285·9	49·2
S17	16·2	137–140° C.	301·4	69·4
S18	5·9	Residue	308·4	70·6
	110·5			

REFRACTIONATION OF S2.

No.	Wt. (grm.).	B.P./1 mm.	Sap. equiv.	Iod. value.
S21	12·1	124–147° C.	289·1	55·3
S22	40·1	147–151° C.	292·4	69·5
S23	17·3	151–150° C.*	306·3	72·4
S24	5·0	Residue	324·2	75·1
	74·5			

REFRACTIONATION OF S3.

S31	5·3	128–146° C.	301·9	73·5
S32	14·8	146–150° C.	312·5	71·8
S33	4·1	150–151° C.	324·0	77·8
S34	5·1	Residue	341·8	79·1
	29·3			

REFRACTIONATION OF S4.

S41	28·8	127–167° C.	333·1	77·9
S42	27·0	167–172° C.	345·3	78·5
S43	5·9	Residue	356·6	79·3
	61·7			

REFRACTIONATION OF S41.

S411	4·6	131–159° C.	311·1	74·5
S412	10·5	159–161° C.	322·4	78·3
S413	10·2	Residue	352·2	78·5
	25·3			

REFRACTIONATION OF S5.

S51	6·2	148–177° C.	347·5	77·5
S52	5·2	177–183° C.	364·5	79·8
S53	7·4	Residue	365·5	79·1
	18·8			

REFRACTIONATION OF S6.

S61	4·2	145–201° C.	362·6	81·4
S62	27·2	Residue	371·3	105·6
	31·4			

METHYL ESTERS OF LIQUID ACIDS L.

PRIMARY FRACTIONATION.

No.	Wt. (grm.).	B.p./1 mm.	Sap. equiv.	Iod. value.
L1	51·9	73–140° C.	273·6	73·1
L2	75·1	140–151° C.	295·5	85·5
L3	50·2	151–186° C.	321·8	91·3
L4	10·0	186–188° C.	342·2	92·6
L5	34·5	Residue	395·0	98·8
	221·7			

* The erratic temperatures in the tables are due to two causes, *viz.* either to minor fluctuations in the pressure of the system, or to the fractionating column becoming somewhat denuded of vapour at the close of the operation.

No.	Wt. (Grm.)	B.p./1 mm.	Sap. equiv.	Iod. value.
		REFRACTIONATION OF L1.		
L11	3·4	68–117° C.	253·0	59·0
L12	8·2	117–118° C.	267·5	61·4
L13	9·3	118–120° C.	279·2	68·3
L14	8·9	120–128° C.	286·9	74·4
L15	8·9	128–136° C.	291·3	83·4
L16	3·2	136–140° C.	299·5	86·1
L17	4·8	Residue	302·6	87·3
	46·7			
		REFRACTIONATION OF L2.		
L21	7·6	104–130° C.	296·7	81·4
L22	18·3	130–131° C.	295·4	85·6
L23	24·8	131–138° C.	301·8	86·6
L24	15·8	138–146° C.	303·1	88·1
L25	4·2	Residue	319·7	89·1
	70·7			
		REFRACTIONATION OF L3.		
L31	4·7	143–156° C.	302·1	87·6
L32	13·1	156–160° C.	312·0	89·3
L33	14·4	160–165° C.	325·7	94·2
L34	7·5	165–170° C.	348·6	97·3
L35	6·3	Residue	357·2	91·5
	46·0			
		REFRACTIONATION OF L5.		
L51	4·4	170–199° C.	365·4	98·1
L52	2·9	199–201° C.	380·0	111·4
L53	23·4	Residue	416·4	102·3
	30·7			

These data afford a basis on which to make an estimate of the quantitative composition of the fatty acid mixtures, if the following conditions are satisfied:

(i) It is necessary to establish by independent tests that each ultimate fraction does not contain more than two homologous members of the saturated and unsaturated acids.

(ii) The presence of particular fatty acids should not be taken for granted unless definite identification, at least of the main fractions, is forthcoming.

In the case of the simpler fatty acid mixtures to which the methyl ester fractionation was originally applied by various groups of workers the isolation of large individual main fractions and rigorous identification of the acids present is a very easy matter; especially is this so in the tropical nut fats, the fatty acids of which are very largely the saturated members of the higher aliphatic series. Fatty acids from marine animal oils are in quite a different category: they are composed of a complex mixture of saturated and unsaturated members, the separation of which by the lead salt method is only partial, so that the final ester fractions frequently consist of a mixture of, at all events, saturated and unsaturated derivatives of the same carbon content. By applying the identification tests described

below, however, we have satisfied ourselves of the general validity of the assumptions on which our calculations are based. Unfortunately, definite qualitative criteria for the unsaturated acids containing more than 18 carbon atoms are in none too satisfactory a condition, and the accuracy of our analytical figures is probably relatively less as the acids of highest carbon content are approached. We believe, however, that, up to and including acids of the C_{20} series, our results are probably accurate to within about 1 per cent. of the total fatty acids; this statement is supported by (i) the results of the two independent analyses of shark-liver oil residues now described, and (ii) the agreement between the analytical figures for a raw and a corresponding hydrogenated oil.

It will be obvious from comparisons drawn later in this paper that, admitting that in the case of these complex mixtures of fatty acids the accuracy of the final results is not so great as in simpler types, the results obtained permit considerable insight to be gained into the variations in general composition in different types of marine animal fats.

Identification of the saturated fatty acids present in methyl ester fractions of low iodine value was established by crystallisation of the liberated fatty acids from ethyl acetate or alcohol, followed by determinations of the melting-point alone and mixed with standard specimens of known acids. For more unsaturated ester fractions, the saponified ester was oxidised in dilute ice-cold alkaline solution with potassium permanganate; the mixture of hydroxylated fatty acids and saturated acids was recovered, and any saturated acids present extracted with petroleum spirit (b.p. 40–50° C.). Both the saturated acids and the hydroxylated acids (corresponding to the unsaturated members originally present) were then purified and examined for melting-point.

FATTY ACIDS PRESENT.—The chief acids whose presence was thus established are recorded below, together with the observed melting-point and (within brackets) the melting point recorded for a mixture of the acid with an authentic specimen.

Ester fraction.	
	FROM SOLID ACIDS S.
S11	Myristic, 52–53·5° C. (52–53·5° C.); palmitic, 60–61° C. (59–61° C.).
S13	Palmitic, 61·5–62·5° C. (61–62° C.); dihydroxypalmitic, 123° C. (123° C.).
S15	Palmitic, 61–62° C. (60–61·5° C.); dihydroxy acids, 125–126° C. (mixture from palmitoleic and oleic).
S17	Dihydroxystearic, 129–130° C. (128·5–130° C.(; saturated acid mixture 66–67° C. (stearic and arachidic ?).
S22	Stearic, 67–69° C. (66–68° C.); dihydroxystearic, 129–130° C. (128·5–130° C.).
S24	Arachidic (?), 66–70° C.; dihydroxyacid, 127–128° C. (depression with dihydroxystearic).
S42	Dihydroxy acid, 127–128° C. (presumably from gadoleic and cetoleic).
	FROM LIQUID ACIDS L.
L11	Myristic, 47–48° C. (46–48° C., impure); palmitic, 60–62° C. (59·5–61·5° C.); dihydroxypalmitic, 124–125° C.
L12	Palmitic, 61–62·5° C. (59–61° C.); dihydroxypalmitic, 124–125° C. (123–124° C.).
L14	Palmitic, 60–61° C. (59–61° C.); dihydroxy acid, 127° C. (mixture from palmitoleic and oleic).
L16	Dihydroxy acid, 128·5° C. (128–129·5° C. with 9, 10–dihydroxystearic).
L22	Dihydroxystearic, 129–130° C.
L23	Dihydroxystearic, 129–130° C. (128·5–130° C.); tetrahydroxystearic, trace.

For the reason already stated, definite identification of the higher unsaturated acids is not possible at present, and we had perforce to assume that the fractionation in these cases had proceeded as completely as in the lower fractions, for which we are able to produce evidence. It is difficult to suppose that the final fractions—nearly fifty in number in the present case—can contain more than simple binary mixtures of homologues; the relationship between the observed boiling-points and equivalents of the final fractions is also consistently in favour of the interpretation we have put upon the results.

The composition of each final fraction has been calculated from its equivalent and iodine value, in conjunction with the above observations. In many cases an ester-fraction has contained three components derived from two homologous series, *e.g.* a mixture of methyl palmitate, palmitoleate and oleate. In such instances, if the weights of the components of a fraction weighing w be x, y, z, the respective equivalents E_w (observed), E_x, E_y, E_z, and the respective iodine values I_w (observed), I_x, I_y, I_z, we have:

$$\text{(i)} \quad x + y + z = w;$$

$$\text{(ii)} \quad \frac{x}{E_x} + \frac{y}{E_y} + \frac{z}{E_z} = \frac{w}{E_w};$$

$$\text{(iii)} \quad x(I_x) + y(I_y) + z(I_z) = w(I_w).$$

In this way it is possible to build up the composition of each primary mixture which was re-fractionated, and thence to arrive at the composition of the original mixture of methyl esters distilled. These figures are summarised in the next table.

PERCENTAGE COMPOSITION OF METHYL ESTERS CALCULATED FROM FRACTIONATIONS.

		(i) From Results of Re-fractionation of Primary Fractions.						(ii) Calculated to Original Mixture.	
		1.	2.	3.	4.	5.	Residue.	As esters.	As fatty acids.
		Esters from Solid Acids (S).							
Weights (grms.)		114·8	79·2	33·0	66·0	22·4	35·5	350·9	—
Myristate	per cent.	4·0	—	—	—	—	—	1·3	1·3
Palmitate	,,	51·5	11·4	—	—	—	—	19·4	19·3
Stearate	,,	—	4·6	8·2	0·8	—	—	2·0	2·0
Arachidate	,,	3·6	3·4	—	—	—	—	2·0	2·0
Palmitoleate	,,	5·9	—	—	—	—	—	1·9	1·9
Oleate	,,	33·5	68·5	29·8	3·2	—	—	29·8	29·7
Gadoleate, etc.	,,	1·5	12·1	50·6	33·7	4·9	—	14·6	14·7 (–2·1H)
Cetoleate, etc.	,,	—	—	11·4	61·3	62·4	33·6	20·0	20·1 (–2·2H)
Selacholeate, etc.	,,	—	—	—	1·0	32·7	66·4	9·0	9·0 (–2·8H)

Esters from Liquid Acids (L).

		1.	2.	3.	4.	5.	Residue.	As esters.	As fatty acids.
Weights (grms.)		51·9	75·1	50·2	10·0		34·5	221·7	—
Myristate	per cent.	2·5	—	—	—		—	0·6	0·6
Palmitate	,,	15·2	—	—	—		—	3·6	3·6
Stearate	,,	—	0·6	—	—		—	0·2	0·2
Myristolate	,,	2·2	—	—	—		—	0·5	0·5
Palmitoleate	,,	25·9	—	—	—		—	6·2	6·1
Oleate, etc.	,,	50·7	80·4	19·5	—		—	44·5	44·3 (–2·1H)
Gadoleate, etc.	,,	3·5	19·0	50·4	—		—	19·1	19·1 (–2·2H)
Cetoleate, etc.	,,	—	—	27·4	33·2		7·2	9·0	9·1 (–2·6H)
Selacholeate, etc.	,,	—	—	2·7	66·8		79·5	16·3	16·5 (–3·2H)
Unsaponifiable	,,	—	—	—	—		13·3	—	—

Hence the composition of the total combined fatty acids of the shark-liver oil is as follows:

Solid acids (S) (61·2 per cent.).	Liquid acids (L) (38·8 per cent.).	Acid.	Combined fatty acids.
0·8	0·2	Myristic, $C_{14}H_{28}O_2$	1·0
11·8	1·4	Palmitic, $C_{16}H_{32}O_2$	13·2
1·2	0·1	Stearic, $C_{18}H_{36}O_2$	1·3
1·2	—	Arachidic, $C_{20}H_{40}O_2$	1·2
—	0·2	Myristoleic, $C_{14}H_{26}O_2$	Trace
1·1	2·4	Palmitoleic, $C_{16}H_{30}O_2$	3·5
18·2	17·2	Oleic, $C_{18}H_{34}O_2$, etc.	35·4 (–2·1H)
9·0	7·4	Gadoleic, $C_{20}H_{38}O_2$, etc.	16·4 (–2·2H)
12·3	3·5	Cetoleic, $C_{22}H_{42}O_2$, etc.	15·8 (–2·3H)
5·6	6·4	Selacholeic, $C_{24}H_{46}O_2$, etc.	12·0 (–3·0H)

The figures in the final column are not, of course, reliable to more than the nearest whole number. The figures in brackets following oleic, gadoleic, erucic, and selacholeic acids indicate the average observed unsaturation in terms of hydrogen atoms—in all cases there was mainly monoethylenic acid present, and probably in no case was there any acid less saturated than diethylenic observed, thus contrasting with the normal types of fish or whale oils (*cf.* p. 257).

ANALYSIS OF COMPLETELY HYDROGENATED ESTERS FROM THE SAME SOURCE.—A quantity (300 grms.) of the mixed fatty acids from the same liver oil residues, from which non-fatty matter had been removed, as described on p. —, was converted directly into methyl esters. After removal of small amounts of unchanged fatty acid from the esters, the latter (301 grms.) were hydrogenated at 170–180° C. in presence of active nickel until hydrogen ceased to be absorbed. The product was filtered and a portion of it submitted to systematic fractional distillation, as in the preceding instance.

The methyl esters possessed the following mean characteristics before, and subsequent to, hydrogenation:

	Sap. equiv.	Iodine value.
Before hydrogenation ..	307·9	76·0
After hydrogenation ..	311·2	8·9

The details of the fractional distillation are as follows:

No.	Wt. (grms.).	B.pt./1 mm.	Sap. equiv.	Iodine value.
		PRIMARY FRACTIONATION.		
1	64·9	100–135° C.	276·9	4·3
2	65·1	135–150° C.	296·7	2·4
3	45·9	150–171° C.	312·3	3·7
4	16·5	171–173° C.	335·1	8·2
5	28·5	173–195° C.	362·7	8·5
6	6·5	195–190° C.	375·4	12·5
7	25·6	Residue	418·6	42·5
	253·0			
		REFRACTIONATION OF No. 1.		
11	9·6	75–111° C.	259·0	
12	9·1	110–118° C.	267·0	
13	20·2	118–120° C.	278·8	
14	17·5	120–135° C.	290·5	
15	4·0	Residue	306·5	
	60·4			
		REFRACTIONATION OF No. 2.		
21	3·7	124–136° C.	281·9	
22	5·4	136–138° C.	290·9	
23	32·1	138–146° C.	299·2	
24	11·9	146–149° C.	300·5	
25	3·1	149–145° C.	307·9	
26	4·8	Residue	317·6	
	61·0			
		REFRACTIONATION OF No. 3.		
31	22·8	130–150° C.	309·0	
32	11·3	150–165° C.	320·2	
33	2·9	165° C.	338·0	
34	5·0	Residue	345·0	
	42·0			
		REFRACTIONATION OF No. 5.		
51	5·2	146–175° C.	354·4	
52	9·5	175° C.	355·9	
53	5·7	175–178° C.	375·0	
54	4·0	Residue	378·2	
	24·4			

It is clear that the small amount of unsaturated material which was not susceptible to hydrogenation was of high molecular weight, and it is probable that it consisted for the most part of non-fatty matter (squalene or complex alcohols).

The ultimate ester fractions were examined qualitatively and the fatty acids identified therein as follows (*cf.* p. 251):

11 Myristic, 53–54° C. (52–53·5° C.); palmitic, 62–62·5° C. (60·5–61·5° C.).
12 Palmitic, 61–62° C. (61–61·5° C.).
13 ,, 60–61° C.
23 Stearic, 68–69° C. (67–69° C.).
24 ,, 68–69° C. (67–68° C.).
32 Arachidic, 73–74° C. (73–75° C.).
34 Behenic, 77–78° C. (78–79° C.).
51 ,, 77·5–79° C. (78–79° C.).
52 ,, 78–79° C. (77–79° C.).
54 Lignoceric, 80–81° C. (78–80° C.; depression to 74–77° C. when mixed with behenic).

The original residue (No. 7) was analysed with respect to its content of non-saponifiable matter; the fatty acids of No. 7, when freed from unsaponifiable matter, had a mean equivalent of 358·7.

The final composition of the mixture of hydrogenated esters was calculated from the results of the fractional distillations with the following results:

PERCENTAGE COMPOSITION OF METHYL ESTERS CALCULATED FROM FRACTIONATIONS.

	(i) From Results of Re-fractionation of primary Fractions.							(ii) Calculated to Original Mixture.	
	1.	2.	3.	4.	5.	6.	Residue.	As esters.	As esters.
Weights (grms.)	64·9	65·1	45·9	16·5	28·5	6·5	25·6	253·0	—
Myristate	7·3	—	—	—	—	—	—	1·9	1·9
Palmitate	53·1	5·4	—	—	—	—	—	15·2	15·0
Stearate	37·5	82·7	36·9	—	—	—	—	38·0	37·9
Arachidate	2·1	11·9	51·6	65·7	—	—	—	17·5	17·6
Behenate	—	—	11·5	34·3	64·9	22·1	28·0	15·2	15·3
Lignocerate	—	—	—	—	35·1	77·9	60·9	12·2	12·3
Unsaponifiable	—	—	—	—	—	—	11·1	—	—

The next table compares these figures with those calculated for a fully-hydrogenated mixture of acids from the data as determined on p. 253 in the analysis of the natural mixture of acids:

Fatty acid.	(i) Found, from hydrogenated esters. Per Cent.	(ii) Calculated, from analysis of original esters. Per Cent.
Myristic	1·9	1·2
Palmitic	15·0	16·7
Stearic	37·9	36·7
Arachidic	17·6	17·6
Behenic	15·3	15·8
Lignoceric	12·3	12·0

Bearing in mind the complexity of the mixture of fatty acids, the agreement is reasonably satisfactory. Effective fractionation becomes increasingly difficult, of course, with increasing molecular weight, and the accuracy of the fractionation method doubtless falls off at the higher end of the scale. On the other hand, the two sets of figures show that, even in a complicated case, such as the present, a fairly complete quantitative picture of the composition of the mixed fatty acids is to be obtained by this process.

Investigation of the Fatty Portion of the Liver Oil of *Scymnorhinus lichia*.

This specimen of liver oil residue (from which most of the squalene had already been removed), still contained 21·1 per cent. of non-fatty matter; it was converted into anhydrous soap and extracted with acetone, as in the first case (p. 247), after which the purified mixed fatty acids had a mean equivalent of 295·1 and an iodine value of 69·0.

The analysis followed the lines already described, except that the lead salts insoluble in alcohol were recrystallised from ether, so that three fractions of fatty acids were submitted to methylation and fractional distillation, namely:

	Percentage.	Mean equivalent.	Iodine value.
Solid acids (S)	27·0	283·2	36·6
Liquid acids, from ethereal solution (E)	31·4	291·2	77·6
Liquid acids, from alcoholic solution (A)	41·6	311·6	82·2

The combined results of the analyses of the methyl ester fractions led to the following compositions for each of these groups:

Acid.	Solid acids (S). Per Cent.	Liquid acids (E). Per Cent.	Liquid acids (A). Per Cent.
Myristic	2·4	—	1·3
Palmitic	39·0	4·9	6·2
Stearic	10·9	1·8	0·2
Arachidic	2·8	0·1	—
Behenic	0·4	0·1	—
Myristoleic	—	—	1·0
Palmitoleic	—	5·0	5·2
Oleic	12·4	30·0	39·0
Gadoleic, etc.	8·2	20·4	4·7
Cetoleic, etc.	13·9	37·7	24·8
Selacholeic, etc.	10·0	—	17·6

The next table shows, in the first column, the composition of the mixed fatty acids of the *Scymnorhynus lichia* oil, calculated from the above figures; and in the second column are repeated, for comparison, the results of the analysis of the mixed oils described on pp. 252, 253:

Acids of:	*Scymnorhynus lichia*. Per Cent.	Mixed shark liver oils (pp. ——). Per Cent.
Myristic, $C_{14}H_{28}O_2$	1·2	1·0
Palmitic, $C_{16}H_{32}O_2$	14·6	13·2
Stearic, $C_{18}H_{36}O_2$	3·6	1·3
Arachidic, $C_{20}H_{40}O_2$	0·8	1·2
Behenic, $C_{22}H_{44}O_2$	0·1	—
Myristoleic, $C_{14}H_{26}O_2$	0·4	0·2
Palmitoleic, $C_{16}H_{30}O_2$	3·7	3·5
Oleic, $C_{18}H_{34}O_2$, etc.	29·1	35·4 (–2·1H)
Gadoleic, $C_{20}H_{38}O_2$, etc.	10·6 (–2·0H)	16·4 (–2·2H)
Cetoleic, $C_{22}H_{42}O_2$, etc.	25·9 (–2·1H)	15·8 (–2·3H)
Selacholeic, $C_{24}H_{46}O_2$, etc.	10·0 (–2·0H)	12·0 (–3·0H)

The agreement between the two sets of figures is fairly close up to the C_{18} acids, but there is a difference of 6 per cent. in the content of oleic acid; the combined amounts of C_{20}, C_{22} and C_{24} unsaturated acids are respectively 46 and 44 per cent., but the proportion of cetoleic acid is much higher in the *Scymnorhinus lichia* oil. Apart from the latter figure, there is a general similarity in the composition of both fatty acid mixtures.

When either series, however, is compared with the fatty acids of marine animal oils in which squalene is not present, very marked differences in characteristics are at once evident. Analyses of fatty acids from the more normal types of marine animal oil have been given by Armstrong and Allan (*J. Soc. Chem. Ind.*

1924, **43**, 207T), Milligan, Knuth and Richardson (*J. Amer. Chem. Soc.*, 1924, **46**, 157), and others, of which the following are typical:

Oil:	Japanese fish.	Menhaden.	Whale.		Whale.
			South Sea.	Newfoundland.	
Observers:	A. & A.	A. & A.	A. & A.	A. & A.	M. K. & R.
Acids:	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Myristic	5·8	5·9	8·0	7·6	4·5
Palmitic	9·7	16·3	12·1	9·7	11·5
Stearic	2·3	0·6	2·3	2·8	2·5
Arachidic	—	0·6	—	—	—
Behenic	—	0·8	—	—	—
Myristoleic	—	—	1·5	1·4	—
Palmitoleic	13·0	15·5 (–3H)	15·0	18·3	17·0
Oleic	14·2	29·6	33·4	35·1	36·5
Linoleic	10·0		9·0	8·8	—
Gadoleic, etc.	26·0 (–5H)	19·0 (–10H)	8·2 (–7·5H)	—	16
Cetoleic, etc.	19·0 (–5H)	11·7 (–10H)	10·5 (–9H)	16·0 (–8H)	10
Selacholeic, etc.	—	—	—	—	1·5

No detailed analysis for a definite marine animal liver oil of this class appears to be available, but it is well known that cod-liver oil, for example, is composed of a mixture of fatty acids very similar to those given above for Japanese fish (sardine) or menhaden oils.

Comparing the above data with those for fatty acids associated with squalene in the shark, etc., livers, it is evident that the proportions of palmitic, stearic, oleic, and linoleic acids are of the same order in both cases, and that here the resemblance ends.

The most striking difference is in the state of unsaturation of the fatty acids of higher molecular weight. Whereas the normal marine animal oil contains 30–40 per cent. of acids of the C_{20} and C_{22} groups, the "average unsaturation" of which is equal to 4 or 5 ethylenic linkings per molecule, the shark liver oil acids are of relatively low unsaturation, and contain but little less saturated than monoethylenic derivatives. At the same time the non-fatty matter of the shark liver oils, squalene, is exceedingly highly unsaturated, and contains six ethylenic bonds per molecule of $C_{30}H_{50}$. It should also be noted that acids of the C_{20} and C_{22} group are present in the shark-liver oil acids in about the same proportion as in other marine animal oils, but they are mainly monoethylenic; also, there is about 10–15 per cent. of a monoethylenic C_{24} acid present in the shark-liver mixture.

Other minor differences are to be found in the much smaller amounts of palmitoleic and myristic acids present in the shark liver oil fatty acids.

The presence of highly unsaturated C_{20} and C_{22} acids and of palmitoleic acid has hitherto been a typical feature of marine animal oils and also exclusive to this class. It would seem probable that there is some connection between the deficiency of these derivatives and the presence of large amounts of squalene in the shark liver oils. Have the acids in question disappeared in the elaboration of the hydrocarbon in the shark, etc., or are they present, in the more familiar marine animals, as decomposition products from squalene (which is further metabolised instead of being secreted as such)? The analytical data given in this paper indicate, at all events, that the biochemical relationships between squalene and the unsaturated fatty acids of typical marine animal oils merit detailed study.

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

X. The Separation of Silica from the Earth Acids.
XI. The Precipitation of Titanium by Tannin.

By W. R. SCHOELLER and A. R. POWELL.

(*Read at the Meeting, February* 1, 1928.)

X. THE SEPARATION OF SILICA FROM THE EARTH ACIDS.

The only recognised method for the separation of silica from tantalic and niobic oxides is that based on its volatilisation by hydrofluoric acid in presence of sulphuric acid, followed by strong ignition and weighing of the residual pentoxides, silica being determined by difference. Whilst it is true to say that an accurate silica determination always involves final hydrofluoric acid volatilisation, we propose to show in this section that the means for the separation under discussion should not be confined solely to an evaporation of the mixed oxides with hydrofluoric and sulphuric acids.

The Disputed Volatilisation of Tantalum and Niobium Fluorides.—It is necessary first to outline the controversy over the volatilisation of the pentafluorides under varying conditions. Rose found that the evaporation of the acid fluoride solution entailed a certain loss of tantalum as well as of niobium, which could be reduced, but not altogether prevented, by addition of sulphuric acid. Marignac, on the other hand, concluded that evaporation to fumes of sulphuric acid of the same solutions caused no loss of earth acid at all. This was confirmed by Levy (Analyst, 1901, **26**, 64), who concluded that "neither commercial tantalic nor niobic oxide volatilises when treated with hydrofluoric and sulphuric acids; niobium does not form volatile compounds even with hydrofluoric acid alone, but tantalic oxide, by action of hydrofluoric acid, loses in weight each time the operation is repeated, resembling titanium in this respect." Again, von John (*Chem. News*, 1909, **100**, 154) reports as follows:—"I have found that on evaporation of hydrofluoric acid [in presence of sulphuric acid] by strong heating, some of the tantalum and niobium is vaporised, TaF_5 and NbF_5; this method gives only good results by most careful evaporation at lowest possible temperatures, and careful regulation of the same." The confusion is increased by Ruff and Schiller (*Z. anorg. Chem.*, 1911, **72**, 349), according to whom tantalum fluoride solutions can be evaporated to dryness and the residue ignited without any loss, both when sulphuric acid is present and when it is not. Their conclusions caused Levy to repeat his tests (Analyst, 1915, **40**, 214), with the result that he confirmed his previous findings.

Our attitude towards the question at issue is that, although our practical experience leads us to take the view that evaporation with hydrofluoric acid does not cause a loss of earth acid, provided an excess of sulphuric acid is present, we hesitate to range ourselves altogether on the side of those who deny the possibility of volatilisation under any conditions. We have had evidence of the volatilisation of tantalum, in the form of an iridescent to opalescent film or coating round the edge of the platinum vessel, during the fusion of potassium fluotantalate, and also when evaporating solutions of tantalic oxide in hydrofluoric acid. Nobody denies that the pentafluorides are volatile: Ruff and Schiller themselves (*loc. cit.*) give the following boiling-points: 217° to 220° C. for NbF_5, and 229·2° to 229·5° C. for TaF_5. It would therefore be rash to assert that the volatilisation reported by a number of investigators is an error in observation. Even such apparently irreconcilable views as Levy's and Ruff and Schiller's may be largely the result of trifling differences in procedure and of *imponderabilia* constituting the personal equation. Therefore, even if we were to re-investigate the subject more fully, our findings need not be held to invalidate the views they contradict.

A certain volatility of titanium in the evaporation of the fluoride solution free from sulphuric acid (b.pt. of TiF_4, 284° C.) has, apparently, never been disputed. Levy (*vide supra*) remarks that tantalum resembles titanium in this respect, whilst niobium does not volatilise with hydrofluoric acid alone, a difference in behaviour for which the ready formation of $NbOF_3$ and the non-existence of the corresponding tantalum compound may provide an explanation. It deserves to be noted here that the deportment of zirconium towards hydrofluoric acid is the same as that of titanium: Wedekind (*Ber.*, 1911, **44**, 1753) reports that zirconia is almost completely volatilised by repeated evaporation with hydrofluoric acid, even in presence of a deficiency of sulphuric acid, but that no loss occurs if an excess (20 parts) of the latter acid is present.

The separation by bisulphate, described below, for which we claim advantages, incidentally avoids the risk—however remote—of volatilisation, as the earth-acid fraction is not treated with hydrofluoric acid.

The Separation.—This is best considered as embracing the usual two propositions: (1) *Small quantities of earth acid from much silica.* In this case, treatment of the mixed oxides with hydrofluoric and sulphuric acids eliminates the predominant constituent and leaves the subordinate as a residue suitable for direct weighing. The major constituent is therefore computed by difference, as it always should be. The manipulation is extremely simple, and the expulsion of the sulphur trioxide from the small pentoxide residue gives no trouble. Hence, hydrofluoric acid is a convenient reagent for the determination of small amounts of earth acid in silica. (2) *Small quantities of silica from much earth acid.* This, the usual case in mineral analysis, is one in which the direct volatilisation method is not only faulty in principle—for the subordinate is determined by difference—but tedious in execution because the expulsion of the sulphuric acid involves serious risk of loss; the earth acids, after the hydrofluoric acid has been volatilised, form a thick jelly which is very apt to spirt unless the heating is done with extreme

caution. The residual earth acids must be repeatedly ignited with ammonium carbonate to constant weight.

AUTHORS' INVESTIGATION.—The object of this investigation was to study the separation of small quantities of silica from much earth acid by a reagent other than hydrofluoric acid, which would yield a weighable silica fraction. The purity of this product (substantially free from, or poor in, earth acid) would then be ascertained by the usual hydrofluoric acid treatment. The processes investigated will be classified into (*A*) fusion with alkaline fluxes, and (*B*) fusion with bisulphate.

(*A*) FUSION WITH ALKALINE FLUXES: (*a*) *Sodium hydroxide* (Rose's proposed method).—Rose (*vide supra*) being satisfied that evaporation with hydrofluoric and sulphuric acids results in a certain loss of earth acid, proposes fusing the mixed oxides with sodium hydroxide, extracting with water, filtering, and washing the residual sodium tantalate and niobate with sodium hydroxide or carbonate solution; the filtrate, containing sodium silicate, is to be acidified and evaporated to dryness for the recovery of the silica. He adds, however, that "the value of this method has not yet been confirmed experimentally."

Rose's proposed method was embodied, without acknowledgment, in von John's article (*loc. cit.*; abstract, ANALYST, 1909, **34**, 508), which contains no numerical data on the reliability or otherwise of the procedure. The insoluble sodium salts are decomposed with dilute sulphuric acid, the earth acids precipitated by hydrolysis, filtered off, ignited, and weighed; silica is taken by difference.

We thought it advisable to submit Rose's process to experimental investigation, with special regard to the direct determination of the silica, as the subordinate constituent. Experiments 1 to 4 (WRS) were carried out in nickel, 5 to 7 (ARP) in a silver crucible. The alkaline extracts were filtered through rubber funnels and received in nickel dishes; they were acidified with hydrochloric acid and the silica recovered by double evaporation in porcelain, the combined precipitates ($P^1 + P^2$) being ignited, weighed, and submitted to treatment with hydrofluoric and sulphuric acid. Results (in grms.):

Exp.		Taken.			Actual SiO_2. (by HF).	SiO_2. Error.
		M_2O_5.	SiO_2.	$P^1 + P^2$.		
Nb	1	0·2222	0·1026	0·0946	0·0900	−0·0126
,,	2	0·1228	0·1004	0·0883	0·0855	−0·0149
Ta	3	0·1240	0·1036	0·0834	0·0817	−0·0219
EA	4	0·2009	0·1054	0·0964	0·0909	−0·0145
,,	5	0·2046	0·0202	0·0217	0·0184	−0·0018
,,	6	0·2512	0·0516	0·0492	0·0467	−0·0049
,,	7	0·1515	0·0086	0·0047	0·0046	−0·0040

A glance at these figures shows that the method is unreliable, as it gives very incomplete silica recoveries, and the silica fractions contain earth acid in every case except Exp. 7. We also recovered the earth acids, obtaining considerable positive errors; it was evident that the precipitates were contaminated, not only with silica, but also with nickel or silver from the crucibles used. In view of these disappointing results, further work was abandoned.

(*b*) *Potassium carbonate.* The success of Schoeller and Jahn's method—fusion with potassium carbonate and precipitation of the earth acids with sodium chloride—for the separation of tungsten from tantalum and niobium (Section VIII, ANALYST, 1927, **52**, 511) seemed to justify the hope that it would also answer for the case under discussion. However, the result of our practical experience is, that it cannot be recommended for the separation of silica from the earth acids. Trouble was encountered when the mass, resulting from the fusion of the mixed oxides with 3 grms. of potassium carbonate, was taken up with water; the solutions, clear at first, soon became cloudy and deposited flocculent precipitates (much more abundantly in the case of tantalum):

	Taken.		
Exp.	M_2O_5.	SiO_2.	Deposit.
8	Ta_2O_5 0·1014	0·1000	0·1539
9	Nb_2O_5 0·1014	0·1014	0·0288
10	Ta_2O_5 0·1019	0·0107	0·0910
11	Ta_2O_5 0·1002	0·0051	0·0539

This flocculation was prevented by solution of the fused mass in a small amount of strong caustic potash, which gave a perfectly clear solution. This was transferred to a nickel dish and saturated with solid sodium chloride; the crystalline precipitate was filtered off after half-an-hour and washed with strong sodium chloride solution. The washing of the niobate precipitate proceeded smoothly, but the filter containing the tantalate precipitate soon became clogged; hence the washing was not completed until the next day, when a flocculent precipitate was again found to have formed in the filtrate. The silica was recovered from the filtrate, and the earth acid from the precipitate, by known methods, the fixed residue from the hydrofluoric acid volatilisation being added to the weight of pentoxide found. Results:

		M_2O_5 in			
Exp.	Taken.	NaCl-*P*.	HF residue.	Found.	Error.
12	Nb_2O_5 0·1563	0·1538	0·0059	0·1597	+0·0034
	SiO_2 0·0545			0·0537	−0·0008
13	Nb_2O_5 0·2562	0·2450	0·0114	0·2564	+0·0002
	SiO_2 0·0538			0·0501	−0·0037
14	Ta_2O_5 0·2967	0·2519	0·0566*	0·3085	+0·0118
	SiO_2 0·0530			0·0435	−0·0095
15	Ta_2O_5 0·2076	0·1778		not completed.	
	SiO_2 0·0103				
15*a*	Ta_2O_5 0·1016	0·0991	—	—	—
	SiO_2 none				

* After repeated HF-evaporation: hence NaCl-precipitate contains SiO_2.

Whilst the results of the niobium-silica separations might almost be passable, the recovery of the silica from the tantalum separation again involves a large negative error. At this stage we suspended further work with alkaline fluxes, as the tests convinced us that a reliable separation would not be achieved. We prefer not to attempt explaining such failure on theoretical grounds, as the exact nature of silicate solutions is not yet perfectly understood. Our inference is

based chiefly on the analogous behaviour of silicate minerals after fusion with alkali carbonate: for some obscure reason, extraction of the fused mass with water —as carried out in Berzelius' method for the determination of silica in presence of fluorine—never achieves a quantitative removal of the alkali silicate from the basic constituents of the mineral. In like manner, the amorphous sodium tantalate (niobate), precipitated by the action of water upon the sodium hydroxide fusion in Rose's process, carries down a considerable amount of silica. The crystalline precipitate produced by sodium chloride in an alkaline solution of potassium niobate was almost free from silica, whereas, in the corresponding case of potassium tantalate, addition of sodium chloride caused some co-precipitation of silica but incomplete precipitation of tantalic acid (slight "loss of individuality"; compare Exps. 15 and 15*a*).

A minor objection against alkaline fusion methods is the familiar difficulty of obtaining quantitative recovery of the silica by evaporation of the acidified silicate solution, more especially—as in the present case—in presence of much sodium chloride. For example, fusion of 0·0218 grm. of silica with potassium carbonate and evaporation of the acidified solution to dryness after addition of 25 grms. of sodium chloride gave 0·0186, a second evaporation, 0·0022 grm.; actual SiO_2 (by HF) 0·0204, error –0·0014 grm. Such losses, it should be added, can be counteracted by a suitable procedure, such as that of Wells (ANALYST, **1922, 47,** 537), who recovers minute quantities of silica from solution by addition of a little alum and neutralisation with ammonia.

(*B*) FUSION WITH BISULPHATE.—The use of this—the acid flux *par excellence* —presents the advantage that, whilst the earth acids can be converted into soluble compounds, the silica is obtained as an insoluble residue or concentrate suitable for hydrofluoric acid treatment. Headden employs acidified hydrogen peroxide to dissolve the bisulphate melt (*Amer. J. Sci.*, **1922, 3,** 297), whilst we have proposed the use of tartaric acid (ANALYST, **1922, 47, 93,** Section I). Obviously any organic acid that forms soluble complexes with the earth acids, or its alkali salts (*e.g.* oxalic acid, ammonium oxalate), can be used instead of tartaric acid.

We fuse the mixed oxides with 3 grms. (or more) of potassium bisulphate; the cooled mass is digested on the water-bath with a solution of about 3 grms. of oxalic (tartaric) acid. The solution, which contains nearly the whole of the earth acids, is filtered, the residue (more or less pure silica) is washed with hot water, ignited strongly in a tared platinum crucible, and weighed. It is then submitted to evaporation with hydrofluoric and sulphuric acids, and again ignited and weighed, the difference giving silica. The small residue is once more fused with bisulphate and the melt dissolved in the organic solvent; this solution being added to the first filtrate, the combined liquors contain the whole of the earth acids.

Whilst it is evident that the above process will separate mechanically admixed silica from earth-acid compounds (*e.g.* quartz from tantalite and kindred minerals), we desired to satisfy ourselves that a molecular mixture of silica and much earth acid (as precipitated from a mixed solution) could be resolved satisfactorily by the same means. Now fusion of the mixed oxides with potassium carbonate,

followed by evaporation to dryness with hydrochloric acid and filtration as for silica, would introduce an uncertain factor, namely, the probability of slightly incomplete recovery of the silica in the evaporation. We eliminated this factor by adopting the following technique.

RESULTS OF TEST ANALYSES.—The mixed oxides were fused with 3 grms. of potassium carbonate in a platinum dish till the fused mass was clear; when cold it was dissolved in a little water, and the contents of the covered dish acidified with dilute sulphuric acid. The cover was rinsed and the liquid evaporated to dryness. After addition of 2 c.c. of strong sulphuric acid, the mass was cautiously heated until it fumed, then more strongly, to fusion of the pyrosulphate. When cold, it was leached, etc., as described above. The quantities taken were unknown to the operator. Results:

Exp.	Taken. M_2O_5.	Taken. SiO_2.	Residue from leach.	Residue from HF.	Found SiO_2.	SiO_2 error.
15	0·2219	0·0235	0·0254	0·0027	0·0227	−0·0008
16	0·2542	0·0575	0·0658	0·0076	0·0582	+0·0007
17	0·3210	0·0208	0·0264	0·0054	0·0210	+0·0002
18	0·5008	0·0139	0·0169	0·0035	0·0134	−0·0005
19	0·5022	0·0060	0·0097	0·0036	0·0061	+0·0001
20	none	0·1012	0·1018	—	—	—

The results are, we submit, within the limit of experimental error, proving that the elimination and determination of a subordinate amount of silica in molecular admixture with the earth acids can be accomplished by means of bisulphate and oxalic (tartaric) acid, without the necessity of contaminating the earth-acid fraction with fluoride.

ANALYTICAL APPLICATION.—The experimental work recorded in this Section has an important bearing on our investigation as a whole, for it confirms our view (see Section I, *loc. cit.*) that for the decomposition of earth-acid minerals "we feel strongly inclined to favour pyrosulphate as having a wider range of usefulness than potassium hydroxide or carbonate, potassium hydrogen fluoride, or hydrofluoric acid." With the greater experience since gained, we now propose to go one step further, and to show that bisulphate has undoubted advantages over the other reagents. The two last-named have nothing to recommend them (except for a determination of the rare earths), (1) because their use does not permit of the silica determination in the mineral, (2) on account of the difficulties involved in the complete removal of the fluorine—an operation resulting in an acid sulphate solution which would have been obtained in the first place with less labour by a bisulphate fusion; and (3) because of the possibility of volatilising some titanium and zirconium, if not tantalum, fluoride (*vide supra*). Potassium hydroxide has found a strong advocate in Simpson (*W. Austr. Geol. Survey Bull.*, **23**, 1906, **72**; *Chem. News*, 1909, **99**, 243), the distinctive feature of whose process for the analysis of tantalite and columbite is hydrolysis of the fusion product with hydrochloric acid. Now our objection against potassium hydroxide fusion of minerals is (and here we include potassium carbonate as being identical in its effects) that cassiterite,

quartz, and silicates are attacked by the alkali, yielding soluble stannate and silicate, which further complicates what already is a sufficiently difficult analytical problem. While we reserve the discussion on the effect of stannate for a future paper, we would here point out that the silica, having been rendered soluble by the alkali fusion, has been converted into a very troublesome constituent as regards recovery and separation; and this because hydrolysis of an acidified solution of alkali tantalate, niobate, and silicate does not result in the quantitative precipitation of the silica. This is in accordance with the known behaviour of silica, complete precipitation of which is difficult even by repeated evaporation to dryness, and is proved by the following experiment:

The fusion from 3 grms. of potassium carbonate, 0·1005 tantalic oxide, and 0·0212 silica, was taken up in water (100 c.c.) and boiled with strong hydrochloric acid (10 c.c.) according to Simpson's directions. The precipitate weighed only 0·1045 grm.; the filtrate after the first evaporation to dryness gave 0·0144 grm.; recovery error, –0·0028 grm. The silica is now divided between the tantalum precipitate (which therefore requires further treatment), and the residue from the first evaporation of the hydrolysis filtrate; a subordinate amount has escaped precipitation in that evaporation, and must be recovered at the cost of further manipulation.

On the other hand, our procedure of bisulphate fusion of the mineral, and tartaric acid extraction of the resultant mass, quantitatively removes the silica in one operation, as shown in this Section; the silica separation precedes all the others, and hydrofluoric acid treatment of the earth acids is obviated.

SUMMARY.—The disputed volatilisation of the fluorides of tantalum and niobium is discussed. Evaporation of the mixed oxides with hydrofluoric and sulphuric acids, whilst suitable for determining small amounts of earth acid in silica, is neither convenient nor accurate for the determination of a small amount of silica in earth acids. In the latter case, fusion of the mixed oxides with sodium hydroxide and treatment of the mass with water, as well as fusion with potassium carbonate, followed by precipitation with sodium chloride, gives low silica recoveries; accurate results are, however, obtained by fusion of the mixed oxides with bisulphate, extraction of the melt with oxalic or tartaric acid, and treatment of the impure silica residue with hydrofluoric and sulphuric acids.

In a discussion on the relative merits of potassium carbonate and bisulphate for the decomposition of earth-acid minerals, preference is given to the bisulphate, chiefly because the silica is not converted into soluble silicate, as is the case in the carbonate fusion; hence it is unnecessary to submit the main earth-acid fraction to hydrofluoric acid treatment.

XI. THE PRECIPITATION OF TITANIUM BY TANNIN.

While the search for a perfected separation of titania from the earth acids is proceeding, this brief Section is intended to record our observations on the precipitation of titanium by tannin, and its effect on the separation of tantalum from

niobium by our tannin method (ANALYST, **1925**, **50**, 485, Section IV), as well as certain conclusions based thereon.

ACTION OF TANNIN ON TITANIUM SOLUTIONS.—As stated in the paper referred to above, tannin produces in solutions of oxalotitanic acid a red precipitate, similar in formation and every other respect to the corresponding niobium compound. In the course of further work, we discovered that tannin is capable of precipitating titanium from tartrate solution; this we believe to be an observation new to science, the only other reagents hitherto known to possess that faculty being cupferron and phosphoric acid (or its salts). Thornton's monograph on Titanium (New York, 1927; ANALYST, **1927**, **52**, 736), published after the completion of this investigation, describes the precipitation of the tannin compound as a qualitative test for titanium; with the remark that "citric acid delays but does not prevent the formation of the precipitate." If iron is also present, Thornton prescribes precipitating it as sulphide from the ammoniacal citrate solution, boiling the acidified filtrate, and removing the precipitated sulphur; the tannin test can then be performed.

We made a quantitative investigation of the reaction. Pure titanic oxide (0·5000 grm.) was fused with potassium bisulphate, dissolved in 250 c.c. of dilute sulphuric acid, and the solution divided into 25 c.c. portions (0·0500 grm.). *Ammonium oxalate* (2 grms.) was added to each of 3 portions. (1) Boiling with 0·2 grm. tannin precipitated 0·0193 grm. TiO_2. (2) The procedure was repeated with addition of excess of sodium acetate, but the recovery was just as incomplete, *i.e.* 0·0189 grm. (3) Addition of ammonia to the formation of a slight turbidity, 5 grms. of ammonium chloride, and excess of solid tannin to the boiling solution gave a yield of 0·0492 grm. *Tartaric acid* (2 grms.) was added in each of the following experiments. (1) Addition of 0·2 grm. of tannin, then ammonia till turbid, and boiling precipitated 0·0222 grm. (2) The solution was neutralised with ammonia against phenolphthalein and boiled with 0·5 grm. of tannin; recovery, 0·0497 grm. (3) The solution was neutralised with ammonia against methyl orange and boiled with 1 grm. of tannin; recovery, 0·0503 grm.

It is concluded that the quantitative precipitation of titanium by tannin from oxalic or tartaric solution requires complete neutralisation and an excess of the precipitant. The precipitate produced is extremely voluminous. Incomplete precipitation is indicated by an orange cloudiness or coloration of the filtrate.

EFFECT OF TITANIUM ON THE TANTALUM-NIOBIUM SEPARATION.—The separation of tantalum from niobium by tannin is a process based on the observation of colour changes; hence it cannot possibly be extended to the separation of niobium from titanium, because the tannin complexes of both elements are red, if for no other reason. Such *a priori* objection could not, however, be raised against a separation of titanium from tantalum by tannin, and it was accordingly investigated; but the results were quite disappointing. Suffice it to say here, that at an acid concentration permitting of the flocculation of the tantalum precipitate, titanium (unlike niobium) appears always to be co-precipitated to a certain extent; and that the admixture—unless minute—discolours the otherwise yellow tantalum

precipitate sufficiently to deprive the tannin method of its vital feature. The discoloration caused by titanium is in the direction of buff or brownish-yellow rather than orange.

RESULTS OF TEST SEPARATIONS.—It remained for us to carry out some separations of tantalum from niobium in presence of small amounts of titanium in order to ascertain how it would affect the accuracy of the method. In the table below, the tantalum fractions are designated as in Section IV (*loc. cit.*).

Exp.		1.	2.	3.	4.	5.	6.
Taken	Ta_2O_5	0·1002	0·2016	0·0211	0·0520	0·0024	0·1686
	Nb_2O_5	0·1017	0·0222	0·2004	0·1811	0·2154	0·0365
	TiO_2	0·0056	0·0023	0·0022	0·0063	0·0054	0·0051
Ratio Ta_2O_5 : TiO_2		8	88	9·6	8·2	0·25	33
	P^1	0·0834[1]	0·1596[3]	0·0191[5]	0·0563[7]	0·0100[9]	0·1571[11]
	ΣP^1	0·1058[2]	0·2043[4]	0·0337[6]	0·0651	0·0166	0·1721
	P^2	—	—	0·0190[6]	0·0465[8]	0·0041[10]	0·1400[12]
	ΣP^2	—	—	0·0263[6]	*a*	—	*a*
	P^3	—	—	—	—	0·0047[10]	—
TiO_2 in last P		0·0039	0·0017	0·0015	0·0032	0·0013	0·0030
Colour of P		[1] orange [2] orange	[3] yellow [4] yellow	[5] reddish [6] orange	[7] pale orange [8] orange	[9] red [10] orange-red	[11] pale buff [12] bright yellow

a Fractionation not completed.

These results require to be studied in conjunction with the Ta_2O_5 : TiO_2 ratio, and the colour of the tantalum precipitates. It will then be seen that Exp. 2, where the quantities taken simulate an oxide mixture obtained from a tantalite, is the only satisfactory one. In Exp. 1, no yellow P^1 was obtained, and hence the rather small final error was not within the operator's control; the test served as a guide for the distribution of the titania, which is shewn to accumulate in the tantalum fractions. Exp. 3 simulates the case of a columbite; though the absolute quantity of titania is small, the Ta_2O_5 : TiO_2 ratio is too low for the formation of a yellow precipitate. In Exps. 4 and 6 the operator—dealing with mixtures unknown to him—felt uncertain about the colour indications, and did not pursue the fractionation of ΣP^1; the balance of the titania in Exp. 6 (*i.e.* 0·0021 grm.) was found in the filtrate from P^2, leaving the small niobium fraction titanium-free. Finally, in the extreme case of Exp. 5, the precipitate was orange-red even at the P^3 stage, and no evidence for the presence of tantalum was obtained during the operations.

ANALYTICAL APPLICATION.—The above tests demonstrate the impossibility of separating tantalum from niobium by tannin in presence of more than an insignificant amount of titanium; we may say that the method works normally, provided the quantity of titania present does not much exceed one per cent. of the tantalic oxide to be determined. Whilst this condition is generally fulfilled in the case of tantalites, the tantalum determination in most columbites must be preceded by the separation of the titania from the earth acids (Section IX, ANALYST, **1927**, **52**, 625). A small portion of the latter (0·02 grm.) should always

be tested colorimetrically for titania as a preliminary step of the tantalum-niobium separation; the weighed final tantalum precipitate is tested in the same manner, and a correction applied.

SUMMARY.—Tannin produces a red precipitate in oxalic or tartaric solutions of titanium; the precipitation is quantitative in the neutralised solution. Titania interferes with the tannin separation of tantalum from niobium, if present in quantities higher than about one-hundredth of the tantalic oxide, by causing a discoloration of the yellow tantalum precipitate.

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The Deposition of Metals on Copper from Cyanide Solutions.

I. A New Method for the Separation and Determination of Small Amounts of Lead.*

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(*Read at the Meeting, February* 1, 1928.)

THE determination of small quantities of lead in, say, copper, has been proved by Dawkins and Weldon (*Proc. Soc. Chem. Ind., Victoria,* 1922, p. 940) to be a very difficult matter; this difficulty is due to the distinct solubility of lead sulphate in dilute sulphuric acid, and these authors only achieve an accurate result in their process only by applying a correction for this solubility. When it is borne in mind that almost all separations of lead depend, at one stage or another, on filtration of lead sulphate, it is at once apparent how urgent is the need of a totally new method of separation. Precipitation as sulphide is apt to be a dangerous proceeding, owing to its comparatively great solubility in quite low concentrations of acid, and, in any case, it is not applicable to most non-ferrous alloys. Precipitation as chromate, though excellent where the conditions allow, requires so strict a regulation of the acidity that it is useless in most cases as an initial separation. Following a clue in Newth's *Text Book of Inorganic Chemistry,* I found that certain metals—notably lead, bismuth, cadmium, and tin—are amenable to a sort of Reinsch test carried out in alkaline cyanide solution; of these, lead and bismuth separate in the cold, the others only on heating. This somewhat curious reaction forms the basis of the method to be described.

As it appeared probable that the reaction would be more likely to go to completion in the hot, than in the cold, solution, experiments were first tried by

* Communication from the Research Department, Woolwich.

boiling coils of copper foil in the alkaline cyanide liquid. Five grm. samples of electrolytic copper were taken, and varying amounts of lead added to them; each was dissolved in 60 c.c. of nitric acid (sp. gr. 1·2), cooled, 10 c.c. of citric acid solution (50 per cent.) added, and the whole made slightly alkaline to litmus with sodium hydroxide. A saturated solution of potassium cyanide was now added until the precipitate formed was all dissolved, the blue colour entirely dispelled, and the solution began to turn brown (any great excess of potassium cyanide was to be avoided). Then 25 c.c. of ammonium chloride* solution (20 per cent.) were added, and an open flat spiral of copper foil, which had been cleaned with nitric acid (sp. gr. 1·2), was dropped in. The liquids in the flasks were boiled for 2 hours, the coppers then lifted out, rinsed with water, and immersed for about 5 minutes in glacial acetic acid. The acetic acid, which contained the lead dissolved off the copper, was poured into a beaker, the copper rinsed twice by covering with water, and the rinsings added to the acetic acid; four drops of dilute sulphuric acid (1 : 3) and about 3 c.c. of nitric acid were added to the lead solution, and the whole was evaporated to dryness on the plate and heated till sulphuric acid fumes were nearly all dispelled. The lead was finally determined by the method described below. The following results were obtained:

Weight of copper taken.	Weight of lead		Percentage of lead	
	Added.	Found.	Added.	Found.
Grms.	Grm.	Grm.		
5·0	0·0040	0·0042	0·080	0·084
5·0	0·0030	0·0030	0·060	0·060
5·0	0·0020	0·0018	0·040	0·036
5·0	0·0010	0·0009	0·020	0·018
5·0	0·0005	0·00056	0·010	0·011

These results, which are of purely academic interest, show that lead can be separated by deposition on copper from a solution containing 10,000 times its weight of copper. It will be noted, however, that several other elements—cadmium, tin, bismuth, and, to a certain extent, zinc and antimony, etc., etc., are also liable to deposit under these conditions, and all or any of these elements may occur in commercial metals. On trying the process on copper to which quantities of these elements, of the order of which they are liable to occur in commercial copper, had been added, it was found that, apart from any other difficulties, the deposit could no longer be made to adhere to the copper. The process was, therefore, abandoned. Further work showed that, especially in the presence of ammonium oxalate, lead will deposit quantitatively in the cold from cyanide solutions, and this reaction forms the basis of the method described in this paper. It was found, however, that in the presence of some metals the lead deposit is not adherent; consequently the apparatus which I described in connection with the determination of mercury was used (Evans and Clarke, ANALYST, 1926, **51**, 226,

* Ammonium chloride was added because there was reason to suspect that the copper occasionally became passive.

and Evans, *Id.*, 1926, **51**, 229). By working in the cold the interference of tin, antimony, zinc, cadmium, and nickel is eliminated; bismuth appears still to be deposited, but, in the amounts present in commercial coppers, does not interfere.

The complete method for copper, brass, bronze, zinc, and nickel is as follows:

GENERAL PROCEDURE.—PREPARATION OF SOLUTION.—A 5·0 grm. sample is placed in a flask (capacity 750 c.c.) suitable for use with the percolator, and is dissolved in 60 c.c. of nitric acid (sp. gr. 1·2), except when tin is present, in which case 35 c.c. of the nitric acid and 25 c.c. of hydrochloric acid are used; the excess acid may with advantage be boiled off somewhat after solution is complete; about 9 grms. of potassium bitartrate are then added, and the solution is cooled. The liquid is next made slightly alkaline to litmus with sodium hydroxide, and a saturated solution of potassium cyanide* is added till the precipitate has redissolved and the solution has changed from its initial blue (where copper or nickel is present) to a light brown colour. The necessary excess of potassium cyanide is then added, being adjusted as follows:

Copper.—Only 2 or 3 c.c. excess are required.

Bronze.—This needs a rather greater excess (say 5 c.c.); if, in the course of the subsequent percolation, the liquid becomes turbid, it is cleared by the addition of a minimum amount of potassium cyanide solution, and percolation is continued rather longer than usual.

Brass and Zinc.—Ten c.c. of the saturated solution are added after the precipitate has dissolved and (with brass) the blue colour has disappeared.

Nickel and Cupro-Nickel.—When nickel is present the colour of the solution seems no longer to provide an indication of the point at which there is a sufficient excess of cyanide. Good results are, however, obtained by adding 30 c.c. of the saturated solution at the point where the precipitate is almost completely dissolved.

As a general rule, it would seem that any great excess of potassium cyanide tends to delay the deposition of the lead.

After adjustment of the potassium cyanide, 25 c.c. of ammonium chloride solution (20 per cent.) and about 4 grms. of ammonium oxalate are added, the liquid is cooled down to room temperature, and the flask is attached to a percolator on which the deposition tube containing the copper has previously been placed in position.

PREPARATION OF DEPOSITION TUBE.—The deposition tube is prepared much in the same way as for determination of mercury (*loc. cit.*). The copper filings used can, with advantage, be rather coarser to avoid clogging (a good plan is to use only filings which will not pass through a 30-mesh sieve); on the other hand,

* As commercial potassium cyanide often contains traces of sulphides, which precipitate some of the lead, it is advisable to treat the saturated solution with a few drops of bromine water until a few c.c. withdrawn no longer give a violet colour when treated with a solution of sodium nitroprusside.

genuine filings must be used, as turnings do not expose enough surface. The tube should be about 8·5 cm. long, and constricted at one end; the constricted end is plugged lightly with cotton wool, about 1 cm. in depth, pushed in through the open end; on this is placed about 4 cm. depth of copper filings, and this is finally held in position by a second plug of cotton wool about half the thickness of the first; this leaves about 3 cm. clear at the top to facilitate washing. The packing of the tube must not be rammed tight, otherwise percolation will be too slow. Glass wool cannot be used in place of cotton wool, because the lead occasionally deposits in a fine powdery form which washes through glass wool. After packing, the copper is cleaned by pouring through (with the aid of gentle suction, if necessary) about 10 c.c. of a mixture of equal parts of dilute hydrochloric acid (1 : 1) and nitric acid (sp. gr. 1·2); this is followed by several washings with cold water. The deposition tube thus prepared is attached, as for mercury (*loc. cit.*), to the end of the stem of the main funnel.

PERCOLATION.—Percolation is normally carried on for 2 hours. Further percolation has not been found to yield more than a trace of lead if cyanide conditions have been properly adjusted; but, as a matter of routine, it might be a safeguard to detach the percolation tube at the end of two hours, replace it with another, and continue percolation for a further hour or two.

TREATMENT OF DEPOSITED LEAD.—After deposition is complete the percolation is stopped, the contents of the main funnel allowed to run completely through into the flask, the deposition tube detached, and its contents washed 4 or 5 times by filling it up with cold water and allowing this to run through. The entire contents of the tube are then transferred to a small beaker, by pushing a thick wire through the constricted end of the tube, then covered with about 10 c.c. of glacial acetic acid and allowed to stand, with frequent agitation, for 10 or 15 minutes. At the end of this time the lead should be completely removed from the copper; the acetic acid is decanted into a beaker, the copper washed twice with water by decantation, the cotton wool plugs squeezed dry against the side of the beaker and removed, the liquid squeezed out being added to the rest, and the copper given a final wash. The liquid now contains all the lead in the original sample; 12 drops of dilute sulphuric acid (1 : 3) and 2 or 3 c.c. of nitric acid are added to it, and the whole is evaporated on the plate till the sulphuric acid fumes strongly. A few drops of nitric acid are then added to destroy traces of organic matter, and it is again evaporated to fumes, and, if any organic brown coloration remains, this nitric acid treatment is repeated; finally the beaker is heated till fumes of sulphuric acid are almost dispelled.

DETERMINATION OF THE LEAD.—The residue in the beaker, which consists, chiefly, of impure lead sulphate, after cooling, is taken up by boiling with 10 c.c. of ammonium acetate solution; it is diluted with 30 c.c. of potassium nitrate solution (5 per cent.), and a few drops of acetic acid are added, followed by an excess of potassium dichromate solution. The liquid is boiled for five minutes and allowed to stand overnight, after which it is filtered through asbestos and the

filter washed with 5 per cent. potassium nitrate solution (4 washings usually suffice). The funnel is then transferred to a clean flask, some nitric acid (sp. gr. 1·2) is boiled for five minutes and cooled, and about 30 c.c. of it are placed in the original beaker, to dissolve any lead chromate that may be adhering to the sides, and then poured four or five times through the filter to dissolve the remainder of the lead chromate. Finally, the beaker is rinsed in, and the filter washed three or four times with cold water. The filtrate is placed in a Nessler glass, and the yellow colour is matched by $N/100$ dichromate solution run into another Nessler glass containing dilute boiled-out nitric acid. (1·0 c.c. $N/100$ $K_2Cr_2O_7$ = 0·00069 grm. Pb.)

As a test of this method of determining lead, various small amounts of lead solution were evaporated with sulphuric and nitric acids, and the lead determined as above:

Lead taken.	$N/100$ $K_2Cr_2O_7$ required.	Lead found.
Grm.	C.c.	Grm.
0·0010	1·5	0·0010
0·0020	2·9	0·0020
0·0030	4·8	0·0033
0·0040	5·9	0·0041
0·0050	7·3	0·0050

The following results have been obtained in trials of the complete process made on various metals and alloys to which varying amounts of lead had been added:

COPPER.—Small amounts of elements liable to occur in commercial copper, and which seemed likely to interfere with the process, were added to electrolytic copper.

Taken.					Lead.		Percentage of lead.	
Cu.	Sn.	Cd.	Bi.	Sb.	Added.	Found.	Added.	Found.
Grms.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.		
5·0	0·010	0·010	0·0005	0·0005	0·0040	0·0039	0·080	0·078
5·0	0·010	0·010	0·0005	0·0005	0·0030	0·0030	0·060	0·060
5·0	0·010	0·010	0·0005	0·0005	0·0020	0·0020	0·040	0·040
5·0	0·010	0·010	0·0005	0·0005	0·0010	0·0009	0·020	0·018
5·0	0·010	0·010	0·0005	0·0005	0·0005	0·0005	0·010	0·010

TIN BRONZE.—Ten per cent. of pure tin was added to electrolytic copper.

Taken.		Lead.		Percentage of lead.	
Cu.	Sn.	Added.	Found.	Added.	Found.
Grms.	Grm.	Grm.	Grm.		
4·5	0·5	0·0040	0·0037	0·080	0·074
4·5	0·5	0·0020	0·0020	0·040	0·040
4·5	0·5	0·0010	0·0013	0·020	0·026
4·5	0·5	0·0005	0·0006	0·010	0·012

BRASS.—A sample of commercial brass was used.

	Lead.			Percentage of lead.	
Brass taken. Grms.	Added. Grm.	Found. Grm.	Found (net). Grm.	Added.	Recovered.
5·08	blank	0·0009	—	—	—
6·61	0·0010	0·0018	0·0007	0·015	0·010
5·37	0·0010	0·0022	0·0013	0·019	0·023
5·26	0·0020	0·0026	0·0017	0·038	0·032
6·14	0·0030	0·0045	0·0034	0·049	0·055

ZINC.—A sample of commercial "pure" zinc gave the following results:

	Lead			Percentage of lead	
Zinc taken. Grms.	Added. Grm.	Found. Grm.	Found (net). Grm.	Added.	Recovered.
5·0	blank	0·0041	—	—	—
5·0	0·0030	0·0072	0·0031	0·060	0·062
5·0	0·0010	0·0050	0·0009	0·020	0·018

It will be observed that these results for brass are far more uneven than those given for either copper or zinc.* This can only be ascribed to segregation of the lead in the sample (which is notoriously liable to occur in the case of lead), and is in line with several results obtained with copper alloys and with nickel.

NICKEL.—In the case of nickel, which follows, the difficulty of obtaining a steady blank was so great that a 20 grm. sample was dissolved and the solution divided into 4 equal parts, to three of which varying amounts of lead were added. The blank sample unfortunately became contaminated and had to be rejected, but the differences between the remaining three were so regular that a blank could be confidently calculated from them. Calculated thus, the three values of the blank are:

0·00066
0·00069
0·00079 } Mean 0·0007 grm.

The following results were obtained:

	Lead.			Percentage of lead.	
Nickel taken. Grms.	Added. Grm.	Found. Grm.	after deduction of mean blank. Grm.	Added.	Recovered.
5·0	0·0030	0·0037	0·0030	0·060	0·060
5·0	0·0020	0·0027	0·0020	0·040	0·040
5·0	0·0010	0·0018	0·0011	0·020	0·022

* It should be noted that whereas the figures given refer to commercial brass, those for copper refer to pure copper, which gave no blank at all. Commercial copper would undoubtedly show variations due to segregation. Lead mixes with zinc without segregation.

NICKEL SULPHATE.—A test was also carried through on a sample of nickel sulphate which was sold as specially pure. Two 10 grm. samples were taken, and to one of them 0·002 grm. of lead (in solution) was added; both were dissolved in water, acidified with sulphuric acid, potassium bitartrate added, the liquid neutralised with sodium hydroxide, and potassium cyanide solution added until the precipitate just redissolved, and then 30 c.c. in excess. The solution was boiled for five minutes, ammonium oxalate added, the liquid cooled, 25 c.c. of 20 per cent. ammonium chloride solution added, and the liquid diluted to about 700 c.c. It was then percolated for four hours, with occasional swirling of the flask to ensure mixing, and finished as usual. The following results were obtained:

Weight of $NiSO_4$ taken. Grms.	Lead added. Grm.	$N/100$ $K_2Cr_2O_7$ required. C.c.	Lead found. Grm.
10·0	—	0·9	0·0006
10·0	0·002	3·7	0·0026
		Lead recovered =	0·0020

The dilution and the larger volume used for percolation were adopted to avoid a difficulty which crops up from time to time. When a sparingly soluble salt is present, crystallisation is apt to take place, the inevitable result of which is the blocking, partial or complete, of the tube which holds the copper powder, thus slowing down or stopping percolation. The volume of solution adopted above seems quite effective in stopping this trouble in the cases of nickel and iron (*vide infra*), which were the worst offenders. In view, however, of the greater volume, it is desirable to continue percolation for three or four hours, and to swirl the flask occasionally.*

IRON.—As iron is frequently a constituent both of metals and other materials, it seemed desirable to find out if lead could be determined by this process in presence of large amounts of that element.

Several 5 grm. samples of "Armco" iron, to which varying known amounts of lead had been added, were dissolved in nitric acid (sp. gr. 1·2); about 9 grms. of potassium bitartrate were added to each, then an excess of ammonia followed by 45 grms. of potassium cyanide in solution. The liquid was boiled for 5 minutes, after which a few c.c. were withdrawn and tested by acidification with hydrochloric acid, a formation of Prussian blue indicating that the conversion of the iron was incomplete; in this event the sample was returned to the flask, a few c.c. of saturated potassium cyanide solution added, and boiling continued for a minute of two, after which a further sample was withdrawn and tested. This procedure was followed until a test failed to give any blue coloration on acidification; by this treatment the iron is converted completely into ferrocyanide. The final sample having been returned to the flask, and ammonium oxalate and ammonium chloride added, it was cooled completely, 10 c.c. of potassium cyanide solution was added, and it was diluted to about 700 c.c., percolated for 4 hours, and finished in the usual way.

* Occasional swirling of the flask is always advantageous when using the percolator.

In two cases the final addition of 10 c.c. of potassium cyanide solution was omitted; these, as will be seen from the table, gave results considerably too high.

	Iron taken. Grms.	Lead added. Grm.	$N/100$ $K_2Cr_2O_7$ required. C.c.	Lead found. Grm.
Final addition of 10 c.c. KCN soln. omitted.	5·0	0·0010	2·4	0·0017
	5·0	0·0040	7·1	0·0049
	5·0	0·0030	4·7	0·0032
	5·0	0·0020	3·6	0·0025

The high results are due, apparently, to a trace of iron remaining in the cotton-wool plugs of the deposition tube, but they are sufficiently accurate to show that iron does not seriously interfere with the process.

INFLUENCE OF PHOSPHATES.—As it was thought possible that phosphates might cause interference, tests were carried out on two 5 grm. samples of ammonium phosphate to which varying amounts of lead had been added; these were dissolved in water, about 4 grms. of potassium bitartrate added, then excess of ammonia followed by 10 c.c. of potassium cyanide solution and the usual amounts of ammonium chloride and oxalate; the remainder of the process was carried out as usual.

Ammonium phosphate taken. Grms.	Lead added. Grm.	$N/100$ $K_2Cr_2O_7$ required. C.c.	Lead found. Grm.
5·0	0·0020	2·4	0·0017
5·0	0·0030	3·4	0·0024

It is evident from this that phosphates exercise a slight restraining influence.

INFLUENCE OF ALKALI SULPHATES.—In view of the possible presence of sulphates in a sample which had to be tested for lead, and also of the fact that large amounts of either sodium or ammonium hydroxide have to be used for neutralisation, two 200 c.c. samples of dilute sulphuric acid (1 : 3), to each of which 0·004 grm. of lead had been added, were made alkaline, one with sodium hydroxide, the other with ammonia; the rest of the process was carried through as in the case of the ammonium phosphate tests, except that a large volume had to be used owing to the crystallisation of the sulphates.

	Lead added. Grm.	$N/100$ $K_2Cr_2O_7$ required. C.c.	Lead found. Grm.
$(NH_4)_2SO_4$	0·0040	6·0	0·0041
Na_2SO_4	0·0040	6·1	0·0042

From these results it appears that large amounts of sulphates of sodium or ammonium have no influence on the determination.

The various results given so far show that, whereas by this process lead can be separated quantitatively from at least

10,000 times its weight of copper,
1,000 ,, ,, ,, ,, tin,
5,000 ,, ,, ,, ,, nickel,
5,000 ,, ,, ,, ,, zinc,
20,000 ,, ,, ,, ,, sulphuric acid or the corresponding weights of alkali or ammonium sulphates,

yet there is a slight loss in separating it from 2000 times its weight of ammonium phosphate, and a slight contamination by iron in the product of the separation from 5000 times its weight of that metal.

In addition to this, it is obvious that certain substances, such as calcium phosphate, will entirely upset the process, owing to the fact that they will mechanically clog the apparatus and prevent circulation.

PROCEDURE IN PRESENCE OF LARGE AMOUNTS OF TIN, PHOSPHATES, OR MECHANICALLY INTERFERING SUBSTANCES.—The following procedure was tried in order to make the process universally applicable. Four 10 grm. samples of calcium chloride were taken, varying known amounts of lead (in solution) and several grms. of ammonium phosphate were added to all; this produced a mixture for which the ordinary process would have been impossible. A solution containing 1 grm. of cupric sulphate (A.R.) was added to each, followed by just sufficient hydrochloric acid to dissolve the precipitate, excess being avoided; hydrogen sulphide was passed into all the solutions, which were then allowed to settle, filtered, and the precipitates washed. The precipitated sulphides were dissolved off the filter with hot dilute *aqua regia*; about 4 grms. of potassium bitartrate were added to each of these solutions, which were then made alkaline with ammonia. The blue colour of the copper was just discharged with potassium cyanide solution, and 5 c.c. were added in excess to each. This was followed by 25 c.c. of ammonium chloride solution (20 per cent.) and about 4 grms. of ammonium oxalate, and the liquids were cooled, percolated and finished in the usual way. The following results were obtained:

	Lead added.	$N/100$ $K_2Cr_2O_7$ required.	Lead found.
	Grm.	C.c.	Grm.
(*a*)	0·0010	1·40	0·0010
(*b*)	0·0020	2·85	0·0020
(*c*)	0·0030	3·95	0·0027
(*d*)	0·0040	5·70	0·0039

In the case of (*c*), the 0·003 grm. quantity, some filter pulp which had got into the solution in dissolving the precipitated sulphides had escaped observation; this clogged the percolation tube and rendered percolation very slow, thus accounting for the somewhat low result. This illustrates the necessity of having the percolation solution free from any precipitate other than the slight haze which seems sometimes to accompany the addition of an excess of cyanide to a lead solution. In the great majority of cases, especially in metallurgical analysis, this is the normal state of affairs; where, however, the necessity arises of filtering out a precipitate, this should be brought into solution and treated by the method described in the latter part of the paper. The latter additional separation will also be necessary or desirable in the presence of large amounts of iron or phosphates.

Modification of Ridsdale's Method for Determining Phosphoric Acid

Introducing a Simple Device for Washing the Ammonium Phospho-molybdate Precipitate.

By A. SCOTT DODD, B.Sc., F.I.C., F.R.S.E.

(*Read before the Association of the Public Analysts of Scotland.*)

Ridsdale's Method for determining phosphoric anhydride is shown by Cameron and Dow (Analyst, 1927, **52**, 576) to be of general application in the analysis of fertilisers. The method has been carefully tested relative to the determination of phosphates in compound manures, and, as a result, it was found to be quite as accurate and reliable as the official process, and is much quicker and more convenient than the latter.

The following results are typical and give an indication of the accuracy of the method:

Compound manure.	Official method. Per Cent.	Ridsdale's. Per Cent.
Total phosphates (as P_2O_5)	13·50	13·49
	13·58	13·50
		13·52
Soluble phosphate (as P_2O_5) ..	6·32	6·33
	6·36	6·35
		6·37

The process is undoubtedly an excellent one, and is worthy of recognition as a reliable method for determining phosphates in fertilisers. There are, however, a few slight alterations in manipulation, which I would suggest as improvements, and which would simplify working when a large number of determinations have to be made at the same time.

The suggested alterations are as follows:

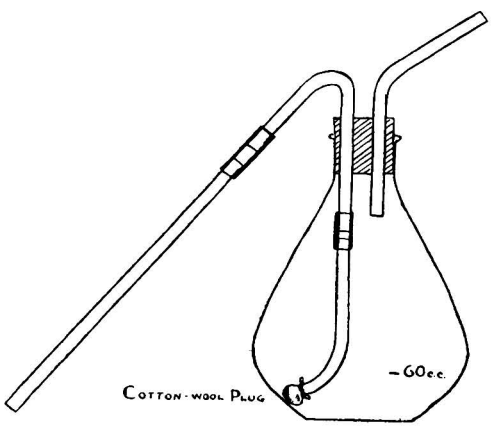
(1) Strong nitric acid, with about 2 vols. of water, in place of acid of sp. gr. 1·20.
(2) $N/2$ sulphuric acid in place of $N/2$ nitric acid.
(3) $N/1$ sodium hydroxide solution in place of $N/2$ sodium hydroxide solution.
(4) The use of a 200 or 250 c.c. wash-bottle flask, in place of a beaker flask (for precipitating).
(5) The use of 5 c.c. dilute nitric acid (1 : 3) instead of 4 c.c. of nitric acid (sp. gr. 1·20).
(6) A special wash-bottle attachment (fitted with cotton-wool pad) for siphoning off supernatant liquid during the washing of the precipitate.

Among the above suggested modifications of Cameron and Dow's details, the most important is the adoption of a simple appliance which will admit of the whole determination from start to finish being made in the same vessel. Centrifuging appears to be quite unnecessary, as the precipitate is heavy and settles well. Much time is saved by using the simple wash-bottle device suggested. The other suggestions are of minor importance and are mainly introduced with a view to saving time and labour.

The following is the suggested modified process in skeleton form:

Solutions required.—(1) Concentrated nitric (sp. gr. 1·42); (2) ammonium molybdate solution (150 grms. per litre); (3) sodium hydroxide solution (about 30 per cent.; (4) dilute nitric acid (1 : 3) (50 c.c. of concentrated acid + 100 c.c. of water); (5) potassium permanganate (about 1 per cent.); (6) a solution of about 2 grms. of potassium nitrate in 2 litres ("Lavol"); (7) nitro-molybdate reagent (290 c.c. of ammonium molybdate solution *poured into* 110 c.c. of concentrated nitric acid); (8) $N/1$ sodium hydroxide solution; and (9) $N/2$ sulphuric acid.

Apparatus required.—(1) Two pipettes (5 c.c. and 25 c.c.); (2) 50 c.c. Nessler tube (with marks at 25 c.c. and 50 c.c.); (3) large glass to catch washings; (4)*



special 200 or 250 c.c. wash-bottle flask (Taylor's pattern) fitted with No. 7 rubber stopper and siphon device, with cotton-wool plug; and (5) 50 c.c. burette.

Method of analysis.—Treat 4 grms. of the fertiliser as directed in the *Official Methods of Analysis*. Make the solution up to 250 c.c., and filter. Of the filtrate, measure 25 c.c. (= 0·4 grm.) into the special flask (4), and add sodium hydroxide solution (30 per cent.) until a precipitate appears. Add dilute nitric acid (1 : 3)

* The flask is marked at the 60 c.c. level. The cotton wool pad is made from a tuft of cotton wool about the size of a shilling, wrapped over the end of the tube, tied on with thread, and clipped at top.

from a 5 c.c. pipette, drop by drop, until the precipitate dissolves, then a further 5 c.c. of the dilute nitric acid. Place the flask on a water bath, and, while heating, add potassium permanganate solution (a few drops) until there is a permanent purple coloration. Add 1·75 grms. of ammonium nitrate, 1·6 grms. ammonium chloride, and 0·25 grm. of ammonium oxalate (No. 7 Analoid Tablet), and make up to 60 c.c. with water. Continue heating on the water bath until the tablet is entirely dissolved. Add a cold mixture of 25 c.c. of nitro-molybdate reagent and 25 c.c. of water (measured for convenience in graduated Nessler tube). Rotate for 1 minute and allow the mixture to settle for 10 minutes. Attach wash-bottle fittings (with cotton-wool pad at end) and siphon off the supernatant liquid. Refill with 0·1 per cent. potassium nitrate solution ("Lavol" solution), rotate and allow the precipitate to settle for a few minutes (2 minutes). Again siphon off the supernatant liquid and repeat the washing with "Lavol" until the washings are found to be neutral to litmus paper. (Three or four washings are usually sufficient.) Remove the cotton-wool pad, tease it out, and drop it into the flask. Add 25 c.c. of *N* sodium hydroxide solution to the contents of the flask, and, when the precipitate is entirely dissolved, titrate the excess of sodium hydroxide with *N*/2 sulphuric acid, using phenolphthalein as indicator (1 c.c. of *N*/2 H_2SO_4=0·001542 grm. of P_2O_5=0·003364 grm. of $Ca_3P_2O_8$).

In order to prevent loss of precipitate in course of washing, it is advisable to drain off without blowing. This may be accomplished satisfactorily by attaching a spring clip to the exit tube and filling the siphon tube with 0·1 per cent. potassium nitrate solution ("Lavol") prior to draining off. The cotton wool pad should be thin enough to allow the liquid to flow readily through it.

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.

THE "KNIGHT TEST" FOR FEATHERS.

In the earlier part of 1923 I was engaged in the examination of feathers, and, amongst other things, it became necessary to be able to determine their degree of cleanliness. After numerous experiments had been carried out with different reagents it appeared that for an easily conducted test, in addition to the chloride test, nothing seemed so suitable as extracting the feathers with distilled water, filtering the extract through glass wool, rendering the filtrate slightly acid with sulphuric acid, and titrating with potassium permanganate until a faint pink colour persisted over a given period of time.

Feathers have been tested in this way ever since, for commercial purposes, in my laboratory, and in view of frequent requests, of late, from many analysts for details, the following particulars of the process, as now carried out, are given:

Twenty grms. of the feathers are weighed into a wide-mouthed bottle, and thoroughly wetted by shaking with one litre of distilled water, the water being allowed to remain on the feathers for one hour, with occasional shaking.

The feathers are then pressed to one side of the bottle, and some of the extract withdrawn and filtered through glass wool. One hundred c.c. of the filtrate are put into a beaker, 1 c.c. of dilute sulphuric acid (1:5) added, and two drops of $N/10$ potassium permanganate solution run in from a burette; should the pink colour disappear in one minute, a further two drops are added, and so on, until the colour persists for one minute.

It is desirable to note the temperature at which these tests are carried out, as, naturally, variations in temperature are likely to cause difference in results; I have found a convenient temperature to be the normal one of 15·5° C.

There is, at present, no actual government standard, but the Air Ministry has, after consultation with me, adopted a standard of 40 parts of oxygen adsorbed per 100,000; in my opinion this is somewhat lenient. I feel that any standard should have both determinations included, and from personal experience I know that a figure of 15 parts per 100,000 both for oxygen and chlorine is easily obtained by proper purification.

The appended table shows some typical results, together with a chlorine figure for comparison; it will be seen that some samples having a low oxygen figure have a very high chlorine figure, showing that the samples have not been washed.

The "Knight" test was introduced because the chlorine test was not altogether acceptable to the trade, as the method of purification did not in all cases include washing.

SOME TYPICAL RESULTS WITH FIGURES FOR SOLUBLE CHLORIDES AND OXYGEN ABSORBED.

Sample.	Oxygen absorbed.	Soluble chlorides, equivalent to chlorine.
	Parts per 100,000.	
Ukrainian down	48–128	145–275
Kosher feathers	176	595
Ordinary trade feathers	18	257
	56	470
	40	337
Down, washed and purified	4	8
Down from down quilts	6	17
	8	8
	26	278
Raw feathers	200	485
Ditto, after purification	8	10
Feather pillow bought from a large London Stores	52	295

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Notes from the Reports of Public Analysts.

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

COUNTY OF ABERDEEN.

Annual Report of the County Analyst for 1927.

The total number of samples examined during the year 1927 was 873, of which 256 were formal samples. Of the formal samples, 21 were adulterated, deficient or doubtful.

Golden Syrup.—The following percentages of sugars were found in 10 samples:

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Sucrose	33·89	34·10	31·92	30·45	30·23	33·00	41·69	32·48	29·66	32·15
Invert sugar	45·00	37·20	36·20	35·20	34·50	36·50	36·00	41·36	26·71	42·50
Total sugar	78·89	71·30	68·12	65·65	64·73	69·50	77·69	73·84	56·37	74·65

The proportion of total sugar in sample No. 9 is low, but no standard exists for sugar in golden syrup. In future amendments of the Food and Drugs Acts minimum limits for syrups, jams and jellies should be prescribed. In former years glucose has been found as an adulterant, but during 1927 none of the samples was found to contain glucose.

Cod-liver Oil Emulsion.—A formal sample was found to contain 26 volumes in 100 volumes of cod-liver oil and was thus deficient in cod-liver oil to the extent of 24 volumes in 100 volumes. According to the statement on the label, the emulsion contained half its volume of cod-liver oil. It was condemned as adulterated.

J. F. Tocher.

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.

THE SALE OF CHOCOLATE LIQUEURS WITHOUT A LICENCE.

On March 16th a confectioner was summoned at St. Helens for selling, without a licence, intoxicating liquor, in the form of sweetmeats. The police took proceedings under Sec. 65 of the Licensing and Accommodation Act (1910), which prohibits the sale of intoxicating liquor without an Excise licence. Evidence was given of the purchase of two boxes of chocolate liqueurs, the contents of which were analysed by Mr. Davies, Public Analyst for St. Helens, who certified that the total amount of fluid in the boxes was 558·9 grains, which contained 6·22 grains weight of pure alcohol. This meant that there was a percentage of 2·45 per cent. of proof spirit by volume.

The managing director of the manufacturing company (a Swiss firm) said that the Customs authorities levied a duty of 1d. per lb. on the whole chocolate, this figure being based on the results of analysis.

Dr. H. E. Cox said that he had analysed a sample of chocolates taken from the defendant's shop, and that he agreed with the figures given by Mr. Davies. The amount of proof spirit in the whole sweetmeat was 1·03 per cent. A newly-baked loaf of bread might contain up to ten times as much alcohol as in the ¼lb. box as purchased. In Report No. 24, issued by the Ministry of Health, there was a list of cordials classified as non-alcoholic. This included peppermint (3·04 to 3·64 per cent. of alcohol), gingerette (2·3 to 3·88 per cent.), and ginger beer, all of which had a higher percentage of pure alcohol than the chocolates. The sample contained 80 per cent. of sugar and artificial essences, and it was practically impossible to make the essences without the alcohol. The word "liqueur" was not restricted to spirits, for "liqueur" drinks were sold in temperance restaurants.

Mr. Fox-Andrews, for the defence, pointed out that, according to Sec. 11 of the Act, liquor was not regarded as intoxicating if the proof spirit did not exceed 2 per cent. The chocolates, taken as a whole, therefore, were not intoxicating. The officer who gave evidence did not go into the shop to buy alcohol, but liqueur chocolates. The prosecution was asking the Bench to take part of a thing, not the whole. The amount of alcohol in the whole chocolates was only about half of the permissible quantity, and in order to get an ordinary drink it would be necessary to buy 2 lb. of the chocolates. If the Customs had adopted the view of the prosecution, they would have levied a duty of 2½d. per lb., because there was about 2·45 per cent. of proof spirit in the liquor. The alcohol did not add to the flavour, but made the manufacture more expensive. He asked the Bench to say that this was not a sale of intoxicating liquor within the meaning of the Act, because the percentage was 1·03, and it was permissible to sell liquor containing up to 2 per cent. of proof spirit.

The Bench, after deliberation, dismissed the case.

MAGNESIA IN A PRESCRIPTION.

On February 24, nine firms of druggists, trading in Islington, were summoned at the North London Police Court for selling a compounded drug, *viz.* magnesium carbonate, in place of magnesium oxide. The solicitor to the Islington Borough Council stated that in each case a prescription, one of the ingredients of which was "Magnesia Pond.," was submitted to nearly every druggist in the borough, and that the majority had complied with the requirements. The nine defendants, and some others, however, had used magnesium carbonate in place of magnesium oxide. Under Sec. 7 of the Food and Drugs Act it was not necessary for him to prove that this was to the prejudice of the purchaser, but the Medical Officer would say that the substitution might cause discomfort to the person taking the medicine, and that the doctor who gave the prescription might be misled by the resulting symptoms.

Mr. Glyn-Jones, for the defence, said that, although the facts constituted an offence in law, there was much to be said for the defendants on the merits of the case. The word "magnesia" was widely used by the public, and even by the medical and pharmaceutical professions, so as to include magnesium carbonate. Even the British Pharmacopoeia had "fluid magnesia" as a synonym for solution of magnesium bicarbonate. The title "heavy calcined magnesia" suggested that the substance which was to be calcined to make the oxide was properly called magnesia. The British Pharmaceutical Codex, under the heading "Magnesia Ponderosa," said that there was no uniform practice when "magnesia" was asked for, and that what was in most cases intended and was supplied was the light

carbonate. Although the pharmacopoeias of the London hospitals included mixtures of "magnesia," the carbonate was prescribed in every instance. With regard to the medicinal properties, the B.P. Codex said: "The medicinal properties of heavy magnesium carbonate are virtually those of Magnesia Ponderosa." It was unfair to choose such a drug as the subject of a test purchase.

Dr. Clark Trotter, Medical Officer of Health, gave evidence supporting what had been said by the Council's solicitor. The oxide, he said, was two-and-a-half times stronger than the carbonate. In his opinion, the defendants had been careless or wanted to save themselves trouble.

The Magistrate (Mr. Basil Watson, K.C.) said that he could not understand how so many defendants could make the same mistake for the same reason.

In cross-examination, the witness admitted that the Codex was a good book, but said that he relied upon the "Pharmacopoeia" as the authority in the matter of prescriptions. He agreed that he had sent notifications to the press that these cases were down for hearing.

The Magistrate observed that the doctor's replies had altered the view he took of these cases. It was proper that the defendants should have brought out the facts they had done. Although he was told that the Council had been put to considerable expense, he considered that there were elements which made it undesirable that costs should be granted in these cases. He would only impose a fine of 10s. on each defendant.

LINIMENT OF TURPENTINE.

On March 9, an appeal was heard at the London Sessions from a decision of the Finsbury Justices, who had convicted the appellant of selling liniment of turpentine which was not of the nature, substance and quality demanded.

The agent of the inspector said that she had asked the druggist's assistant for "four ounces of liniment of turpentine." When asked which of the three kinds of liniment she required, she replied that the doctor had told her to ask for liniment of turpentine, whereupon the assistant told her that she had better have the white one, and to this she had agreed. The bottle handed to her was labelled "Turpentine Liniment L.I.P." The inspector then entered the shop and told the assistant that the liniment had been bought for the purpose of analysis.

The inspector, in cross-examination, admitted that there was very little difference in the cost of the liniment, whether it was made according to the B.P. formula or the London Insurance Pharmacopoeia formula.

Mr. Eustace Fulton, for the appellant, produced a copy of the London Insurance Pharmacopoeia, and pointed out that among its compilers was the Medical Officer of Health for the inspector's district (Islington).

The inspector agreed that in this book liniment of turpentine was described as "Lin. Tur. Alb.," whereas in the B.P. it was simply "Lin. Tur."

Mr. Fulton pointed out that the London Insurance Pharmacopoeia formula was used to a much greater extent by panel doctors than the B.P. formula. The assistant had thought that the inspector's agent was a panel patient, and had therefore given her the L.I.P. prescription, and had told her what it was.

Evidence was given to this effect by the assistant and by the appellant, who said that it was quite exceptional for a customer to ask for liniment made up on the B.P. formula.

The Chairman of the Bench, Sir Robert Wallace, K.C., said that the majority of the justices were of opinion that the appellant's assistant had supplied the agent of the inspector with what he honestly believed she had asked for. They therefore quashed the conviction, but refused to allow costs. (*Cf.* ANALYST, 1928, 220.)

Ministry of Health.

CONDITIONS OF THE PRODUCTION OF MILK

(Used in Preparing Condensed Milk)

IN THE

NETHERLANDS AND DENMARK.

REPORTS OF THE COMMISSION APPOINTED BY THE MINISTRY.*

A COMMISSION, consisting of Dr. J. M. Hamill, Mr. Hole (a Milk Inspector of the Ministry of Health) and Professor J. Mackintosh, visited Holland and Denmark in August, 1927, and have issued this Report on the observations made during their inspection of the condenseries, creameries and farms in the two countries. The Report covers the conditions which determine the systems of production, the conditions under which the milk is produced, the methods of milking, the regulations for the purity of the milk supply, the administration of the regulations, non-official control organisations, and conclusions.

THE NETHERLANDS.

DUTCH REGULATIONS.—The purity of the milk supply is controlled by a Royal Decree of June 23, 1925, made in pursuance of Articles 14 and 15 of the Food Act (Warenwet), 1919, and amended by a further decree of August 4, 1926. According to Article 34, the decree does not apply to milk and/or milk products which, as such, are clearly intended for export. In Article 1, milk products are defined as all fluid products obtained from milk, *except* condensed milk and whey; consequently condensed milk, not being a "milk product," is not included in the exemption from the decree.

The decree contains provision for the sanitary production of milk, and its proper storage, and provisions prohibiting the sale of milk from cows suffering from certain diseases.

Certain provisions, such as those enabling a local authority to enforce the sealing of milk cans, the compulsory bottling of milk and the pasteurisation of milk, may be adopted by the local authorities. The decree also lays down definitions and standards for milk and certain milk products, including the chemical and physical characteristics; dirt or sediment must not exceed a trace, pathogenic micro-organisms must be absent, and streptococci must not be present in noticeable quantities. On the other hand, the decree lays down no specific requirements as to the structure of cowsheds.

ADMINISTRATION OF THE REGULATIONS.—For the administration of the Food Law and Milk Decree, Holland is divided into 20 districts, each of which has a staff to carry out the work. This service is called the Keuringdienst van Waren (Food Control Service). Each district service is controlled by a director, with a staff of three or four chemists, a bacteriologist, and five or more assistant chemists. As many as 20,000 to 30,000 samples annually may be examined chemically and bacteriologically in a district laboratory. When a sample of milk is found to contain pus and streptococci the farmer is notified and instructed to call in a veterinary surgeon to examine the herd at his own expense. If the directors' instructions are not complied with, another sample is taken; and should evidence of pathological contamination again be found, proceedings are taken. Such inspection would

* H.M. Stationery Office, 1928. Price 6d. net.

detect cows suffering from advanced tuberculosis, but there is no systematic examination of milk for tubercle bacilli. When samples show excessive dirt, the farmer is warned; if no improvement is effected, an inspector is sent to give advice, and if, after this, the milk is still unsatisfactory, legal proceedings are instituted.

NON-OFFICIAL CONTROL ORGANISATIONS.—In addition to Government control, the Co-operative Societies have their own organisations for controlling the health of the cattle and improving the quality of the milk, and these organisations work in close co-operation with the Food Control Service. Samples are commonly taken on delivery at the creameries, and are examined at the Hygienic Organisation's laboratory. The usual tests applied are for dirt and sediment, and these are supplemented by the reductase test. A number of samples are also examined bacteriologically for *B. coli*, and microscopic examination of the samples is made for evidence of mastitis among the cows. If such evidence is obtained, an inspector visits the farm; milk from a cow suffering from mastitis may not be sent to a creamery, but is denatured, and not allowed to be used for human consumption. Cattle are only tested with tuberculin by the organisation, the ophthalmic test alone being employed. About 70,000 cows are thus tested each year, and about 10 per cent. react to the test. Cows with advanced tuberculosis are slaughtered. The whole of the milk supply of a creamery is pasteurised at 90° C. for a brief period, and all separated milk and whey returned to the farmer for stock feeding must be pasteurised before leaving the creamery.

CONCLUSIONS.—The cowsheds in Holland are generally superior to the average English cowshed, but the general management and cleaning of utensils is on a somewhat higher level in England. On the whole, however, the average cleanliness of the Dutch milk is as high as that of English milk. Enterprise on the part of English producers and distributors similar to that of the Dutch organisations would do much to improve the milk supplies in this country.

DENMARK.

The manufacture of condensed milk is on a much smaller scale than in Holland.* The co-operative movement is highly developed, and it is estimated that approximately three-quarters of the total milk produced is handled by co-operative interests.

TESTS AT THE CREAMERIES.—Reliance appears to be placed mainly on the reductase test, and also upon a simple acidity test. The filtration test for visible dirt does not seem to be so universally or systematically employed as in Holland.

REGULATIONS.—Under the Food Law of April 18, 1910, the Minister of Justice is authorised to make regulations prescribing definitions and standards for foods intended for sale. Under this authority a Ministerial Decree (Oct. 22, 1925) has been issued dealing with milk and cream; this decree supersedes a previous decree dated Jan. 10, 1921. In the recent decree definitions for milk, cream, sweet milk, skimmed or partially skimmed, homogenised, pasteurised, sterilised or heated milk, and soured milk are given. Children's milk (Boernemaelk) is also defined as sweet milk coming from animals which have undergone the tuberculin test at least one year previously, and which are under the control of a veterinary surgeon.

By Sec. 11 of the Law relating to Contagious Diseases of Animals (Apr. 14, 1920) it is the duty of every person in possession or in charge of any cattle to notify

* During the year 1926 the amounts of condensed skimmed milk and condensed full cream milk imported from Holland were 1,321,979 and 157,847 cwts., respectively, and from Denmark 358,686 and 33,605 cwts. respectively.

without delay the police or a veterinary surgeon if hard painless swellings in the udder cause a suspicion that the cow suffers from tuberculosis of the udder. Until it has been proved whether or not the udder is tuberculous, the milk of such cows must not be used for human food or for the preparation of food.

Another decree, dated April 12, 1924, deals with the preparation of condensed milk and dried milk. The factory must have a satisfactory water supply and drainage system, and must conform with the requirements of the Minister of Agriculture with regard to cleanliness. Definitions of condensed milk (full cream and skimmed), dried milk, homogenised milk and sterilised milk, are given. Rules are laid down for the labelling of containers, and standards of purity are prescribed for the metal of which these are made. Provision is also made for the sampling of the products by officials of the Ministry of Agriculture and their examination at the laboratory of the Ministry.

The first of these decrees has been superseded by a decree made under the Law of May 4, 1927. This decree, which came into force on Nov. 1, 1927, extends the scope of the first decree, notably in prohibiting the use of milk from cows suffering from clinical tuberculosis and some other diseases which may injuriously affect the milk. In addition to these laws, the local authorities may make regulations controlling the supply of raw milk for consumption in their district, but such regulations must not be less stringent in any particular than the general decree applicable to the whole country. There are, then, two systems of milk control in force in Denmark, the first being concerned only with milk and cream intended for consumption in Denmark, and the second applying to all milk intended for conversion into dairy products, such as condensed milk, butter and cheese.

CONCLUSIONS.—The views as to conditions under which milk is produced in Denmark are similar to those expressed in regard to Holland, with the exception that Danish cowsheds appear to be even superior to the average Dutch cowshed.

So far as regulations are concerned, milk, whether intended for consumption as such or for conversion into milk products, is subject to certain minimum requirements in common, and, in addition, milk intended for human consumption as such may be subject to regulations very similar to those in the English Milk and Dairies Order. Milk intended for conversion into condensed milk is exempt from these regulations, but is subject to other regulations of a less specific and detailed character, which, however, if properly administered, may be as effective ultimately in attaining the same end. Notwithstanding the relative paucity of regulations dealing with milk for manufacturing purposes in Denmark, the Commission does not think that the milk delivered at condenseries in Denmark differs, in any notable respect, from the average milk produced in England.

Report of the Medical Research Council*

FOR THE YEAR 1926–1927.

STUDIES IN CLINICAL AND EXPERIMENTAL MEDICINE.—The studies of Sir Thomas Lewis on the intimate physiology of the capillary blood vessels and their responses to mechanical, thermal, chemical and nervous influences have been collected and published as "Blood Vessels of the Human Skin and their Responses." The main argument points to the conclusion that almost all forms of injury to the human skin, or irritation of it, act similarly by causing liberation of a chemical

* Obtainable at Adastral House, Kingsway, W.C.2. Price 3s. 0d. net.

substance akin to, if not histamine itself, and this produces reddening and other familiar phenomena of local irritation.

STUDIES OF FILTER-PASSING VIRUSES.—Dr. Gye's work on the filterable *virus* of sarcoma has continued, and experimental details are shortly to be published. At the request of the Harvard Cancer Commission, Dr. Gye has gone to America to demonstrate his methods.

ARTIFICIAL VITAMIN PRODUCTION.—Dr. Rosenheim and Mr. Webster have succeeded in producing the so-called vitamin "D" by the action of ultra-violet light upon a sterol—ergosterol. It had been found that chemically purified cholesterol no longer gave any trace of vitamin on irradiation, and that the essential impurity accompanying natural sterols must itself be a sterol. Ergosterol is found to be an abundant and readily available source of preparation of vitamin *D*, a daily dose of one ten-millionth of a grm. inhibiting rickets in a rat. Efforts are now being directed to the increase of yield of vitamin by selecting the regions of the spectrum in which the formative outweighs the destructive action. Ordinary sunlight, although containing no ultra-violet rays of so short a wave length as correspond to the absorption band of ergosterol, nevertheless produces vitamin from it, and since cholesterol from the skin contains the vitamin-yielding impurity, and the vitamin is known to be absorbed by the skin when artificially applied, it is suggested that the curative effects of sunlight on rickets are due to the natural production in, and absorption from the skin, of vitamin *D*.

FAT-SOLUBLE VITAMINS "A" AND "D" AND THE NATION'S FOOD SUPPLY.—Vitamin *A*, the chemical nature and affinities of which are still unknown, has been found, in proportions far exceeding that in cod-liver oil, in salmon and halibut-liver oils, and the liver fats of birds, such as grouse, etc. In sheep, calf and ox liver fats it is present to about 10 times the extent that it is found in cod-liver oil, and sheep or ox liver fats contain 200 to 1000 times more vitamin *A* than an average sample of butter. Since there is in this country an apparently inevitable shortage of milk fat, it is necessary to supplement the supply of vitamin *A* by adding it to margarine, etc., and this problem is nearing solution. The question of the supply of vitamin *D* is now easily solved, as it can be readily produced artificially; it may be noted that herbivorous animals, unlike fish, do not appear to store vitamin *D* in the liver. Eels contain a large proportion of both vitamins *A* and *D*. Yeast fat has been re-examined by a new method, and vitamin *A* found to be absent, as also is vitamin *D*, unless there has been irradiation with ultra-violet light. Vitamin *D* was found to be present with vitamin *A* in the stomach oil of the Australian mutton bird. The study of a satisfactory method for avoiding the disturbing influence of some natural pigments, particularly of the carotene group, in estimations of vitamin *A*, has received attention.

NUTRITIONAL STUDIES IN GENERAL.—Studies of the other vitamins are being pursued and are under the supervision of a special Committee. Modern studies show that vitamin actions are vitally related to subtle factors of balance among themselves, and between them and other factors in diet. Some constituents of diet appear to nullify their action. Further problems under consideration include the factors to be used in determining so-called "man-value"; the actual energy requirements of the adult, and the question of "luxus" consumption. Investigations of the action of vitamin *B* have shown that the physiological effects of administering concentrates from yeast are complex, and due to at least two substances, one sensitive to heat, especially in alkaline solution, and which apparently is the curative agent in beri-beri convulsions, and the other very stable to temperature and in reaction.

BIOCHEMISTRY AND PHARMACOLOGY.—About 50 purely organic substances, themselves colourless, but related to complex dyes, have now been prepared and tested systematically and quantitatively with respect to their trypanocidal activity. A relation in the series between appearance and intensification with varying structure has been traced, on the one hand of curative action in experimental trypanosomiasis, and on the other, of affinity for cotton fibres. A method of rapidly testing organic nuclei for their potential value as starting points in the preparation of trypanocidal remedies is suggested. A study of the gold and mercury derivatives of the thiolglyoxalines has led to the testing of one for curative action in experimental tuberculosis, with promising results. The study of organic compounds of arsenic for structural characteristics associated with trypanocidal action has been continued. A search for insulin substitutes has produced diguanidylnonane (synthalin), which is undergoing clinical trials; it has been shown to accelerate the disappearance of glucose from the blood circulation, but the sugar is not deposited as glycogen.

NATIONAL COLLECTION OF TYPE CULTURES.—During the year over 4000 cultures were distributed, and over 200 new strains added to the collection.

The Report includes details of the research schemes in specific subjects, and of the research work of clinical units.

D. G. H.

New Zealand.

SIXTIETH ANNUAL REPORT OF THE DOMINION LABORATORIES.

IN his Report for the year 1926 the Dominion Analyst (Dr. J. S. Maclaurin) mentions that during the year a Department of Scientific and Industrial Research was created, and that the Dominion Laboratory is now under the control of the new Department.

The work during the year involved the examination of 5471 samples, of which 4048 were for the Public Health Department, 496 for the Customs, 467 for the Mines Department, and 34 for the Police, the remainder consisting almost entirely of samples from other Government Departments. In addition, 2300 samples were analysed at the Auckland Branch Laboratory, and 1252 at the Christchurch Branch Laboratory.

MILK.—The number of samples analysed at the Wellington Laboratory was 3995, at the Auckland Branch 1747, and at the Christchurch Branch 916. The amount of visible dirt in the Auckland samples was considerably less than in previous years, but the quality of the farm milk, as indicated by the reductase test, showed no improvement. The outstanding feature of the Auckland City milk supply was the large number of samples below the standard in fat, notwithstanding numerous warnings.

The number of samples taken in Christchurch City and suburbs was quite insufficient to provide a satisfactory check on the supply. There are over 600 registered vendors in the city, and only 546 samples were taken, indicating that the milk of each vendor had not been sampled even once during the year. The percentage of non-compliances (not including samples containing excessive amounts of visible dirt, which would add to the number considerably) is 10·6, indicating that the city supply is far from satisfactory.

ARSENIC AND APPLES.—In New Zealand orchards it is customary to spray apples and pears with a mixture containing arsenate of lead. A typical mixture

would be 100 gallons water, 2 lb. to 4 lb. arsenate of lead (paste), 1 gallon lime-sulphur containing 1 lb. to 2 lb. quicklime, 5 lb. atomised sulphur. This is applied several times in the course of a season. Determinations made in this laboratory several years ago indicated that the amounts of arsenic remaining on the ripened fruit were negligible. In view, however, of recent reports by English analysts that some imported (American) apples contained dangerously large amounts of arsenic, it seemed advisable to make a further examination of New Zealand apples.

A variety of typical samples was obtained from orchards in Auckland, Hawke's Bay, Nelson, and Otago. Two of each variety were selected for analysis, peeled, and the skin (with the calyx and stem) and the pared apple treated separately with a mixture of nitric and sulphuric acid, as directed in the Kerbosch process Arsenic was determined in the resulting solutions by means of the electrolytic Marsh apparatus, with the use of a platinum anode and lead cathode.

No.	Lead Arsenate in 100 Gallons Spray, lbs.	Number of Applications of Spray.	Interval between last Spraying and Picking.	Arsenic found, expresssd as Grains of As_2O_3, per Pound of Unpeeled Fruit.		
				In Peel.	In Pared Fruit.	Total in Unpeeled Fruit.
1	Not given	6	2 hours	$^1/_{80}$	$^1/_{800}$	$^1/_{70}$
2	Not given	5	12 days	$^1/_{200}$	$^1/_{1500}$	$^1/_{200}$
3	2	6	1 day	$^1/_{70}$	$^1/_{700}$	$^1/_{60}$
4	2	4	26 days	$^1/_{400}$	$^1/_{3000}$	$^1/_{400}$
5	1½	4	8 weeks	$^1/_{1000}$	$^1/_{1400}$	$^1/_{600}$
6	2	4	17 days	$^1/_{160}$	$^1/_{3000}$	$^1/_{1500}$
7	4	3	5 weeks	$^1/_{180}$	$^1/_{1000}$	$^1/_{170}$
8	4	3	6 weeks	$^1/_{1600}$	$^1/_{3000}$	$^1/_{1000}$
9	2	6	15 days	$^1/_{100}$	$^1/_{1600}$	$^1/_{100}$
10	3	7	7 days	$^1/_{400}$	$^1/_{2500}$	$^1/_{400}$

It will be seen that in only two cases does the total arsenic exceed $^1/_{100}$ grain to the pound. In both these picking took place within a few hours of spraying, and patches of dry spray were easily visible on the skins. No dry spray was noticed on the other apples. The arsenic in the peeled apple has no significance when compared with the amount on the skin. Experiments with wiping to remove arsenic from the skin indicated that the practice would be of little value, except for removing patches of visible spray.

Various samples of pears were also examined, and the results were similar to those obtained with apples.

It is evident that if an interval of several days is allowed to elapse between the final spraying and the picking, the arsenic remaining on the fruit is far too small to have any harmful effect.

VINEGAR FROM TAPIOCA.—A number of samples of vinegar from one vendor, labelled and sold as malt vinegar, gave unusual analytical results, and it was ascertained that tapioca was being used in the manufacture of the vinegar. Tapioca is not a cereal, and its use in the manufacture of malt vinegar is hence not permitted by the New Zealand regulations, which are in accordance with those generally in force throughout the world. A prosecution followed, resulting in a conviction being recorded.

LIME WATER.—Two of the three samples examined at the Wellington Laboratory did not comply with the B.P. standard. Four samples analysed in the Auckland Branch Laboratory had not been prepared from distilled water. In view of the widespread use of lime water, especially for infants, a much larger number of samples should be taken.

CAMPHOR MONOBROMATE.—A number of powders were examined in connection with a case of reputed camphor poisoning. The powders were found to be camphor monobromate, as claimed, and of an average weight of 2 grains. A single powder had been sufficient to produce almost fatal results, with symptoms typical of camphor poisoning, and the case was considered to be one of idiosyncrasy to camphor.

KAURI GUM.—Three tins of freshly exuded kauri gum were examined in comparison with two samples of fossil kauri gum, No. 1 being a clear high-grade gum, and No. 2 an opaque, very "chalky," highly-oxidised gum. In order to determine the effect of "running" the gums, portions of each sample were heated to about 350° C., and the residues ("run" gums) examined. Portions of each sample were also distilled with superheated steam up to 200° C., and the distilled oils examined. The following results were obtained:

	Fossil gums.		Freshly exuded gums.	
	1.	2.	3.	4.
Moisture (Dean & Stark method), per cent.	1·05	4·40	0·95	1·60
Approximate loss on "running," per cent.	21	25	20	21
Oil distilled at 200° C., per cent. ..	9·3	10·1	15·2	17·5
Sp. gr. of this oil	0·865	0·923	0·862	0·873
Refractive index, n_D^{40} of oil	1·4615	1·4996	1·4690	1·4634
Acid value, raw gums	56	76	74	66·6
,, ,, "run" gums	37·6	48·9	41	45·4
Saponif. value, raw gums	63·6	97·7	86·8	76·0
,, ,, "run" gums	48·9	51·5	52·6	52·6
Iodine value, raw gums	136·9	93·7	137·4	149·3
,, ,, "run" gums	96·5	82·8	94·6	100·0

The results obtained with the "run" gums indicate that the freshly exuded gums may be almost, if not quite, as good as the best fossil gum for varnish making, provided they can be collected free from impurity, and that the "running" on a commercial scale is not attended with greater difficulties or does not give a darker product than fossil gums.

Thirty-fourth Annual Report of the Committee on Atomic Weights.

DETERMINATIONS PUBLISHED DURING 1927.*

INVESTIGATIONS have recently been made on boron, carbon, nitrogen, neon, chlorine, scandium, potassium, argon, silver, yttrium, antimony, and dysprosium. The table of atomic weights for 1928 differs in several respects from that of the German Atomic Weights Commission (ANALYST, 1928, 159). The atomic weight 175·0 is assigned to lutecium, that of 222 to radon, and 93·1 to columbium. The following weights are slightly higher than the German figures:—Cadmium, 112·41; cerium, 140·25; helium, 4·002; iodine, 126·932; nickel, 58·69; lead, 207·22; platinum, 195·23; rhodium, 102·91; samarium, 150·43; thorium, 232·15; uranium, 238·17; ytterbium, 173·6; whilst the figures for cobalt (58·94), dysprosium (162·46), gadolinium (157·26), potassium (39·096), neon (20·183), osmium (190·8), phosphorus (31·027), radium (225·95), sulphur (32·064), vanadium (50·96), yttrium (88·92), and zirconium (91·22) are lower. Thulium (169·4) is given the symbol Tm, not Tu.

D. G. H.

* G. P. Baxter (*J. Amer. Chem. Soc.*, 1928, **50**, 603–617.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Studies on the Effect of Heat on Milk. IV. The Iodine Content. H. E. Magee and A. E. Glennie. (*Biochem. J.*, 1928, **22**, 11–14.)—An investigation has been carried out on the effect of heat on the iodine content of milk. As the investigation proceeded, the question of the physico-chemical state of the iodine content was raised, and ultra-filtration and dialysis experiments were accordingly made. Heat caused the disappearance by volatilisation of 20 per cent. or more, according to the duration of heating, of the total iodine of separated milk. The ratio of diffusible to non-diffusible iodine was the same in the milk after heating as it was before. Approximately 83 per cent. of the total iodine of separated cows' and goats' milk was found to be in diffusible form. P. H. P.

Degree of Acidity (Hydrogen Ion Concentration) of Honey and Artificial Honey. J. Fiehe and W. Kordatzki. (*Z. Unters. Lebensm.*, 1928, **55**, 59–63.)—The acidities and P_H values of a large number of genuine and artificial honeys and their mixtures have been determined by titration of 10 grms. with 0·1 *N* sodium hydroxide solution, with phenolphthalein as indicator, and by Tödt's colorimetric drop method (*Chem. Ztg.*, 1927, **51**, 302) respectively. Brom-phenol blue (P_H 2·8 to 3·8) and brom-cresol green (P_H 3·8 to 5·4) were used in the latter case. No relation was observed between the two sets of values, but the P_H values of genuine and artificial honeys ranged from 3·8 to 4·3 and 3·0 to 4·0 (the majority being 3·9 and 3·2), respectively. Though the P_H value of the former was lowered very little by the addition of the latter, a value of less than 3·8 may be taken as an indication of its presence. Apart from this, the P_H determination is of value only in conjunction with the analytical numbers. J. G.

Separation of Honey. J. Fiehe. (*Z. Unters. Lebensm.*, 1928, **55**, 64–65.)—Analyses of portions taken from the top, middle and bottom of the container of a sample of separated honey showed that the top layer, which was sharply defined, and white in colour, contained most sucrose, dextrose, salts and non-sugars. Microscopical examination showed it to consist of crystals of sugar, and in the case of the less refined varieties, of small particles of wood, wax or bees' wings. The separation is probably caused by the slow rise to the surface of air bubbles occluded in the mixture. The low water-contents of the top and bottom portions, as compared with the middle portion (6·6, 11·25 and 15·7 per cent., respectively), are due to evaporation and to concentration of the sugar by crystallisation, respectively. J. G.

Carbonyl Number of Wines. H. Strache and A. Brandl. (*Z. Unters. Lebensm.*, 1928, **55**, 50–53.)—The bouquet of a wine is due to the esters, aldehydes and ketones, etc., produced during fermentation and storage, and the " carbonyl

number," *i.e.* the number of mgrms. of carbonyl oxygen per litre of wine, may be determined by a modification of the authors' method (*Brennstoff-Chem.*, 1926, **7**, 341) in which the carbonyl groupings react with phenylhydrazine, the excess of which is oxidised by boiling Fehling's solution, and the nitrogen evolved measured. Preliminary experiments showed that the majority of the carbonyl compounds were contained in the first two-thirds of the distillate from 100 c.c. of wine. This, and the steam-distillate from the residue were therefore used for the determination. For the relatively few varieties of wine examined, the results show that the carbonyl number is to some extent related to the vintage and aroma. Muscatel and sweet wines (Chablis) alone, gave residues whose steam-distillates contained carbonyl compounds, and the high total carbonyl number obtained in the former case is attributed to the presence of carbonyl compounds in the original grape, whilst in other wines they are produced subsequently in the vinting process. J. G.

Detection and Determination of *p*-Hydroxybenzoic Acid Methyl Ester in Foods. F. Weiss. (*Z. Unters. Lebensm.*, 1928, **55**, 24–31.)—This ester, which is used under the names of " Solbrol " and " Nipagin " as a preservative for foodstuffs, is very soluble in alcohol or ether, moderately soluble in oils, and sparingly soluble in water. It is weakly acidic, steam-volatile, melts at 131° C., boils at 270 to 280° C., with decomposition, and gives the Millon reaction slowly (a deeper red than with salicylic acid) by virtue of its hydroxyl group. These properties may be slightly modified in the commercial product. Ferric chloride solution gives a violet colour. It is extracted from fat-free substances (50 grms.) by prolonged extraction with hot water. The extract is strained, clarified with 1 c.c. (or 3 c.c. if proteins are present) of Carrez reagent (a mixture of solutions of 150 grms. of potassium ferrocyanide per litre and of 300 grms. of zinc sulphate per litre), diluted to 100 c.c. and filtered. Fatty substances are treated similarly, but 5 c.c. of the Carrez reagent are required for meat-foods, and fats and oils are steam-distilled on an oil-bath at 100° C. and 200 c.c. of distillate collected. In each case 20 c.c. of the clear extract are shaken twice with 50 c.c. portions of a mixture of equal volumes of petroleum spirit and ether. If the residue, after removal of the solvent below 40° C., gives no reaction with Millon's reagent after 4 hours, the ester may be taken to be absent, but if a positive result is obtained, a test must be made for salicylic acid. If this is absent, the colour from the Millon reaction may be matched after 24 hours in a volume of 50 c.c. against a standard. It is preferable, however, to saponify the ester with 10 c.c. of 2 per cent. potassium hydroxide solution, and to determine the methyl alcohol in 6 c.c. of the distillate by Von Fellenberg's method (ANALYST, 1918, **43**, 37). The factor 4·75 gives the amount of ester. Quantitative results were obtained except for fatty foods, which gave low results. A modification of Zeisel's method is also described.

J. G.

Halibut and Flat Fish Liver Oils. M. Tsujimoto. (*J. Soc. Chem. Jap.*, 1928, **31**, 38–40B.)—Halibut liver oil (*Hippoglossus vulg. Flem.*), (*a*) rendered and (*b*) extracted, and (*c*) flat fish liver oil (*Paralichthys olivaceus T. and S.*) had the

following characteristics: Sp. gr., 15/4° C., (*a*) 0·9428, (*b*) 0·9320, (*c*) 0·9326; saponification value, (*a*) 166·0, (*b*) 174·9, (*c*) 164·7; iodine value, Wijs, (*a*) 163·1, (*b*) 160·3, (*c*) 150·1; $n_D^{20°}$, (*a*) —, (*b*) 1·4780, (*c*) 1·4800; unsaponifiable matter, (*a*) 10·48, (*b*) 11·08, (*c*) 10·77 per cent.; acid value, (*a*) 96·5, (*b*) 100·8, (*c*) 9·9; colour reaction with sulphuric acid, (*a*) dark reddish violet, (*b*) violet. The fatty acids from (*a*) and (*c*) showed m.pt. 33° and 30–30·5° C.; neutralisation values, 190·5, 195·8; iodine values, 165·0, 155·0; ether-insoluble bromides, 46·6 and 42·5 per cent.; bromine content of bromides, 71·09 and 70·65 per cent. By the lead salt and ether method the fatty acids gave for (*a*) about 76 per cent. of liquid acids (iodine value 16), and for (*c*) 73·0 per cent. By the lithium salt and acetone method (*a*) yielded 27 per cent. of highly unsaturated acids of neutralisation value 164·9, iodine value 324·2 and $n_D^{20°}$ 1·4916; (*c*) 22·5 per cent. of unsaturated acids of neutralisation value 177·3, iodine value 355·6, and $n_D^{20°}$ 1·4930. For (*a*) the fatty acids appear to consist mainly of C_{18} acids, and in the higher boiling fractions appreciable amounts of highly unsaturated acids, possibly C_{18} and C_{22} acids. The unsaponifiable matter in each case was of an orange yellow colour, and the m.pt. above 100° C. It contained (*a*) 72·1 and (*c*) 85·5 per cent. of cholesterol, corresponding to (*a*) 7·5 and (*c*) 9·2 per cent. on the oil. Vitamin *A* appeared to be present in each oil. D. G. H.

Reaction between Phenacetin and Acetaldehyde. O. Carletti. (*Giorn. Chim. Ind. Appl.*, 1928, **10**, 66.)—When a small amount of phenacetin is moistened with acetaldehyde and stirred with 2 to 3 c.c. of concentrated sulphuric acid, a red coloration gradually develops; the reaction is accelerated if the mixture is gently heated on a water-bath. Dilution of the liquid yields a bluish-brown substance, which gives the red coloration when dissolved in concentrated sulphuric acid. The same reaction is given by paraldehyde and metaldehyde, but not by formaldehyde, trioxymethylene, or hexamethylenetetramine. T. H. P.

Biochemical, etc.

New Test for Ergothioneine. G. Hunter. (*Biochem. J.*, 1928, **22**, 4–10.)—A new and apparently highly specific colour test, which is a modification of the well-known diazo-reaction and depends on the use of diazotised sulphanilic acid, is described, by which it is possible to detect ergothioneine in a dilution of more than one in five millions. The following solutions are necessary:—(1) *Ergothioneine standard.* An aqueous solution of ergothioneine saturated with chloroform and containing 1 mgrm. in 1 c.c., if stored in an ice-chest, remains unchanged for a month. From this, standards may be prepared which contain 0·005–0·050 mgrm. in 2 c.c. (2) *Artificial standard of phenolsulphonephthalein.* (*a*) *Stock.* In 5·7 c.c. of *M*/20 sodium hydroxide solution in a 100 c.c. volumetric flask is dissolved 0·10 grm. of pure vacuum-dried phenol red and water added to the mark. (*b*) *Standard.* Into a 100 c.c. volumetric flask is measured 0·40 c.c. of the stock solution, and diluted to the mark with a buffer solution at $P_H = 8·0$, which consists

of 50 c.c. $M/5$ boric acid solution in $M/5$ potassium chloride solution, and 3·97 c.c. $M/5$ sodium hydroxide solution diluted to 200 c.c. with water according to Clark. The colour of this is indistinguishable in daylight from that developed in the test. A test solution having the same depth of colour as this standard contains 0·015 mgrm. of ergothioneine. (3) *The diazo-reagent.* In a 50 c.c. volumetric flask, immersed in running water under 10°, or ice, are placed 1·5 c.c. of a solution which contains 9 grms. of sulphanilic acid and 90 c.c. of 37 per cent. hydrochloric acid per litre, followed by 1·5 c.c. of 5 per cent. sodium nitrite. The mixture is left for 5 minutes, a further 6 c.c. of nitrite solution then added, and again left for 5 minutes, when cold water is added to the mark and the contents mixed. This reagent, if kept cold, is good for 2–3 days. (4) One grm. of anhydrous sodium carbonate and 10 grms. anhydrous sodium acetate made up to 100 c.c. with water. (5) 10 N sodium hydroxide, from which carbonate has been allowed to settle. For the test, 1 c.c. of the diazo-reagent is delivered into a test-tube, the time noted, 0·5 c.c. of the carbonate-acetate solution added, followed after 15 seconds by 2 c.c. of the solution to be tested, and the contents of the tube are mixed and kept cold. A clear yellow-colour develops. Thirty seconds after the test portion has been added, 2 c.c. of 10 N sodium hydroxide solution are added, and the mixture is quickly shaken. A beautiful red colour with a purple tinge rapidly develops, and is at a maximum after 15 minutes, and is stable for at least 40 minutes. This can be matched against the standards. A method for the quantitative determination of ergothioneine in simple solution and in protein-free blood-filtrates has been based upon the test. The ergothioneine contents of a number of human and animal bloods are recorded. P. H. P.

Biological Significance of the Unsaponifiable Matter of Oils. III. Fish-Liver Oils. H. J. Channon. (*Biochem. J.*, 1928, **22**, 51–59.)—A study has been made of the yields of unsaponifiable matter from a number of fish-livers and fish-liver oils ; the sterol contents of these materials have been determined, and they have been examined for the presence of squalene ; similar observations have been made on a number of samples of plankton, and a comparison has been drawn with the unsaponifiable fraction of certain mammalian livers. The liver oils of the *Selachii* differ from those of the *Teleostei* in that, in many cases, very large amounts of unsaponifiable matter occur in the former. A relationship seems to exist between the percentage of unsaponifiable matter in the liver-oils of the *Selachii* and their sterol content. The higher the percentage of unsaponifiable matter in a given oil, the lower is the percentage of sterol in that fraction. It is concluded from this, that oils of approximately the same content of unsaponifiable material will contain approximately the same amount of sterol. The relationship is only apparent among the *Selachii*, where the unsaponifiable fraction is very high, but presumably it is a general one. Squalene was not detected in the liver oils of any of the fish studied, save in those from three members of the *Squalidae* family. The question as to whether squalene is synthesised or is derived by the fish from its food is briefly discussed. P. H. P.

Note on the Unsaponifiable Matter from the Stomach Oil of *Scymnorhinus Lichia*. **E. D. Kamm.** (*Biochem. J.*, 1928, **22**, 77–79.)—The oil, which was obtained by Heilbron, Kamm and Owens (*J. Chem. Soc.*, 1926, 1630) from the stomach of the elasmobranch fish *Scymnorhinus lichia*, and which contains the hydrocarbon squalene, has now been examined in some detail. The fish is known as " Darkie Alf," and each specimen used averaged 1 m. in length and 5 to 6 kgrm. in weight. The stomach was full, either of clear oil, or, if the fish had been feeding just before capture, of an oily mass of undigested food. The content of oil was usually about 250 c.c. The oil is almost identical with the liver oil. All the specimens examined were obtained during three months of the year (March to May), and all contained the oil, but members of closely related species of shark or dog-fish did not. It is tentatively suggested that some of the liver oil may have come into, and been temporarily stored in, the gall bladder, hence it may have been forced through the bile duct into the small intestine, and thence into the stomach. Whether this process is a normal one of the living animal, or takes place *post mortem* on the release of pressure consequent on the sudden ascent from its normal habitat of more than 100 fathoms to sea level, must still be a matter for conjecture. The unsaponifiable matter from the oil was extracted, and its constitution may be summarised as follows :—Squalene (by distillation), 1000 grms. +residue (by saponification), 45 grms. =1045 grms. =50·6 per cent. of original oil. This consists of :—Squalene (distillation), 1000 grms. ; squalene (distillation of unsap.), 23 grms. ; and squalene (estimated as present in residue), 1 grm. = 1024 grms. =98 per cent. ; batyl alcohol, 3 grms. =0·28 per cent. ; and residue (chiefly selachyl alcohol), 8 grms. =0·96 per cent. P. H. P.

The Vitamins of Orange Juice. **S. G. Willimott.** (*Biochem. J.*, 1928, **22**, 67–76.)—An investigation has been made in order to determine as accurately as possible, under carefully controlled conditions, the minimum adequate dose of fresh orange juice of known origin as a source or vitamin *A* and vitamin *B* respectively for the rat. In previous investigations the supply of vitamin *D* in testing for vitamin *A* has not been controlled. Work on vitamin *C* was omitted, since other workers have examined this. Orange juice from a known source (California navel and Valencia, Sunkist brand), and representative of 600 fruits, was used throughout the work. Complete analyses were made and the results are tabulated. Under carefully controlled conditions 5 c.c. of navel orange juice were found to contain a sufficiency of vitamin *A* for growth and well-being in the rat ; thus, at any rate in the case of the California fruit, orange juice is further demonstrated to be more potent in vitamin *A* than has previously been supposed. Ten c.c. of Valencia orange juice appeared to be adequate for the vitamin *B* requirements of the rat. Although the work on vitamin *D* is incomplete, the results obtained by the Zucker method appear to indicate the absence of this factor from navel orange juice. This result, if confirmed, is of obvious importance in clinical medicine. P. H. P.

Chemical Composition of the Milk of Cows Receiving Cod-Liver Oil. E. C. V. Mattick. (*Biochem. J.*, 1928, **22**, 144–149.)—Since the butter from the milk of cows fed on cod-liver oil is much higher in antirachitic properties than that from cows on ordinary diet, and since rickets is a calcium deficiency disease, it was thought that if any of the mineral salts were affected by the feeding of cod-liver oil the most probable ones would be the calcium salts, and that it was therefore desirable to determine the amounts of the total and diffusible calcium present in the milk of cows receiving cod-liver oil in comparison with that of cows on a normal diet. Analyses have been made of the milk of cows which have been fed on well-balanced diets to which varying quantities of cod-liver oil and arachis (pea-nut) oil have been added. They indicate that the addition of the cod-liver oil results in changes in the chemical composition of the milk, particularly an increase in the percentage of total calcium. Insufficient results have as yet been obtained to justify any very definite conclusions, but the results already obtained seem to be of sufficient interest to warrant further analyses. No suggestion is as yet put forward as to the source of the extra calcium which is found in the milk. Further work on the subject is in progress. P. H. P.

Influence of the Cow's Diet on the Fat-Soluble Vitamins of Winter Milk. II. J. Golding and S. S. Zilva. (*Biochem. J.*, 1928, **22**, 173–182.)—Experiments have been carried out to ascertain whether it is possible to give cows doses of cod-liver oil of such a magnitude that they will not depress the milk-fat but will raise the antirachitic value of the milk. A winter ration for cows which contains silage and hay is described. This ration produced an antirachitic butter of moderate potency. The daily addition of 2 ozs. of cod-liver oil to this ration did not significantly depress the percentage of milk-fat, nor did it raise the vitamin *D* of the butter to any appreciable extent. Higher doses of cod-liver oil depressed the percentage of milk-fat and raised the antirachitic potency of the butter. The authors are now engaged in further work on this subject.
P. H. P.

Vitamins in Tinned Strawberries. E. F. Kohman, W. H. Eddy and N. Halliday. (*Ind. Eng. Chem.*, 1928, **20**, 202–204.)—Strawberries contain vitamin *C*, and the quantity is not reduced when the fruit has been preserved in tins for over one year. About 2·5 grms. of the fruit are required daily to protect a guinea pig against scurvy and to insure normal growth. Strawberries contain about one-fortieth the amount of vitamin *C* found in tomatoes and about one-fourth the amount of vitamin *B*. W. P. S.

Vitamins in Oysters. D. B. Jones, J. C. Murphy and E. M. Nelson. (*Ind. Eng. Chem.*, 1928, **20**, 205–210.)—Oysters are a good source of vitamins *A*, *B* and *D*, but are deficient in the vitamin required for reproduction and the rearing of young. Dehydration of oysters at 40° C. under reduced pressure (10 to 15 mm.) considerably reduces the activity of the vitamins *A* and *B*.
W. P. S.

Bacteriological.

The Rancidity of Coconut Oil Produced by Mould Action. W. N. Stokoe. (*Biochem. J.*, 1928, **22**, 80–93.)—The following experimental work has been carried out:—(1) An investigation of the products of the action of a *Penicillium* organism on coconut oil, (2) physiological experiments with *Penicillium* and *O. lactis*, (3) a repetition of the method of Dakin (*J. Amer. Chem. Soc.*, 1910, **44**, 41) for the oxidation of fatty acids, to determine, if possible, whether secondary alcohols are formed as intermediate products, and (4) a more complete investigation of the " échappées " of Haller and Lassieur (*Compt. rend.*, 1910, **150**, 1013). The results of this last subject will be described in another paper. The rancidity of coconut oil, caused by a typical *Penicillium* organism, is due essentially to the presence of methylamyl, methylheptyl and methylnonyl ketones; the former occurs in greatest quantities and causes the characteristic " perfume." There are also present secondary alcohols which correspond to the ketones, ethyl alcohol (probably by fermentation of sugar), esters of the secondary alcohols and ethyl alcohol, with caprylic acid (and probably other fatty acids), and free fatty acids. The production of methyl ketones by moulds shows that oxidation of a chain compound takes place primarily at the β-carbon atom, with formation of a keto-acid. A keto-acid is normally decomposed by moulds to a fatty acid which contains two carbon atoms less, and acetic acid; with *Penicillium* the absorption of poisonous fatty acids on the mycelium impedes respiration, and the keto-acid is decomposed to methyl ketone and carbon dioxide. The poisoning capacity of the fatty acids towards *Penicillium* increases with the molecular weight up to caprylic acid, then decreases. Only acids up to lauric acid are absorbed, and thus ketones up to methylnonylketone are formed. The fatty acids, with the exception of butyric acid and lower acids, are more poisonous to *O. lactis* than to *Penicillium*. *Oidium*, owing to its greater enzymic activity, decomposes a keto-acid normally to a lower acid and acetic acid. It is probable, but not definitely concluded, that secondary alcohols are intermediate products of the mould oxidation. Dakin's oxidation of saturated fatty acids has been repeated, but the formation of secondary alcohols as intermediate products could not be satisfactorily demonstrated.

P. H. P.

Identification of Fungi causing Mildew in Cotton Goods. The Genus Aspergillus. G. Smith. (*J. Text. Inst.*, 1928, **19**, T92–T100.)—Under difficult or abnormal conditions of growth, as for example, on cloth of almost normal moisture content, the fruiting organs of most *Aspergilli* are dwarfed and of non-characteristic appearance. It is, indeed, impossible to identify an *Aspergillus* species by microscopic examination of mildewed cotton, and isolation of the mould in pure culture becomes necessary. Where a mould is growing freely on the exposed surface of cotton material, pure culture is often possible by direct transference of a portion

of the growth to a tube of suitable medium, but even then purity must be checked by the preparation of a series of plate cultures. With cloth which is merely stained and shows no surface growth, a small portion of the sample is cut into pieces as small as possible, further teased out, and the fibres mixed thoroughly in a test-tube with liquefied agar medium at about 45° C. From three to five tubes of medium are inoculated from this by successive dilution and poured into Petri dishes, which are incubated at 25° C. until the highest dilution gives characteristic but well separated colonies. The media used by the author were wort-agar and prune-juice-agar for isolation of species, and Dox's medium for the final cultures of all species except those of the *A. glaucus* group, for which wort-agar gave better results.

For microscopic study all species may be mounted in lacto-phenol, containing 2 parts (by vol.) of lactic acid, 2 pts. of phenol (melted crystals), 1 part of glycerin, and 2 parts of distilled water. This serves for determining the colours of stalks and conidia, but substitution of the water by saturated aqueous picric acid is of advantage for micrometry and photomicrography. Preliminary treatment with alcohol is advisable with one or two particularly fragile forms.

The species described are divided into: (I) *Aspergillus* species, which have been identified as the causal agents of mildew damage of yarns and cloths. These comprise: *A. flavus* Link, occurring fairly regularly as spore infections of yarns, but recorded only once, as a cause of mildew, in Queensland raw cotton; *A. fumigatus* Fresenius, occurring infrequently; *A. glaucus*; *A. niger* Van Tieghem, a common cause of black spots in dhooties shipped to the East; *A. repens* (Corda) Saccardo, the commonest species of the *A. glaucus* group found on cotton goods; *A. ruber* (Spieckermann and Bremer), Thom and Church, found as principal infection in several cases of mildew in dhooties; *A. sydowi* (Bainier and Sartory), Thom and Church; *A. terreus* Thom, regarded as one of the most dangerous organisms; *A. versicolor* (Vuillemin), Tiraboschi; and *A. wentii* Wehmer. (II) Species occurring commonly as spore infections of commercial yarns, but not yet found growing on cotton goods. *A. candidus* Link; *A. chevalieri* (Mangin), Thom and Church; *A. effusus* Tiraboschi; *A. flavipes* (Bainier and Sartory), Thom and Church; *A. nidulans* (Eidam), Winter; *A. ochraceus* Wilhelm; *A. tamarii* Kita.

T. H. P.

Microbic Flora of Frozen Eggs. J. Verge and E. Grasset. (*Compt. rend.*, 1928, **186**, 718–719.)—An examination of Chinese eggs imported into France showed that the frozen eggs compared advantageously with eggs in shells as to the number of colonies developing on incubation, but when left for 24 hours at laboratory temperature before incubation the number of colonies per grm. were: White of egg, on gelatin at 20° C., 360,000, gelose at 37° C., 35,000; yolk, 3,600,000; 3,500,000, and whole egg, 4,000,000 and 2,000,000 respectively. Besides bacteria which had lost all pathenogenic power, others of the paratyphoid and coli groups were isolated, so that such frozen eggs should only be used in products that will be subjected to heat. D. G. H.

Toxicological and Forensic.

Chemical Constitution and Toxicity. E. Walker. (*Biochem. J.*, 1928, **22**, 292–305.)—The relationship between chemical constitution and toxicity has been studied; toxicity has been measured against the unicellular organism, *Colpidium colpoda*, and, to a less extent, against *Glaucoma scintillans*. The principle of the method adopted has lain in the determination of the concentration of substance to be tested which killed all the organisms in a given amount of culture in a fixed time. The bulk of the compounds examined are derivatives of arsenic; a lesser number of antimony, bismuth, and mercury compounds have also been tested. The following general rules, appertaining to arsenic compounds, have been established:—(*a*) Aromatic derivatives are more toxic than aliphatic derivatives, (*b*) trivalent derivatives are more toxic than pentavalent derivatives, (*c*) secondary derivatives are more toxic than primary and tertiary derivatives, and (*d*) primary derivatives are more toxic than tertiary derivatives. It appears probable that antimony compounds are more toxic than the corresponding arsenic compounds. The most toxic arsenic compounds are the tervalent secondary derivatives, and, within this class, compounds of the diphenylarsine type of structure are the most toxic. Unicellular organisms are considered only to afford a measure of general protoplasmic toxicity. The protozoal test fails to give any indication of poisons exerting a specific action upon mammals; for example, the cyanides, certain amines and the alkaloids. Evidence is brought forward to show that the toxicity of arsenicals is intimately concerned with the sulphydryl constituents of the cell. Organisms which have ceased all movement under the influence of arsenic can be revived at once, and continue to live for periods up to 2 hours, by the addition of a suitable sulphydryl compound. P. H. P.

Organic Analysis.

Rapid Determination of Carbon, Nitrogen, and Hydrogen in Organic Substances. R. Vandoni and M. Algrain. (*Bull. Soc. Chim.*, 1928, [IV], **43**, 255–260.)—In this method, which admits of accurate results being rapidly obtained, the combustion of the organic substance for the determination of the carbon and nitrogen is carried out in a small quartz U-tube containing cupric oxide. The total amount of oxygen introduced only slightly exceeds that necessary for complete combustion. The U-tube is inserted between a gas-measuring apparatus and an absorption pipette and is heated by a powerful gas burner, the gaseous products of combustion mixed with the excess of oxygen being passed backwards and forwards through the tube until combustion is complete. This occupies only a few minutes, measurements of the carbon dioxide and nitrogen then giving the proportions of carbon and nitrogen present in the substance. In a second combustion for determining the hydrogen, the water formed is collected in a small Sommelet tube immersed in a freezing mixture at about 0° C., and followed by a calcium chloride U-tube serving as a guard. Here, too, oxygen is used in small

amount, and is prepared just when wanted from oxylith, and by means of small Cloez bubblers containing mercury and a Drehschmidt gas burette and levelling tube also charged with mercury, the gases are repeatedly passed in the same direction through a closed circuit comprising a calcium chloride tube, the combustion tube, the Sommelet tube, and the calcium chloride guard tube. Diagrams of the apparatus are given. T. H. P.

Determination of Oxygen in Organic Compounds. G. Glockler and L. D. Roberts. (*J. Amer. Chem. Soc.*, 1928, **50**, 828–831.)—The amount of oxygen consumed during combustion of an organic compound is measured gasometrically, so that carbon, hydrogen and oxygen may be determined in one operation. A modification of Wise's semi-micro combustion method is used. The system is closed, and any gases due to cracking or incomplete combustion are carried back through the combustion tube several times in the period allowed for combustion, so that complete combustion is assured. A volatile oil obtained from ethane, under the influence of electric discharge in an ozoniser, was found by the ordinary semi-micro method to contain carbon and hydrogen, together amounting to 87 per cent., but by the adapted method it was shown that no oxygen was present. D. G. H.

Rapid Quantitative Removal and Determination of the Carbonic Acid Radicle. F. W. Foreman. (*Biochem. J.*, 1928, **22**, 222–229.)—The high retentiveness of 87 per cent. alcohol for volatile acids when steamed, even though the temperature was probably as high as 85° C., coupled with another observation that carbon dioxide escapes extremely readily from its partially saturated solution in alcohol on exposure to the air at room temperature, gave rise to the suggestion that at temperatures well below 85° C., a current of air passed through a solution of carbonic acid and " free " volatile acids in 87 per cent. alcohol, causing little change in the alcohol concentration, might very rapidly remove the carbon dioxide completely and leave the whole of the volatile acids behind. On investigation it was found that strong alcohol, in which carbonic acid and small quantities of " free " volatile acids are dissolved, very readily parts with the whole of the carbon dioxide, but completely retains the volatile acids on aeration. In this solvent, bicarbonates of " weak " nitrogenous bases and " free " carbonic acid lose their carbon dioxide on aeration with equal readiness. A simple, rapid room temperature process and a useful modification, applicable to fluids such as bacterial cultures, for the determination and elimination of the carbonic acid radicle, are based upon these observations. There is no risk of loss or change in any of the other constituents, and subsequent determinations are more precise. P. H. P.

Oxidation of certain Poly-alcohols by Periodic Acid. Applications. L. Malaprade. (*Compt. rend.*, 1928, **186**, 382–384.)—Glycol, glycerol, erythritol, adonitol, and mannitol reduce periodic acid in the cold to iodic acid, the reaction being complete after, at most, 12 hours. The reaction coefficients are ascertained

by treating an acid solution of potassium iodide with a definite quantity of periodic acid and titrating the liberated iodine with thiosulphate, a second test being carried out with the same amount of periodic acid solution and the poly-alcohol in quantity insufficient to reduce the whole of the periodic acid. The numbers of molecules of periodic acid reduced by one molecule of each of the poly-alcohols mentioned above are respectively 1, 2, 3, 4, and 5. These results furnish a basis for determining the poly-alcohols, especially in small proportions, and for determining iodic and periodic ions present together, the procedure in the latter case being as follows :—One portion of the liquid is acidified, treated with potassium iodide, and titrated with thiosulphate to determine the iodine liberated. A second portion of the acidified solution is mixed with a sufficient quantity of mannitol to reduce the periodic acid, and left for 30 mins. before treatment with iodide and titration with thiosulphate ; in this case only six, instead of eight, atoms of iodine are set free per molecule of periodic acid, the amount of which is thus easily calculated.

The proportions of acid formed in the reaction between periodic acid and the different poly-alcohols are in agreement with the equation :

$$(CH_2.OH)_2\,(CH.OH)_n + (n+1)HIO_4 = 2H.CHO + nH.CO_2H + (n+1)HIO_3.$$

T. H. P.

Determination of Sulphur in Volatile Fuels. H. T. Kennedy. (*Ind. Eng. Chem.*, 1928, **20**, 201–202.)—The liquid fuel is placed in a tapped pipette holding 5 c.c. between the two graduation marks ; the stem of the pipette enters a small combustion chamber containing a plug of glass-wool and provided with an inlet for air and an outlet tube leading to a burner. The combustion chamber is fitted with a heating coil, and is embedded in alundum cement. At the commencement of a test the pipette is filled to above the upper mark with the liquid fuel, the heater is started, the air supply adjusted, and the fuel allowed to enter the combustion chamber at a regulated rate. The vapour and air issuing from the burner are ignited, and when the level of the liquid has fallen to the upper mark an absorption vessel for the gases is placed over the flame, and is removed as soon as 5 c.c. of fuel have been burnt. The sulphur is then determined in the contents of the absorption vessel. W. P. S.

Rapid Detection of Fatty Oils in Green Cells. K. B. Blackburn and M. Thomas. (*Proc. Univ. Durham Philosoph. Soc.*, 1927, **7**, 202–207.)—Osmic acid (osmium tetroxide) not only gives a black stain with oil in the cells of plants, but also gives a dark coloration with tannins and other constituents of the green cell. To prevent the speckled effects thus produced, the cells are first treated with osmic acid, and then with chlorine water, with the result that even very small oil drops appear as dark spheres against the bleached background. The specimen under examination is immersed in a drop of 2 per cent. osmic acid and left on the slide for at least 1 minute, after which it is treated with chlorine water until bleached. Finally, it is washed with water, and examined under a cover

glass with the microscope. Good results are thus obtained with the cells of green algae, with whole leaves of mosses and liver worts, and with sections of the leaves of higher plants.

Composition of Ivy Seed Oil. A. Steger and J. Van Loon. (*Recueil Trav. Chim. des Pays Bas*, 1928, **47**, 471–476.)—The yield of oil obtained by extracting ivy seeds was 20 per cent., and its analytical constants were :—Solidification pt., 13·8° C. ; sp. gr. at 35° C., 0·9151 ; $n_D^{20°}$, 1·4670 ; saponification value, 181·1 ; iodine value (Wijs), 102·2 ; Reichert-Meissl value, 1·0 ; unsaponifiable matter, 6·58 per cent. ; acid value, 11·0 ; glycerol (as C_3H_5), 4·0 per cent. The distilled fatty acids had : M.pt., 23–24° C. ; solidif. pt., 19·9° C. ; n_D^{40}, 1·4592 ; iodine value (Wijs), 97·2, (Kaufmann) 85·4 ; acid value : 199·0 ; mol. wt., 281·9. The composition of the fatty acids was found to be : higher saturated fatty acids, 5·1 ; petroselinic, 62 ; 9 : 10-oleic acid, 20 ; and linolic acid, 13·1 per cent.

D. G. H.

Micro-method for the Determination of the Copper Number of Cellulose. T. F. Heyes. (*J. Soc. Chem. Ind.*, **47**, 1928, 90T.)—This method is based on that of Braidy, modified as follows :—The moisture in 0·25 grm. of the air-dry cellulose is determined by drying it at 105° for 3 hours. Three solutions are necessary : (1) 150 grms. of anhydrous sodium carbonate and 50 grms. of sodium bicarbonate are dissolved and diluted to 1 litre ; (2) 100 grms. of copper sulphate crystals in 1 litre ; (3) 40 grms. of ferric sulphate and 100 c.c. of concentrated sulphuric acid in 1 litre. The sample (0·25 grm.) is placed in a test-tube ($4'' \times \frac{3}{4}''$), treated with a heated mixture of 9·5 c.c. of solution No. 1, and 0·5 c.c. of solution No. 2, and the whole immersed in a boiling water-bath for 3 hours, the mouth of the tube being covered with a glass pear, and the contents being stirred occasionally. The tube is cooled, the cellulose and precipitated cuprous oxide filtered through a fritted Jena glass or a Gooch crucible, and washed 3 times. One-and-a-half c.c. of solution No. 3, after being placed in the reaction tube, and shaken till the cupric oxide is dissolved, are poured on to the cellulose on the filter, and left till the darkening in colour has passed away. The filter is sucked into a clean 100 c.c. flask, the vacuum released, and the reaction-tube and cellulose washed with a further 1 c.c. of solution No. 3, followed by three or four washings with 2 c.c. lots of water. The filtrate and washings are titrated in the filter flask with 0·04 *N* potassium permanganate, a 2 c.c. burette reading to 0·005 c.c. being used. The end-point, which is quite sharp, consists in a change from faint green to colourless. A blank test is carried out on 2·5 c.c. of solution No. 3, and usually shows 0·025 to 0·03 c.c. of the permanganate solution. The results are calculated as percentages of copper on the dry material (1 c.c. 0·04 *N* permanganate solution = 0·002543 grm. Cu.). The results agree well with those given by the macro-method. Normally bleached cotton yarn gives a copper number of 0·2, whereas in the case of a badly tendered hank it was 5·94. This result suggests that the tendering was due to local over-bleaching, and not to acid tendering, since the latter would have caused the yarn to fall to powder on drying.

R. F. I.

Inorganic Analysis.

Applications of Ceric Sulphate in Volumetric Analysis. N. H. Furman. (*J. Amer. Chem. Soc.*, 1928, **50**, 755–764.)—Dilute sulphuric acid solutions of ceric sulphate were found to possess at least a moderate degree of stability, and the reaction between such solutions and a standardised ferrous sulphate solution was suitable for the accurate potentiometric determination of either ion. The reaction is applicable to the standardisation of ceric solutions. These may also be standardised by titrating them, while hot, with standardised oxalic acid, but the reverse reaction is not satisfactory. A potentiometric study of the determination of cerium shows that oxidation of bismuthate or persulphate, followed by potentiometric titration with ferrous sulphate, is rapid and satisfactory. D. G. H.

Antimony Enamels. K. Beck and W. A. Schmidt. (*Z. Unters. Lebensm.*, 1928, **55**, 1–24.)—Antimony trioxide or sodium antimoniate ("Leukonin") are often used as cheaper substitutes for zinc oxide in white enamels. Antimony is detectable in such cases by the orange-yellow precipitate produced on the addition of sulphuric acid to a solution of the enamel in a 3 per cent. solution of tartaric acid, and 1 mgrm may be detected in 100 c.c. of solution, even in the presence of zinc and zirconium oxides. The change in valency during the heating process of antimony compounds, both in the pure state and mixed in an enamel, has also been investigated for various methods of heating in order to find the most suitable solvent for the antimony, and a method is described for the accurate determination of small quantities of tri- and penta-valent antimony in the presence of one another. For enamelled vessels of 1 litre capacity, 200 c.c. of a 3 per cent. solution of tartaric acid are used. The solution is boiled in the vessel over a naked flame for 30 minutes, with a round-bottomed flask full of cold water as a combined cover and condenser, well shaken, and made up to a suitable volume with the tartaric acid. (1) Fifty c.c. are then titrated with 0·001 *N* potassium bromate solution in the presence of 20 c.c. of hydrochloric acid (sp. gr. 1·126), and one drop of methyl orange (1:1000), till the colour disappears. (2) This solution, or another 50 c.c. portion with 20 c.c. of acid, is then heated almost to the b.pt., 10 drops of a 10 per cent. solution of phosphotungstic acid added immediately, and then enough of a 0·1 *N* solution of titanium trichloride to produce a cobalt blue colour permanent for 2 minutes. After a further 3 minutes, 2 drops of a 0·01 per cent. solution of copper sulphate are added, and, after a further 5 minutes, the red colour produced on the addition of a drop of methyl orange solution may again be removed by titration with the bromate solution. The titrations (1) and (2), in c.c., less those given by the respective blank experiments, give the trivalent and total antimony, respectively, in 0·001 mgrm. equivalents, and this, multiplied by 0·0609, gives the amount in 50 c.c. of solution. The potassium bromate should be recrystallised and dried at 125° C., and a 0·1 *N* solution (2·784 grms. per litre) standardised iodimetrically against a 0·1 *N* solution of potassium dichromate.

The titanium chloride solution is made from 100 c.c. of a commercial 15 per cent. solution and 200 c.c. of hydrochloric acid (sp. gr. 1·126), diluted to 1 litre. J. G.

Determination of -SOOH (sulphinic) Group and of Ferric Iron. S. Krishna and H. Singh. (*J. Amer. Chem. Soc.*, 1928, **50**, 792–798.)—Sulphinic acids yield insoluble ferric sulphinates and the formation is quantitative. A known volume of ferric chloride solution of definite concentration is acidified with hydrochloric acid, a known volume of the sulphinic acid added, the orange-coloured precipitate filtered off, washed, and the iron determined. The strength of the sulphinic acid is then calculated according to the equation $3R\text{SOOH}+\text{FeCl}_3=(R\text{SOO})_3\text{Fe}+3\text{HCl}$. Ferric iron in ferric chloride was determined by titrating a known volume of ferric chloride solution against a standard sulphinic acid solution in the presence of dilute hydrochloric acid with a dilute solution of potassium thiocyanate as external indicator. The error ranged from 0·0001 to 0·0004 grm. of ferric iron. Ferrous iron may also be determined in the presence of ferric iron and *vice versa*, and ferric ions in the presence of aluminium, chromium, nickel and cobalt. D. G. H.

Detection and Determination of Beryllium. H. Fischer. (*Z. anal. Chem.*, 1928, **73**, 54–64.)—1.2.5.8.-Tetrahydroxyanthraquinone, which forms a bright blue lake with magnesium salts (ANALYST, 1925, **50**, 35), reacts in the same manner with beryllium, an alkaline solution of which strikes a cornflower-blue coloration with a few drops of the 0·05 per cent. dye solution in 0·25 *N* caustic soda ; the reagent should always be freshly made. The alkaline solution of the dye is violet. The limit of sensitiveness is 1:2,000,000 ; for the detection of small quantities it is recommended to use two test tubes, one containing the test, the other an equal volume of caustic soda of the same concentration as that in the test ; the same amount of reagent is added to each tube. The colours are compared against a white background. Alkali salts do not interfere, but ammonium salts decrease the sensitiveness. The presence of aluminate at any concentration is immaterial ; it is only necessary to increase the alkalinity of the liquor (to about 0·5 *N*) for large quantities. An admixture of 0·03 per cent. of beryllium in aluminium can be readily detected. Phosphoric acid, lead, zinc, and tin are likewise without influence. Cyanide does not interfere, tartrate only in so far as it depresses the sensitiveness to 1:335,000. On the other hand, the simultaneous presence of tartrates and aluminium spoils the reaction, as it causes a violet coloration ; iron should not be present in a tartrate solution in quantities exceeding 0·001 grm. per c.c. In presence of magnesium, beryllium is detected as follows : The nearly neutral solution (10 c.c.), free from aluminium and iron, is treated with about 1 grm. of ammonium chloride and a few drops of a 0·05 per cent. solution of the dye in 2*N* ammonia, next with 10 drops of strong ammonia and, during agitation, with 5 c.c. of saturated bromine water. If magnesium only is present, the colour is entirely discharged, but beryllium causes a stable violet-blue coloration ; after some time the beryllium lake flocculates. The test detects 1 part of beryllium in presence of 1000 parts of magnesium.

Determination. The principle underlying the determination is a matching of tints, not comparison of the same tint at varying intensities. Two standard solutions are required : (1) pure beryllium nitrate in 0·25 *N* caustic soda (0·1 grm. BeO in 1000 c.c.) ; and (2) a 0·05 per cent. solution of the dye in 0·25 *N* caustic soda, made on the day the determination is made. The dye solution (theoretically 0·0332 mgrm. Be per c.c.) is standardised as follows : (*A*) Ten c.c. are diluted in a conical flask with a suitable volume of 0·25 *N* caustic soda (*e.g* to 200 c.c.). (*B*) The solution serving as the colour standard is prepared like the preceding, but with an excess of the standard beryllium solution as well ; it has a pure blue colour. The standard beryllium solution is now added in small quantities to solution *A*, and a sample withdrawn after each addition and compared in a colorimeter with a sample of solution *B*. The sample from *A* is returned to the bulk before each addition of standard beryllium solution. The operations are repeated until the blue tint of *B* is matched by that of *A*. The unknown solution (0·25 *N* alkali) is tested by being added to another 10 c.c. of the standard dye solution, and the liquid again made up to 200 c.c. with the alkali (solution *A'*) ; this is matched against *B* in precisely the same manner as *A*. A smaller volume of standard beryllium solution is now required to equalise the tints, from which data the unknown is calculated. The error is stated to be smaller than in most other colorimetric determinations. Its great advantage is applicability in presence of much aluminium. With more than 100 parts of aluminium, the tint of the assay does not coincide with that of the standard ; in that case a solution containing aluminium must be used as the standard. Sufficient sodium hydroxide is added to re-dissolve the alumina precipitate ; the solution is then diluted to the desired bulk with 0·25 *N* alkali. Alloys of copper or nickel with beryllium (3 per cent.) are analysed as follows : 0·1 grm. of sawings is dissolved in a little cold hydrochloric acid and hydrogen peroxide, and the solution evaporated to dryness on the water-bath. The residue is dissolved in a little water and treated with cyanide until the precipitate first formed has re-dissolved and the liquid is colourless. It is diluted in a graduated flask with 0·25 *N* caustic soda and an aliquot portion assayed colorimetrically. For the determination of beryllium in beryl, 0·2 grm. of the very finely powdered mineral is fused with sodium carbonate (twice). The melt is taken up with hydrochloric acid, and the silica rendered insoluble by evaporation. The filtrate is made up to 200 c.c. with alkali, etc., as above. The small quantity of ferric hydroxide does not interfere ; it is left to settle, and the clear liquid pipetted off for the colorimetric assay. W. R. S.

Determination of Fluorine in Blende. L. Fresenius, K. Schröder, and M. Frommes. (*Z. anal. Chem.*, 1928, **73**, 65–69.)—A critical examination of the methods proposed led to the conclusion that Olivier's etching test ("funnel" method, *Z. anal. Chem.*, 1923, **62**, 299) is the best process for fluorine percentages of 0·05 and less. For high percentages (0·5 per cent. and more), a volatilisation method gives the best, but always low results, due to traces of moisture ; for this reason the method is not reliable for the lower percentages (ANALYST, 1923, **48**,

628). For the interval 0·5 to 0·05 per cent., the authors recommend their modification of Steiger's colorimetric method, based upon the bleaching action of fluorine upon pertitanic acid. It gives fair results even with quantities of 0·5 to 1 per cent. The sample is first submitted to the etching test, which gives an approximate figure. For the colorimetric determination, 2 grms. of the fine powder are fused with sodium peroxide and carbonate (5 grms. of each). The product is extracted with hot water, and the liquid evaporated to 50 c.c. after addition of 8 grms. of ammonium carbonate. The precipitate is filtered off and washed with hot water, the cold filtrate is acidified with an excess of 10 c.c. of sulphuric acid (1 : 1), violent stirring being avoided. The solution should remain perfectly clear; if lead sulphate is precipitated in the acidification, the liquid should be made feebly alkaline, and filtered. For the standard, the same quantity of flux is dissolved in water and evaporated with the same amount of ammonium carbonate, etc., as with the assay sample. The solutions are placed side by side in hemispherical 500 c.c. porcelain dishes, and treated with 5 c.c. of 3 per cent. hydrogen peroxide and 5 c.c. of titanic sulphate solution (1 c.c. = 0·001 grm. TiO_2). The standard is titrated with a solution of sodium fluoride (0·0010 grm. F per c.c.) until the tint matches that of the assay. The method is stated to be sensitive to 0·0001 grm. F; the quantity present should not exceed 0·003 to 0·004 grm.; if it does, the liquid should be divided into halves. W. R. S.

Iodimetric Determination of Phosphorous Acid, and the Use of Sodium Hydrogen Carbonate in Iodimetry. P. Carre. (*Compt. rend.*, 1928, **186**, 436–438.)—Rupp's method of determining phosphorous acid by treating the aqueous solution with excess (5 to 15 mols.) of sodium hydrogen carbonate and excess of 0·1 *N* iodine solution, and, after the lapse of 90 minutes, titrating the residual iodine with sodium thiosulphate (*Ber.*, 1902, **35**, 3691), is found to give practically exact results only when the excess of iodine used is small (less than 5 c.c. of 0·1 *N* iodine) and the amount of sodium hydrogen carbonate less than 5 mols. (per mol. of phosphorous acid). This result is due to the fact that the action of iodine on the excess of the carbonate yields iodate, so that it is necessary to acidify the liquid with hydrochloric acid before determining the excess of iodine with thiosulphate. Moreover, during the oxidation of the phosphorous acid by the iodine, the mixture should be kept in a flask with a ground stopper, since otherwise the carbon dioxide gradually escaping entrains appreciable amounts of iodine. Similar precautions are advisable in all cases when excess of iodine is left in contact with bicarbonate, the latter being used in minimum quantity. The above method serves for the determination of free phosphorous acid when mixed with mono-esters of the acid, these remaining unoxidised by the iodine. T. H. P.

Physical Methods, Apparatus, etc.

Burette-reading Device. M. Hyman. (*J. Soc. Chem. Ind.*, 1928, **47**, 100T.)—The lower portion of a piece of white celluloid (about $3'' \times 1\frac{1}{2}''$) is blackened so that the blackened portion measures about $3'' \times 1''$. Over the blackened portion is fixed by eyelets a strip of transparent celluloid, so that its upper edge coincides with the upper margin of the blackened area, and so that there is sufficient space between the eyelets to allow the device to be slipped over a burette. The blackened portion of the celluloid is brought to just below the meniscus, which will then appear as a sharp black crescent. The level of the eye is such that the upper edge of the transparent strip in front and the upper edge of the blackened area behind the burette are seen to be in line. The device is then gradually raised till this line forms a tangent to the black crescent of the meniscus, when the reading is clearly indicated. Of nine independent observers, seven returned a given reading as 6·03, and two as 6·02. R. F. I.

Use of Liquid Sulphur Dioxide in Laboratory Cooling Device. A. F. Gill. (*Ind. Eng. Chem.*, 1928, **20**, 212.)—In the usual " cold test " for castor oil a constant temperature of –10° C. may be maintained by the use of boiling sulphur dioxide. This boils at –10° C., and slow boiling is attained by placing the liquid in a Dewar flask of about 5 cm. internal diameter. The test-tube containing the oil under examination is placed in the liquid, and the only attention required is the addition of about 100 c.c. of liquid sulphur dioxide every second day. The actual consumption of sulphur dioxide during a ten days' test is less than 500 c.c. The stopper closing the test tube containing the oil should be coated thickly with vaseline to exclude moisture and sulphur dioxide. W. P. S.

Rapid Method of Drying Laboratory Preparations. M. Hyman. (*J. Soc. Chem. Ind.*, 1928, **47**, 86T.)—A substance may be directly dried on the Buchner funnel by fitting over it an inverted filter funnel with a side tube from the stem, connected with a supply of warm air, and with a thermometer fitted through the stem. The junction of the funnels is made air-tight by means of a rubber band. Nitrogen may be used instead of air when a substance is easily oxidisable; it is passed through alkaline sodium hyposulphite and over calcium chloride. D. G. H.

Measurement of the Fluidity of Cotton in Cuprammonium Solution. D. A. Clibbens and A. Geake. (*J. Text. Inst.*, 1928, **19**, T77–T92.)—Descriptions are given of the procedure and methods of expression, referring to the measurement of the rate of flow of solutions of cotton in cuprammonium hydroxide solution, in use in the laboratories of the British Cotton Industry Research Association, a critical account of the reasons for their adoption being included. T. H. P.

References to Scientific Articles not Abstracted.

CELLULOSE LACQUERS. By S. SMITH. *J. Soc. Dyers & Col.*, 1928, **44**, 106 (April).

Description of methods of preparation—Cellulose nitrate—Resins—Solvents—Plasticisers—Pigments.

AFFINITY OF DIFFERENT TYPES OF ENZYME FOR THEIR SUBSTRATES. By J. B. S. HALDANE. *Nature*, 1928, **121**, 207.

Apparent dissociation constants for 44 enzymic reactions classified—Enzymes fall into three groups, with low, medium, and high affinities.

Reviews.

A HANDBOOK OF ELEMENTARY CHEMISTRY. By J. C. ATTIX, M.D., M.S. 2nd edition. Pp. 278. Philadelphia and New York: Lea & Febiger. 1926. Price 3 dollars.

From the preface of this volume we gather that it is intended as a reference book for the use of the student in acquiring a working knowledge of chemistry. As such it may reasonably be expected to confirm and supplement the information contained in the larger works, but it is soon evident to the reader that the author has compiled his text hurriedly, and, further, that the proof reading has been carried out with insufficient care. Not only are numerous typographical errors present, but, in addition, many inaccurate statements and infelicities of expression are met with which induce the belief that the author has but little regard for scientific truth or for grammar.

The volume is divided into three parts, the first of these dealing with physics, chemical philosophy and laboratory methods, the last comprising only a few experiments on the Bunsen flame and the use of flame tests, borax beads and charcoal reactions in analysis. The second is devoted to the chemistry of the elements and their commonly occurring compounds, and contains much concentrated instruction, although this is often duplicated even on the same page. Throughout this portion numerous experiments are described which the student should perform, but even here several errors occur. The third and smallest portion of the book includes directions and tables for use in qualitative analysis, with a brief section of four pages describing standard and normal solutions. This is by far the most reliable part of the work, but, even here, reference is made to the solubility of silver iodide and chloride in dilute sodium hydroxide solution instead of ammonia, and to the precipitation of silver nitrate by hydrofluoric acid.

Among the misprints the following are noticeable: "alloptropic," "choride," "exposion," and "di-methyl glycine," as a reagent for nickel salts. Yet more inexcusable are various incompatible statements; thus on p. 81 the crith is given two values, *viz.* 0·0898 and 0·0896 grms.; on p. 102 we find "the halogens do not combine with each other," and on p. 108, "Compounds of chlorine with every other element except F and A and other rare gases are known," whilst on p. 200 it is correctly stated that hydrochloric acid does not act on mercury, but p. 202 provides the information that "Hg . . . on coming in contact with the HCl of the gastric juice is converted into $HgCl_2$."

The quality of the instruction provided for the use of the student may be gauged from the following extracts, which represent but a fraction of the errors contained in the volume: "The acidity of a base is determined by the number of hydrogen atoms it contains"; "electricity is thought to be a form of molecular motion"; "without it (oxygen) heat and energy cannot exist"; "one volume of hydrogen can be combined with 50 of water"; "it (CO_2) gives to water its palatable taste, most noticeable when it is absent"; "inanimate objects evolve immunity when subjected to inimical circumstances." Such expressions and mis-statements would not be tolerated in the notebook of an elementary student, and it is almost incredible that such errors should be included in a text-book which has reached a second edition, and on the title-page claims to be "thoroughly revised." The next revision will require to be of a far more drastic nature before it will be possible to recommend the volume for the use of anyone except as an example of "how not to write a book."

T. J. WARD.

A LABORATORY MANUAL OF QUALITATIVE CHEMICAL ANALYSIS. By THEODORE J. BRADLEY, A.M., B.S., Ph.G. 4th edition. Philadelphia and New York: Lea & Febiger.

Professor Bradley's manual has reached its fourth edition, and therefore, presumably, has proved of value in America; it is, however, difficult to perceive in it any superiority over many other text-books of qualitative analysis in common use, and there are certain features which will hardly commend it to teachers in this country. The opening section of some twenty pages, entitled "Elementary Theory of Chemistry," is quite inadequate for giving the student any real grasp of the subject, and seems out of place in a book which claims to be a laboratory manual. The usual tests for metals and acids are fully given, but there is much unnecessary repetition of the analysis tables. It is difficult to see any advantage in the inversion of the usual procedure; the student is plunged straight away into the separation of metals in the same group, whilst directions for getting solids into solution come near the end of the book. It seems unlikely that students of pharmacy should have to detect compounds of vanadium, selenium and palladium, and not have to test for compounds of more common occurrence, yet no

instructions are given which would enable them to detect chromates and permanganates or the phosphates., etc., of the alkaline earth metals. The book, therefore, cannot be regarded as in any way preferable to those already well known to teachers.

A. F. KITCHING.

ANALYTICAL TABLES. By A. O. BENTLEY, Ph.C., and J. E. DRIVER, M.Sc.(Lond.), A.I.C. Oxford University Press. London: Humphrey Milford. 1927.

A small pamphlet giving in a compact form the usual tables for the analysis of mixtures; it is printed on one side of the paper only, the other side being left blank for notes. It should be handy for use in the laboratory.

A. F. KITCHING.

ATOMS AND MOLECULES. By Prof. R. M. CAVEN. Pp. 141. London: Blackie & Son, Ltd. 1927. Price 7s. net.

As this little book includes a separate issue of Part I and Chapter XII of the author's well-known work, "The Foundations of Chemical Theory," it needs no introduction or commendation, and is assured of a good reception. All chemists are interested in atoms and molecules, and, as the subject is now so complex, those of us who do not move in academic circles will welcome a clear, concise exposition, such as this, of recent and current doctrines. The book is, in the main, extremely lucid; the diagrams, too, are helpful in Chapter VI, though there is at times a lack of precision in some statements; for example, on p. 98 we are told that when salt is dissolved in water "the electrostatic attraction gradually gives way"; this does not convey a very clear idea of what actually happens, but it must be admitted that there is very great difficulty in being precise in matters which are yet imperfectly understood. So an occasional lapse may well be overlooked, particularly when occurring in a really good and readable little book. One sin of omission cannot be overlooked—the absence of an index.

H. E. Cox.

FERTILISERS AND SOIL IMPROVERS. By W. GARDNER. Pp. 184. 1927. London: Crosby Lockwood & Sons. Price 7s. 6d.

The author of this work, according to the preface, has endeavoured to classify and briefly describe the chief fertilisers of commerce and their value as plant food.

The opening chapter deals with soil and soil conditions, but the information given is too curtailed to be of real utility. Indeed, it is impossible to summarise existing knowledge of the soil in 20 small pages, and so, in the circumstances, some statements require qualification and others further explanation . For instance, that "nitrogen in the form of nitrate is the best nitrogenous food for plant life," may be in theory correct, but in practice the use of a nitrate may be very inadvisable. A paragraph on soil reaction at once plunges into acidities measured

as hydrogen-ion concentrations and certain P_H values are given. Such information may be intelligible and of use to the soil chemist, but, surely it is of doubtful value to most people who would be likely to use a small manual on fertilisers. It is with surprise that one reads that the application of too little fertiliser results in such a lowering of the quality of crops that they will not contain the proper amounts of albuminoids, carbohydrates and fat necessary for the animals fed on them to be sufficiently nourished. Another passage which requires qualification states that too liberal an addition of a fertiliser causes land to become sour and the crops of poor quality.

The list and description of nitrogenous, phosphatic and potassic fertilisers is comprehensive and of unquestioned utility. The amount of phosphates in the various fertilisers is sometimes given in terms of P_2O_5, and at others as $Ca_3P_2O_8$; some confusion would be obviated if authors would adopt one term or, perhaps preferably, give the phosphorus content of a fertiliser in terms of P_2O_5, and its equivalent in terms of $Ca_3P_2O_8$. The method of converting P_2O_5 into terms of $Ca_3P_2O_8$ is, of course, simple, and it seems, therefore, scarcely necessary to give the process twice on one page.

Formulæ and equations are frequently made use of in the book; and though they are of an elementary character, they appear formidable to those unaccustomed to them, and their presence will not further the popularity of the manual among farmers and gardeners for which the author hopes.

Nevertheless, the book contains much useful information.

F. W. F. ARNAUD.

MODERN CEREAL CHEMISTRY. D. W. KENT-JONES, Ph.D., B.Sc., F.I.C. Revised and Enlarged Edition. Pp. vii + 446. Liverpool: The Northern Publishing Co., Ltd. 1927. Price 25s. net.

It is no matter for surprise that within three years of the first issue of this most interesting book a new and enlarged edition should be required. The author is to be congratulated on this fact, as also that he has managed to add another 120 pages to the volume without making it unwieldy or detracting from its readable character. Its twelve chapters deal successively with (1) Wheat and Flour and their Composition (42 pp.); (2) Nutritive Value of Bread (26 pp.); (3) Cereals other than Wheat (23 pp.); (4) Colloidal Chemistry (16 pp.); (5) Hydrogen-ion Concentration (20 pp.); (6) Strength and the Colloidal Chemistry of Flour (35 pp.); (7) The Chemistry of the Baking Process (39 pp.); (8) Composition of Mill Products (21 pp.); (9) Bleaching and Flour Improvers (36 pp.); (10) Conditioning and the Effect of Heat on Wheat and Flour (21 pp.); (11) Moisture in Wheat and Flour (21 pp.); (12) Analysis of Flour, etc. (89 pp.); Appendix; Bibliography (20 pp.); and Indexes.

The book is concerned very largely with the modern methods of milling wheat, and the chemistry of white flour and bread. It is replete with tables of figures,

and with the results of the author's investigations on the materials with which the miller, the cereal chemist and the baker deal. The importance of colloidal chemistry and of hydrogen-ion concentration in connection with flour and bread-making are exemplified by the prominence given to these subjects, and the author discusses them in a comprehensive manner, beginning with the theories and principles underlying them, and passing to their possible practical applications, especially as regards the relationship of "strength" of flour to its colloidal condition. Owing to the slight knowledge of physics and chemistry of many of those for whom the book is primarily written, much elementary matter appears in these chapters, but the material is handled in an interesting way which is wholly commendable.

The chapter on the nutritive value of bread shows a strong bias in favour of white bread, which is considered superior to other breads prepared from flour of a higher extraction percentage. The views of authorities differing from the author in this respect are, however, fairly set out, and it is admitted that persons living sedentary lives may find "brown" bread of special value. The oft-repeated and erroneous statement that white flour and bread consist mainly of starch with little or no protein, is quite properly traversed by the author. Though the differences in composition between white and brown bread are appreciable, chemically they are usually very slight, and largely concerned with the content of mineral matter, fibre, and vitamin *B*. Though we do not yet know enough of the chemistry of foods to dogmatise about the respective food values of different breads, it must be agreed that, so far as our present knowledge goes, white bread, when made from pure white flour, is a good and valuable food, and need not be replaced in the varied diet of most people by any form of "brown" bread. Many persons, however, like a little of the latter variety as a change from all white bread; and, from the point of view of flavour, there is much to recommend brown bread made from flour containing a little of the finely-ground bran and germ of the wheat-berry.

When the author comes to deal with the modern methods of chemical treatment of flour, it may be permitted to differ from him, especially in view of the fact that the report on flour treatment issued last year by the Departmental Committee appointed in 1924, undoubtedly shows a preference for an untreated flour. The author is on surer ground when he discusses the truly remarkable results which he has himself obtained by the heat treatment of wheat and flour. Weak flours are those in which the proteins are in an insufficient degree of aggregation. By heating flour in an enclosed space to a high temperature, say 180° F. for ten to twelve hours, it acquires peculiar properties which render it valuable as an improver when added to untreated weak flours to the extent of about 0·7 per cent. Thus Dr. Kent-Jones has in all probability made a contribution to the problem of flour treatment which will prove to be of the greatest possible value, and may make the addition of chemical "improvers" of any kind quite unnecessary.

Although some portions of this work will make difficult reading for those with little or no chemical training, to the cereal chemist it will be of great value—a book to keep always at hand. In no other British work known to the reviewer is quite the same ground covered, and the author's intimate knowledge of the industry of which he writes make him a reliable authority. The cereal industry owes the author a debt of gratitude for putting the chemistry of wheat and flour so clearly and fully before it.

The concluding chapters on moisture in wheat and flour, and on the analysis of flour and other cereal foods, are of considerable importance. The various analytical methods form a valuable feature of the volume. There is a full bibliography to complete what is certainly an important book of outstanding merit.

ARNOLD R. TANKARD.

Publications Received.

A TEXTBOOK OF ELEMENTARY QUALITATIVE ANALYSIS. By C. J. ENGELDER. New York: Wiley; London: Chapman & Hall. Price 11s. net.

THE CHEMISTRY OF CHEMATHERAPY. By G. M. DYSON. London: Ernest Benn, Ltd. 1928. Price 32s. 6d.

CHEMICAL ENCYCLOPAEDIA. By C. T. KINGZETT. 4th Edition. London: Baillière, Tindall & Cox. 1928. Price 35s. net.

OILS, FATS AND FATTY FOODS. By E. R. BOLTON. 2nd Edition. London: Churchill. 1928. Price 30s.

RADIATION IN CHEMISTRY. By R. A. MORTON. London: Baillière, Tindall & Cox. 1928. Price 15s. net.

THE STRUCTURE OF AN INORGANIC CRYSTAL. By Sir W. H. BRAGG (Fison Memorial Lecture, 1928). London: Longmans. Price 1s. 6d.

THE MANUFACTURE OF ARTIFICIAL SILK. By E. WHEELER. London: Chapman & Hall. Price 12s. 6d. net.

PRACTICAL SEROLOGY. By L. VIGANI. Cambridge: W. Heffer & Sons. 1928. Price 12s. 6d. net.