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Deaths.

WE deeply regret to have to record the death of a Past-President of the Society:

Alfred Smetham, on October 11th,

and of the following members:

William Plenderleith Lewellen Hope, on August 28th,
Maurice S. Salamon, Member of Council, on September 19th.

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

XIII. A New Method for the Separation of Zirconium and Hafnium from Tantalum and Niobium.

BY W. R. SCHOELLER, Ph.D., AND E. F. WATERHOUSE.

(*Under the Analytical Investigation Scheme.*)

(*Read at the Meeting, October* 3, 1928.)

IN the earliest of these papers on earth-acid analysis (Section II, *J. Chem. Soc.*, 1921, **120**, 1931; ANALYST, 1922, **47**, 93), Schoeller and Powell describe a method for the separation of zirconium from tantalum and niobium, based on the action of fused potassium carbonate on the mixed oxides. The earth acids are thereby converted into soluble potassium salts, whilst the zirconia remains insoluble. In this manner a quantitative separation of zirconium from niobium was achieved after one or two fusions, but the separation from tantalum was less satisfactory, the zirconia results after three fusions being from 0·002 to 0·008 grm. too high,

and the tantalum results correspondingly low. This Section is the result of our successful endeavours to improve and supplement the earlier method; the additional method here given is the one referred to in the preceding Section (XII, ANALYST, 1928, 468).

Hafnium.—Since the first-mentioned paper was published hafnium has been proved to occur in all zirconium minerals; although comparatively abundant, it had been overlooked for so long because its deportment to all known reagents is exactly the same as that of zirconium. We may, therefore, safely assume that any procedure that separates the earth acids from zirconia will separate them from hafnia also; that being so, the term "zirconia," as used in this and other sections, applies to the oxide mixture (Zr, Hf)O_2.

It should be recorded here that the zirconia used in our tests was prepared from zircon sand, obtained as the non-magnetic fraction of the Travancore beach deposit (ilmenite-zircon-monazite). The zircon was fused with sodium carbonate and converted into zirconyl chloride by known methods (*cf.* ANALYST, 1921, **46**, 344); the re-crystallised salt, on being ignited, yielded the pure oxide (Zr, Hf)O_2.

AUTHORS' INVESTIGATION.—The incomplete separation of tantalum from zirconium by Schoeller and Powell's method must be ascribed mainly to hydrolytic decomposition of potassium tantalate when the fusion product is dissolved in water, tantalic acid being precipitated; the fact that the niobium-zirconium separation is satisfactory is readily explained by the greater stability of potassium niobate. With the experience gained in the study of the alkali salts of the earth acids (VI, ANALYST, 1926, **51**, 613), we improved the original procedure by adopting extraction of the carbonate fusion with potassium hydroxide solution, as detailed below. Still, we had to recognise that total separation by carbonate fusion would be tedious and protracted, if not impracticable. The solution of the problem lay in the discovery of an auxiliary method, *i.e.* one that would readily separate the small quantity of earth acid remaining in the zirconia residue from the carbonate fusion.

In the preceding Section (*loc. cit.*) we proved that the pyrosulphate hydrolysis method cannot serve as a reliable means for the separation of zirconia from the earth acids. We then turned our attention to the precipitation of the earth acids by tannin from slightly acid oxalate solution as a reaction on which a quantitative separation might be based, the non-interference of zirconia in the separate identification of tantalum and niobium by that reaction having been previously established by Powell and Schoeller (Sect. V, ANALYST, 1925, **50**, 495). Zirconyl oxalate is a much more stable compound than the oxalo-earth acids; it was found to resist precipitation by tannin as long as the solution remained feebly acid. At that stage oxalotantalic acid is readily and completely decomposed, with precipitation of the yellow tannin complex. Oxaloniobic acid is intermediate in stability, almost complete neutrality and a larger excess of tannin being required before it is wholly converted into the red tannin complex; at this point there is a risk of co-precipitation of zirconium. Fortunately, niobium is readily separable

by carbonate fusion, whilst, with tantalum, the position is reversed, the tannin separation succeeding where carbonate fusion fails. What has been said of tantalum applies equally to the mixed earth acids. We have now at our disposal two complementary methods for the separation under discussion.

METHOD A: TANNIN PROCEDURE. (SEPARATION OF SMALL QUANTITIES OF EARTH ACID FROM MUCH ZIRCONIA.)—The mixed oxides (as much as is thought necessary) are fused with potassium bisulphate in a silica crucible, and the product of the fusion dissolved in a saturated solution of ammonium oxalate containing approximately as much of this salt as the bisulphate taken.

The boiling liquid is treated with 0·2 grm. of tannin dissolved in hot water, and dilute ammonia (1:1) drop by drop, during constant agitation. At or before the neutral point a precipitate will be formed; if the $(Ta, Nb)_2O_5$: $(Zr, Hf)O_2$ ratio in the oxides is very low, the precipitate will be whitish or slightly discoloured (pure zirconia gives a white tannin precipitate); if the ratio is higher, the precipitate will be yellow, orange, or red (depending on the Ta:Nb ratio of the pentoxide). If so, the cautious dropwise addition of the ammonia is continued until the discoloration of the precipitate indicates incipient co-precipitation of zirconia. The beaker is left in a warm place until the liquid becomes clear; the precipitate, P^1, is then collected, washed with 2 per cent. ammonium chloride solution, and ignited in the same silica crucible.

For the precipitation of zirconia-free pentoxide, the ignited precipitate is treated in the same way as the original mixed oxides, though with less bisulphate and oxalate. The clear solution (50 c.c. or less) is stirred and neutralised, while boiling, with the dilute ammonia until a cloudiness is perceptible. This is at once removed with a minimum of hydrochloric acid (1:1). The boiling solution, once more perfectly clear, is treated with one grm. of ammonium chloride and a freshly-made one per cent. solution of tannin, which imparts at first a yellow, orange, or red coloration to the clear liquid. Further gradual addition of the reagent and boiling cause flocculation of the coloured precipitate and decolorisation of the solution. When this has taken place, further addition of tannin is undesirable; the amount required is generally below 0·1 grm. After an hour or two at 50° to 70° C. the liquid is filtered, and the precipitate, P^2, washed, ignited, and weighed as $(Ta, Nb)_2O_5$.

All the reagents used should, of course, be free from lime; such contamination is indicated by a pulverulent residue of calcium oxalate when the bisulphate fusion of P^1 is dissolved in the oxalate solution. If present, it is filtered off at that stage. Complete precipitation of the earth acids may be tested for by re-treatment of the boiling filtrate from P^2 with a little more tannin and a drop of ammonia, if necessary; this should produce no change or only a whitish zirconium precipitate. The freedom of the earth-acid precipitate from zirconia may be ascertained by a third precipitation (P^3) or, if considered necessary, by carbonate fusion (Method B).

RESULTS OF TEST ANALYSES.—The table below gives the results of twelve consecutive test separations of quantities of oxides unknown to the operator, and

comprising three series of four tests with tantalic, niobic, and mixed (61·4 Ta_2O_5: 38·6 Nb_2O_5) oxides, respectively.

Exp.	M_2O_5.	ZrO_2.	P^1.	P^2.	P^3.	M_2O_5 Error.
Ta 1	0·0046	0·2684	—	0·0048	—	+0·0002
,, 2	0·0122	0·2218	—	0·0124	—	+0·0002
,, 3	0·0030	0·4190	0·0058	0·0033	—	+0·0003
,, 4	0·0047	0·3485	0·0068	0·0043	—	−0·0004
Nb 5	0·0035	0·3385	0·0105	0·0053	0·0031	−0·0004
,, 6	0·0071	0·2023	0·0133	0·0107	0·0065	−0·0006
,, 7	0·0055	0·1004	0·0358	0·0069	0·0061	+0·0006
,, 8	0·0016	0·3686	0·0474	0·0032	0·0030	+0·0014
EA 9	0·0019	0·3067	0·0239	0·0029	—	+0·0010
,, 10	0·0064	0·1022	0·0242	0·0064	—	0·0000
,, 11	0·0030	0·2004	0·0070	0·0032	—	+0·0002
,, 12	0·0044	0·2052	0·0118	0·0050	—	+0·0006

In Exps. 1 and 2 we applied Procedure *B* of the tantalum-niobium separation (ANALYST, 1925, **50**, 490), *i.e.* collection of the bulk of the tantalum as the zirconium-free yellow precipitate, and re-adjustment of the filtrate with dilute ammonia; the weight given under P^2 is that of P^1+P^{1a} (the latter very subordinate). This procedure answers quite well for tantalum, but not for niobium.

ACCURACY.—In actual practice it is unnecessary to weigh P^1. It was done here for the purpose of demonstrating the elimination of the bulk of the zirconia by the preliminary precipitation.

An analysis of the above results shows the tantalum-zirconium separation to be reliable. In the earth-acid series the first result (No. 9) is unduly high; the others are good, with a general tendency towards positive errors. As regards the niobium-zirconium separation, the operator had to be advised in each case to re-treat P^2 so as to reduce the positive error, with results as above. Therefore, the tannin reaction is rather uncertain for the quantitative separation of zirconia from tantalum-free niobic oxide; but it must not be forgotten that it will be used in conjunction with the carbonate fusion method, which is quite satisfactory in that special case.

The great advantage of our process is, that it constitutes a most delicate test for the smallest quantities of earth acid in zirconia, thanks to the coloured precipitates produced and the preliminary concentration of the earth acid in P^1.

The tannin and earth acid precipitate being very bulky, we prefer to separate zirconia from quantities of earth acid exceeding 0·02 to 0·03 grm. by a procedure embodying the two complementary methods applied in the following order: (1) Potassium carbonate fusion (single or double); (2) tannin process. The improved carbonate fusion will now be described.

METHOD B: POTASSIUM CARBONATE FUSION. (SEPARATES ANY QUANTITY OF ZIRCONIA FROM MUCH EARTH ACID.)—The mixed oxides are fused with six parts of potassium carbonate in a platinum or gold crucible over a blast burner. The mass is allowed to solidify against the sides of the crucible and to disintegrate

completely by digestion with a ½ inch-stick (about 1 grm.) of pure potassium hydroxide and enough water to cover the melt (1 to 2 hours in the covered crucible on a hot plate). The crucible contents are transferred with water to a small beaker; filter pulp is well stirred into the turbid liquid, which is then filtered. The first portion of the filtrate may be cloudy, but is readily cleared by being poured once more through the filter. The zirconia residue, after thorough washing with 2 per cent. potassium carbonate solution, is ignited in the crucible previously used. If heavy and derived from a mixture rich in tantalic oxide, it is submitted to another carbonate fusion followed by the operations so far described.

The alkaline filtrate (or combined filtrates) is acidified with hydrochloric acid and boiled with a very small excess of ammonia; the precipitate, *CP*, is mixed with filter pulp, collected, washed with dilute ammonium nitrate solution, ignited, digested with hot water acidulated with hydrochloric acid, again collected, ignited strongly, and weighed as $(Ta, Nb)_2O_5$.

The zirconia residue from the carbonate fusion is ignited in the platinum crucible, moistened with dilute sulphuric acid, and dried; it is then fused with bisulphate and the product dissolved in ammonium oxalate solution. The liquid is poured through a small filter for the removal of slight quantities of impurities (*e.g.* silica), after which, it is submitted to the tannin process (Method A). The balance of M_2O_5 is thus obtained as the small precipitate TP^2.

The direct determination of the zirconia offers no advantages over the determination by difference where it forms a substantial proportion of the mixed oxides. Small quantities should, of course, be actually determined: to this end the combined filtrates from the two tannin precipitations are evaporated with sulphuric and nitric acids for the destruction of the oxalate and tannin (*cf.* Moser and Niessner, ANALYST, 1928, **53**, 401). The residual sulphate liquor is diluted, filtered, and the zirconia precipitated by hydrolysis with thiosulphate after sodium carbonate neutralisation.

RESULTS OF TEST SEPARATIONS.—Four separations were made of quantities unknown to the operator; the very small deviations observed prove that the object of this investigation—an improved separation of zirconia from the earth acids—has been accomplished.

	Taken.					Found	M_2O_5
Exp.	M_2O_5.	ZrO_2.	No. of K_2CO_3 fusions.	*CP*.	TP^2.	M_2O_5.	Error.
Ta 13	0·2400	0·2770	2	0·2366	0·0038	0·2404	+0·0004
,, 14	0·3060	0·2030	2	0·3010	0·0046	0·3056	−0·0004
,, 15	0·1049	0·2338	1	0·0955	0·0087	0·1042	−0·0007
EA 16	0·2154	0·3160	1	0·2110	0·0049	0·2159	+0·0005

SUMMARY.—A new method is described for the separation of small quantities of earth acids from large amounts of zirconia (hafnia). The process is based on the precipitation of the oxalo-earth acids by tannin in weakly acid solution, zirconyl oxalate remaining dissolved. The method described in an earlier Section—fusion of the mixed oxides with potassium carbonate—has been perfected, with

the result that a single fusion may be sufficient for the separation of the bulk of the earth acids. The balance is then separated from the zirconia residue by the tannin procedure. This is a delicate test for the detection of the smallest quantities of earth acids in zirconia.

The authors and their collaborators have much pleasure in acknowledging a generous grant made by the Analytical Investigation Scheme Committee of the Society of Public Analysts, which is being used to defray part of the cost of these investigations. Messrs. Daniel C. Griffith and Co. also have given financial support in the acquisition of material.

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The Fatty Acids of Egyptian Butter Fats.

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

IT has been pointed out by Trimen (ANALYST, 1913, **38**, 242), that the examination of butter fat in Egypt presents difficulties which are not ordinarily met with by the food chemist.

Thus a glance at the following figures, quoted from analyses made by Lucas*, Hogan and Griffiths-Jones,* Trimen, Knowles and Urquhart (ANALYST, 1924, **49**, 509), and from analyses made recently in this laboratory, will show the limitations of the Reichert–Meissl and Polenske figures:

Butter.	Reichert–Meissl value limits.	Polenske value limits.	Ratio (mean) 100 Polenske value / Reichert–Meissl value.
Gamoos ..	24–37	0·8–2·8	4·8
Cow	21–32	1·2–3·0	8·0
Goat	20–28	4·0–8·7	23·5
Syrian samn (sheep?)	24–31	4· –8	22·0

It is evident then that the ratio of Muntz and Coudon (see Lewkowitsch, Vol. II) will afford little help. In fact, taking his ratio 12·0 as a limit for a genuine butter, it is possible to add 10 per cent. of coconut oil or more of palm kernel oil to an average sample of gamoos butter without the adulteration being detected by this method. Goat butter and Syrian samn, on the other hand, would appear (judged by the results of the method) to contain one of these oils. Kirschner's method, excellent as it is in detecting small quantities of butter in margarines, fails equally here; for, even if the Kirschner number were equal to the whole of the

* Lewkowitsch, *Chemical Technology of Oils, Fats and Waxes*, Vol. II (butter).

Reichert–Meissl value in a sample of goat butter, the Polenske value would fall outside the Kirschner limit for a pure butter.

My aim has been to find a "butter constant" which varies within narrow limits in butters of different types, and which is appreciably altered by the addition of a small proportion of coconut and palm kernel oil.

It was considered at first that the butter acids whose magnesium or barium salts were insoluble in water might be a useful starting point, but as the magnesium and barium salts of capric acid, which appears to be a variable constituent of butters of different type, are practically insoluble in cold water, this was abandoned, and the following procedure substituted:

The acids have been sorted out into the following four groups, which naturally show no definite lines of demarcation between any two acids, with the exception of oleic acid:

(1) Volatile acids distilled from 1 grm. of saponified fat with 210 c.c. of water* (acidified) (AD. See the chart). (2) Acids insoluble in aqueous alcohol of a definite strength at 15° C.—EF. (3) Oleic acid—DE. (4) Residual acids—FO.

(1) Separation of Volatile Acids.—Taking a glance at the chart, it will be seen that when 1 grm. of saponified coconut oil is distilled with 210 c.c. of water, the acids distilled require about 93 mgrms. of potassium hydroxide for neutralisation. Now, comparing this with the value in Table III, calculated from the results of Elsdon (see Lewkowitsch, Vol. II), the total acids below lauric acid would require 71 mgrms. of potassium hydroxide for neutralisation, and, therefore, roughly speaking, the whole of the caproic, caprylic and capric acids are volatilised, and the greater part of the lauric acid remains in the non-volatile portion.

In the case of cow's butter, the proportion of volatile acids is about 50; and as the acids up to and including capric acid, calculated from the results of Holland and Buckley (Lewkowitsch, Vol. II), account for about 35 mgrms. of potassium hydroxide (see Table III), these acids, and some of the lauric acid, are volatilised. The procedure is on the same lines as the Reichert–Meissl method, but with the following quantities:—1 grm. of fat, weighed accurately within 2 or 3 mgrms.; 10 grms. of glycerin; 1 c.c. of 50 per cent. sodium hydroxide solution.

After saponification, 110 c.c. of boiled distilled water, pumice, and 25 c.c. of 2·5 per cent. (v/v) sulphuric acid are added; 110 c.c. are distilled in the usual way, and the distillate transferred to a stoppered flask of about 600 c.c. capacity. The 110 c.c. flask is then replaced below the condenser, 100 c.c. of boiled water added to the residue in the distillation flask, and another 100 c.c. distilled. Meanwhile, the first distillate is titrated with $N/10$ sodium hydroxide solution, which is added in excess to the extent of about 1 c.c. after shaking, and is then heated on the hot plate with loosely fitting stopper, to melt the water-insoluble acids that are yet to be neutralised. The second 100 c.c. distillate is poured in, the solution

* This volume is not claimed as being preferable to, say, 200 or 220 c.c., and the difference between the volatile acids in the 3 cases would be almost negligible. The volume 210 c.c. was chosen because the 110 c.c. distilled in a Reichert–Meissl apparatus were not sufficient, and another 100 c.c. were distilled.

again titrated with sodium hydroxide to a slight excess, and about 1 c.c. of approximate normal neutral solution of calcium chloride added. The object of this addition is two-fold: It prevents frothing, and also, by precipitating the higher acids, prevents hydrolysis of the soaps. The titration is then completed, with vigorous shaking, until just pink, the 110 c.c. flask and the condenser are washed with the warm neutral solution, the washings being returned to the large stoppered flask, and the end point finally arrived at after vigorous shaking.

From this result is deducted the blank value determined on the glycerin and sodium hydroxide solution, and the result, multiplied by 5·6, gives the total volatile acids in term of mgrms. of potassium hydroxide.

(2) Acids Insoluble in Aqueous Alcohol.—This is the basis of many other methods of analysis of butter fat, but many of the drawbacks to these methods have, it is hoped, been avoided.

The strength of the alcohol and the temperature have been chosen as closely as possible to precipitate the stearic acid and the greater part of the palmitic acid, and to leave in solution practically all the oleic, myristic and lower acids.

The alcohol used is redistilled from potassium hydroxide, and has a specific gravity of 0·814 (about 95·5 per cent. by volume), and this alcohol is used for the preparation of $N/2$ alcohol potassium hydroxide by dissolving in it the sticks of anhydrous potassium hydroxide, without addition of any water. The filtered solution is adjusted to approximately $N/2$ by the addition of redistilled alcohol, and allowed to stand at least 24 hours before use. Five grms. of fat are then saponified with 50 c.c. of this solution in the usual way.

The alcoholic solution is now titrated with N hydrochloric acid, giving the saponification value, and the addition of normal acid is continued until sufficient has been added to neutralise the alcoholic alkali originally used. The solution is transferred to a 100 c.c. flask, with the aid of about 12 c.c. of alcohol, and then enough water is added to bring the total volume of added water (*i.e.* N hydrochloric acid and water) to 34 c.c.

The warm solution will be slightly less than 100 c.c., and will be quite clear on shaking. It is cooled with gentle rotation in a water bath at 17–18° C. for 15 minutes, made up to 100 c.c. with alcohol, shaken vigorously, and cooled at 14–15° C. for 45 minutes.

With alcohol of this concentration the insoluble acids separate as beautiful shining crystals, unless the oleic acid content is abnormally high, in which case the separation of saturated acids is preceded by a turbidity. A slight divergence from the correct ratio of alcohol to water does not, at this concentration, make a great difference. For instance, with a cow's butter having an iodine number of 35, the addition of 34 c.c. of water precipitated acids equivalent to 63 mgrms. of potassium hydroxide, whilst 35 c.c. of water precipitated acids equivalent to 65 mgrms. of potassium hydroxide.

These acids in the ordinary way are rejected, and the amount determined by difference, but in a determination on a cow's butter, with an EF value of 66, the

acids were filtered off by suction, and pressed thoroughly between filter paper, and then gave, on analysis, a molecular weight of 267, and iodine value of 6·6, corresponding to a mixture of palmitic, stearic and oleic acids in the following proportions, calculated as percentages on the original fat:—Palmitic acid, 19·0; stearic acid, 10·3; and oleic acid, 2·3 per cent. (Compare the results of Holland and Buckley: Palmitic acid, 19·23; stearic acid, 11·4 per cent.)

After 45 minutes the flask, cooled to 14–15° C., is again vigorously shaken, the contents filtered rapidly through a dry folded filter paper, and the insoluble acids rejected. If the atmospheric temperature is more than 2 or 3 degrees higher than 15° C., the filtration is conducted in a low temperature incubator.

Ten c.c. of the clear filtrate are titrated with $N/10$ sodium hydroxide solution, giving the "soluble acids." The end-point is disturbed somewhat by hydrolysis, but, as different butters are affected to approximately the same extent, and since all results are expressed in whole numbers, no greater accuracy than 0·1 c.c. of $N/10$ sodium hydroxide solution is required, and no important error is introduced. The titration figure, multiplied by $2 \times 5{\cdot}6$, gives the soluble acids, expressed in mgrms. of potassium hydroxide, and the difference between this and the saponification value gives the "insoluble acids" (EF).

(3) Oleic Acid.—Ten c.c. of the filtrate are run into a stoppered iodine flask and the iodine value determined by the Wijs method, a blank determination being made on 5 c.c. of alcoholic potassium hydroxide, 1 c.c. of distilled alcohol, and enough N hydrochloric acid to neutralise the alkali. No difficulty arising from the use of alcohol has been met with, and not only do coconut and palm kernel oils (the insoluble acids of which are *nil*), give practically the same iodine value, when determined in this way, as on the original oil, but known mixtures of butter with these oils also give iodine values agreeing closely with the calculated amounts, as is seen in the following table:

Table I.

	Saponification value.	D.E. Oleic No.	E.F. Insol. acids.	D.F. Sum.	Decrease per 10 per cent. coconut oil.
Butter I, pure	226	69	78	147	—
,, containing 10 per cent. coconut oil	230	64	70	134	13
,, ,, 30 ,, ,, ,, ,,	235	54	51	105	14
,, ,, 60 ,, ,, ,, ,,	245	40	27	67	13
					calculated=13.
Butter II, pure	232	73	70	143	—
,, containing 10 per cent. palm kernel	233	69	64	133	10
,, ,, 20 ,, ,, ,, ,,	235	66	55	121	11
,, , 30 ,, ,, ,, ,,	236	63	49	111	11
					calculated=11.

It appears, then, that addition of coconut oil or palm kernel oil to a butter fat will reduce the sum (D.F. Acids) by 11 to 13 units for every 10 per cent. of added oil, and if these acids were constant in samples of pure butter fat, these two figures alone would be sufficient. Unfortunately this is not the case, and, in general, the number decreases in the order gamoos, cow, sheep and goat butters, while abnormal iodine values also introduce complication, as is seen in Table II. Fortunately, however, the butters which have a low "D.F." value have also a low value for non-volatile acids "D.O.," and the difference, which is the residual acids "F.O.", is a fairly concordant value for all these butters.

Since the non-volatile acids for coconut and palm kernel oils are respectively 164 and 173, and the mean value for cow's butter is about 178, it might be concluded that addition of a small proportion of one or other of these oils to a butter would not make very much difference to this value, and this actually is the case. In fact, the presence of the non-volatile acids appears to depress the vapour pressure of the volatile acids of the coconut oil to such an extent that the non-volatile acids of the mixture are in most cases actually higher than those of the pure butter fat, as is seen in Table II.

Table II gives the results of these determinations on a few fats of each type and of mixtures of known composition. It is admitted that considerably more samples of every type must be examined before any definite limits can be laid down for genuine butter fats, and, since it has not yet been possible to make experiments on the butter fats of animals which have been artificially fed, particularly on substances rich in coconut or palm kernel oil, the effect of these foods on the "F.O." acids number is yet to be investigated. In spite of this, however, the value of this number is not lessened in a country like Egypt, where the milk fats of all these animals are sold as butter fat.

VARIATION IN BUTTERS OF DIFFERENT ANIMALS.—My aim has been to take cases as extreme as possible as regards the values usually determined, particularly the Reichert–Meissl, Polenske ratio, which has so often been claimed as superior to any of the methods subsequently put forward.

The extreme cases in Table II are:

	Reichert–Meissl value.	Polenske value.	100 Polenske R.–Meissl ratio.	F.O. residual acids.
Goat III	21·9	6·0	27	37
Syrian samn 2	27·9	6·5	23	34
Gamoos 1	30·8	1·2	4	35
Gamoos 3	33·2	1·3	4	38

Compare with these the mixtures:

Gamoos 4 with 20 per cent. palm kernel oil	27·8	2·8	10	55
„ 5 „ 40 „ „ „ „ „	21·0	4·1	19·5	79

TABLE II.

BUTTER.	Reichert-Meissl value AB 5/5.6	Polenske value BC 5/5.6	Saponification AO	Total Volatile Acids AD	Non-Volatile Acids DO	Oleic Acid DE	Insoluble Acids EF	Sum DF	Residual Acids FO	
Cow:										
Australian I. ..	29·9	2·3	229	51	178	74	66	140	38	
,, II. ..	27·9	1·4	226	49	177	74	63	137	40	
,, III. ..	27·7	2·1	228	48	180	76	67	143	37	
Danish	27·9	2·1	228	46	182	83	61	144	38	
Egyptian I. ..	27·3	1·9	229	54	175	65	75	140	35	
,, II. ..	—	—	226	43	183	81	67	148	35	
,, III. ..	26·3	2·7	226	44	182	81	62	143	39	
Gamoos:										
I. ..	30·8	1·2	226	44	182	69	78	147	35	
II. ..	27·9	1·4	224	44	180	75	74	149	31	
III. ..	33·2	1·3	232	55	177	65	74	139	38	
IV. ..	30·1	1·3	226	47	179	80	68	148	31	
V. ..	32·0	1·8	226	47	179	80	68	148	31	
VI. ..	35·6	2·0	232	54	178	73	70	143	35	
Goat:										
I. ..	21·9	6·0	235	70	165	64	64	128	37	
II. ..	22·9	4·6	229	55	174	81	55	136	38	
III. ..	24·0	4·1	228	55	173	72	66	138	35	
Syrian samn:										
I. ..	30·6	6·8	242	73	169	73	59	132	37	
II. ..	27·9	6·5	234	63	171	73	64	137	34	
III. ..	29·1	3·9	233	59	174	63	75	138	36	
IV. ..	29·2	6·6	240	70	170	67	69	136	34	
Cheese:										
Roquefort ..	28·4	5·2	240	71	169	69	61	130	39	
Salonica ..	28·0	5·8	236	59	177	82	57	139	38	
									Mean = 36	
Beef fat: ..	—	—	198	4	194	74	106	180	14	
Coconut oil: ..	—	—	257	93	164	18	—	18	146	
Palm kernel oil ..	—	—	245	72	173	35	—	35	138	
MIXTURES.										Calculated percentage added oil FO − 36 / 1·2
Gamoose:										
VI + 10 Palm kernel	32·5	2·7*	233	53	180	69	64	133	47	9
VI + 20 ,,	29·4	3·3*	235	53	182	66	55	121	61	18
V + 10 Coconut	30·1	2·5*	230	50	180	74	61	135	45	8
V + 40 Palm kernel	21·0	4·1	234	52	182	62	41	103	79	36
I + 30 Coconut	—	—	235	55	180	54	51	105	75	33
IV + 20 Palm kernel	27·8	2·8*	230	50	180	71	54	125	55	16
Cow:										
A_3 + 10 Coconut	—	—	231	49	182	70	60	130	52	13
Gamoose:										
VI + 15 Beef fat 15 Palm kernel	26·0	2·6*	230	48	182	62	71	133	49	11

* Genuine butters according to Polenske's limits.

TABLE III.

MILLIGRAMMES OF POTASSIUM HYDROXIDE REQUIRED TO NEUTRALISE THE ACIDS OF ONE GRM. OF FAT.

Acids.	Coconut oil. (Elsdon, see Lewkowitsch, Vol. II.)			Butter. (Holland and Buckley.)		
Butyric ..	–	AB=8	AD=93	20	AB=31	AD= 43–51 cow 44–55 gamoos 55–70 goat
Caproic ..	9	BC=19		6		
Caprylic ..	32			4	BC=2	
Capric ..	30			6		
Lauric ..	117			19		
Myristic ..	45	EF=Nil		56	EF=63–75	
Palmitic ..	14			42		
Stearic ..	9	DE=18		22	DE=63–80	
Oleic ..	4			54		
Total ..	260			229		

The chart, drawn from mean values of butters of each type, shows at a glance how far the so-called constants vary in butter of different animals. The value S.B. is the "Silver Insoluble Value," and is arrived at by adding to the neutral solution, after determination of the Reichert–Meissl value, 2 drops of $N/10$ sulphuric acid and 10 c.c. of $N/10$ silver nitrate solution, making up to 200 c.c., leaving for about 20 minutes, with frequent shaking, filtering 100 c.c. through a dry filter paper, and determining the excess of silver by the Volhard method. A blank determination is made on the reagents in the absence of butter fat, and the difference, multiplied by $2 \times 11/10$, gives the silver insoluble value. The sum of this value and the Polenske value is of the same order as Blichfeldt's value, but a greater divergence is shown when the silver insoluble value is expressed as a percentage on the Reichert–Meissl value, giving a ratio which is not widely affected by addition of oils having no Reichert–Meissl value:

Cow's butter gives a percentage between 4·5 and 7, with a mean value of 6
Gamoos ,, ,, ,, ,, ,, 2 and 4·5, ,, ,, ,, ,, ,, 3
Goat's ,, ,, ,, ,, ,, 10·5 and 14·5, ,, ,, ,, ,, 12
Coconut oil gives a percentage about 70

The main fact brought out by the chart is that the difference between the total volatile acids and the volatile acids of the Reichert–Meissl process is less in cow's butter than in sheep or goat's butter, and, in general, they are present in still smaller quantity in gamoos butter, so that any method of analysis which does

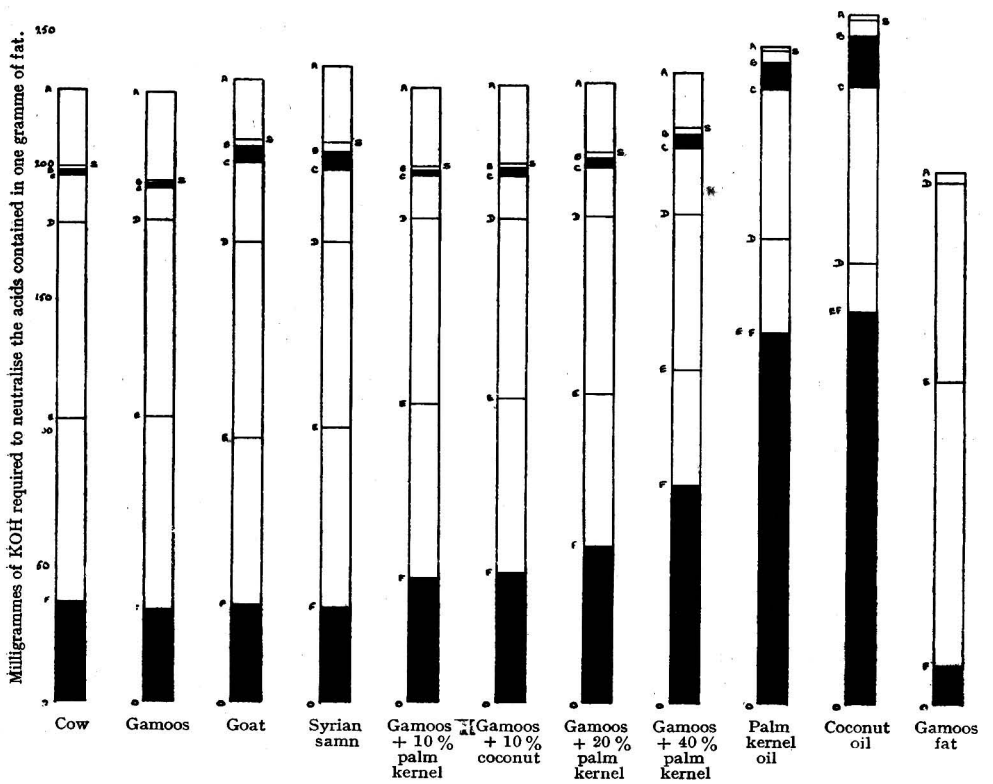
not take into account this fact will break down when the source of the butter is not known.

A comparison of some of the values in the chart, with those of some of the methods already put forward, would not be out of place here.

THE ACIDS OF EGYPTIAN BUTTER FATS

COMPARED WITH THOSE OF COCONUT AND PALM KERNEL OIL.

AO	Total acids.	= Saponification value.
AB	Water-soluble acids.	= Reichert-Meissl value × 5·6/5·0.
BC	Volatile acids insoluble in water.	= Polenske value = 5·6/5·0.
AD	Total volatile acids.	One grm. saponified fat distilled with 200 c.c. water.
EE	Oleic acid.	= Iodine value × 250/127.
EF	Acids insoluble in 62 per cent. aqueous alcohol at 15° C.	
FO	Residual acids.	



BLICHFELDT'S METHOD.—The figures are of the order of the "S.C." values of the chart (*i.e.* silver insoluble value+Polenske value).

His results are:

	Silver sol.	Silver insol.	Total.
Butter	29	3	32
Coconut oil ..	4	16	20

Compare with these the "S.C." values [reduced to the same units]:

	Volatile acids, minus SC.	SC.	Volatile acids.
Cow's butter	28·5	3·5	32
Coconut oil	2·5	21·5	24
Gamoos butter ..	29·5	2·5	32
Goat's butter.. ..	19	8	27
Syrian samn ..	25·0	10	35

FENDLER'S METHOD.—The value DF of the chart is of the order of the acids remaining insoluble in aqueous alcohol in this method, and as he starts with the non-volatile acids remaining after determination of the Reichert–Meissl and Polenske values, the value OC—DF should be of the same order as his numbers when reduced to the same units.

His numbers are: Butter, 40–48; coconut oil, 192–205.

Compare the value OC—DF, multiplied by 5/5·6: Cow's butter, 48; gamoos butter, 41; coconut oil, 193; goat's butter, 58.

SHREWSBURY AND KNAPP'S METHOD.—The same criticism applies to their results, since the acids lower than lauric acid will remain in solution in the aqueous alcohol.

CASSAL AND GERRANS' METHOD.—The value, total volatile acids, minus Reichert–Meissl acids, *i.e.* BD should be comparable with their values.

Their numbers are: Butter, 15; coconut oil, 66.

Compare:

	BD.	Ratio, taking cow's butter as 15.
Cow's butter	20	15
Coconut oil	85	64
Gamoos butter	15	12
Goat's butter	36	27

EWERS' METHOD.—That the barium- and magnesium-soluble acids remaining unextracted by petroleum spirit are of the same order as those remaining in solution in the presence of silver nitrate (see p. 526) is shown by the following results, calculated from the Reichert–Meissl and barium soluble values of 19 butters quoted by Bolton and Revis ("Fatty Foods," p. 126), and for coconut oil in the same work, the units being calculated as c.c. of $N/10$ solution per 4 grms. of fat.

The proportion of the Reichert–Meissl acids remaining in solution in presence of silver nitrate is calculated from the mean values quoted on page 526. The results for sheep and goat's butters are calculated from the Reichert–Meissl values and barium-soluble values of Trimen (ANALYST, 1913, **38**, 242).

Ewers' results are:

	Water soluble.	Petroleum spirit sol.	Sum.	Difference.
Butter	18–21	7·7–10·1	25·5–30·4	+11
Coconut oil	1·3–1·4	25·3–25·9	26·7–27·2	−24

RESULTS CALCULATED FROM THE FIGURES OF BOLTON AND REVIS AND FROM TRIMEN.

	Silver sol.	Barium sol. minus silver sol.	Sum barium soluble.	Difference.
Cow's butter	23	9	32	+14
Coconut oil	1·8	28·2	30	−26·4
Gamoos butter	25·5	6	31·5	+19·5
Goat's butter	16	10·5	26·5	+5·5

To summarise the above results, the values regarded as constants for cow's butter may be arranged as follows:

Reichert–Meissl, Kirschner, Gilmour* } Palm-kernel oil, coconut oil, butter of sheep, goat, cow, gamoos.

Polenske, Blichfeldt, Ewers, Cassal and Gerrans, Muntz and Coudon's ratio, Fendler, Shrewsbury and Knapp } Butters of gamoos, cow, sheep and goat, palm-kernel, coconut oil

In confirmation of the above summary, numerical determinations were made on:

(1) Pure cow, or gamoos butter.
(2) Cow or gamoos butter, containing 10 per cent. of coconut oil.
(3) Syrian samn, or goat butter,

by the methods of Kirschner, Ewers, Fendler, and Shrewsbury and Knapp, and in every case butter No. 3 appeared to contain more coconut oil than mixtures No. 2.

Sheep and Goat Butter.—It has not yet been possible to obtain authentic specimens of sheep butter; and, though Syrian samn is supposed to consist almost entirely of this fat, there is no proof that goat's butter is absent. Consequently, sheep and goat have been grouped together, and no attempt at differentiation can be made until several specimens of pure fat can be obtained.

Animal Fat.—Column 11 of the chart shows the acids of beef fat examined in the same way as butter fats, and the residual acids (FO) were found to be 14. Consequently, admixture of animal fat with butter fat would tend to lower the residual acids value. The decrease, however, is slight, unless the animal fat is present in sufficient proportion to make its presence known in other ways.

* ANALYST, 1925, **50**, 272.

Consequently, a mixture in equal proportions of coconut oil and beef fat, which is a common adulterant, and which has little effect on the refractive index, saponification value or iodine value, would increase the value of the F.O. number by about 80 per cent. of the amount due to the addition of coconut oil alone.

SUMMARY.—(1) The usual analytical methods, including Reichert–Meissl value, Polenske value, saponification value, iodine number and refractive index, do not supply sufficient information to lead to a conclusion as to the purity of a butter fat when the origin of the fat, whether from the milk of the gamoos, cow, sheep or goat, is not known.

(2) Analyses based on the Polenske value, or the ratio of this value to the Reichert–Meissl value, give widely divergent results in the butter fats of different animals; and, while sheep and goat's butter appear to contain coconut or palm kernel oil, it is possible, on the other hand, to add an appreciable proportion of one of these oils to individual samples of gamoos butter, without its presence being detected by this method.

The same criticism applies to the methods of Kirschner, Blichfeldt, Ewers, Cassall, and Gerrans and Gilmour.

(3) Analyses based on the solubility of the water-insoluble acids (Shrewsbury and Knapp), or of the non-volatile acids (Fendler) in aqueous alcohol, necessarily give results varying in the same order, since the acids which differentiate the butter fats of sheep and goat from those of cow and gamoos (*i.e.* caprylic and capric acid) are soluble in the aqueous alcohol. Furthermore, the results are complicated by the appreciable solubility of oleic acid in aqueous alcohol.

(4) It has been found that when 1 grm. of saponified fat is distilled with 210 c.c. of water the titration value of the non-volatile acids obtained by subtracting that of the volatile acids, expressed in mgrms. of potassium hydroxide, from the saponification value, is, in general, lower in the butter fats of sheep and goat than in those of cow and gamoos.

(5) If the sum of the two values, oleic acid and acids insoluble in 62 per cent. aqueous alcohol, is subtracted from the non-volatile acids, a number is obtained (residual acids) which is, within reasonable limits, constant for the butter fat of all these animals.

(6) Addition of coconut oil or palm kernel oil has little effect on the non-volatile acids, but decreases the "sum" mentioned in paragraph 5 to an extent practically in proportion to the amount present, and the residual acids are increased by about 12 units for every 10 per cent. of added oil.

(7) Addition of beef fat decreases the residual acids by about 2 units for every 10 per cent. of added fat, but, as this effect is comparatively small, the increase due to the presence of coconut or palm kernel oil is perceptible in a mixture of the two with butter fat.

(8) The purity of a butter fat having been established by this method, its origin can be deduced from almost any of the results cited on page 529, and, in particular, from the Polenske and Reichert–Meissl ratio, or the "insoluble silver value (page 526).

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 DETERMINATION OF VANADIUM IN STEEL.

In my test experiments on the method of Evans and Clarke (ANALYST, 1928, 475), I have obtained excellent results with an alloy steel containing chromium, molybdenum, tungsten, nickel and cobalt, in addition to vanadium. It is unfortunate that many commercial steels contain considerable quantities of nickel, because, according to the description of the process, nickel ferrocyanide is practically unfilterable, and is therefore removed by means of glyoxime. I found that the glyoxime precipitate, obtained from a solution containing all the other metals, could not be readily filtered off, and was not easy to wash. Hence, in the case of an alloy steel containing about 0·5 per cent. each of vanadium and nickel, together with cobalt, molybdenum, chromium and tungsten, I decided not to remove the nickel, and found that the filtration from the mixture of the two ferrocyanides was less difficult than from vanadium ferrocyanide alone. In this experiment, however, I did not use a pulp filter, as recommended, but *two* Munktell 15 cm. filters on a ribbed funnel.

F. IBBOTSON.

DEPARTMENT OF APPLIED SCIENCE,
UNIVERSITY OF SHEFFIELD.

THE KEEPING PROPERTIES OF SPECIFIC ANTI-SERA FOR THE PRECIPITIN TEST.

In view of Mr. Shrewsbury's interesting note (ANALYST, 1928, 380) on the keeping properties of anti-sera in hot climates, our experience in Cairo may be worth recording.

We have in our laboratory a few specimens of anti-sera, prepared by the Lister Institute and despatched by them to Cairo on June 5th, 1923. The anti-sera are, of course, in sealed ampoules, each containing 1 to 1·5 c.c. For nearly five years they were kept in an old-fashioned ice-chest, in which the summer temperature was frequently as high as 15° C. Only within the last few months have they been transferred to a modern refrigerator.

They have been tested periodically during this time, and every specimen has been found potent and specific. The latest test was made on a sample of anti-fowl serum on August 10th, 1928, and a very definite reaction was obtained in a capillary tube with a solution of fowl-blood serum diluted to 1 in 2000 of normal saline. The zone was plainly visible after about 17 minutes.

This titre, admittedly, falls far below the standard set by some workers, but, in our experience, such anti-sera can be used with confidence, provided that there is no suspicion of a reaction with sera of other blood diluted to 1 in 50; and provided that controls with other anti-sera of at least equal sensitiveness and specificity are rigidly applied.

We have this year purchased from another manufacturer anti-sera which were quite useless when they reached Egypt, although some of the consignments were

sent in winter, and others, sent later, were most carefully packed and forwarded in cold storage, arriving almost ice-cold.

Other specimens, sent in May by a Continental maker, without any special precautions, were, owing to a mistake on the part of the local agent, kept in an office at a temperature of, probably, 30° to 35° C. for about twelve days before they reached me. The titre was then 1 in 2000 in less than 20 minutes, and the specificity of all samples was good, except that there was some danger of confusing sheep- and cow-blood at high concentrations (1 in 50).

It would appear, therefore, that temperature variations are not in themselves sufficient to cause instability in anti-sera; and that certain samples (possibly owing to imperfect sterilisation), are unstable, in spite of the utmost precautions against temperature changes.

FRANK BAMFORD.

CHEMICAL LABORATORY
MEDICO-LEGAL DEPARTMENT, CAIRO.

METHYLENE BLUE FOR THE MILK REDUCTASE TEST.

THE dye generally recommended for this test is supplied by Messrs. Blauenfeldt and Tvede in tablets; one of these makes 200 c.c. of solution, and 1 c.c. of solution is used per 40 c.c. of milk in the test. Hence practical dairymen can easily dissolve and use the dye. The provision of these tablets has caused some confusion in the minds of chemists. Thus Arup (1913) advises the use of a 0·35 per cent. solution of pure methylene blue in water, and Davies (1928) refers to a standard solution of methylene blue, roughly 0·3 per cent.

When used as prescribed, these tablets yield a solution equivalent to a 0·02 per cent. solution of medicinal methylene blue, which is also the equivalent strength of the solution used in the official New Zealand test (ANALYST, 1926, **51**, 459).

For some years now we have been using in this laboratory a solution of the British Drug Houses methylene blue standard stain, and our experiments indicate that the working strength of the dye solution may vary to a considerable degree without appreciably affecting the results of the milk tests.

For a discussion of the value of this test as a substitute for bacterial counts in the grading of milk, see Löhnis and Fred (*Agricultural Bacteriology* (1923), pp. 172–174).

D. W. STEUART.

LABORATORY, MAYPOLE MARGARINE WORKS,
SOUTHALL.

A CURIOUS CASE OF ANTIMONY POISONING.

THE proprietors of a large general store, in Newcastle, decided, during the recent hot weather, to serve round to their staff a cooling drink. They purchased fruit crystals or lemonade powder, made up the lemonade ready for consumption, and stored it overnight in enamelled buckets provided with lids to keep out the dust.

Shortly after taking it, during the following morning a number of the staff were very sick, and between fifty and sixty of them had to be taken away and treated at the Royal Infirmary; fortunately, nearly all speedily recovered, although complete recovery, in some cases, was only after some days.

Investigation of the lemonade powder showed it to contain approximately 80 per cent. of sugar, 18·5 per cent. of tartaric acid, and 1·5 per cent. of sodium bicarbonate—enough to produce a slight effervescence when the powder was dissolved in water. It contained nothing of an injurious nature. The made up lemonade, however, which had been standing in the buckets, contained antimony compounds, and also a minute quantity of zinc. The amount of zinc was so small as hardly to be worth determining; but the antimony compounds, expressed as metallic antimony, amounted to 0·013 per cent. This would be equivalent, in an ordinary 10 oz. tumblerful of the liquid, to 0·57 grain of metallic antimony, or over 1·5 grains of tartar emetic. The "Emetic dose" of tartar emetic is given in the B.P. as 0·5 to 1·0 grain, so that the cause of the sickness of those who drank even a third or half a tumblerful of this liquid is sufficiently clear.

The enamel of the buckets had obviously been acted on by the liquid, for the glazed surface was gone from those portions that had been exposed to it, and the roughened coating left could be completely removed from the metal as a fine powder by merely rubbing with a finger. This powder contained antimony oxide equivalent to 5·0 per cent. of metallic antimony, or 6·1 per cent. of Sb_2O_3.

Analysis of the untouched portions of the enamel, chipped off from the bucket, gave:—

Silica	39·48
Alumina	9·78
Antimony oxide (Sb_2O_3)	2·88
Zinc oxide	2·23
Nickel oxide	0·08
Ferric oxide	2·17
Lime	2·66
Magnesia	0·41
Soda	19·63
Boron trioxide	20·43
	99·75

It is interesting to note that the enamel remaining on the bucket, after being acted on by the liquid, contained twice as much antimony as the untouched enamel. Clearly the liquid had dissolved out preferentially large quantities of the other constituents of the enamel, especially, no doubt, the sodium borate which forms nearly 40 per cent. of it; in fact, the corroded enamel contained nearly 60 per cent. of silica and under 8 per cent. of boron trioxide, whilst the lemonade contained 0·12 per cent. (10·5 grains per pint) of boron trioxide. Monier Williams, in his report on glazes and enamels (Ministry of Health Reports on Public Health and Medical Subjects, No. 29, ANALYST, 1925, **50**, 133), mentions an enamel from which citric acid dissolved large amounts of boron compounds.

The incident shows the need for caution in the use of vessels for containing such liquids—though experience shows that enamels which vegetable acids will corrode so considerably are exceptional, and the makers of these buckets might contend that, as buckets, they were not intended to contain such liquids. I have kept the same lemonade solution for a week in a small pie-dish coated with an antimony oxide enamel, and found that no action whatever occurred, and that the liquid was free from any trace of antimony.

J. T. DUNN.

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.

ALLEGED EVAPORATION OF MOISTURE FROM FLOUR AND RICE.

On August 4th a grocer was summoned at Luton for selling flour of less weight than was purported. The inspector stated that he had weighed 12 packages of flour at the defendant's shop, and had found the total weight to be 26 lb. 4 oz., making a total deficiency of 10 oz., or an average deficiency of 2·38 per cent. One package, in respect of which a summons was issued, bore a label stating that the net weight was $1\frac{3}{4}$ lb., and this was 1 oz. 2 drms. short; the other, labelled net weight $3\frac{1}{2}$ lb., was 1 oz. 14 drms. short.

The solicitor for the defence submitted that the inspector, having already weighed the bags, knew what he was purchasing, and, therefore, there was nothing purported to be sold to him other than the actual weights he bought. The Bench, having over-ruled that point, the solicitor then contended that, if it could be satisfactorily proved that reasonable precautions were taken to prevent evaporation, the deficiency came within the wording of the Act, "unavoidable evaporation."

Defendant said that he himself had obtained the flour, and that he was prepared to swear that the amount he had weighed into the bags was absolutely accurate. A number of the packages had been placed on a shelf in the shop, and during the hot weather the blinds had been drawn while the windows and door were kept open.

Dr. E. A. Fisher, F.I.C., said that for several years he had made a scientific study of wheat and flour. He had tested the contents of certain bags of flour sealed with the seal of the inspector, and had found the moisture in one to be 13·53 per cent., and that in the other 13·52 per cent. He would not be surprised to hear that the moisture content of the flour, when it left the millers, was 16·5 per cent. The loss by evaporation might be anything up to 3 or 4 per cent., according to the weather conditions. The defendant's shop was a small one, and the sun would stream through the window on to the bags of flour placed on the shelf. If the defendant drew the blinds, he had, in witness's opinion, taken reasonable precautions to prevent evaporation. He was not surprised at the variations in the deficiencies in the 12 packets, since those in the front row would be more exposed to the sun.

A representative of the firm of millers, who had originally supplied the flour, said that moisture tests were made at the mills from time to time, and that the average moisture content of the flour during the preceding three months had been 16 to 16·5 per cent. Under certain conditions he would expect a decrease of 4 per cent. in the amount of moisture. It was not the practice to put extra flour in bags to allow for evaporation.

The Bench decided to convict, and imposed a fine of 20s. in each case. Notice of appeal was given.

On August 11th another grocer was summoned at Luton for selling four lots of flour of less weight than was stated, and there was a similar summons in respect of rice.

The inspector gave evidence that he had weighed 48 bags of flour on the defendant's premises, and in 21 bags, each purporting to be 3½ lb. net weight, he had found a total deficiency of 1 lb. 8 oz. 10 drms., equal to an average deficiency of 2·09 per cent. There was no uniformity in the deficiencies, and one package, in respect of which a summons was issued, was 3·11 per cent. deficient. A 3½ lb. bag of wholemeal flour was 2 oz. deficient, and two others 1 oz. each.

The witness stated that he had also examined 27 packets of rice. Ten were correct in weight, 10 were each 2 drms. deficient, three were ¼ oz. short in weight, and four 5 drms. short each, an average deficiency of 0·75 per cent.

In cross-examination the witness said that he knew that evaporation was suggested in regard to flour, but he was not aware that rice was affected. He did not know that the moisture content of rice was about 12 per cent., and that according to climatic conditions it would be possible for a purchaser to get a slightly larger weight than was stated, as well as less weight. He was not concerned with what what people gave away.

The solicitor for the defence said that, as in the previous case, the deficiency was due to the spell of hot weather. The deficiency in the flour was only half of what Dr. Fisher told the Court recently he would expect to find as the result of evaporation, and it was not unreasonable to expect an evaporation of 0·75 per cent. from rice. As it would not be policy for him to contest the charges, he pleaded guilty, but he asked the Bench to remember that Dr. Fisher had also stated, that when the moisture had left the flour the actual food received by the purchaser was not lessened.

The Bench considered that there was no intention to defraud, and dismissed the cases on payment of 25s. costs.

As an outcome of these cases, experiments have been made by Mr. W. Simmons, miller, of Eaton Bray, Bedfordshire, and the following results have been obtained.* The flour contained 14·6 per cent. of moisture at the beginning of the tests:

Test of loss of weight by evaporation on eight bags of flour, weighed at 2 lb. each (gross). Date of commencement of test, July 25, 1928.

(A) Two bags were placed in a very hot and very dry room, the temperature of which was taken every other day (approximately), the temperatures being 107°, 105°, 90°, 95°, 95°, 98°, 96°, 85°, and 99° F. By August 1 (eight days) one bag showed a loss of 2 oz. 0¼ drm., the other a loss of 2 oz. 1¼ drm. By August 15 (22 days) one bag showed a total loss of 2 oz. 6¼ drm., the other a total loss of 2 oz. 7¼ drm.

(B) Two bags were placed in a cool and damp place. These actually gained in weight. There were no means of ascertaining the humidity of the various places. Temperatures taken approximately every other day were:—72°, 73°, 63°, 63°, 63°, 63°, 61, 66°, 63° F. By August 1 one bag showed a gain of 3 drm., the other a gain of 2¾ drm. By August 15 one bag showed a total gain of 4¼ drm., the other showed a total gain of 3¼ drm.

(C) Two bags were placed in a room where the temperature and general atmospheric conditions were as nearly as possible normal, varying with the weather. Temperatures taken approximately every other day were:—75°, 74°, 67°, 66°, 56°, 66°, 58°, 72°, 67° F. By August 1 one bag showed a loss of 1¼ drm., the other a loss of 1¼ drm. By August 15 both bags still showed a total loss of 1¼ drm. each.

(D) Two bags were placed in a somewhat similar place to the two bags in "C." Temperature readings were 78°, 78°, 69°, 69°, 65°, 70°, 59°, 76°, and 70° F. By August 1 one bag showed a loss of 1¾ drm., the other a loss of ¾ drm. By August 15 one bag showed a total loss of 2¼ drm., the other a total loss of 3¼ drm.

* *The Times*, August 30, 1928.

Government of Madras.

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1927.

In the absence of Dr. Clive Newcomb, the Acting Chemical Examiner reports that the number of analyses made during the year was 5476, which broke all previous records; in the previous year the number was 4637. The cases investigated included 252 of suspected human poisoning, with 1646 articles, and 618 stain cases, with 2800 articles, all of which figures were larger than ever before. This does not indicate any material increase in serious crime, but is due to increased activity on the part of the police or to the establishment of a routine practice of submitting cases to the Chemical Examiner. For example, whilst the number of stain cases has increased five-fold in the last 20 years, charges of murder have not increased to this extent, if at all.

Human Poisoning Cases.—Of the 252 cases investigated, poison was detected in 116. In 136 cases in which no poison was found, 107 were fatal, involving the deaths of 121 persons. Mercury was found in 15 cases, arsenic in 9, arsenic and mercury together in 8, opium in 19, and datura (atropine) in 12. The unusual poisons detected were veronal, *Citronellus colocynthus*, and oduvan. In one case a decoction of datura was drunk to cure a cold. In one fatal case a man took powdered nux vomica to cure a skin complaint. In another case a man suffering from syphilis bought a powder from a medicine quack in the streets. He took the powder mixed with sugar and ghee, and collapsed with symptoms of strychnine poisoning, but recovered after treatment.

Cannabis indica Poisoning.—Ganja and milk were boiled in a teapot, and the milk was given to four persons. Some time afterwards they became intoxicated and restless. They then went out into the road, leaving their property behind them in the house, and fell down unconscious. They recovered after treatment in hospital.

Animal Poisoning.—There were 54 cases, with 208 articles, as compared with 41 cases and 136 articles in the previous year. The most common poisons found were arsenic with 13 cases, and yellow oleander with 8 cases. An unusual poison was picrotoxin (*Cocculus indicus*), which was detected in the stomach of 11 goats which had died 2 hours after taking the suspected conjee water.

New South Wales.

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1927.

In this Report the Government Analyst (Mr. T. Cooksey) states that 17,646 samples were examined during the year, of which 15,409 were collected under the provisions of the Pure Food Act, and the remainder in connection with the public services.

Of the food and drug samples, 14,103 were milk, of which 426 contravened the requirements of the Pure Food Act, 1·40 per cent. being deficient in fat, 1·40 per cent. in solids-not-fat, and 0·37 per cent. in both fat and solids-not-fat. The

value of the systematic inspection of the milk supply is shown by the low percentage of adulterated samples.

The proportion of adulterated food substances was 32·1 per cent. of the total, the increase being partly explained by the fact that 136 samples of meat were illegally preserved, and 106 samples of sausages contained excess of preservative. Two samples of coffee and chicory essence were deficient in caffeine, and nine samples of "pure fruit" essences contained flavouring derived from sources other than the fruits specified on the labels. Nine samples of "fruit jelly crystals" also contained artificial flavouring and were reported as adulterated, as was also a sample of tomato sauce containing a farinaceous thickening agent.

"PROPERLY BAKED" BREAD.—In order to give a specific value to the requirement of the standard that bread shall be "properly baked," an attempt was made to determine the relationship between the specific gravity of the crumb and the general quality of the bread. The following method was devised:—A cube of 3 inches is cut as nearly as possible from the centre of the loaf, a wooden mitre box provided with two vertical slits exactly 3 inches apart, to guide the knife, being used for the purpose. The cube can thus be cut with a variation in size that is negligible in practice. It was ascertained from a number of determinations that the weights of the cubes of bread, having a moisture content ranging from 40·6 to 43·6 per cent., and which were regarded as satisfactory, varied from 125 to 135 grms., the average weight being approximately 130 grms. It was therefore considered that 135 grms. could be taken as a useful limiting figure for the weight of a cube of bread of the size stated, as it was found with all the samples examined that a cube possessing a greater weight than this was an unsatisfactory article.

It is of some advantage to allow fresh bread to remain some time before testing, say from 24 to 36 hours, provided that the loaf is so wrapped that the loss of moisture is not appreciable. This allows the crumb to be cut more easily and also permits all samples to be tested under approximately uniform conditions. It has been found in practice that where any slight loss of moisture occurred it was compensated for by a corresponding shrinkage, the weight of a definite volume of the crumb remaining practically unaltered. In certain types of loaf, *e.g.* the long French roll, it is not possible to obtain so large a sample for the determination, and in such cases a cube of 2 inches may be used, the results obtained being reasonably comparable.

Acidity of Bread.—The method of determining the acidity of bread, as described in various text books, in which the bread is allowed to remain in the liquid during the titration, is unsatisfactory, owing to the indefiniteness of the end-point obtained. The method given in Allen's *Commercial Organic Analysis* (5th ed., p. 577) for the determination of the acidity of flour, gives consistent results, but occupies too much time, it being necessary to shake the sample for two hours. The A.O.A.C. Official Method for flour has also the disadvantage of requiring at least one hour for the determination.

The method for the determination of the water-soluble acidity can be considerably shortened by the following procedure:—

Take 20 grms. of the crumb from the centre of the loaf (preferably 24 to 36 hours old), place it in a strong glass beaker of 400 c.c. capacity; add 200 c.c. of distilled water (free from carbon dioxide), and, by means of an ordinary egg beater with reversely revolving paddles, whirl briskly for 1 minute, or until the bread completely disintegrates. Allow the liquid to stand until the crumb has settled (about 2 minutes); then decant carefully 100 c.c. of the upper liquid and titrate in the ordinary way with $N/10$ sodium hydroxide solution, with phenolphthalein as indicator.

The following results were obtained by this method and by Allen's method:

Sample No.	Allen's Method. (*N*/10 NaOH for 10 grms. of crumb.) c.c.	Method given above. (*N*/10 NaOH for 10 grms. of crumb.) c.c.
1	1·25	1·2
2	0·9	0·95
3	1·0	1·0
4	1·2	1·25

As the method proposed gives lower results than one in which the crumb is not removed, the standard limit for acidity (*N*/10 NaOH) should be lowered to (say) 1·5 c.c. of *N*/10 NaOH.

TOMATO SAUCE, ETC.—*Determination of Non-Sugar Organic Tomato Solids in Tomato Sauce, etc.*—During the past year an investigation was carried out to ascertain the composition of the various tomato sauces offered for sale in New South Wales, with the object of fixing a minimum standard for the amount of tomato solids to be required. After consultation with manufacturers, a scheme of analysis, including some of the A.O.A.C. Official Methods, was drawn up, with the object of prescribing a standard method for the determination of non-sugar organic tomato solids. The chief difficulty experienced with the analysis was in regard to the total solids content; undoubtedly the A.O.A.C. vacuum oven method of drying at 70° C. gives the most satisfactory result, but, to meet the convenience of manufacturers, it was decided, for the present at least, to recommend that the total solids be determined by drying for 4 hours in a steam oven at 95 to 100° C. In practice, this gives concordant results, but about 6 per cent. lower than those obtained by the vacuum oven method. The following table gives the results obtained by the use of the two methods in question:

Sample No.	TOTAL SOLIDS. Dried for 4 hrs. at 100° C. in steam oven. Per Cent.	TOTAL SOLIDS. Dried for 4 hrs. at 70° C. in vacuum. Per Cent.
9	28·4	30·1
10	39·2	41·9

Should it be decided to adopt the vacuum oven method, a proportionately higher figure for the minimum tomato solids content will have to be prescribed.

The following is the method recommended to be prescribed:—

1. *Preparation of Sample.*—Proceed as directed in A.O.A.C. Methods of Analysis (1925 edition, Method No. 12, p. 220).

2. *Total Solids.*—Weigh about 5 grms. into a flat-bottomed glass dish having a diameter of approximately 7 cm. and a depth of 3 c.m. Distribute evenly in a thin layer over the bottom of the dish. If the sample is very thick, it is advisable to add 1 c.c. of distilled water to aid the even distribution. Evaporate on a steam bath for 30 minutes, and dry in a steam oven for 4 hours at a temperature of 98–100° C. Cool in a desiccator and weigh.

3. *Ash.*—Evaporate 5 to 10 grms. of the sample to dryness in platinum on a steam bath. Char thoroughly, being careful to avoid loss of salt. Exhaust the char with 25 c.c. of hot distilled water, breaking the material with a glass rod, if necessary. Collect the insoluble residue on a 9 c.m. ashless filter paper. Wash the dish and filter paper with successive portions of 15 c.c. and 10 c.c. of hot distilled water. Return the filter paper and its contents to the dish, dry, and ignite at a temperature not exceeding dull redness until free from carbon. Add the filtrate to the dish; evaporate on a steam bath, dry to constant weight in an air oven at a temperature of 100 to 105° C. Cool in a desiccator and weigh.

SUGARS.

4. *Reducing Sugars before Inversion.*

For products containing 10–20 *per cent. of invert sugar.*—Weigh 10 grms. of the sample. Dilute with about 100 c.c. of distilled water, and transfer to a 500 c.c. graduated flask. Clarify, using a slight excess of neutral lead acetate solution; dilute to the mark and filter. Remove the excess of lead with dry potassium oxalate. Filter and determine reducing sugar by Method No. 35, A.O.A.C. Methods of Analysis (1925 edition, p. 190), using 50 c.c. of the filtrate.

For products containing less than 10 *or more than* 20 *per cent. of invert sugar.*—Vary the amount of sample weighed, so that the 50 c.c. of the filtrate will give a reduction of about one-half the Fehling's solution used (50 c.c.). Express the results obtained as percentage of *invert sugar before inversion.*

5. *Reducing Sugars after Inversion.*—Proceed as directed in Method No. 21, A.O.A.C. Methods of Analysis (1925 edition, p. 221), using 50 c.c. of the final filtrate obtained in (4), for the determination of reducing sugars before inversion. Express the results obtained as percentage of *invert sugar after inversion.*

6. *Sucrose.*—The difference between the percentages of invert sugar before and after inversion, (4) and (5), multiplied by 0·95, gives the percentage of sucrose (cane sugar).

7. *Total Sugars.*—Total sugars are the sum of invert sugar before inversion and sucrose (cane sugar).

8. *Non-Sugar Organic Tomato Solids.*—The percentage of non-sugar organic tomato solids is obtained by subtracting the sum of the percentages of total sugars and ash from the percentage of total solids.

NOTE.—If apple or other fruit is used in the preparation, the non-sugar organic solids are calculated as fruit solids. If starch or other thickening agent is used, the amount present must be taken into consideration when calculating non-sugar organic tomato solids.

The analyses given hereunder were obtained by the use of the above method. No allowance was made for the small amount of condiments (usually less than 0·5 per cent.) present.

It will be seen from the attached table of analyses that only two samples, Nos. 4 and 10, contained more than 5 per cent. non-sugar organic tomato solids; two contained between 4·0 and 4·4 per cent.; five contained between 3·0 and 3·9 per cent.; and two less than 3 per cent. Two samples prepared with apple contained 3·4 and 3·5 per cent. of non-sugar organic fruit solids, respectively.

As the result of the investigation, it is proposed to fix a standard of not less than 4 per cent. of non-sugar organic tomato solids in tomato sauce or ketchup.

AMOUNT OF SULPHUR DIOXIDE LOST IN THE COOKING OF DRIED FRUITS.—In connection with the request that the question of the desirability of raising the amount of sulphur dioxide in dried fruits from 7 grains to 14 grains per lb. (as permitted under the British Regulations) be taken into consideration, an investigation was carried out to determine the loss of sulphur dioxide in the fruit after cooking in the manner recommended by the Fruitgrowers' Association.

The dried fruit was soaked in 5 times its weight of tap water and allowed to stand overnight (about 18 hours). This water was strained off, and fresh water sufficient to cover the fruit (about an equal weight of water to the weight of the wet fruit) and sugar were added. The whole was brought to boiling point and allowed to simmer gently for 5 minutes, with the cover off the cooking vessel. The fruit was allowed to cool by standing for 10 minutes, before analysis.

Tomato Sauce, Tomato Ketchup and Tomato Chutney.

Sample. No.	Total solids (4 hrs. at 100°C.) Per Cent.	Sugars. Total. Per Cent.	Sugars. Invert. Per Cent.	Sugars. Cane. Per Cent.	Ash. Per Cent.	Chlorine as sodium chlorine. Per Cent.	Phosphoric acid (P_2O_5). Per Cent.	Acidity as acetic acid. Per Cent.	Non-sugar organic tomato solids. Per Cent.	Non-sugar organic fruit solids. Per Cent.	Remarks.
Sauce 1	25·8	17·2	6·7	10·5	4·6	3·9	0·083	1·3	4·0	—	No apple present
Sauce 2	29·0	20·4	12·7	7·7	4·3	3·5	0·074	1·3	4·3	—	No apple present
Sauce 3	28·9	21·4	12·9	8·5	3·6	2·8	0·078	1·1	3·9	—	No apple present
Sauce 4	33·8	23·9	15·4	8·5	4·0	3·0	0·082	1·5	5·9	—	No apple present
Sauce 5	26·8	20·4	10·5	9·9	3·0	2·3	0·067	1·1	3·4	—	No apple present
Ketchup 6	28·6	22·6	14·8	7·8	3·2	2·4	0·071	1·0	2·8	—	Few cells resembling apple present
Sauce 7	25·3	17·4	11·8	5·6	4·2	3·2	0·088	1·4	3·7	—	No apple present
Sauce 8	25·4	19·2	13·1	6·1	3·0	1·95	0·090	1·5	3·2	—	No apple present
Sauce 9	28·4	19·4	7·7	11·7	4·2	3·1	0·076	1·3	3·3	—	No apple present. Sample contains approx. 1·5 per cent. starch
Sauce 10	39·2	29·1	20·0	9·1	4·2	3·6	0·057	2·0	5·9	—	No apple present
Chutney 11	25·2	18·8	12·9	5·9	2·9	2·2	0·048	0·9	—	3·5	Apple present
Sauce 12	23·8	18·3	13·3	5·0	2·9	2·4	0·044	0·9	2·6	—	A few cells resembling apple present
Ketchup 13	28·3	21·9	12·4	9·5	3·0	2·2	0·11	1·1	—	3·4	Apple present

The sulphur dioxide present was determined by the volumetric method, all necessary precautions being taken, with the following results:—

Sulphur Dioxide.

Fruit.	In uncooked dried fruit. Grains per lb.	Remaining in fruit after cooking. Calculated on original dried fruit. Grains per lb.	Remaining in fruit after cooking. Calculated on fruit and syrup as eaten. Grains per lb.
Apricots	16·9	6·6	1·1
Peaches	1·2	0·4	0·07
Pears	7·6	3·9	0·7

It was found that one-third to one-half of the sulphur dioxide originally present remained after cooking in the manner recommended. The dried fruit absorbed about two parts of water during soaking and cooking, and this, with an equal weight of syrup added, reduced the sulphur dioxide content of the prepared article, as actually eaten, to one-tenth to one-sixteenth of the amount originally present.

Preservative Regulations in Germany.

DR. H. ZELLNER, Public Analyst, Berlin, informs us that the following regulations as to the use of preservatives in Germany have been in force since October 1, 1927:

Article of Food.	Preservative.	Maximum allowed per 100 grms. of Article of food. Grm.	Declaration of Preservative Content.
1. Meat Salad.	Benzoic acid.	0·125	No.
2. Fish preserves (anchovy).	Boric acid.	0·5	Yes.
3. Caviare.	Hexamethylenetetramine.	0·1	Yes.
4. Crabs, fresh.	Boric acid.	0·9	Yes.
Crabs preserved.		0·75 (0·9)	
5. Preserved eggs, yolk for exclusive consumption in bakeries or for manufacture of macaroni.	Boric acid.	1·5	No.
Yolk.	Benzoic acid.	1·0	No.
6. Edible fats, margarine.	Benzoic acid.	0·2	No.
7. Mayonnaise.	Benzoic acid.	0·25	No.
8. Grits and groats.	Sulphurous acid.	0·044	No.
9. Preserved fruit, dried fruit.	Sulphurous acid.	0·125	No.
Fruit juice.	Benzoic acid.	0·15	No.
Fruit juice.	Formic acid.	0·25	No.
Fruit pulp.	Benzoic acid.	0·15	No.
Fruit pulp.	Formic acid.	0·25	No.
10. Wine.	Sulphurous acid in gaseous form or its solution in distilled water, and technically pure potassium metasulphite containing at least 5 per cent. SO_2.	Provided that only small quantities of sulphuric acid are contained in the beverage.	No.
11. Imported wine.	Sulphurous acid in gaseous form or its solution in distilled water, and technically pure potassium metasulphite containing at least 5 per cent. SO_2.	According to the regulations for the sale in the countries of origin.	No.
12. Edible gelatin.	Sulphurous acid.	0·125	No.

Parliamentary Notes.

GOVERNMENT CHEMIST'S FEE.—On August 1, Mr. A. V. Alexander asked the Minister of Health whether the fee charged by the Government Analyst had recently been raised from one guinea to two guineas; and whether, as this charge was altogether out or proportion to the work involved and was likely to cause the denial to some individuals of the right to appeal under the Sale of Food and Drugs Acts, he would consider the reduction of that fee.

The Financial Secretary to the Treasury (Mr. A. Michael Samuel), in reply, said that the fee charged by the Government Chemist for samples submitted to

him under the Sale of Food and Drugs Acts was increased on April 1st, 1927, from one guinea to two guineas per sample. He was advised that the present fee was amply justified by the work involved, and that there was no reason to suppose that its retention would have the effect suggested. The Government Chemist was regarded as a referee, and it was absolutely necessary that he should have accurate and experienced assistants. For the work they did the fee was only just adequate.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

The Copper Content of Milk. G. N. Quam and A. Hellwig. (*J. Biol. Chem.*, 1928, **78**, 681–684.)—Several different investigators have reported the presence of copper in cow's milk, the amounts found by Supplee and Bellis (*J. Dairy Sci.*, 1922, **5**, 455) ranging from 0·2 to 0·8 mgrm. per litre, and showing no apparent relationship to the food. The variation in results obtained in widely different localities, however, suggested the possibility of the influence of the copper content of native feeding products, and the authors have therefore tested the milk of cows, sheep and goats. The possibility of contamination by copper during the analysis was always checked by means of equivalent quantities of copper-free water, which were treated in the same manner as the milk. The copper was determined by the xanthate colorimetric method, as modified by Supplee and Bellis (*loc. cit.*). Analyses of milk from 14 cows collected from four states showed a fairly constant copper content for raw cow's milk, the quantities ranging from 0·26 to 0·52 mgrm. per litre. Apparently the possible variation in copper content of native feeds, such as the grass in Kentucky, has little or no effect. The copper content of milk of the sheep was found to be about the same as that for the cow (0·45 to 0·50 mgrm. per litre). The copper content of goat milk was low in six cases (0·19 to 0·25 mgrm. per litre), but always easily detectable, notwithstanding the report to the contrary by Titze and Wedemann (*Arb. k. Gesundsheitsamte*, 1911, **38**, 125). The copper content of milk that has been passed through a manufacturing process may vary between wide limits. Of four common brands of condensed or evaporated milk, the copper in all cases was greater than could probably be accounted for in the original raw product (*e.g.* 1·80 to 2·32 mgrms. in concentrated milk). The variation in copper content can be traced to the amount of copper surface exposed to the milk product. In one factory 3 samples of pasteurised whole milk showed 0·60 to 0·73 mgrm., whilst 3 samples from another factory gave 1·50 to 1·60 mgrm. per litre, and 3 samples of buttermilk from this second factory gave 2·40 to 2·50 mgrms. per litre. P. H. P.

Standard for Beriberi-preventing Rices. E. B. Vedder and R. T. Feliciano. (*Phil. J. Sci.*, 1928, **35**, 351–390.)—Two hundred samples of rice were examined by inspection, after staining with Gram's iodine solution, for the percentage of external layers still adhering; by analysis for moisture, ash, fat,

phosphorus pentoxide, nitrogen, amino and albuminoid nitrogen; and by feeding experiments on pigeons; and, as a result, a tentative standard for beriberi-preventing rice is given. "Any rice having 1·77 per cent. of phosphorus pentoxide plus fat, but not less than 0·4 per cent. phosphorus pentoxide; or any rice having not less than 0·62 phosphorus pentoxide; or any rice having not less than 0·50 per cent. phosphorus pentoxide, and with at least 75 per cent. of the external layers of the grain remaining." Rices in the process of milling or as sold may be classified as highly milled, 0·20 per cent. of external layer present, medium milled, 31–49 per cent., or undermilled with 50–100 per cent. No rice of the standard given above produced polyneuritis in pigeons, and the standard excluded only nine rices out of 200 that afforded protection to pigeons. Thorough washing of rice (10 samples) reduced the phosphorus pentoxide content from an average of 0·447 to 0·197 per cent., and presumably the vitamin content is similarly reduced. Storage of insect-infested rice may convert undermilled rices into highly milled rices producing polyneuritis. D. G. H.

Fats of Japanese Birds. R. Koyama. (*J. Soc. Chem. Ind., Japan.*, 1928, **31**, 140B.)—The physical and chemical constants of the fats of three species of Japanese birds are given in the following table:

Constants of the fats.	Bird:	Little Bittern. *Nannocus eurythmus* (Swinhoe).	Gray Night Heron. *Nycticorax nycticorax nycticorax* (Linn.).	
	Sex:	♂	♂	♀
	Colour:	Faint yellow.	Faint yellow.	Faint yellow.
Melting-point		19·0–22·1°	30·0–34·0°	29·8–33·4°
Sp. gr. ($d.\ ^{40°}_{4°}$)		0·89825	0·90091	0·89936
Refrac. index ($n^{40°}_{D}$)		1·4670	1·4678	1·4673
Saponification value		194·23	196·39	195·00
Acid value		2·57	4·86	2·87
Iodine value		47·98	46·96	48·13
Unsaponifiable matter, per cent.		4·08	2·12	2·78
Polybromide insoluble in ether, per cent.		1·22	small quantity	0·40
M.pt. of polybromide		246–247° (decomp.)		

Constants of the fats.	Bird:	Red-checked Starling. *Sturnia violacea* (Boddaert).			
	Sex:	♂	♂	♀	♀
	Colour:	Yellow.	Yellow.	Yellow.	Yellow.
Melting-point		34·2–36·0°	34·0–35·7°	33·6–35·5°	33·2–36·2°
Sp. gr. ($d.\ ^{40°}_{4°}$)		0·89861	0·89687	0·90051	0·89852
Refrac. index ($n^{40°}_{D}$)		1·4649	1·4654	1·4647	1·4651
Saponification value		199·65	199·07	200·91	199·52
Acid value		—	1·29	—	1·52
Iodine value		38·01	37·62	41·21	39·52
Unsaponifiable matter, per cent.		2·26	1·90	1·07	2·05
Polybromide insoluble in ether, per cent.		0·38	0·30	0·60	0·56

R. F. I.

Grape Seed Oils. E. André and H. Canal. (*Bull. Mat. Grasses*, 1928, **5–6**, 131–144.)—An examination of 52 varieties of grape seed has shown considerable variations, particularly in the percentage of oil in the seed (6·5 per cent. for Muscadet seed, up to 20·6 for Hebremont variety), and in the acetyl value of the oil. The saponification values were below 180 in 11 cases, and erucic acid should be looked for in such oils, but the iodine values were then higher than those found for cruciferous oils. The specific gravity was higher in the presence of high proportions of acidity, such as are found in some industrial oils, but for oils extracted in the laboratory varied from 0·912 to 0·926. The iodine value was always over 130, and for 87 per cent. of the samples examined was between 135 and 142, whilst in one it reached 157. In 22 out of 46 cases the acetyl value was below 10, in 17 between 10 and 20, and in 2 between 20 and 35. Industrial oils showed values of 40·0, 42·0, and 72·0. Some varieties of grape vines are particularly influenced by climatic conditions; *e.g.* the grape seeds from Praysass in Lot-et-Garonne gave in 1921, 18 per cent., in 1922, 10·6, and in 1926, 16·6 per cent. of oil, with acetyl values of 21·5, 11·9, and 6·1, respectively. A hot climate seems to favour production of oils rich in acid-alcohols, but the castor-oil type of grape-seed oil is rare, and the majority of grape-seed oils must be regarded as semi-drying. D. G. H.

Composition and Solubility of Strychnine Hydrochloride. J. E. Driver and S. P. Thompson. (*Quart. J. Pharm.*, 1928, **1**, 37–43.)—The conclusion of Dott (*Pharm. J.*, 1926, **117**, 760), as to the composition of strychnine hydrochloride crystals, has been confirmed. When dried to constant weight in moist air the salt has a composition agreeing with the formula $C_{21}H_{22}O_2N_2$, HCl, $1\frac{3}{4}H_2O$. Commercial samples were found to contain rather less water of crystallisation than required by this formula, but more than that required by a compound with $1\frac{1}{2}H_2O$. The solubility has been determined at temperatures up to 61° C. By extrapolation it was found to be 2·32 grms. per 100 grms. of water at 15·5° C. This may be expressed approximately in the form in which solubilities are given in the British Pharmacopoeia (solute in grm. and solvent in c.c.) as 1 in 43 for the anhydrous salt, or 1 in 39·5 for the hydrate ($1\frac{3}{4}H_2O$). Hence the solubility recorded in the B.P. stands in need of revision. The solubility is considerably diminished by the presence of hydrochloric acid or metallic chlorides. In *N*-hydrochloric acid the solubility is only about one-sixth of the solubility in water.

Salts of Pelletierine. G. Tanret. (*J. Pharm. Chim.*, 1928, **8**, 112–120.)—On account of the loose definition of pelletierine sulphate by the French Codex, and of the tannate by other Pharmacopoeias, the products marketed under these names are complex mixtures of the pomegranate alkaloids which vary in composition, and often contain very small quantities of the active principle. Pseudopelletierine tannate ($C_9H_{15}NO$, $2C_{14}H_{10}O_9$) is best prepared by liberation of the alkaloid from a 1 per cent. solution of the sulphate by the addition of 0·17 grm.

of sodium hydroxide per grm. of sulphate, the tannate then being precipitated as a white, granular powder which contains 11·5 to 16·5 per cent. of alkaloid, by the slow addition of tannin (4 parts). The tannate, which is easily dissociated, and differs from that prepared by the Codex method, is given the minimum number of washes, and dried between filter papers below 40° C., and finally over sulphuric acid. It is determined by extraction of a solution of 3 grms. in 10 c.c. of 15 per cent. sodium hydroxide solution with 100 c.c. and 25 c.c. portions of chloroform, the total extract being shaken with 20 c.c. of 0·2 *N* sulphuric acid, which is then separated and titrated with sodium hydroxide solution, with nitrophenol as indicator; the factor is 0·3122. Pelletierine tannate (C_8H_5NO, $2C_{14}H_{10}O_9$) is prepared and determined similarly, the factor for analysis being 0·2877. Both tannates are soluble in organic acids, warm mineral acids, cold water (300 parts), ether (500 parts), and alcohol at 90° C. (8 to 15 parts), but not in chloroform. The dose is 1·3 to 1·75 grms. of pelletierine tannate containing 17 per cent. of alkaloid.

J. G.

Assay of Trional Tablets. L. E. Warren. (*J. Assoc. Off. Agric. Chem.*, 1928, **11**, 404–407.)—This method, which is suggested for use in the absence of chloroform-soluble substances other than trional, avoids losses of trional due to evaporation, but gave slightly high results for a number of commercial samples and a mixture of trional with 50 per cent. of starch. The equivalent of 5 grains of trional is extracted in a Soxhlet apparatus or macerated repeatedly with chloroform, and the total filtered extract evaporated in a slow current of air, the vessel being rotated in an inclined position. The residue is dried in a desiccator over sulphuric acid till constant in weight. J. G.

Determination of Adrenalin in the Suprarenal Glands. M. Paget and P. Lohéac. (*J. Pharm. Chim.*, 1928, **120**, 159–169.)—Variations obtained by different workers in the determination of adrenalin in the suprarenal glands are regarded as due to lack of knowledge of special phenomena, particularly *post-mortem* changes, and the time of the removal of the organs should be known. Removal should take place as quickly as possible after death, and the organs kept for 24 hours *in vacuo* over sulphuric acid. The weighed suprarenal glands are chopped, mixed with three times their weight of anhydrous sodium sulphate, powdered, triturated for 5–10 minutes with 5–10 c.c. of 0·1 *N* sulphuric acid, left for 5 minutes, made up to 50 or 100 c.c. with water, shaken at intervals for 15 minutes, and filtered. Ten c.c. of filtrate are poured into a test tube containing 1 grm. of sodium acetate, and, after solution, 10 drops of 5 per cent. mercuric chloride are added. After shaking gently, a rose colour is formed very slowly if the reaction is positive, reaching maximum intensity in 45 minutes. This colour is compared with that produced from 10 c.c. of adrenalin, containing 0·1 grm. per 1000, and treated with the same reagents, by taking 5 c.c. of each solution and diluting the type sample to match the solution being tested. E. G. H.

Determination of Synthetic Camphor in Pharmaceutical Preparations. J. Bougault and (Mlle.) B. Leroy. (*J. Pharm. Chim.*, 1928, (viii), **8**, 49–55.)—Synthetic camphor, being optically inactive, cannot be determined by means of its rotation. The use of the semicarbazone is likewise unsuitable, since any isofenchone present also gives semicarbazone, and the camphene and borneol remain mixed with the semicarbazone. The oxime is found to give satisfactory results, use being made of its solubility in alkaline solutions. The procedure is as follows: 0·5 grm. of the camphor is dissolved in 5 c.c. of 90 per cent. alcohol in a test-tube, and the liquid mixed with a solution of 1 grm. of hydroxylamine hydrochloride in 5 c.c. of water, and 2 c.c. of 20 per cent. sodium hydroxide solution. The tube is sealed in a flame and immersed for 2 hours in a boiling water-bath. When cold, the contents of the tube are transferred to a decantation vessel, together with a few c.c. of the sodium hydroxide solution (diluted 1 in 10) used to rinse out the tube. The liquid is mixed with 20 c.c. of water, which causes turbidity owing to precipitation of part of the camphoroxime. Any turbidity persisting after addition of 3 c.c. of sodium hydroxide solution consists of camphene and borneol, which are removed by filtration, the filter being washed with dilute alkali solution. The alkaline liquid is neutralised exactly with hydrochloric acid and the precipitated camphoroxime taken up in 20 c.c. of ether, which is decanted off, washed with 5 c.c. of water, and again decanted into a tared dish 7 cm. in diameter. The aqueous liquid is extracted with two further 10 c.c. quantities of ether, which are washed as before and added to the first. The dish is left in the air for 12 hours, and then under a bell-jar in presence of calcium chloride for 12 hours, and weighed. The resultant weight is increased by 4 per cent. to compensate for loss of the oxime by evaporation.

This method may be applied directly to the strong and weak tinctures of camphor of the Codex. With camphorated oil, 20 grms. are introduced, together with 50 c.c. of water and a few fragments of pumice stone, into a 500 c.c. flask. The water, which carries the camphor with it, is then slowly distilled off from an oil-bath at 120–130°. The camphor seems to be distilled completely in two hours, but, to make more certain, 30 c.c. of 95 per cent. alcohol are introduced into the flask through a tapped funnel and distilled off. The condenser is finally washed down with a few c.c. of alcohol, and the distillate made up to 100 c.c., giving a weak tincture of camphor. T. H. P.

Determination of Alcoholic Extractive in Gum Benzoin. T. N. Bennett and C. F. Bickford. (*J. Assoc. Off. Agric. Chem.*, 1928, **11**, 386–388.)—Of the six methods proposed, the following is quickest, simplest, gives highest results, and is preferable to the U.S.P. method, in that it avoids loss of benzoic acid during drying. The sample (2 grms.) is extracted for 5 hours in a tared dry thimble with 95 per cent. alcohol containing 0·5 grm. of sodium hydroxide. The alcoholic extractive matter is calculated by difference from the weight of the dried thimble and contents, the water content (determined by xylol distillation) being deducted. J. G.

Yeast Method for Silver Proteins. H. Wales. (*J. Assoc. Off. Agric. Chem.*, 1928, **11**, 396–398.)—In the official method (*id.*, 1927, **10**, 74, 374, and Pilcher and Sollmann, *J. Lab. Clin. Med.*, 1924, **9**, 256), 10 c.c. of a suspension of 8 grms. of pressed yeast in 200 c.c. of 10 per cent. sucrose solution are placed in test tubes with suitable quantities of silver protein and made up to 20 c.c. with water. After 1 hour at 38° C. the concentration of silver protein, just sufficient to inhibit the action of yeast, is shown by that tube which contains least protein, and in which no gas has been formed, and the concentration of silver nitrate to produce the same effect on the same yeast suspension is then determined. It is now shown that, since silver nitrate differs in its effect from silver proteins, and since the inhibitory action of the latter is not due to the concentration of the silver ion, the expression of the results in terms of the former is not justified. (*Cf.* Taylor, *J. Amer. Pharm. Assoc.*, 1927, **16**, 820). J. G.

Biochemical.

Determination of Aluminium in Animal Tissues. V. C. Myers, J. W. Mull and D. B. Morrison. (*J. Biol. Chem.*, 1928, **78**, 595–604.)—A colorimetric method for the determination of the minute amounts of aluminium, which may be found in the various body tissues and fluids, is described. Although it is less accurate than gravimetric methods where large amounts are to be determined, it is unquestionably better suited to the determination of minute amounts of aluminium in animal tissues. It was necessary to remove all the other inorganic constituents from the tissues before the colorimetric tests were made, but it was found that iron must be present at the time of the first precipitation of the aluminium, otherwise the aluminium is not completely precipitated. The essential features of the method, which is described fully, are: (1) The digestion of the tissues with a sulphuric and perchloric acid mixture, (2) the precipitation of the aluminium along with a very small amount of iron, and the subsequent complete separation from the iron, and (3) the development of a colour reaction upon the aluminium with the ammonium salt of aurin tricarboxylic acid. This delicate colour reagent for aluminium was described by Hammett and Sottery (ANALYST, 1925, **50**, 152), and their method, with certain modifications, has proved most suitable. The method is adequate for the determination of the aluminium present in tissues under various conditions; *i.e.* amounts which vary from less than 0·01 to 0·5 mgrm. per 100 grms. of tissue. It is not suited to amounts of aluminium which exceed 1·0 mgrm. per 100 grms. of tissue. Owing to the delicacy of the method only reagents of the very highest purity can be used, but with suitable reagents and careful manipulation the error of the method should not exceed 10 per cent. P. H. P.

Influence of Administration of Aluminium upon Aluminium Content of the Tissues, and upon Growth and Reproduction of Rats. V. C. Myers and J. W. Mull. (*J. Biol. Chem.*, 1928, **78**, 605–613.)—Experiments have been carried out on rats in order to study the influence of aluminium administration

upon the content of aluminium in the tissues and upon growth and reproduction. The results are shown in tables and a chart. The aluminium content of the tissues of rats has been determined on four groups of animals: (1) On a control diet, (2) on a diet with high aluminium content, (3) on an aluminium-free diet, and (4) after the intraperitoneal administration of aluminium. Minute traces of aluminium were shown to be present in the tissues normally, and these show only a slight increase on a diet which contains considerable aluminium; aluminium persists in the tissues even on an aluminium-free diet, so that it is either retained in the body, or else is very difficult to exclude from the food. Following intraperitoneal administration, aluminium is found in increased amounts throughout the body, the largest amounts apparently being in the liver. It appears to be excreted chiefly by way of the intestine. For the liver the average findings of aluminium per 100 grms. of tissue were: (1) Control diet, 0·14 mgrm.; (2) aluminium diet, 0·18 mgrm.; (3) aluminium-free diet, 0·08 mgrm., and (4) aluminium administered intraperitoneally, 8·22 mgrms. Observations have been made which covered four generations of rats that were receiving 2 mgrms. of aluminium in the form of potassium aluminium sulphate per rat daily, in addition to the stock diet. The growth curves of these animals compare well with those of the controls, but the aluminium-fed rats show a slightly greater initial growth. So far as could be ascertained, the addition of aluminium to the diet was without other influence.

P. H. P.

Fractionation of Serum Proteins by means of Ammonium Sulphate. A. Muschel. (*J. Biol. Chem.*, 1928, **78**, 715–718.)—The method proposed for the fractionation of serum proteins by Van Slyke and Cullen (*J. Biol. Chem.*, 1920, **41**, 587; ANALYST, 1920, **45**, 226), and modified by Petschacher, Berger and Schretter (*Z. ges. exp. Med.*, 1926, **50**, 449), has now been further modified by aeration at 60–70° C., and by the use of superoxol. Tables show that the new method gives satisfactory results on ammonium sulphate, on urea, and on serum. It is also shown that for the same person the ratio globulin : albumin remains constant for a period of about 2 months, if the technique for obtaining blood is correct. The dilutions used for the determinations corresponded, for total nitrogen to 0·1 c.c. of serum, for albumin plus non-protein nitrogen to $\frac{1}{6}$ c.c. of serum, and for non-protein nitrogen to 0·5 c.c. of serum. Total nitrogen is determined in serum diluted tenfold with 0·9 per cent. sodium chloride solution. One c.c. of the dilution is digested with 2 c.c. of concentrated sulphuric acid and 2·5 c.c. of 2 per cent. copper sulphate solution. If the oxidation is finished by addition of 0·2 c.c. of superoxol, almost the same figures for nitrogen result. The globulin is precipitated by half saturation with ammonium sulphate in serum diluted threefold with distilled water. The supernatant fluid obtained after centrifuging is used for determination of albumin plus non-protein nitrogen. Magnesium oxide in 50 per cent. alcohol decomposes the ammonium sulphate, and a vigorous air current, washed free of ammonia, carries off the liberated ammonia while the flasks are kept in a water-bath at 60–70° C. (not higher lest the flask contents dry out) for 2 to 3 hours, until all the ammonia is removed. To the residue in the flasks

a few c.c. of distilled water, 2·5 c.c. of 20 per cent. copper sulphate solution and 2 c.c. of concentrated sulphuric acid are added, and the flasks are heated over a low flame until the contents are in fine suspension; then the water is boiled off, and when white fumes appear, 0·2 c.c. of superoxol is added; after a few minutes the mixture clears up, but without superoxol the oxidation takes a few hours and requires much supervision. Non-protein nitrogen is determined by the usual precipitation with tungstic acid. For distillation use is made of the apparatus of Fuchs (*Biochem. Z.*, 1926, **176**, 32), modified by a block tin coil and Pyrex tubing instead of Jena glass tubing, and by a Hopkins trap. It is advisable to start with a volume of about 40 c.c. and distil over half the volume, slowly at first, and with the tin coil well cooled to save repeated testing for the end-point. Excess acid is titrated with 0·05 *N* sodium hydroxide, with methyl red and methylene blue as indicators. A micro burette of 5 c.c. capacity, with subdivisions of 0·02 c.c., is used. P. H. P.

Determination of Succinic Acid in Blood. P. W. Clutterbuck. (*Biochem. J.*, 1928, **22**, 745–748.)—The method of Moyle (*Biochem. J.*, 1924, **18**, 351), for the determination of succinic acid in muscle, by which it was claimed to be possible to determine very small amounts with an accuracy of 95 ± 5 per cent., has been adapted to its determination in blood with a view to following the succinic acid content of the blood perfusing a surviving liver under various conditions. However, in the early experiments, the determination by the Moyle method of a known amount of succinic acid present in blood filtrates always gave very low results, both when the proteins were removed by acid (mercuric sulphate + sulphuric acid) and by alkaline (zinc sulphate + sodium hydroxide) precipitants. Therefore, the accuracy of Moyle's method for succinic acid in tissue was investigated. Determinations were made of standard solutions of the acid by direct titration by the silver method and after putting the acid through the Moyle technique. Small amounts of succinic acid, after precipitation as the silver salt and titration of the silver against potassium thiocyanate, were determined with an accuracy of 99 ± 1 per cent. For the Moyle technique the solution which contains succinic and sulphuric acids is saturated with ammonium sulphate, made up to 20 c.c. with saturated ammonium sulphate solution, extracted 5 times by shaking out with ether, and then the extracted material is oxidised to remove lactic acid, etc., re-extracted with 5 more portions of ether, and determined by the silver method. Under the optimal conditions the amount recovered was 86 ± 2 per cent., and was not as high as that obtained by Moyle for succinic acid in muscle. With the revised method which was finally adopted for the determination of succinic acid in blood, and which is described fully, the amount of acid recovered was 87 ± 3 per cent. The first series of hand extractions was replaced with a constant ether extraction, and under these conditions fairly consistent results were obtained of a somewhat greater accuracy than those obtained when the two sets of hand extractions were employed; a constant ether extraction for each set of hand extractions gave untrustworthy results. P. H. P.

Studies on Colour Tests for Sterols and Vitamin *A*. I. Sterol Tests. **F. Wokes.** (*Biochem. J.*, 1928, **22**, 830–835.)—Since evidence is gradually accumulating in favour of vitamin *A* being a sterol derivative, and as "vitamin" reagents seem closely related to sterol tests, and give similar, though more transient, colours, a comparative study has been made of some of these colour tests. A table gives the analytical data obtained on the sterols and their derivatives which were employed, and a second table shows the colour test results which are summarised as follows:—Pure cholesterol (freed from ergosterol), cholesteryl acetate and chloride, α-cholesterylene, cholestene and ψ-cholestene give with the "vitamin" reagents (concentrated sulphuric acid, arsenic and antimony trichlorides) red colours which persist for many hours, but the last two may take longer for the colour to develop. Cholesterol, cholesteryl acetate or chloride, cholestene and ψ-cholestene in chloroform solution, left in contact with concentrated sulphuric acid for some hours, and then diluted with more chloroform, give a purple or violet colour, and similar colours are obtained by removal of the chloroform solution from the acid after less than a minute's contact, and addition to the former of a drop of formalin. No colours are produced by formaldehyde alone with chloroform solutions of cholesterol or its derivatives which have not been in contact with concentrated sulphuric acid. Irradiation of sterol derivatives generally renders the colours more transient, but cholesterol, irradiated under certain conditions, may produce with the "vitamin" reagents blue colours, changing to red on standing for some hours. Activation with other agents, such as acetic anhydride, benzoyl peroxide or formaldehyde, may lead to the production of blue or purple colours on addition of the "vitamin" reagents. Cholestenone gives transient red colours with the "vitamin" reagents, and negative results (including red instead of blue with Liebermann's and Lifschutz's tests) with all other tests. The other oxidation products of cholesterol which have been tested give negative results in all cases (dicholesteryl ether can be made to give red colours with modified Lifschutz's, Liebermann's, Tschugaieff's and "vitamin" tests). Antimony pentachloride gives the colour sequence red —> blue —> red with all cholesterol derivatives examined, except the oxidation products. Of these, dicholesteryl ether, containing one proportion of oxygen, gives both red and blue; cholestenone and hydroxycholesterylene, containing 2 proportions of oxygen, give red only; and β-hydroxycholestenol acetate, with 4 proportions of oxygen, gives negative results. Introduction of sulphur into the side chain, as in cholesterylmethylxanthogenic ester, retards development of the colours, but does not necessarily prevent it after liberation of sulphur compounds has taken place. Ergosterol differs from cholesterol only in its results with the "vitamin" reagents. With ordinary concentrations of ergosterol these give the usual red, but if a higher initial concentration is employed (about 0·05 grm. to 1 c.c. of reagent) the red colour given by arsenic or antimony trichloride changes to purple or blue, on diluting with more reagent after a few moments. Sitosterol gives similar results to cholesterol, but more slowly. Other workers have suggested that the initial blue colour is indicative of vitamin content. The results show that blue colours may be obtained from sterols: (1) With antimony

pentachloride, (2) with acetic anhydride and concentrated sulphuric acid, (3) with "vitamin" reagents on ergosterol in high initial concentration, and (4) with "vitamin" reagents on sterols treated with "oxidising" agents, formaldehyde or acetic anhydride. Sterol colours are usually fairly stable and "vitamin" colours transient, but irradiation of sterols may cause transient colours, and a "vitamin" blue has been made to persist for nearly 1 hour by Wokes and Willimott (*Pharm. J.*, **1927**, **1**, 752). A characteristic property of the "vitamin" colours is their sequence, blue —> red. In the case of antimony pentachloride, of acetic anhydride and concentrated sulphuric acid, and of arsenic or antimony trichloride on ergosterol in high concentration, the initial colour obtained is red, but cholesterol irradiated at its melting point or oxidised under given conditions has given blue —> red. The optimum concentration of a fraction for "vitamin" tests does not differ much from that for sterol tests. Of the 4 classes of blue colours given by sterols and their derivatives, those obtained by addition of "vitamin" reagents to cholesterol or certain of its derivatives or to ergosterol, after "oxidation" with benzoyl peroxide or nascent formaldehyde, most closely resemble the "vitamin" colours. It does not seem probable that cholestenone is the chromogen formed on irradiation of cholesterol, which is responsible for the initial blue colour. It has not yet been possible to isolate from the oxidation products of cholesterol pure substances giving initial blue colours with the "vitamin" reagents, and only red chromogens have so far been obtained. With sterols, as with the "vitamin" colours, the blue chromogen is unstable, and is destroyed by attempts to isolate it.

P. H. P.

Specificity of Ergosterol as Parent Substance of Vitamin *D*. O. Rosenheim and T. A. Webster. (*Biochem. J.*, 1928, **22**, 762–766.)—Evidence is presented which strengthens the assumption that only a molecular structure such as that possessed by ergosterol enables a sterol to be photochemically converted into vitamin *D*, and confirms the evidence already available for the view that ergosterol is the specific parent substance of vitamin *D*. Experiments were carried out to find whether, besides ergosterol, other substances with three or more double bonds, but without the sterol ring-structure, would yield the vitamin on irradiation. It was known that squalene, nerolidol and *pseudo*-ionine cannot be activated. Sphingosine, $C_{17}H_{35}NO_2$, an unsaturated open-chain amino-alcohol, and a cleavage product of the cerebrosides, was prepared by hydrolysis of pure phrenosin, but neither the cerebroside phrenosin, to which antirachitic properties had been ascribed by Stepp and Woenckhaus, nor sphingosine possessed any antirachitic action either before or after irradiation. Oxycholesterylene, with 2 double bonds, was another substance prepared and found to be quite inactive. There remained the possibility that isomers of ergosterol, differing from it in the relative position of the three double linkages, might be activable. Other workers have failed to activate *neo*-ergosterol, and zymosterol would hardly be expected to be activable. However, *iso*-ergosterol was prepared and this was also found to be devoid of antirachitic activity. Ergosterol, therefore, seemed to be the specific

parent substance of vitamin *D*, except for a report by Windaus (*Z. angew. Chem.*, 1927, **40**, 697) and Windaus and Holtz (*Nachr. Ges. Wiss. Göttingen*, 1927, 217) that digitaligenin, $C_{23}H_{30}O_3$, a substance structurally related to cholic acid, and therefore to the sterols, could also be activated by irradiation. Since digitaligenin, the anhydro-aglucone of the digitalis glucoside *digitalinum verum*, is a hydroxy-lactone which contains three double linkages, its activation would seem probable. However, digitaligenin was prepared and tested biologically and spectroscopically. A critical repetition was made of the experiments of Windaus and Holtz, and irradiated digitaligenin was entirely devoid of antirachitic properties, even when given in doses 10,000 times larger than effective doses of irradiated ergosterol. Windaus and Holtz irradiated the substance in olive oil, and found that olive oil itself acquires antirachitic properties on irradiation; also, in their negative control experiment, the oil was irradiated for 3 hours, and prolonged irradiation is known to destroy the antirachitic activity of vegetable oils and vitamin *D*. Therefore, apparently, from these facts and previous work, not only a typical ring-structure, but also the specific relative positions in which the three double bonds are present in the molecule of ergosterol are essential for the photochemical conversion of a sterol into vitamin *D*. P. H. P.

Ergosterol in Human Blood. L. H. Dejust, Van Stolk and E. Dureuil. (*Compt. rend.*, 1928, **187**, 311–313.)—Cholesterol was separated from samples of human blood serum, and examined by optical methods. It was found that three bands were present in the spectrograms, corresponding to 2926, 2810 and 2687 Å, which are in close agreement with the accepted figures for ergosterol. In addition, the spectrograms indicate the presence of another absorptive substance in the portion of the spectrum of shorter wave length than 2700 Å. D. G. H.

The Antiscorbutic Fraction of Lemon Juice. VII. S. S. Zilva. (*Biochem. J.*, 1928, **22**, 779–785.)—Experiments show that when phenolindophenol is added to decitrated lemon juice until the indicator is no longer reduced and the solution is adjusted immediately to P_H 7, the antiscorbutic activity disappears within 24 hours. Purified antiscorbutic fractions from lemon juice lose their activity much more rapidly than does decitrated lemon juice of similar activity. The capacity of decitrated lemon juice for reducing phenolindophenol is lost when the juice is dialysed in collodion thimbles of a permeability which leaves the solution inactive after 3 days, but retained to a great extent when the juice is dialysed in thimbles of a permeability which yields an active juice at the end of the dialysis. Acidity retards the deterioration, on storage, of the antiscorbutic activity in anaerobically autoclaved decitrated lemon juice. On storage at P_H 3 the deteriorating effect of autoclaving is hardly perceptible. Lemon juice autoclaved anaerobically, even in a very acid medium, deteriorates much more rapidly at P_H 7 on storage than similar solutions which have not been autoclaved. Very little loss is registered in decitrated lemon juice which has been autoclaved at 40 lbs. pressure (143° C.) for 1 hour under *strictly* anaerobic conditions. These results strengthen the suggestion made by Zilva (ANALYST, 1927, **52**, 552) that the

stability of the antiscorbutic factor in lemon juice is conditioned by the presence of a reducing principle and of a factor, the functioning of which is destroyed by heat; and that the reducing property of the solution acts as a "reduction buffer" for the antiscorbutic vitamin. After the reducing properties are destroyed the activity does disappear much more rapidly. This confirms the dependence of the reducing agency, and consequently of the antiscorbutic factor, on the heat-labile factor. The following points stand out from the complex mechanism:— The antiscorbutic factor, a principle which can withstand such drastic treatment as heating at 143° C. in the absence of air, becomes very labile in the presence of air, on changing the protective conditions of its natural medium. The process of chemical purification is one of the means of removing this protection. P. H. P.

Bacteriological.

The Black Yeasts. G. K. Burgwitz. (*Woch. Brau.*, 1928, **45**, 213–214; *J. Inst. Brew.*, 1928, **34**, 415.)—The term "black yeast" is used provisionally for certain polymorphous fungi which do not form spores or possess fermentative power, but have been included among the pigment-secreting fungi occurring in milk, air, the blood of insects, etc. Pribram describes two such black yeasts, in addition to a polymorphous fungus which he terms *Torula variabilis*. The torula, *Cryptococcus niger*, isolated by Uaffucci and Sirleo from a guinea pig, and *Nadsoniella nigra*, discovered by Issatchenco in the Arctic regions, are of similar character. When grown in liquid media the latter fungus form black flocks on calcium carbonate, and produces on the side of the glass vessel head-like growths, from which secondary shoots develop. In pure cultures on meat peptone with glucose and sodium chloride the fungus forms a thick black layer composed of single oval cells which resemble yeast cells, both in propagating by budding and in containing fat globules. On solid media small round or ovoid conidia may separate, and mycelia develop. The fungus also grows readily on potato. It does not liquefy gelatin unless the culture is old; it does not ferment glucose, sucrose, maltose or lactose, and does not reduce nitrates. Several other black yeast-like fungi resembling torula and monilia have been isolated and described by Treillard.

Germicidal Powers and Capillary Activities of Certain Essential Oils. S. Rideal, E. K. Rideal and A. Sciver. (*Perf. Ess. Oil. Record*, 1928, **19**, 285–304.)—The Rideal-Walker coefficients of some twenty-six well-known essential oils have been determined, and in some cases, *e.g.* palmarosa (9·0), cinnamon leaf (7·5) and cloves (8·0), these are considerably greater than those of a number of commercial disinfectants. Although the oils are very complex, in a few cases it has already been established that the germicidal power is roughly proportional to the percentage of one chemical substance; *e.g.* oil of cloves contains 90 per cent. eugenol, and has a R–W coefficient of 8·0, cinnamon leaf oil contains 85 per cent. with a coefficient of 7·5, and bay oil 60 per cent. and has a coefficient of 5·5. Disinfectants may roughly be classed by their surface tension lowering effects, although

Japanese mint oil and kananga oils seem to be exceptional in their behaviour. In some cases stable peroxides appear to be formed of some of the constituents of the oil, with larger germicidal effects than the oils themselves, *e.g.* white camphor and eucalyptus. Drop number curves are given for concentrations of the oils in pure B.P. paraffin. D. G. H.

Microbiology of Wool. L. Burgess. (*J. Textile Inst.*, 1928, **19**, T315–T322.)—The preliminary work carried out on "mildew" by the British Research Association for the Woollen and Worsted Industries is described. Growth of conidia of *Aspergillus* and spores of *B. mesentericus* or *B. subtilis*, the mildew organisms, is inhibited by formalin (20 per cent.), phenol (10 per cent.), benzoic acid (5 per cent.), mercuric chloride (2·5 per cent.), salicylic acid (2·5 per cent.), and certain silicofluorides, of which the sodium salt (0·5 per cent.) is preferable, since, unlike some of the above compounds, it imparts no discoloration or undesirable odour. Sodium fluoride, chloramine T, borax with formalin, and chlorinated phenols were not effective, and mineral acids were more successful than organic acids. Chrome dyeing increases the powers of resistance of a cloth, probably owing to the waterproofing properties it imparts. The ideal antiseptic, however, which should be cheap, easily absorbed and retained by the wool, and yet produce no colour or odour nor irritate the wearer, has yet to be found. Species of *Actinomyces, Fusarium, A. fumigatus, Penicillium brevicaule, Acrostalagmus*, and *Trichoderma*, and *B. mesentericus ruber, B. mycoides, A. niger* and *Cephalothecium* also attack to different extents ordinary commercial worsted cloth, slightly alkaline in reaction and sterilised by discontinuous steaming. Complications are introduced by migration of alkali in the cloth and the difficulty of determining the moisture requirements of the organisms, since, in very humid atmospheres, condensation on the cloth occurs. In order to determine the actual condition of the fibres to be treated it is proposed to standardise damaged samples of fleece and commercially handled wool (1) in the mass by colour gradations, and (2) quantitatively by the direct microscopic method of Thaysen and Bunker (*Biochem. J.*, 1921, **15**, 407), in which the percentage of damaged fibre units (*i.e.* those damaged portions of a fibre limited by a standard microscopic field) is estimated. Pauly's diazo reaction for tyrosin (*Z. physiol. Chem.*, 1904, **42**, 508), which is present in the inner layers but not in the epithelial scales of the fibre, may be used for the former purpose, since the reagent (alkaline diazobenzene sulphonic acid) is able to stain the cortical tissue of a fibre only where the outer scale has been ruptured, and the depth of colour (pale yellow to deep red) is proportional to the extent of the damage. Benzopurpurine 10 B, which is more stable, has also been recommended. J. G.

Organic Analysis.

General Reaction of Amino Acids. II. H. D. Dakin and R. West. (*J. Biol. Chem.*, 1928, **78**, 745–756.)—An account is given of further experiments on the reaction which occurs between amino acids and a mixture of pyridine and

acetic anhydride, which was described by Dakin and West (*J. Biol. Chem.*, 1928, **78**, 91; ANALYST, 1928, **53**, 452). Other types of amino acids and their derivatives have now been treated with the mixture. The following amino acids were found to yield substituted acetylaminoacetones which were characterised by appropriate derivatives: aspartic acid, glutamic acid, histidine and tryptophane; yet methylaspartic acid gave no trace of either ketone or carbon dioxide, owing to the absence of an unsubstituted α-hydrogen atom adjacent to the amino group. The behaviour of methylaspartic acid is analogous to that of α-amino-hydratropic acid. Phenyl-β-alanine, chosen as a representative of the β-amino acids, gave neither ketone nor carbon dioxide, but underwent simple acetylation. Serine, typical of the β-hydroxy-α-amino acids, gave evidence of ketone formation, but the amount was small, as the product seemed unstable. Phenylserine gave traces of carbon dioxide but no ketone, and was largely converted into the anhydride (azlactone) of acetaminocinnamic acid. The fact that α,β-unsaturated azlactones of this type are not acted upon by pyridine and acetic anhydride was confirmed by experiments with the azlactone of benzoylaminocinnamic acid, prepared by the condensation of benzaldehyde with hippuric acid, which was entirely unacted upon and was recovered unchanged. However, azlactones, or cyclic anhydrides, of saturated α-amino acids were prepared from leucine, phenylalanine and aspartic acid by the action of acetic anhydride on the amino acids according to the method of Bergmann, Stern and Witte (*Ann. Chem.*, 1926, 277), and all reacted with acetic anhydride and pyridine to give carbon dioxide and the same acetylamino-ketones as are furnished by the amino acids themselves. Possibly these azlactones represent an intermediate stage in the pyridine and acetic anhydride reaction. This hypothesis offers a satisfactory explanation of the curious failure of α-alkylamino acids to undergo a reaction analogous to that of the unsubstituted amino acids for the former compounds obviously cannot yield azlactones which contain a hydrogen atom in the position capable of replacement by an acetyl group; on the other hand, it is not improbable that the azlactones only represent one of several intermediate steps in the reaction. P. H. P.

Aromatic Allyl and Propenyl Compounds. I. Safrol and Isosafrol. H. I. Waterman and R. Priester. (*Rec. trav. chim. Pays-Bas*, 1928, **47**, 849–860.)—A number of commercial samples of safrol and of isosafrol were purified, the former by fractionation in a cathode vacuum or by production of the mercury addition compound with mercuric acetate, and the latter by the formation of the picric acid compound. The physical constants were determined, and the m.pt. for safrol given in the literature (11·0° C.) was obtained for the product derived from the mercury compound. In the absence of light, pure safrol or isosafrol does not absorb iodine, but the presence of impurities of an unsaturated nature may produce a slight absorption. The fact that in daylight safrol absorbs more iodine than isosafrol, equilibrium being reached at room temperature after 2 and after more than 5 days, respectively, is made the basis of a method of evaluation of mixtures of these substances. At lower temperatures the

difference is greater, so that by adjustment of the temperature and the intensity of the light the errors inherent in the method (such as those due to side reactions which may affect the point of equilibrium) may be compensated. In practice, a 1 per cent. solution of the mixture in carbon tetrachloride is mixed with 5 c.c. of the solvent and 20 c.c. of a 0·1 *N* solution of iodine in carbon tetrachloride, and the excess of iodine titrated after appropriate periods with 0·1 *N* sodium thiosulphate solution. A linear curve is shown relating the iodine absorption and composition of the mixture. J. G.

Citronellal and the Citronella Oils. H. I. Waterman and E. B. Elsbach. (*Rec. trav. chim. Pays-Bas*, 1928, **47**, 764–775.)—The change in properties of commercial samples of Java and Ceylon citronella oils, prepared differently and of different origins, has been measured by fractionation in the cathode vacuum (*cf. id.*, 1927, **46**, 509), and by determinations of the refractive index. The purest product was obtained from Java oil. In the absence of air there was no change, but atmospheric oxygen produced a slight rise in refractive index and specific gravity after 6 months, which could be wholly or partly inhibited by exclusion of air (*e.g.* by fusion), or by the addition of stabilisers, such as traces of hydroquinone (1 in 1,000) or larger quantities of geraniol. The absorption of oxygen by citronellal at ordinary temperatures is a function of time and results in the production chiefly of citronellic acid, which may be determined by titration with 0·1 *N* potassium hydroxide solution, with phenolphthalein as indicator, and isolated and identified by means of its silver salt. Since analysis showed an unduly high proportion of oxygen, it is concluded that the geraniol present in citronella oil has a stabilising effect on the citronellal. J. G.

Detection of Small Quantities of Alcohol in Oil of Cassia. Schimmel and Co. (*Perf. Ess. Oil Rec.*, 1928, **19**, 353.)—The bisulphite method of determining cassia oil not only determines the cinnamic aldehyde, but also the alcohol content, so that a poor oil adulterated with alcohol will give a good "cinnamic aldehyde figure." The flash-point of the oil is lowered by addition of alcohol, pure cinnamic aldehyde having a flash point of 118° C., and rectified cassia oil 117°. The addition of 1 per cent. of 90 per cent. alcohol to the aldehyde results in a flash point of 73°; of 2 per cent., 48° C.; and of 5 per cent., 39°, and the flash point of the rectified oil is reduced to 70° by the addition of 1 per cent. of alcohol, and to 45° C. by 3 per cent. For practical purposes the flash point of cassia oil should not be below 75° C. D. G. H.

Colorimetric Method for Determining Ethylene Chlorhydrin. M. B. Sapadinsky. (*Z. anal. Chem.*, 1928, **74**, 273–275.)—The refractometric determination of ethylene chlorhydrin (Gomberg, *J. Amer. Chem. Soc.*, 1919, **41**, 1414; Berry, ANALYST, 1919, **44**, 305) is slow, owing to the necessary neutralisation and distillation, and uncertain, owing to the difficulty of ascertaining when distillation of the substance is complete. Moreover, the ordinary methods for determining alcohol by acetylation, benzoylation, or treatment with magnesium methyl iodide

are inapplicable here, but Rosenthaler's method for the detection of alcohols may be modified to render it quantitative. The reagent used is prepared by mixing 1 part of 0·7 per cent. nitrite solution, with cooling, with 4 parts of a solution of 1 grm. of sulphanilic acid in 150 grms. of water and 50 grms. of 0·2 *N* hydrochloric acid. Of the solution to be tested, 0·5 c.c. is mixed, in a test-tube 1 cm. in diameter, with so much of the reagent that the total volume after neutralisation is 6 c.c., the liquid being heated and compared with standard tubes. Solutions containing more than 20 per cent. of the chlorhydrin should be suitably diluted before testing. The standards are kept in sealed tubes away from the light, and should be occasionally checked. The method requires only a few minutes and gives results accurate to about 0·25 per cent. T. H. P.

Differentiation of Raw and Bleached Cotton in Mixtures. W. Sieber. (*Textilber.*, 1928, **9**, 404–406; *J. Soc. Dyers & Col.*, 1928, **44**, 220.)—The material (0·1 grm.) is boiled for 30 seconds to 1 minute with a solution of Victoria Blue B (3 per cent. on the weight of the fibre) in 10 c.c. of water, and then washed with cold water until the washings are only faintly alkaline. The material is then boiled for 30 seconds to a 1 minute with water, again washed several times with cold water until the washings are only faintly blue, and finally dried. Raw cotton is dyed deep shades, whilst bleached cotton is only very slightly coloured.

Determination of Sulphuric Acid in Vegetable Leather. R. F. Innes. (*J. Inter. Soc. Leather Trades Chem.*, 1928, **12**, 256.)—The method in most general use at present is the Procter-Searle method, and in Great Britain leathers shown to contain 0·5 per cent. or more of sulphuric acid by this method are considered to be unsuitable for many purposes, especially if stored for any length of time. Used alone, this method is likely to be misleading, because it may return as sulphuric acid many sulphur compounds other than sulphuric acid, *e.g.* synthetic tans, sulphonated oils and compounds of sulphuric acid with ammonia or basic organic compounds present in the leather.

In order conclusively to establish the presence of sulphuric acid in a leather it is necessary also: (1) To determine the percentage of SO_4 radicle in the leather, and (2) to prove that the aqueous extract of the leather contains a highly ionised acid. (1) The percentage of SO_4 radicle is determined as follows:—Two grms. of the sample are treated for 24 hours at laboratory temperature with 400 c.c. of 0·2 *N* sodium bicarbonate solution, the bottle being occasionally shaken. This extract is then filtered off, an aliquot portion taken, acidified with hydrochloric acid, and the SO_4 radicle determined gravimetrically with barium chloride in the usual manner. (2) The presence of a highly ionised acid is demonstrated as follows:—One grm. of the leather is treated for 24 hours at laboratory temperature with 50 c.c. of water, and the P_H value of the decanted unfiltered extract determined by the hydrogen electrode (*a*). The extract is diluted tenfold, and the P_H value again determined (*b*). All aqueous extracts of vegetable leather are more or less acid, and if the acid present is only slightly ionised (such as lactic, acetic, gallic), the difference between *a* and *b* is 0·6 or less. But, if sulphuric or some other

highly ionised acid is present, the difference between *a* and *b* is between 0·7 and 1·0. It may be that a positive result is only obtained by one or two of the three methods. In such cases sulphuric acid cannot be present. The following table shows how such results should be interpreted:

Diff. between *a* and *b*.	Procter–Searle method.	Gravimetric method.	Conclusion.
0·7 to 1·0	+	+	Sulphuric acid present
0·7 to 1·0	+	—	Sulphuric acid absent, Syntans present
0·7 to 1·0	—	+	Sulphuric acid absent
0·7 to 1·0	—	—	Sulphuric acid absent, Oxalic acid probably present
0·6 or less	+	+	Sulphuric acid absent
0·6 or less	+	—	
0·6 or less	—	+	
0·6 or less	—	—	

From this table it will be seen that it is only justifiable to conclude that a leather contains free sulphuric acid *when a positive result is obtained by all three methods.* R. F. I.

Inorganic Analysis.

The Indicator Question. K. Linderstrom-Lang. (*Comptes-rend. Lab. Carlsberg*, 1928, **17**, 7, 24.)—The compound 2, 4, 2′, 4′, 2″-pentamethoxy-triphenyl carbinol, with a basic hydrolysis constant of 0·03, prepared from Lund's triphenylmethane dyes, gave a colour intensity of the same order as phenolphthalein at a concentration of 2 c.c. of 0·5 per cent. acetone solution per 110 c.c. of solution under investigation. Titrations of glycocoll and peptic hydrolysates of casein with the use of this indicator, gave similar results to naphthyl red, and the indicator is to be preferred to naphthyl red unless a control is used. D. G. H.

New Indicators of the Sulphonphthalein Series. (*Hyg. Lab. U.S. Public Health Service*, Reprint No. 1131.)—The sulphonphthaleins in the subjoined list have been synthesised, and their characteristics as indicators studied.

Sulphonphthalein.	Common name.	P_H range.	Colour change.
m-Cresol	*m*-Cresol purple	7·4–9·0	Yellow—purple
Tetrabrom-*m*-cresol	Brom-cresol green	3·8–5·4	Yellow—blue
Tetrachlor-*m*-cresol	Chlor-cresol green	4·0–5·6	,, ,,
Dibrom-phenol	Brom-phenol red	5·2–6·8	Yellow—red
Dichlor-phenol	Chlor-phenol red	4·8–6·4	,, ,,
Dibrom-dichlor-phenol	Brom-chlor-phenol blue	3·0–4·6	Yellow—blue

Separation of Gallium from Iron. J. Papish and L. E. Hoag. (*J. Amer. Chem. Soc.*, 1928, **50**, 2118–2121.)—The solution of the chlorides is neutralised with ammonia, re-acidified with one or two drops of hydrochloric acid, treated with an excess of acetic acid or ammonium acetate, and the iron precipitated with a slight excess of a freshly prepared solution of α-nitroso-β-naphthol (1 grm. in

50 c.c. of 50 per cent. acetic acid). After standing for several hours, the precipitate is collected and washed, first with cold 50 per cent. acetic acid, then with water. The dried precipitate is ignited in a tared porcelain crucible to constant weight over a Méker flame. The ignition must be started very carefully so as to prevent mechanical loss. The separation is quantitative. W. R. S.

Volumetric Determination of Germanic Acid. Study of certain Hydrated Forms of the Acid and its Salts. A. Tchakirian. (*Compt. rend.*, **1928**, **187**, 229–231.)—Two methods serve for the volumetric determination of germanium. (1) In presence of alcoholic compounds, such as mannitol, glycerol, or glucose, the solubility of germanium dioxide is increased owing to the formation of a germano-organic compound, and on titration of the liquid with sodium hydroxide, using phenolphthalein as indicator, one atom of germanium corresponds with one molecule of the alkali. For 10 grms. of germanium dioxide, 20 grms. of mannitol are required. If the alcoholic compound is replaced by a strong electrolyte, such as calcium or strontium chloride, in concentrated solution (20 grms. of the salt per 10 c.c. of the solution), one atom of germanium corresponds with two molecules of sodium hydroxide on titration. (2) This method is based on the property of the mannitol-germanic acid compound of liberating one atom of iodine per one atom of germanium from the mixture $KI+KIO_3$; the reaction is complete in three hours. In presence of strong electrolytes, the amount of iodine set free is doubled, this reaction being finished in twelve hours. This method is applicable in presence of strong acids. The acid is eliminated by means of the iodide-iodate mixture, and the solution decolorised exactly with thiosulphate, then treated with mannitol, and titrated with thiosulphate after three hours.

Both methods give results accurate to about 1 per cent. T. H. P.

Detection of Vanadium in Systematic Qualitative Analysis. J. Röll. (*Z. anal. Chem.*, **1928**, **74**, 342–345.)—In presence of sufficient ferric iron, vanadium is precipitated quantitatively by ammonia. If necessary, therefore, some ferric chloride is added before the precipitation of the ammonia group. The washed precipitate is digested with hot sodium hydroxide solution. One portion of the filtrate is strongly acidified with sulphuric acid and tested with hydrogen peroxide for vanadium. The other portion is neutralised and the precipitate formed tested for alumina by ignition with a little cobalt nitrate. The washed residue from the last extraction is digested with sodium carbonate solution and the extract tested for uranium; the final residue consists of the hydroxides of iron, chromium, and titanium, for which separate tests are made. W. R. S.

Micro Method for the Determination of Potassium as Iodoplatinate. A. T. Shohl and H. B. Bennett. (*J. Biol. Chem.*, **1928**, **78**, 643–651.)—A procedure is outlined for the determination of 0·1 mgrm. or more of potassium. The method depends upon the precipitation of the potassium as potassium chloroplatinate in the ash of physiological material. The potassium chloroplatinate is

converted into potassium iodoplatinate by the addition of potassium iodide. Quantitative determination can then be made either by colorimetric or titrimetric procedure or by both. Because of the deep rich wine colour of the iodoplatinate in solution, amounts as small as 0·1 mgrm. of potassium in this form can be determined with an accuracy of $\pm$ 4 per cent., by colorimetric comparison with known amounts of potassium chloroplatinate converted in the same way. By titration of the iodoplatinate solution with 0·01 *N* sodium thiosulphate in a micro burette, 0·4 mgrm. of potassium or more can be determined with an accuracy of $\pm$ 2 per cent. Colorimetric determination is convenient for 0·1 to 0·4 mgrm. of potassium as the chloroplatinate, and titrimetric procedure is convenient for 0·4 to 1·0 mgrm. of potassium. The titrimetric result can be checked colorimetrically by re-oxidation of the solution. Some results for blood, serum, milk and urine are given, and all results with the present method were checked by gravimetric determination according to the Lindo-Gladding method. All known potassium solutions were determined correctly, and varying amounts of material yielded the same percentage analysis for potassium by the new method. P. H. P.

Reviews.

RADIATION IN CHEMISTRY. By R. ALAN MORTON, B.Sc., Ph.D., F.I.C. Pp. 284+ xvi. London: Baillière, Tindall & Cox. (Industrial Chemistry Series.) Price 15s.

This is an interesting and useful book. Although primarily an account of the investigations of the Liverpool school, the author reviews the results of recent years of radiation and photochemical research. It is encouraging to realise what a large array of results of industrial importance has been obtained from work in this field, in spite of the fact that the theoretical development of this subject has suffered many reverses, and is not yet beyond controversy. The chapters on the photographic industry, and on "Biochemistry and Light," are particularly interesting, and the results of irradiation in vitamin work are summarised in a manner which will interest all chemists.

The author writes as an enthusiast; he clearly loves the subject, and understands it. This leads to certain drawbacks; thus the theoretical side of the book might, with advantage, be amplified and made more clear for the benefit of those who are not quite up-to-date in chemical physics. Too much is taken for granted, and there is insufficient appreciation of the importance of facts which do not fit in with current theory. Some of the drawings are rather crude.

H. E. Cox.

A COMPREHENSIVE SURVEY OF STARCH CHEMISTRY. Vol. I. Compiled and edited by R. P. WALTON 1928, Pp. 360. The Chemical Catalog Company, Inc., New York, U.S.A. Price $10·0.

This book is in a way unique in type. Of its six hundred pages, two hundred and forty are devoted to a symposium of the various phases of starch chemistry and technology, and the remaining three hundred and sixty to a bibliography and author and subject indexes.

The symposium consists of nineteen sections, each treated by an authority on the special branch of the subject. These authorities are of a variety of nationalities, *e.g.* Pictet, Irvine, Ling, Arlsberg, Katz, Pringsheim, Fernbach, Preuss, Takamine, Alexander, etc. The first seven sections deal with the chemical and physical properties of starch, and include discussions by Pictet, Irvine, Ling and Pringsheim on its molecular constitution. These sections will be of particular interest to those engaged in research problems connected with starch. Somewhat divergent views are expressed by these authorities, and it is apparent that its molecular constitution has not been finally determined. This is not surprising, in view of the fact that the further investigations are carried into the nature and constitution of starch, the more complex is it found to be. It has long been recognised that at least two substances, *viz.* amylopectin and amylose, are present in the starch grain, and recently Schryver has shown that a third substance is sometimes present, *viz.* amylo-hemicellulose. Again, Samec's assertion, that the amylopectin portion is a phosphoric ester, further complicates the problem.

It will be obvious from these remarks that some of the earlier work on the molecular constitution of starch is valueless, because it was based on the assumption that the substance of starch grains is a chemical individual. In fact, some of the work described in this book is not free from this criticism.

It is unfortunate that in the literature of starch chemistry, as in that of pectin, a variety of names is used by the different investigators for what is probably the same substance. This confusion is, perhaps, inevitable until the subject has been investigated more fully, but it undoubtedly adds to the difficulties of those who attempt to follow the progress of these investigations.

It is not possible in the space available to deal adequately with all sections in this symposium, even if the writer were qualified to do so. There are, however, several sections of special interest to most chemists. For example, there is a section on the gelatinisation and retrogradation of starch in relation to bread "staling" by J. R. Katz, which is published here for the first time in English. It describes an investigation into the causes and prevention of "staling" in bread which arose out of a demand by the union of the bakery workers in Holland that night work should be prohibited. Katz found that he could prevent staling by controlling humidity and temperature conditions. The results of this investigation are of interest to all who have to deal with starch in a gelatinised form, where retrogradation changes may affect the qualities of the product adversely or otherwise.

To those unfamiliar with the methods of manufacturing starches, dextrin gums, and adhesives, and their uses in industry, the respective sections will be of interest, but, as a general rule, they are unlikely to teach the specialist much which he does not know, as the articles are mainly of a descriptive nature intended for the general reader. The section on starch-converting enzymes—to which four specialists have contributed—will be found interesting, as it indicates the comparatively new, but rapidly increasing, use of commercially prepared enzymes as catalysts in various industries.

The bibliography contains 3485 references, the period covered being from 1811 to 1925 inclusive. The list is believed to be as complete, as regards starch chemistry, as it is possible to make it. An attempt was made to test the completeness of these references over a period of years, but no important omission was detected.

These references are generally on the card index principle, *i.e.* they give the name of the author and the original title of each article, followed by the name of the journal, etc.; also in most cases a very brief abstract of the article, and very often a note as to where a copy of the original paper or a fuller abstract of it may be seen. This latter reference is obviously intended for the use of American readers.

There are very complete author and subject indexes, but the analyst will be disappointed in finding that there is no section dealing with the analysis or testing of starch or its products, except in one section on viscosity. In this Njvling gives a description, with illustrations, of various forms of viscometers suitable for determining the viscosity of starch pastes. There are, however, numerous analytical references in the bibliography.

The book will appeal most to those research workers who are investigating problems connected with starch, to whom the bibliography should be particularly useful, as it should save them much time and trouble otherwise necessary in searching the literature.

The volume is well printed and is remarkably free from printers' errors. One of these, noted in the index of authors' names, was that of placing all references to J. L. Baker's work under J. C. Baker. There are numerous illustrations and photo-micrographs, which have been very well reproduced.

T. MACARA.

PRACTICAL SEROLOGY. By LUIGI VIGANÒ. Translated by E. MARY HEFFER. Cambridge: W. Heffer & Sons. 1928. Pp. x+221. Price 12s. 6d.

The vast amount of labour which must have been spent in making such a good translation of this book from the original Italian has not been justified by the result. It is obviously intended for the student, to help him in his practical classes, but, as it contains many incorrect statements, it is more likely to mislead than help him. As a work of reference it has little to commend it to the practising serologist.

If we were reviewing the book for a medical journal we should criticse adversely much of the technique, such as the dangerous method of obtaining blood samples by wet cupping and the use of dangerous live cultures, such as *M. militensis* and *B. mallei*, for agglutination reactions. The *B. proteus* × **19** is not used in this country for the diagnosis of cerebro-spinal fever, but may be used for the diagnosis of typhus fever.

Many of the numerous reactions given for the diagnosis of syphilis are mere refinements; on the other hand, Lange's colloidal gold reaction, which is now in almost universal use, and of proved value, is dismissed in half a page, and there is no explanation of how the reaction occurs or of its significance.

The book is well and clearly printed, and has numerous illustrations, which are well reproduced, but some, especially those on pp. 59 and 135, are meaningless.

J. H. MACLEAN.
G. ROCHE LYNCH.

STANDARDS AND TESTS FOR REAGENT AND "C.P." CHEMICALS. By BENJAMIN L. MURRAY. Second edition. Pp. 560. London: Constable & Co., Ltd. 1928. Price 25s. net.

It will be appreciated that the value of a book of standards depends not a little on the authoritative position of the body or author producing it. Mr. Murray appears to represent only himself, but pleads the past experience of many years when he was in charge of the control laboratory of Merck & Company, as the justification for preparing such a text. In the first edition (1920) the work dealt entirely with reagent chemicals. There are now treated two categories, "Reagent" and "C.P."; it is not quite clear what is the essential point of difference, except that the C.P. standard is in each case less stringent than for the Reagent quality, although both are said to be standards for chemicals which the manufacturers can produce economically on a commercial scale.

About 450 substances are included, and there is given a description of the substance, a note as to its analytical or reagent uses, a list of its maximum impurities, and details of how each test for these impurities is to be carried out. The substances include a large variety of organic and inorganic chemicals, "fine" and otherwise; and inasmuch as the author puts forward standards and tests for many for which there is no other published specification, even if we do not agree with the proposed standard, we are indebted to him, and shall find his work valuable. It is surprising, however, that the author should propose standards widely different from, and more lax in many cases (*e.g.* Sulphuric acid) than those of an authoritative work, such as the B.P. and the U.S.P. To multiply standards for chemicals included in the pharmacopeias is undesirable, nor does there seem any good reason for so doing.

Considering the detail of the book, we find that it bristles with controversial points and presents many inconsistencies which ought to be eliminated in a future

edition. For example, sulphuric acid (Reagent) is allowed 30 parts per million of lead (and no heavy metals), whilst diluted sulphuric acid, 10 per cent., also of "Reagent" quality, is allowed 50 parts, similar relaxation is evident in many instances, so that all the manufacturer has to do if his product is not up to standard is to dilute it. Another curious feature is the number of grades prescribed; thus we have five potassium hydroxides, (1) purest (Reagent and C.P.), (2) pure, also Reagent and C.P., (3) purified (Reagent), and, in addition, there is a 30 per cent. solution. Potassium iodide is distinguished from potassium iodide neutral, and it is difficult to understand why the former may have up to 0·069 per cent. of carbonate, 0·238 per cent. of chloride and 0·0016 per cent. of nitrate. There are numerous curious limits, the *raison d'être* of which is not apparent; thus glycerin must contain 0·0000 per cent. of substances reducing ammoniacal silver nitrate, but is allowed 0·04 per cent. of sugars and 0·1161 per cent. of esters, with 7·5 parts per million of arsenic (As).

Space does not permit of detailed examination of the various tests, but many of them leave much to be desired, and, as a whole, the specifications are not such as would be accepted by most analysts accustomed to the handling of pure chemicals.

H. E. Cox.

Publications Received.

TECHNICAL METHODS OF CHEMICAL ANALYSIS. Vol. II. Edited by C. A. KEANE and P. C. THORNE. London: Gurney & Jackson. Price £3 3s. 0d. net.

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

PHOTOMETRIC CHEMICAL ANALYSIS. Vol. I. COLORIMETRY. By J. H. YOE. London: Chapman & Hall. Price 42s. 6d. net.

INDUSTRIAL CATALYSIS. By S. J. GREEN. London: Ernest Benn, Ltd. Price 50s. net.

THE PRINCIPLES AND PRACTICE OF THE DILUTION METHOD OF SEWAGE DISPOSAL. By W. E. ADENEY. Cambridge University Press. Price 12s. 6d. net.

PRACTICAL PHYSIOLOGICAL CHEMISTRY. By S. W. COLE. 8th Edition. Cambridge: Heffer. Price 16s. net.

GLYCEROL AND THE GLYCOLS. By J. W. LAWRIE. New York: Chemical Catalog Co. Price $9.50.