THE ANALYST

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

Death.

We greatly regret to have to record the death of one of the original members of the Society, Professor John Robinson Leebody, who died on August 21st. He was born in 1840, educated at Queen's College, Belfast, and in 1865 was appointed Professor of Mathematics and Physics in Magee College, Londonderry. At the time of his death he was President of the College.

Food Colouring Materials Sub-Committee.

UNIFORMITY OF ANALYTICAL METHODS.

ARSENIC, LEAD, Etc., IN FOOD COLOURING MATERIALS.

The above-mentioned Committee will be glad to receive from Chemists (at home or abroad) who have had experience in the estimating of poisonous metals in food colouring materials, details of the methods which they have found to be of service. In addition, correspondence is invited from all those who can in any way offer useful suggestions relative to this subject.

Communications to the Hon. Secretary of the Sub-Committee, Mr. S. G. Clifford, A.I.C., Midways, Deepdene Avenue, Dorking, Surrey.

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

VII. The Precipitation of Tungstic Acid by Tannin.
VIII. The Separation of Tungsten from Tantalum and Niobium.

By W. R. SCHOELLER and C. JAHN.

(*Read at the Meeting, May* 4, 1927.)

VII. THE PRECIPITATION OF TUNGSTIC ACID BY TANNIN.

The analytical recovery of tungstic acid from tungstate solutions containing excess of alkali carbonate or hydroxide, or both, is generally effected by mercurous nitrate, after neutralisation with nitric acid or boiling with excess of ammonium nitrate. If the tungstate solution contains an undue quantity of chloride, the precipitation of mercurous chloride renders the process impracticable. In such cases recourse can be had to the salt of an organic base or alkaloid (*e.g.* benzidine, cinchonine, quinine), the more commonly used reagent being apparently cinchonine hydrochloride. However, the literature contains indications to the effect that this precipitant is not infallibly successful: thus, Ledoux and Co. (*Bull.* 212, *U.S. Bureau of Mines*, Washington, 1923, 160) point out that "small quantities of tungsten are slowly precipitated by cinchonine in the presence of alkaline chlorides"; Cremer (*ibid.*, 144) found that "48 hours was required for the cinchonine precipitate to settle."

Cinchonine Precipitation.—In our investigation into the separation of tungsten from tantalum and niobium (see Section VIII of this paper), the proposition was to recover small quantities of tungstic acid (generally below 0·05 grm.) from liquors containing 20 to 30 grms. of alkali chloride and possibly a few mgrms. of earth acids. The latter, it was assumed, would be precipitated as such on acidification, and flocculate out together with the cinchonine tungstate. We satisfied ourselves as to the efficacy of the reagent used, namely, a 5 per cent. solution of the base dissolved in a small excess of hydrochloric acid. Pure tungstic oxide (0·2000 grm.) was dissolved in a small quantity of hot potassium carbonate solution, and the liquid diluted to 200 c.c. Three 50 c.c. portions were treated with a very small excess of hydrochloric acid; 10 c.c. of the reagent were required to bring about rapid flocculation. The precipitate was collected next day, washed with 0·2 per cent. cinchonine solution, and ignited. Results: 0·0499; 0·0501; and 0·0500 grm.

When the same procedure was applied in our test separations, the recoveries were, as a rule, from less than 0·001 to 0·004 grm. short; the clear cinchonine filtrates were occasionally seen to deposit a further small precipitate after some days' standing. Evaporation of the filtrates, after addition of ammonia and re-acidification, when tried, generally gave an additional yield of oxide, but not quite enough to satisfy us that a full recovery had been reached. Precipitation by

benzidine was tried in two experiments, but the results were lower still. The inference seemed justified that the recovery by any organic base might not reach the full amount taken for analysis.

TANNIN PRECIPITATION.—Now the action of tannin on tungstic acid is similar to that on the earth acids, in that it produces a voluminous, coloured precipitate. On investigation we found that the recovery of tungstic acid from the acidified solution in the form of the bulky, brown tannin adsorption complex is not quite quantitative, but that the brown coloration of the filtrate renders visible the few mgrms. that have escaped precipitation. This small fraction, we argued, must be in colloidal suspension, therefore amenable to precipitation by such flocculating and collecting agents as yield insoluble tannin compounds, *e.g.* alkaloids. By boiling the filtrate, containing excess of tannin, with cinchonine hydrochloride solution, we obtained a precipitate containing the remainder of the tungstic acid. In this procedure the presence of alkali chloride, far from being prejudicial, is necessary for satisfactory flocculation. As the precipitate is very bulky, the method is more suitable for the determination of small amounts of tungsten, that is, the very case in which the other processes are less certain in operation.

DESCRIPTION OF AUTHORS' METHOD.—In the method given below, the tannin and the cinchonine precipitations are carried out simultaneously; hence the whole of the tungstic acid is obtained in one operation. The alkaline tungstate solution, (100 to 150 c.c.) containing alkali chloride, is neutralised with dilute hydrochloric acid to the bicarbonate stage (phenolphthalein indicator) and treated with a freshly-made solution of 0·5 grm. of tannin, part of which flocculates as a white precipitate if the chloride ion concentration is high. The addition of the dilute acid is now continued until the solution is acid to litmus paper; at this stage the brown turbidity due to the formation of the tungsten complex appears. The liquid is heated to boiling, when the precipitate becomes dark brown and flocculent. After a few minutes' gentle boiling, a 5 per cent. solution of cinchonine hydrochloride (5 c.c., diluted with water) is added, and the boiling continued for another 5 minutes, during which the pale cinchonine precipitate blends thoroughly with the tungsten precipitate. After standing in the cold for 6 hours or overnight, the clear liquid is decanted through a 9 or 11 cm. ashless filter; the precipitate in the beaker is then well mixed with pulped filter fibre, transferred to the filter, and thoroughly washed for the removal of the alkali salt; this is done with a cold 5 per cent. ammonium chloride solution containing a little tannin. The white turbidity that appears when the washings run into the filtrate is of no consequence. Should a small part of the precipitate adhere to the beaker in a plastic condition, it is easily detached with the help of a little filter pulp and warm wash liquor. The precipitate is dried in a tared porcelain crucible, heated gently till charring is over, then over a Bunsen burner till yellow, and weighed as WO_3.

RESULTS OF TEST DETERMINATIONS.—In experiments 1, 2 and 5, the solution was precipitated with tannin, the precipitate filtered off, and the filtrate precipitated with cinchonine; the two precipitates were ignited and weighed separately.

In the other experiments, the determination was made as described above, the tungstic oxide being obtained in one precipitate. The quantities taken in experiments 3 to 6 were unknown to the operator.

Expt.	WO_3 taken. Grm.	Tannin precipitate. Grm.	Cinchonine precipitate. Grm.	Sum. Grm.	Error. Grm.
1	0·0364	0·0336	0·0023	0·0359	−0·0005
2	0·0532	0·0490	0·0046	0·0536	+0·0004
3	0·0044	—	—	0·0047	+0·0003
4	0·0229	—	—	0·0233	+0·0004
5	0·0444	0·0371	0·0072	0·0443	−0·0001
6	0·0440	—	—	0·0443	+0·0003

The ignited cinchonine precipitate in Exp. 1 was black, and the test resulted in an error of +0·0013; the cinchonine fraction was therefore dissolved and reprecipitated with cinchonine. In this operation a loss occurred, which explains the negative error. We submit that the results are accurate, tending towards a small positive error. This method should prove very useful in the assay of low-grade tungsten ores, tailings, and the like.

SUMMARY.—A method is described for the precipitation of small quantities of tungstic acid from solutions containing alkali chloride. The acidified solution is boiled with tannin, and complete flocculation of the brown tungsten precipitate is accomplished by addition of cinchonine hydrochloride; the precipitate is ignited to tungsten trioxide. The results are accurate.

VIII. THE SEPARATION OF TUNGSTEN FROM TANTALUM AND NIOBIUM.

The separation of tungsten from tantalum and niobium is a problem frequently encountered in earth-acid analysis; the usual directions for the analysis of tantalite and kindred minerals prescribe fusion with bisulphate and extraction of the hydrolysis precipitate with ammonium sulphide, a treatment originally devised by Berzelius, and supposed to extract the whole of the tungsten, tin, or antimony, or tin and antimony, from the precipitate. Though riddled with adverse criticism, this method still survives in the text-books.

This Section is divided into two parts. In the first, the published methods are reviewed and criticised; in the second, we introduce our new separation methods, based on the precipitation of tantalum and niobium as sodium salts (Section VI, ANALYST, 1926, **51**, 613).

1. OBSERVATIONS ON THE PUBLISHED METHODS OF SEPARATION.

The available information on the separation in question is not extensive and, as we propose to show, almost wholly unreliable. The published methods, five in

number, will be discussed *seriatim*. It should be noted that the criticisms of the separation of tungsten by ammonium sulphide (see *Method A*) and by fusion with sodium carbonate and sulphur (*Method C*) apply equally to the separation of tin and antimony from the earth acids.

METHOD A: *Extraction of the hydrolysis precipitate with ammonium sulphide or ammonia.*—The use of this method, mentioned in the preamble to this Section, is still advocated by Meyer and Hauser. In their monograph, *Die Analyse der seltenen Erden und der Erdsäuren* (Stuttgart, 1912, p. 301), they even defend it against some of its critics in the following translated passage: "As small quantities of stannic and tungstic acid occur in probably all the natural titanoniobates and tantalates, it is pertinent to inquire whether extraction with ammonium sulphide effects the complete removal of tin and tungsten from the earth acids. Roy D. Hall (*J. Amer. Chem. Soc.*, 1904, **26**, 1235) disputes the possibility of the complete extraction of tin by this process. In his experience, niobic acid must be fused with sodium carbonate and sulphur, several times if necessary. Edgar F. Smith (*Proc. Amer. Phil. Soc.*, 1905, **44**, 151) is of the same opinion. However, more recent confirmation of these observations is lacking, so that the question remains undecided for the present. In any case, the errors by this method are not very considerable."

Meyer and Hauser were evidently unaware that additional evidence corroborating that of Hall and of Smith was available. As long ago as 1862, Rose (*Traité Complet de Chimie Analytique*) observed that tantalic acid could not be completely freed from tungstic acid by extraction with ammonia or ammonium sulphide, whilst niobic acid was not quite insoluble in the same reagents. Our own experiments, recorded under *Method B*, confirm Rose's observations. The treatment therefore gives rise to the following errors:

> Positive for Ta, negative for W, in the Ta-W separation;
> negative for Nb, positive for W, in the Nb-W separation.

If these errors happen to compensate one another more or less, seemingly good results may ensue in the analysis of earth-acid minerals; but it must also be borne in mind that the tungstic acid content of such minerals is generally reported as less than one per cent.; hence what is in reality a considerable relative error may appear as a small absolute error. That the principle of the method is faulty becomes apparent when substantial quantities of tungstic and earth acid have to be separated. Thus Bedford (*J. Amer. Chem. Soc.*, 1905, **27**, 1216), in determining the composition of a niobotungstate, found that "concordant results were not obtained by the usual methods." Finally, Giles (*Chem. News*, 1909, **99**, 1) observed that ammonia dissolved "a surprising amount" of niobic acid when acting on the hydrolysis precipitate.

We conclude that the evidence here cited constitutes ample proof of the unreliability of the method, which should therefore be expunged from the literature, together with its applications. Among these we may instance the determination

of the earth acids in wolframite, as given in Treadwell's *Analytical Chemistry*, Vol. II: the mineral is decomposed by *aqua regia*, ferric and manganous chlorides are removed by filtration and washing, and the tungstic acid eliminated by solution in ammonia; the residue is assumed to contain the whole of the earth acids free from tungsten. In view of what precedes, the separation achieved by the procedure cannot be regarded as quantitative, for, in addition to the adsorption of tungsten by tantalic acid and the solubility of niobic acid in ammonia, the presence of a form of tungstic acid insoluble in ammonia (Hutchin, ANALYST, **1911**, **36**, 398) constitutes another source of error. This ammonia-insoluble tungstic acid may even have been mistaken in some analyses of wolframite for niobic acid. Quantitative data obtained by Treadwell's ammonia method (*e.g.* by Carobbi, who found 0·1 per cent. of earth acids—chiefly niobic—in Traversella scheelite (*Gazz. Chim. Ital.*, 1924, **54**, 59) must for the present be regarded as more or less approximate.

METHOD B: *Action of ammonium nitrate on alkaline solutions of the metallic acids.*—When an alkaline solution containing tungstate, niobate, and tantalate is boiled with ammonium nitrate, soluble ammonium tungstate is formed, whilst the earth acids are assumed to be precipitated. Bullnheimer (*Chem. Zeit.*, 1900, **24**, 870) proposes the reaction for the purification of tungstate solutions in the assay of tungsten ores, though he does not say that it removes the earth acids. In the absence of published data we decided to investigate the method experimentally.

In the following test separations the weighed mixed oxides were fused with 3 grms. of potassium carbonate, the mass dissolved in water, and the solution boiled with 5 grms. of ammonium nitrate until the escaping steam no longer smelt of ammonia. The precipitates were collected, washed with dilute ammonium nitrate solution, ignited, and weighed. Results:

Exp.	1.	2.	3.
Grm. Ta_2O_5 taken	0·1048	—	0·0555
,, Nb_2O_5 ,,	—	0·1050	0·0557
,, WO_3 ,,	0·0223	0·0222	0·0222
,, NH_4NO_3 ppt.	0·1180	0·0018	0·1195
Earth-acid error	+0·0132	−0·1032	+0·0083

The precipitates from Exps. 1 and 3 were fused with potassium carbonate, and the solution of the mass saturated with sodium chloride for the precipitation of the earth acid; the acidified filtrate was precipitated with cinchonine, the precipitate fused with sodium hydroxide, and the aqueous solution treated with hydrochloric acid and stannous chloride; in both cases a strong blue colour characteristic of tungstic acid was obtained.

The conclusion reached is that the separation is unreliable: tantalic acid, as well as the mixed earth acids, adsorbs tungstic acid freely, whilst niobic acid alone is apparently not precipitated. We confirmed the different behaviour of the two earth acids in absence of tungstic acid towards ammonium nitrate by fusing

weighed amounts, given below, with potassium carbonate, and boiling as before with ammonium nitrate:

Exp. 4. Took 0·1044 grm. Ta_2O_5; Wt. of NH_4NO_3 ppte 0·1033 grm.
,, 5 ,, 0·1518 ,, ,, ; ,, ,, ,, ,, 0·1516 ,,
,, 6 ,, 0·1035 ,, Nb_2O_5; ,, ,, ,, ,, 0·0044 ,,
,, 7 ,, 0·1550 ,, ,, ; ,, ,, ,, ,, 0·0054 ,,

This proves that potassium tantalate is quantitatively precipitated by boiling with ammonium nitrate, whereas potassium niobate is not precipitated. In Exp. 3, a 1:1 mixture of tantalic and niobic oxides, converted into potassium salts, was completely precipitated by the same treatment, which shows that tantalic acid here causes "loss of individuality" of niobic acid. Hence, an excess of niobic acid may be expected to prevent the precipitation of tantalic acid. We thought it interesting to determine the interference the two acids exert on each other according to their relative proportions in a mixture, by means of Exps. 8 to 12, which were carried out in the same manner as Exps. 1 to 7:

Exp.	Taken: Ta_2O_5. Grm.	Taken: Nb_2O_5. Grm	Sum. Grm.	NH_4NO_3 Ppt. Grm.	Ratio. Ta_2O_5:Nb_2O_5.	Deportment.
8	0·1026	0·0220	0·1246	0·1236	5:1	as Ta_2O_5
9	0·0803	0·0420	0·1223	0·1208	2:1	,, Ta_2O_5
10	0·0610	0·0612	0·1222	0·1200	1:1	,, Ta_2O_5
11	0·0408	0·0795	0·1203	0·0856	1:2	intermediate
12	0·0212	0·1084	0·1296	0·0026	1:5	as Nb_2O_5

To sum up, if a solution containing potassium tungstate, niobate, and tantalate is boiled with ammonium nitrate, the tungsten result will be low if tantalum predominates, and high if niobium is the more important constituent. The method is of no analytical value.

We made a final unsuccessful attempt at a separation by means of ammonia after converting the metallic acids into oxalo-complexes, the difference between this procedure and the ammonia treatment in Method *A* being that, in this case, the ammonia is made to act on a solution of the metallic acids, whereas in Method *A* a precipitate is submitted to extraction. The mixed oxides were fused with bisulphate, the mass dissolved in ammonium oxalate solution, and the boiling liquid treated with a slight excess of ammonia. Results:

Exp.	Taken: Ta_2O_5 Grm.	Taken: Nb_2O_3 Grm.	Taken: WO_3 Grm.	Ammonia precipitate. Grm.	Earth-acid error.
13	0·1024	—	—	0·1039	+0·0015
14	—	0·1016	—	0·0990	−0·0026
15	0·1018	—	0·0218	0·1121	+0·0103

The ammonia precipitate from Exp. 15, tested as in Exp. 1, was found to be strongly contaminated with tungstic acid.

METHOD C.: *Fusion of the mixed oxides with sodium carbonate and sulphur.*— This method was devised by H. Rose (*op. cit.*) to supplement or replace Method *A*.

Yet it has fared badly at the hands of its critics, who unite in pronouncing it defective. Smith (*loc. cit.*) ascertained, like Hall (*loc. cit.*), that "two or even three refusions with these reagents were found necessary" for the removal of tungsten and tin. Bedford (*loc. cit.*), who attempted to use the method, reports that the results varied "within wide limits." Blomstrand (*J. prakt. Chem.*, 1866, **99**, 40) pointed out that if the fusion was conducted at low temperature, tin and tungsten were not extracted completely, whilst at higher temperatures tantalum and niobium were rendered soluble. It is easy to account for this behaviour by the following considerations. The mixed oxides, having been precipitated simultaneously, are in the state of molecular admixture. Hence, if the action of the flux is not as complete as possible, some tungsten (tin) will still remain with the unattacked pentoxides. If on the other hand the attack is complete, the tantalic and niobic acids are converted into sodium salts, which are rather sparingly but distinctly soluble; yet Rose's method is silent as to the recovery of this soluble fraction from the solution of the thiosalts. We submit that this argument, based on the findings of several independent observers, dispenses us from undertaking fresh experimental work, and would justify the excision of Rose's method from the literature.

METHOD D: *Action of magnesia mixture on alkaline solutions of the metallic acids.*—This is the method devised by Bedford (*loc. cit.*) for the analysis of a niobotungstate. It consists in fusing the weighed mixed oxides with potassium carbonate and treating the alkaline solution of the melt with excess of magnesia mixture. After standing some hours the precipitate is collected, washed with the precipitant, ignited, fused with bisulphate, and the mass boiled with water. The hydrolysis precipitate, after the usual treatment, is weighed as Nb_2O_5; tungstic oxide is obtained by difference (Abstract: ANALYST, 1905, **30**, 415). The results of five test separations are given; four are very close, the fifth shows a negative earth-acid error of 0·0053 grm. Bedford did not try the method for the separation of traces of tungsten from much niobium, nor did he investigate the separation of tantalum from tungsten.

The success of our own method—precipitation of tantalum and niobium as crystalline sodium salts, followed by the direct determination of tungsten in the filtrate—rendered a further study of Bedford's method and the investigation of its extension to the tantalum-tungsten separation unnecessary for the present. In the course of some trial experiments we observed that the magnesium niobate precipitate (which flocculates and settles well after digestion on the water bath) showed a slight tendency to give a cloudy filtrate on being washed; this may explain the above-mentioned low result obtained by Bedford.

METHOD E: *Action of salicylic acid and ammonia on an alkaline solution of the mixed acids.* This reaction, studied by Muller (*J. Amer. Chem. Soc.*, 1911, **33**, 1506) completes the list of the published processes. Muller found that the separation of much niobium from small amounts of tungsten was satisfactory, whereas large quantities of tungsten interfered with the precipitation of the niobium.

2. Authors' Separation Methods.

The new methods take advantage of the fact that sodium tungstate is freely soluble, whilst sodium tantalate and niobate are practically insoluble, in solutions of high sodium ion concentration. The precipitates do not adsorb tungstic acid, and the precipitation is carried out in alkaline solutions free from heteropoly-acids. In mineral analysis the separation requires two different modes of procedure: Method *A* for earth-acid minerals poor in tungsten; Method *B* for tungsten minerals poor in earth acids.

Method A: *Separating small quantities of tungstic oxide from large quantities of earth acids.*—This method consists in the application of the technique described in Section VI (*loc. cit.*). The mixed oxides (0·5 grm. or more) are fused with 3 grms. of potassium carbonate in a platinum crucible at high temperature until the molten mass is perfectly clear. When the crucible is cold, a small lump of potassium hydroxide (rather less than 0·5 grm.) is introduced; the crucible is half filled with hot distilled water, and left on a hot plate until everything has dissolved. The solution is transferred to a 250 c.c. beaker with a little hot water, and precipitated hot with an excess of solid sodium chloride added gradually (about 17 grms. for 50 c.c. of solution). The sides of the beaker are rinsed down with a little half-saturated sodium chloride solution. The precipitate is allowed to stand overnight, collected on a 9 or 11 cm. filter, washed by decantation with half-saturated sodium chloride solution till the solid sodium chloride has dissolved, then transferred to the filter and well washed with the same solution.

If the direct determination of the earth acids is desired, the filter containing the sodium chloride precipitate is returned to the precipitation vessel, and the paper disintegrated by stirring with hot distilled water. The suspension is acidified with dilute hydrochloric acid (methyl orange indicator) and digested for some hours on the water bath. The precipitate is collected, well washed with dilute ammonium nitrate solution, ignited strongly in a tared porcelain crucible, and weighed as pentoxides (P^1).

The filtrate from the sodium chloride precipitate contains the tungstic acid and a few mgrms. of non-precipitated earth acid. The latter is recovered by hydrolysis in bicarbonate solution as follows (*cf.* Section VI, *loc. cit.*, p. 618): the cold liquid is treated with a drop of phenolphthalein and dilute hydrochloric acid until the red colour just disappears. The solution is then digested on the water-bath, and if the pink colour returns on heating, it is just discharged by another drop or two of dilute acid. The remainder of the earth acids is thus precipitated in a flocculent form, leaving the supernatant liquid perfectly clear after a few hours' digestion. The precipitate is collected on a small filter containing a little filter pulp, and washed with half-saturated sodium chloride solution, after which it is returned to the beaker and digested for two hours with a little dilute acid for the removal of adsorbed alkali. It is then collected on the same filter, washed with dilute ammonium nitrate solution, and ignited to pentoxides (P^2). The sum P^1+P^2 represents the tantalic *plus* niobic oxide present in the mixed oxides.

The filtrate from the bicarbonate hydrolysis precipitate, containing alkali tungstate, is treated with 0·5 grm. of tannin, etc., according to the procedure given in Section VII of this paper, and the ignited tannin-cinchonine precipitate weighed as WO_3.

The appearance of the tungstic oxide is a good indication of its purity, as the yellow colour is very sensitive to a small admixture of earth acids. On digestion with a little hot, strong sodium hydroxide in the porcelain crucible, the weighed tungstic oxide should give a clear solution. If turbid, the liquid is transferred to a small beaker, neutralised to the bicarbonate stage as before, and digested hot until flocculation has set in. The small precipitate, P^3, is collected, washed, leached with dilute acid, and ignited exactly as described for P^2; the weight found is deducted from that of the tungstic oxide and added to the weight of pentoxide. This purity test is more important in the niobium-tungsten separation (incidentally, a very rare occurrence in mineral analysis), because a little niobic acid may escape precipitation at the P^2 stage.

The ignited precipitate, P^1, is pure white, whilst P^2 is generally dark, owing to adsorption of a trace of platinum. If a gold crucible is used in the fusion, the flocculated P^2 is lilac (a Cassius purple).

RESULTS OF TEST ANALYSES.—The subjoined table gives the results of 5 tantalum-tungsten separations (Exp. 1 to 5), 5 niobium-tungsten separations (6 to 10), and 6 separations of tungstic oxide from a mixed earth-acid preparation containing 61·4 per cent. Ta_2O_5 and 38·6 per cent. Nb_2O_5, as determined by Powell and Schoeller's tannin method. In almost every case the quantities of oxides taken were unknown to the operator.

		Taken:		M_2O_5 fractions:		Found:		Errors:	
Exp.		M_2O_5. Grm.	WO_3. Grm.	P^1. Grm.	P^2. Grm.	M_2O_5. Grm.	WO_3. Grm.	M_2O_5. Grm.	WO_3. Grm.
Ta	1	0·1022	0·0202	0·1018	—[1]	0·1018	0·0215	−0·0004	+0·0013
,,	2	0·0995	0·0204	0·0970	0·0020	0·0990	0·0206	−0·0005	+0·0002
,,	3	0·1002	0·0264	0·0980	0·0016	0·0996	0·0254	−0·0006	−0·0010
,,	4	0·1500	0·0543	0·1510	0·0008	0·1518	0·0536	+0·0018	−0·0007
,,	5	0·2848	0·0245	0·2798	0·0066	0·2864	0·0249	+0·0016	+0·0004
Nb	6	0·1031	0·0224	0·1012	0·0009	0·1021	0·0220	−0·0010	−0·0004
,,	7	0·3296	0·0090	0·3282	—[2]	0·3282	0·0092	−0·0014	+0·0002
,,	8	0·2055	0·0421	0·2022	0·0022	0·2044	0·0424	−0·0011	+0·0003
,,	9	0·3004	0·0338	0·2976	0·0035[3]	0·3011	0·0334	+0·0007	−0·0004
,,	10	0·2766	0·0125	0·2701	0·0048[3]	0·2749	0·0116	−0·0017	−0·0009
EA	11	0·4562	0·0582	0·4558	0·0009	0·4567	0·0574	+0·0005	−0·0008
,,	12	0·4772	0·0380	0·4760	0·0015	0·4775	0·0376	+0·0003	−0·0004
,,	13	0·3128	0·0255	0·3106	0·0024	0·3130	0·0256	+0·0002	+0·0001
,,	14	0·2237	0·0475	0·2227	0·0016	0·2243	0·0478	+0·0006	+0·0003
,,	15	0·3221	0·0353	0·3188	0·0028	0·3216	0·0349	−0·0005	−0·0004
,,	16	0·3724	0·0072	0·3696	0·0025	0·3721	0·0067	−0·0003	−0·0005

[1] Ta_2O_5 recovery by P^1 only, which stood 5 days before being filtered off: high WO_3 result.
[2] No P^2 was obtained.
[3] This is P^2+P^3.

In some of the earlier tests here recorded, the filtrate from P^1 was precipitated with cinchonine, the ignited impure tungstic oxide fused with a little potassium carbonate, and the resulting solution submitted to bicarbonate hydrolysis, which gave P^2. The separation method described above is more expeditious, as it saves a second fusion; it answered particularly well in the tests on the mixed earth acids (Exp. 11 to 16).

METHOD B: *Separating small quantities of earth acid from large quantities of tungstic acid.*—In this case the separation is carried out in a solution free from potassium ion, the weighed mixed oxides (1 grm.) being fused with sodium hydroxide (2 grms.) in a nickel crucible. In order to avoid dusting caused by the strong reaction of the melting alkali upon the tungstic oxide, we moisten the oxides and alkali in the crucible with a few drops of water, and dry the contents by gentle heating; the bulk of the oxide is thus dissolved before the water is expelled. The fluid melt is brought to a red heat, which need not be maintained for more than half a minute. The cold mass is taken up in the crucible with 10 c.c. of half-saturated sodium chloride solution by digestion on a hot plate, and the liquid allowed to stand a few hours at ordinary temperature. A little filter pulp is stirred in, and the small precipitate collected on a minute, tightly-packed pad of filter pulp in a tiny funnel; it is washed with half-saturated sodium chloride solution (1 to 1·5 c.c. at a time) till the washings hardly blue a litmus paper, *i.e.* 8 to 10 times. The total volume of combined filtrate and washings is 20 to 30 c.c. The pulp containing the precipitate is rinsed into a 50 c.c. beaker, and digested hot with a few drops of dilute hydrochloric acid for about half-an-hour; after some standing it is collected on a 5 cm. filter, washed with ammonium nitrate solution, ignited and weighed as $(Ta, Nb)_2O_5$. Tungstic oxide, as the predominant constituent, is taken by difference.

TESTING THE WEIGHED PRECIPITATE.—For the certain identification of the earth acids, the weighed oxides are fused with a little potassium carbonate on platinum foil; the mass is dissolved in a few drops of water, and the solution, transferred to a watchglass, is saturated with sodium chloride, when a white crystalline precipitate is obtained. Alternatively, the oxides are fused with bisulphate, the mass dissolved in ammonium oxalate, and the solution treated with tannin according to Powell and Schoeller's method (Sections IV and V, ANALYST, 1925, **50**, 485).

RESULTS OF TEST ANALYSES.—In spite of the relatively large amount of tungstic oxide present, the manipulations have almost the character of micro-analytical work, the tungstic acid being easily soluble in 2 grms. of sodium hydroxide, and readily eliminated with about 15 c.c. of wash-liquor. Results of four determinations (quantities unknown to operator):

Taken. Grm.	WO_3 added. Grm.	Found. Grm.	Error. Grm.
0·0108 Nb_2O_5	1·000	0·0107	−0·0001
0·0083 Nb_2O_5	1·000	0·0082	−0·0001
0·0062 Ta_2O_5	1·000	0·0061	−0·0001
0·0018 $(Ta, Nb)_2O_5$	1·000	0·0019	+0·0001

In each case the precipitate obtained was tested by fusion with potassium carbonate, etc., as prescribed above; a positive reaction was readily given. In a parallel test, 0·0050 grm. of the mixed earth-acid preparation was fused with 2 grms. of sodium hydroxide, etc., without addition of tungstic oxide; the recovery was 0·0047 grm. $(Ta, Nb)_2O_5$.

SUMMARY.—The following methods for the separation of tungsten from tantalum and niobium are shewn to be unreliable:—(1) Extraction of the precipitate, obtained by hydrolysis after bisulphate fusion, by ammonium sulphide or hydroxide (Berzelius); (2) precipitation of the solution of the potassium salts by boiling with ammonium nitrate; and (3) fusion of the mixed oxides with sodium carbonate and sulphur (Rose).

The authors' separation methods are based on the precipitation of sodium tatalate and niobate. The separation of small quantities of tungsten from considerable amounts of the earth acids is effected by fusion of the mixed oxides with potassium carbonate, precipitation of the resulting solution with sodium chloride, recovery of the small quantity of non-precipitated earth acid by hydrolysis in bicarbonate solution, and precipitation of the tungstic acid in the filtrate by tannin and cinchonine. For the determination of small quantities of earth acid in tungsten trioxide, the latter is fused with sodium hydroxide, and the fused mass dissolved in sodium chloride solution; sodium tantalate and niobate remain undissolved. The two methods give satisfactory results.

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A Study of Antimony Trichloride as a Possible Quantitative Reagent for Vitamin A.

By F. WOKES, B.Sc., F.I.C., and S. G. WILLIMOTT, Ph.D., B.Sc., A.I.C.

(*Read at the Meeting, May* 4, 1927.)

Kahlenberg (*J. Biol. Chem.*, 1922, **52**, 217) appears to have been the first investigator to observe the colours given by different sterols, when using antimony trichloride as the reagent to distinguish between them. While testing a series of cholesterols of different origin with a number of anhydrous inorganic chlorides, he noticed that one of them (origin not stated) gave a blue colour with arsenic trichloride, and when rubbed in a mortar with antimony trichloride gave pink colours, changing to brown. No attempt was made to use antimony trichloride in solution.

In 1920 Rosenheim and Drummond (*Lancet*, 1920, **198**, 862) recorded an observation of great interest in the light of the many recent additions to our knowledge of colour tests for vitamin *A*. These authors found that the colour reactions given by liver oils with sulphuric acid appeared to be proportional to the amount of vitamin present, as determined by feeding experiments with rats. Following up this observation, Drummond and Watson (Analyst, 1922, **48**, 341) put forward concentrated sulphuric acid as a test for vitamin *A* in cod-liver oil. Attempts were then made to match the colour against standard solutions of dyes, but the evanescent nature of the colour, and its masking by charring of other constituents in the oil, prevented their success. Later, Rosenheim and Drummond (*Biochem. J.*, 1925, **19**, 753) proposed the use of Kahlenberg's reagent, arsenic trichloride, which gives bright blue colours lasting one or two minutes, without charring. This was a great advance on Drummond and Watson's reagent, but in unskilled hands arsenic trichloride can be a somewhat dangerous reagent. Continuing the search for colour tests for vitamin *A*, Carr and Price (*Biochem. J.*, 1926, **20**, 497) then tried antimony trichloride in solution in chloroform. They found that this reagent gave blue colours lasting several minutes, and was a much safer reagent. These colours were matched against blue units in a Lovibond tintometer, and the readings thus obtained on two oils agreed approximately with their content of vitamin *A*, as determined by feeding experiments.

Considerable time is needed for the assay by feeding experiment of a foodstuff for vitamin *A*. In the vitamin-testing department of the Pharmaceutical Society's laboratories, opened in London this year, a minimum period of 6 weeks is required to carry out such a test, and another 5 weeks for preparing the animals may also be required (*Pharm. J.*, 1927, Jan. 15, 49). But animal experiments, however tedious and expensive, cannot be displaced by chemical tests until the specificity of the latter has been proved beyond doubt. A great deal of

evidence in favour of the specificity of the arsenic trichloride and antimony trichloride tests for vitamin *A* has already been collected. On various fish oils the results of these tests have been found to agree with the content of vitamin *A* as estimated by feeding experiments on rats. (Rosenheim and Webster, *Lancet*, 1926, Oct. 16, 211; *Biochem. J.*, 1926, **20**, 1342; *Biochem. J.*, 1927, **21**, 111.) Moreover, colour tests and animal experiments agree in indicating that the vitamin is concentrated in the unsaponifiable fractions of these oils, freed from cholesterol by digitonin. When this fraction is distilled with super-heated steam in an atmosphere of nitrogen, or in high vacuum, both colour tests and animal experiments agree in showing that the vitamin can be recovered unchanged from the distillate (Rosenheim and Drummond, *Biochem. J.*, 1925, **19**, 753). Parallel results are also obtained when the vitamin is destroyed by aeration at 100° C. (Rosenheim and Drummond, *loc. cit.*), or at various other temperatures between 88° C. and 125° C. (Wokes and Willimott, *Biochem. J.*, 1927, **21**, 419), by treatment in the cold with concentrated sulphuric acid or phosphorus pentoxide, or by exposure to ultra-violet light (Willimott, Moore and Wokes, *Biochem. J.*, 1926, **20**, 1292).

When, however, these colour tests are applied to vitamin *A*-containing foodstuffs from the vegetable kingdom, difficulties immediately arise on account of the fact that certain plant pigments also give blue colours with reagents (Wokes and Willimott, *Pharm. J.*, 1927, 752). Rosenheim and Drummond noticed this effect with carotin, a pigment found in carrots and in many green leaves. We have recently observed a similar permanent blue colour with xanthophyll, another carotinoid pigment found in the yolk of eggs, and have also discovered that a transient blue colour is given by either arsenic trichloride or antimony trichloride with bixin, the pigment of the seeds of *Bixa Orellana* (Willimott and Wokes, *Pharm. J.*, 1927, Feb. 26, 217). Methods are being worked out for the removal of these interfering pigments by adsorption with suitable agents, which may enable colour tests to be applied eventually to the many vegetable sources of vitamin *A* (*Lancet*, 1927, **213**, 8). At present, however, we suggest applying quantitative colour tests only to oils such as cod-liver oil. In the laboratories of the Pharmaceutical Society the routine procedure has been adopted of first applying colour tests to all oils sent in for physiological assay of vitamin *A*, and, if the result of these tests is unsatisfactory, the manufacturers are recommended not to incur the expense of a feeding experiment.

Although comparatively little is yet known of the chemistry of vitamin *A*, it appears probable that the colours given by this vitamin with arsenic trichloride or with antimony trichloride are due to these substances acting as condensing agents. If the action be purely chemical, it should be affected in a normal manner by the usual factors influencing chemical action, such as time, temperature, purity and concentration of reagents. A study of the effects of these factors has therefore been made.

1. NATURE OF COLOUR CHANGE.—Solid antimony trichloride, when mixed with substances rich in vitamin *A*, gives a pink colour changing rapidly to brown.

If, however, the antimony trichloride be used in solution, under suitable conditions, the action may be retarded, and it will then be seen to consist of three distinct stages:—(*a*) Formation of the blue colour. (*b*) Change from blue to yellow. (*c*) Change from blue or yellow to red, finally to red-brown. These three stages overlap to a greater or less degree, and it is possible to observe various intermediate shades, such as green, orange pink, or purple. As will be shown later, it is possible to retard or accelerate each of these stages (for instance, conditions can be arranged so that the first perceptible colour change is from blue to red), but the final colour reached is always red-brown. It has been suggested by Rosenheim and Drummond (*loc. cit.*) and by Takahashi *et al* (*Inst. Phys. Chem. Research*, Tokyo, 1923, **3**, 81) that the blue colour is indicative of vitamin content, and this suggestion has been adopted in a proposed colorimetric method of estimating vitamin *A* in cod-liver oil recently drafted by the Medical Research Council.

2. Purification of Antimony Trichloride.—This substance, when pure, should consist of white deliquescent prisms melting at 73° C. Commercial samples are sometimes tinged with yellow, and if improperly protected from atmospheric moisture, may be coated with oxychloride. For vitamin testing, antimony trichloride should be purified by recrystallisation from anhydrous chloroform, overheating being carefully avoided, and should then be stored in a stoppered bottle over anhydrous calcium chloride. Any adherent oxychloride should be washed off with anhydrous chloroform immediately before use. Adopting these precautions, we have not observed any difference in the results obtained with several batches of reagent obtained from either of the makers mentioned in the list published by the Association of British Chemical Manufacturers.

3. Purification of Solvent.—Antimony trichloride is readily soluble in many organic solvents; a number of these were tried, including benzene, toluene, xylene, chloroform, monochlorbenzene, *o*- and *p*-monochlortoluene. Of these, the best results were obtained with chloroform, thus agreeing with the findings of Kahlenberg who investigated the colours produced with antimony pentachloride on cholesterol (*J. Biol. Chem.*, 1926, **67**, 425).

It is stated by Cocking and Price (*Pharm. J.*, 1926, Aug. 7, p. 177) that phosgene in chloroform solution, while giving no colour alone with vitamin *A*, if added in minute quantities to other reagents greatly accelerates the reaction and tends to increase the amount of blue in the colour produced. It is advisable, therefore, to test the chloroform used to dissolve the antimony trichloride for the absence of this substance by the barium hydroxide test, and to protect the reagent from light so as to obviate risk of its formation.

If the reaction between antimony trichloride and vitamin *A* is a condensation it should be affected by removal from the reagents of traces of moisture. We have investigated this point by using chloroform dried over anhydrous sodium sulphate and over calcium chloride. Contrary to the experience of Carr and Price (*loc. cit.*), we find that drying the reagent slows down the colour change, and also obviates a tendency to clouding which had previously given us much trouble in

obtaining accurate readings. Moreover, the calcium chloride also removes the ethyl alcohol usually present in commercial samples of chloroform. The purified chloroform thus obtained had sp. gr. at 15°/15° C. of 1·495 to 1·500, and gave negative results when tested for moisture with calcium carbide, and for phosgene with barium hydroxide. It must be carefully protected from light.

4. PREPARATION OF SOLUTION.—Using these purified materials, we made a saturated solution by shaking 30 grms. of dry antimony trichloride with sufficient anhydrous chloroform to make a total volume of 100 c.c. in a dry stoppered bottle for several days at room temperature. Carr and Price (*loc. cit.*) state that they used a 30 per cent. solution, weight in volume. We have not been able to make a solution of this strength without using heat, which we find tends to decompose

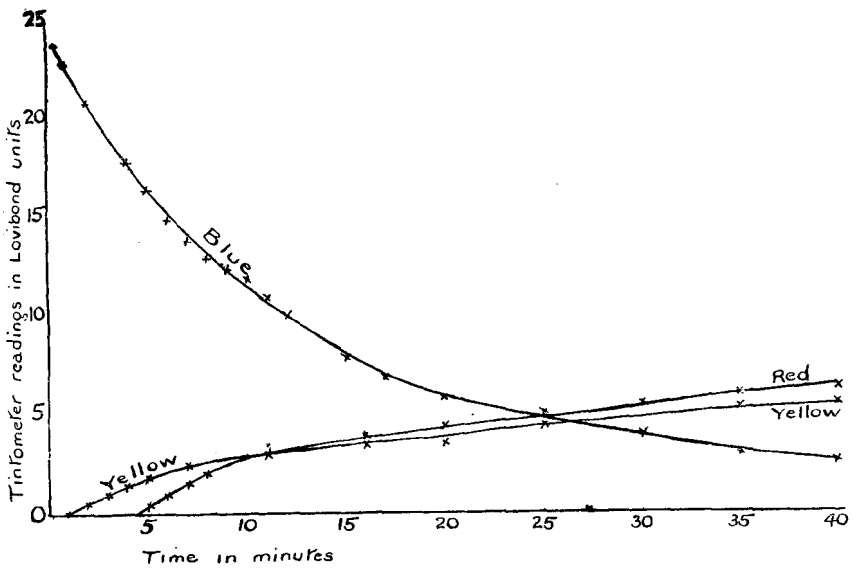

Fig. 1.

the antimony trichloride and to produce an unstable reagent. We have therefore made all our solutions in the cold, and have found them to contain 25 to 26 per cent. of anhydrous antimony trichloride, weight in volume, and to have a sp. gr. of 1·590 to 1·610. The reagent should be stored in well-stoppered bottles, carefully protected from light and moisture, and will then keep for several months. Small amounts of a heavy yellow liquid gradually separate, and for this reason the reagent should not be shaken up; the separation of this liquid, however, does not appear to affect the reliability of the reagent. The liquid probably consists of complex basic chlorides of antimony and is being further investigated.

TIME EFFECT.—A 20 per cent. solution (volume in volume) of a sample of Newfoundland cod-liver oil (see Wokes and Barr, *Pharm. J.*, 1927, **118**, 758) known by previous feeding experiments to be potent in vitamin *A*, was made in anhydrous chloroform. Two c.c. of the antimony trichloride solution were put

in a dry half-inch cell in position in a Lovibond tintometer. To this was added 0·20 c.c. of the cod-liver oil solution, and the liquids mixed immediately with a dry glass rod. Exactly 30 seconds after mixing, a reading was taken of the blue and yellow units required to match the colour of the reaction mixture. This reading was repeated every 30 seconds, with frequent stirring. It was found that the blue units gradually decreased, while the yellow increased. After 4 minutes it was necessary to add red units also. After 25 minutes the reading of each colour was approximately equal. Beyond this, the red colour predominated, and the colour at the end of an hour consisted largely of red, with smaller amounts of yellow and practically no blue. This experiment was repeated with fresh lots of the same oil, and also with fresh reagents, and series of readings were taken by

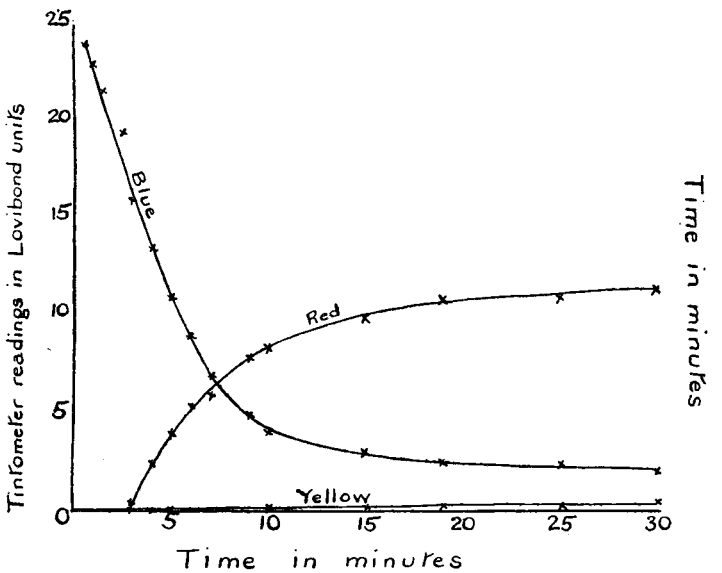

Fig. 2.

different observers. Similar results were obtained, and these findings are plotted in Figure 1. The following were the conditions in the reaction mixture:— Concentration of antimony trichloride, 24·0 per cent.; concentration of cod-liver oil, 1·8 per cent.; temperature, 16° C.

A similar series of experiments was carried out on a number of different oils. It was found that the yellow colour developed more rapidly in oils in which the vitamin had been rendered unstable (*e.g.* by exposure to sunlight). On the other hand, by using high concentrations of stable oils, it was possible to retard considerably the development of the yellow colour, and to obtain a change from almost pure blue to almost pure red. In Figure 2 are plotted the results obtained with a fresh Iceland oil, with which a concentration of 4·5 per cent. in the reaction mixture was used, but otherwise conditions were the same as before.

When any of the stable oils was treated for a short time with any agent which might set going vitamin destruction, it was found that the colours obtained with antimony trichloride were enhanced in yellow, and diminished in red. In all cases, however, there was a rapid drop in blue units within the first few minutes after mixing.

These results showed us that before proceeding further with quantitative work it would be necessary to fix a time after mixing at which readings should be taken. This time effect seems to have been overlooked by previous workers. Cocking and Price (*loc. cit.*) state that a solution of antimony trichloride in ordinary B.P. chloroform produces with cod-liver oil an intense ultramarine blue, "stable for at least 3 minutes." Our experience has been that ordinary B.P. chloroform of several different makes often contains enough moisture to render an accurate reading impossible at the end of 3 minutes. Even when the chloroform is thoroughly dried over calcium chloride, the reading in blue units at the end of 3 minutes may be 20 or 25 per cent. less than at the beginning, as indicated by our curves. The Medical Research Council, apparently recognising this difficulty, has fixed a time limit of one minute after mixing in which the reading is to be taken. After some experience of this technique, we decided to reduce this to half a minute in our work. Our experience has been that when one is working with an oil in which the vitamin has been rendered unstable, *e.g.* by inadvertent exposure to sunlight, the colours may change so rapidly that the brown stage may be reached in little more than one minute. If our procedure is adopted of having the cell and reagent already in position in the tintometer, it is quite possible to obtain readings 15 seconds after mixing, and certainly no difficulty should be experienced in securing a reading at the 30 second limit. We have therefore used the time limit of 30 seconds after mixing throughout the work described in this paper.

6. Temperature Effect.—If the reaction between antimony trichloride and vitamin *A* is a chemical one, the reaction velocity should be roughly doubled for each ten degrees' rise in temperature. In order to investigate this point, a series of experiments was carried out in which the reagent and solution of oil were heated or cooled separately to fixed temperature, mixed in the cell by stirring with a thermometer, and the temperature of the reaction mixture recorded when each reading was taken. When cooled below about 15° C. the reagent clouded, and accurate readings could not be obtained. Above 25° C. the colours changed too rapidly to be correctly matched. Between these limits, several sets of readings were taken at different temperatures, and the average figures are plotted in Figure 3. It will be noticed that the temperature coefficient, over the range investigated, is approximately 2, thus supporting the suggestion that the reaction is a chemical one.

7. Effect of Varying the Concentration of Antimony Trichloride.—Since the condensing agent in this action is greatly in excess, it might be thought that a little antimony trichloride more or less in the reaction mixture would not make much difference to the colour produced. Cocking and Price (*loc. cit.*) state

that the blue colour is not affected by the addition of more chloroform, and that a fully saturated solution is not essential. However, we tested this point by carrying out a series of experiments in each of which the same quantity (0·04 c.c.) of a potent Norwegian oil was mixed with 2 c.c. of antimony trichloride solutions of different concentration, taking readings 30 seconds after mixing, and correcting for temperature. In Figure 4 are plotted the results, showing that when the

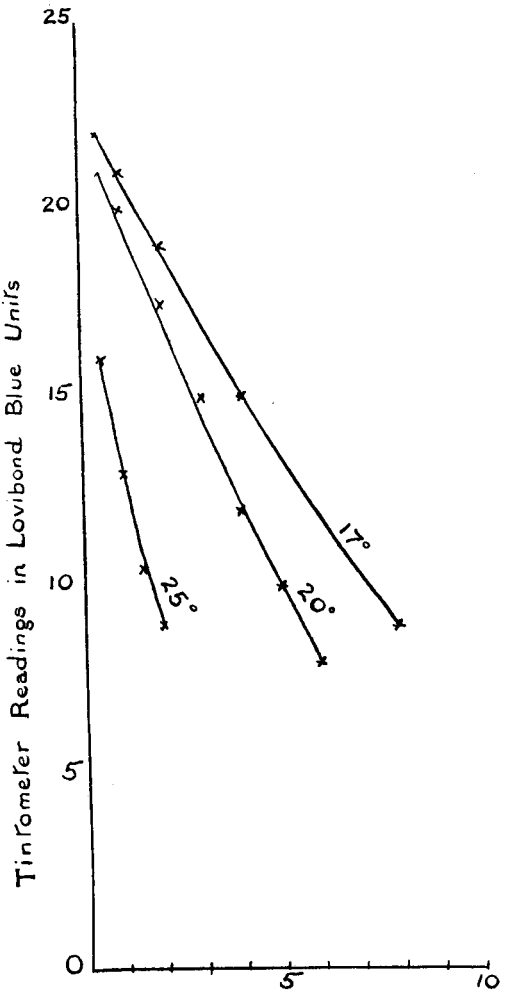

Fig 3.

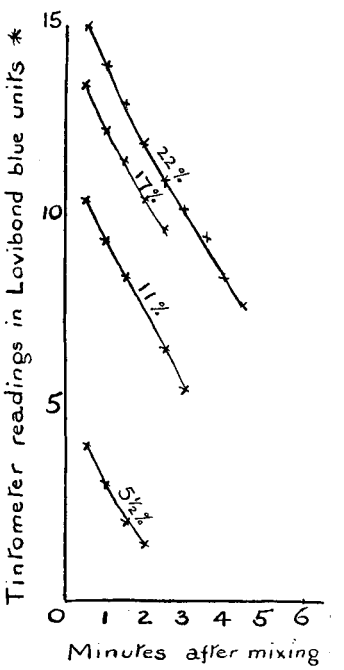

Fig. 4.

concentration of antimony trichloride is halved, the readings of blue colour obtained are markedly reduced to about two-thirds their original value. Since low concentrations of antimony trichloride make the colour change more rapid, we suggest that the concentration of antimony trichloride in the reaction mixture be kept between 22 and 24 per cent.

8. Effect of Varying Concentration of Vitamin.—In this part of the investigation we used three samples of cod-liver oil of entirely different origin. One was a Norwegian oil, the second a Newfoundland, and the third from Iceland. All had been prepared in 1926. Their constants were as follows:—

Table I.

	Norwegian.	Newfoundland.	Iceland.
Sp. gr.	0·927 (15° C.)	0·926 (17° C.)	0·928
Refractive index	1·480 (15° C.)	1·4733 (40° C.)	1·4782 (20° C.)
Saponification value	185·2	186·2	186·0
Iodine value	173·0	168·0	160·0
Acid value	1·19	0·75	1·45
Unsaponifiable matter, per cent.	1·30	—	0·66
Tintometer reading of natural colour, in ½ in. cell:			
Yellow	1·05	1·75	1·5
Red	nil	0·15	0·05

The results of feeding experiments indicated that all these oils were highly potent sources of vitamin *A*, while at the same time differences were observed between them within the somewhat wide limits of experimental error incident to animal experiments. We now estimated their content of vitamin *A* by means of antimony trichloride, adopting all the precautions previously described. A large number of experiments were carried out on each oil over a wide range of concentrations. In order to avoid undue dilution of the antimony trichloride in the reaction mixture, 50 per cent. solutions of oil were used for the higher concentrations, and for convenience in measuring, 5 per cent. solutions were used for the lowest concentrations. Thus the total volume of the reaction mixture was kept between 2·1 and 2·4 c.c., and the concentration of antimony trichloride in it between 22 and 24 per cent. In every case, the reading was taken at the end of 30 seconds after mixing. Several readings were taken at each point, frequently by different observers, and were found to vary less than 10 per cent. The mean of these was used in each case to build up the three curves in Figure 5. (In the upper parts of the curve a ¼ in. cell was used, and the resulting readings were doubled in order to make them equivalent to those obtained in the remainder of the work where a half-inch cell was employed.)

The comparative values obtained with these three oils agree fairly well at different concentrations. The general form of curve, however, indicates a possible source of error in comparing the vitamin content of different oils by colour tests. A Norwegian oil, for example, which gave a reading of 26 blue units under these conditions would contain twice as much vitamin as one which gave a reading of 17·5 units, but the comparative vitamin contents, as judged by direct comparison of colour tests, would be 26:17·5 or approximately 10:7. In such a case an error of about 30 per cent. would arise. This error can be greatly reduced by arranging the concentration of oil in the reaction mixture so as to give readings on the lower linear part of the curve.

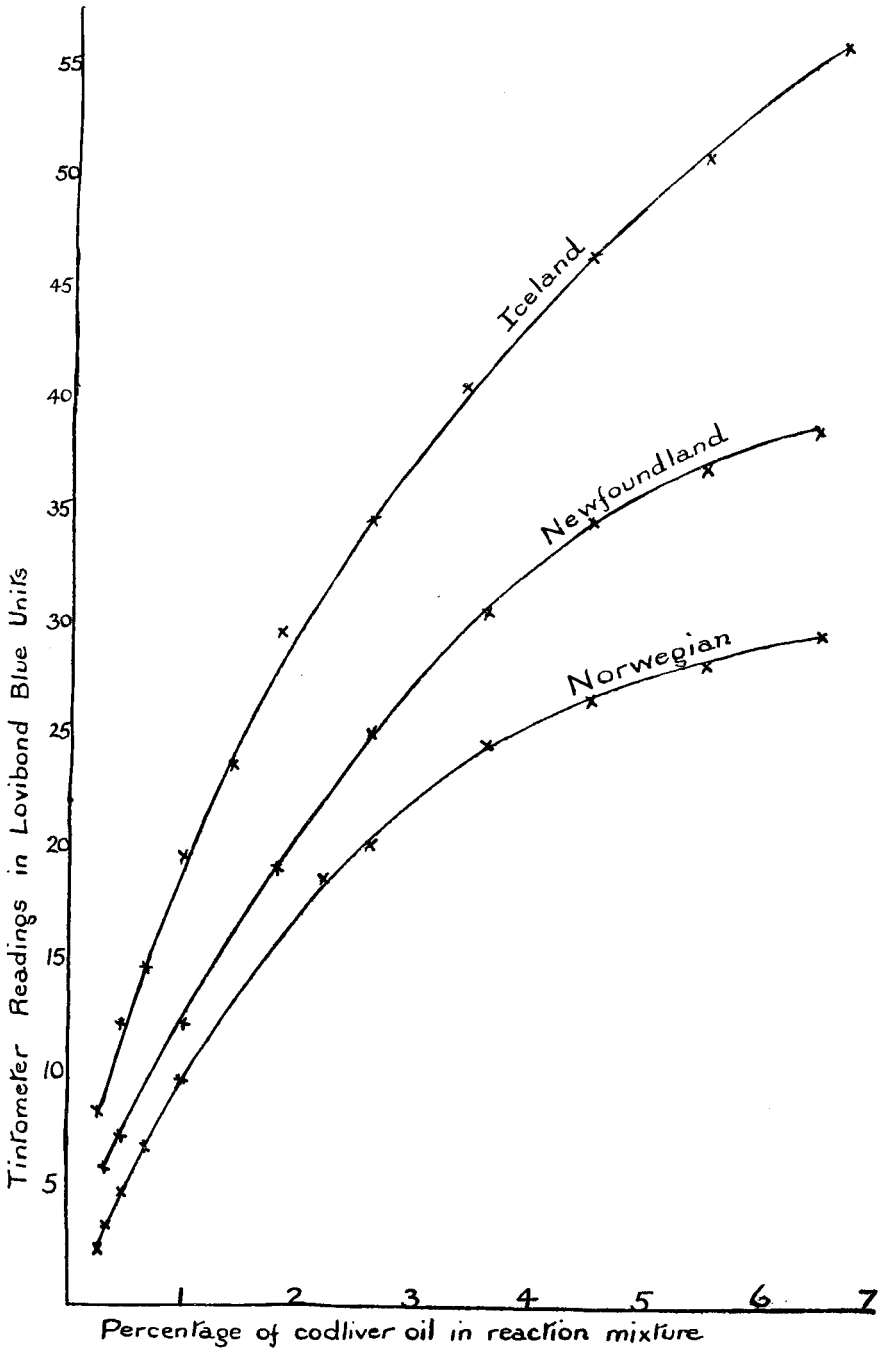
Tintometer Readings in Lovibond Blue Units
55
50
45
40
35
30
25
20
15
10
5
Iceland
Newfoundland
Norwegian
1
2
3
4
5
6
7
Percentage of codliver oil in reaction mixture

Fig. 5.

A number of readings were also taken with arsenic trichloride, with similar precautions; parallel results were obtained. This fact, added to all the evidence obtained in regard to the behaviour of antimony trichloride with vitamin A, leads us to the conclusion that, when the precautions indicated in this work are observed, antimony trichloride in chloroform solution can be used as a reliable reagent for the quantitative estimation of this vitamin.

Our thanks are due to Professor E. C. C. Baly, F.R.S., of Liverpool University, and to Professor T. M. Lowry, of Cambridge University, for kindly affording us facilities for doing this work. Samples of cod-liver oil obtained under different conditions were kindly supplied by Messrs. Allen & Hanburys; Messrs. Evans, Sons, Lescher & Webb; Messrs. Parke, Davis & Co.; and Messrs. Southall Brothers & Barclay. Part of the expenses of this investigation were defrayed by a grant from the Pharmaceutical Society of Great Britain, to whom our thanks are due.

SUMMARY AND CONCLUSIONS.—A quantitative study has been made of the reaction between antimony trichloride and vitamin *A* in cod-liver oil. The effects of the following factors were separately investigated; purity of reagent, nature and purity of solvent, time, temperature, concentration of reagent and concentration of vitamin. The following conclusions were reached:—

1. The reaction consists of a series of colour changes; blue—yellow—red with intermediate shades. The blue is probably characteristic of active vitamin, and the depth of blue colour has therefore been used to measure vitamin content.

2. The reaction, which is probably a condensation, can be retarded (and thus more closely examined) by dehydration of the solvents. Of the latter, chloroform dried over anhydrous calcium chloride has given the best results.

3. The reaction is a chemical one, with a temperature coefficient of approximately 2.

4. The following conditions are suggested for the application of this reaction in the quantitative estimation of vitamin *A*:—

(*a*) *Reagent.* A saturated solution of pure antimony trichloride (recrystallised from chloroform), concentration 26 or 27 per cent. weight in volume, in anhydrous chloroform. The reagent should be protected from light and moisture, and decanted for use. Two c.c. to be put in a clean dry ½ in. cell.

(*b*) *Solution of Oil.* To be prepared on the day when required, with anhydrous chloroform. Strength to be adjusted so as to keep the amount to be added between 0·1 and 0·3 c.c. This to be run into the cell already in position in the tintometer, and containing the reagent. To be mixed immediately by stirring with a clean dry glass rod, and time of mixing noted.

(*c*) *Tintometer Readings.* To be taken in Lovibond blue units, 30 seconds after mixing.

(*d*) *Temperature.* To be kept at about 16° C. Divergence of more than one degree from this to be noted, and a correction applied.

(*e*) *Conditions* to be adjusted so that reading of blue units is below 18, using half-inch cell.

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 POLARIMETRIC DETERMINATION OF SUCROSE IN SWEETENED CONDENSED MILK.

IT is to be regretted that Dr. Honegger (ANALYST, 1926, **51**, 496) did not consult the earlier literature on the polarimetric determination of cane sugar in sweetened condensed milk. The method attributed to Revis and Payne (ANALYST, 1914, **39**, 476) is really that of Harrison (ANALYST, 1904, **29**, 248), and Revis and Payne only introduced modifications in the procedure and formulae for calculation. Dr. Honegger has now modified Revis and Payne's procedure largely in the direction of going back to Harrison's original method; one error of Revis and Payne's is, however, perpetuated, viz. the incorrect factor 1·11 for converting the weight of fat into volume. This factor, 1·11 (which I introduced in many formulae), is really the volume occupied by 1 grm. of fat per 100 c.c. of milk of mean specific gravity, and is the value of $\frac{1{\cdot}032}{0{\cdot}93}$; when fat is expressed as percentage by weight the factor should be $\frac{1}{0{\cdot}93} = 1{\cdot}076$. The error introduced is not very great, but it helps to explain why Revis and Payne used an empirical value in place of the Herzfeld value which was used by Harrison (*loc. cit.*), and also substantially by Cochran (*J. Amer. Chem. Soc.*, 1907, **29**, 555).

Dr. Honegger shows that there is a seasonal variation of the error (or rather difference between polarimetric and gravimetric results), and attributes this to a difference in the volume of the elements of the condensed milk derived from the original fresh milk. This difference is stated to have reached as much as 0·60 per cent., or about 1½ per cent. on the total. I decline utterly to believe that a variation of volume due to such vague causes as "the nature of lactic elements" can cause so great a difference.

It is noted that the variation is seasonal and greatest in hot weather and least in cold; I suggest that there is an explanation which fits in with known facts. If calculated by Harrison's formula, the incidence of variation would be largely reversed.

The fat globules of milk condense round them a layer of serum of the same composition as the milk serum held by surface energy (*cf.* ANALYST, 1904, **29**, 186); the extent of this layer will vary very greatly and inversely as the temperature, and it will take some considerable time for it to become diffused on dilution of the milk. In the winter the milk will have become throughly cooled and the fat globules solid, and the layer will be comparatively great around them, whilst in the summer the globules may even be liquid with very much less layer. The process of dilution and precipitation is directed to be hurried through, with the result that insufficient time is given for the sugars in the condensed layer to diffuse and become equally distributed through the solution. I would suggest that the best procedure is:—

1. When diluting the condensed milk the solution should be left to stand while warm (say at 60° C.) for at least half-an-hour.

2. It should then be cooled to 10° C. and the acid mercuric nitrate added, and the mixing and polarisation carried out at as low a temperature as possible, to delay inversion.

3. Harrison's method and formula should be used.

4. The milk sugar results will be slightly low; I have shown (ANALYST, 1910, **35**, 516) that acid mercuric nitrate is not a complete precipitant of proteins. The final filtrate should be treated with phosphotungstic acid, and the difference between the readings before and after this treatment used as a correction for the initial polarisation.

H. DROOP RICHMOND.

THE DETERMINATION OF SULPHUR DIOXIDE IN DRIED FRUIT.

THE figures quoted by Miller (ANALYST, 1927, 338) show that the method described by him is an accurate one for determining the total amount of sulphur dioxide obtained in the distillate. Unfortunately, the results by this method do not give a correspondingly accurate result for the total sulphur dioxide in the fruit. As pointed out by Monier-Williams (*Ministry of Health Report*, No. 43, p. 48; ANALYST, 1927, 416), dried fruits require a prolonged boiling with fairly strong acid to liberate all the sulphur dioxide, and the amount of acid in Miller's process is too low to do this in a reasonable time, as can be seen by the following figures :—

Apricots.	Sulphur dioxide—parts per million.			
			Miller's Method.	
Samples.	Monier-Williams' Method (ANALYST, p. 415).	May's Method (ANALYST, p. 272).	Vol.	Grav.
A	2960	2670	2290	2180
B	690	625	510*	542
			522*	574
C	2860	—	2610	—

An attempt was made to get more accurate results by largely increasing the acidity in the distillation flask by using 20 c.c. of strong hydrochloric acid instead of the phosphoric acid, but, as might have been expected, considerable quantities of organic acids distilled over, making a volumetric estimation impossible.

Miller's method should be of value as a quick sorting process, but when the amount found is near the prescribed limit, it would appear necessary to repeat the determination, using a considerable quantity of acid with a reflux condenser as recommended by Monier-Williams, or using a gravimetric method such as that previously described by me.

PERCY MAY.

MONUMENT CHAMBERS,
KING WILLIAM STREET, E.C.4.

* Sample B gave a result of 510 when the distillation took 1¾ hours, and 592 when the distillation was carried out more slowly so as to take 2½ hours.

FURTHER NOTES ON THE SEPARATION OF VANADIUM FROM TUNGSTEN.*

In addition to the references cited in my paper (ANALYST, 1927, 466) mention should also be made of the statement in two American papers that vanadium is retained by tungstic oxide in steel analysis. In one of these, by Kelly and his collaborators (*J. Ind. Eng. Chem.*, 1919, **11**, 633), the impure tungstic oxide is dissolved in ammonia solution, the solution made just acid and the vanadium precipitated by the addition of uranium nitrate followed by ammonia. In the other (Lundell, Hoffman and Bright, *J. Ind. Eng. Chem.*, 1923, **15**, 1064) there is described in a footnote a method similar to the above, except that 1 grm. of alum is recommended instead of uranium nitrate; no test results are given. I have tested this process on a solution containing 1 grm. of tungsten (as sodium tungstate) and 0·0020 grm. of vanadium (as ammonium vanadate) prepared to simulate an impure tungstic oxide; a low result was obtained (0·0014 grm. of vanadium), and it was found impossible to wash the aluminium hydroxide precipitate free from tungsten. The hydrogen peroxide method for determining vanadium colorimetrically fails in presence of tungsten, for, on acidification of an alkaline tungstate and vanadate solution, a strong yellow colour is produced which remains practically unchanged after the addition of hydrogen peroxide. It is stated by Singleton (*Chem. Age, Met. Suppl.*, July, 1927) that the addition of phosphoric acid overcomes this interference of tungsten; this is not the case, as the colour produced is not comparable with the brownish-red tint of peroxidised vanadium.

Small Amounts of Vanadium.—The process for small amounts of vanadium of the order to be expected from an impure tungstic oxide in steel analysis is similar to that described in my paper for larger amounts, except that, before adding cupferron, it was found desirable to dissolve 50 grms. of ammonium chloride in the solution to assist the separation of the somewhat small precipitate. In test experiments this precipitate, after filtration and thorough washing, was burnt off, and the residue fused with fusion mixture. The vanadium was determined colorimetrically in the aqueous extract of this fusion by the hydrogen peroxide method, according to the directions of Meyer and Pawletta (*Z. anal. Chem.*, 1926, **69**, 15), *i.e.* treatment of the solution containing 20 per cent. sulphuric acid with 1 drop of 3 per cent. hydrogen peroxide, and comparison with the standard after some minutes' standing. Some results are given in the subjoined table.

Added.		In 300 c.c. solution.		
Vanadium. Grm.	Tungsten. Grm.	HCl. C.c.	HF. C.c.	Found. Vanadium. Grm.
Nil	1·0	25	10	Nil
0·0030	1·0	25	10	0·0027
0·0020	1.0	25	10	0·0018
0·0010	1·0	25	10	0·0009
0·0005	1·0	25	10	0·0004

In each test 50 grms. of ammonium chloride were added.

S. G. CLARKE.

* Communication from the Research Department, Woolwich.

A CASE OF METACETALDEHYDE POISONING.

ON June 8th, 1927, at 8 p.m., a boy of 16 swallowed, in mistake for a sweet, a portion (about 5 grms.) of a double tablet of the solidified fuel used as a substitute for methylated spirit.

No ill effects occurred till 3 a.m. on June 9th, when the patient became flushed, restless and delirious. The temperature rose to 100° F. at 6 a.m. Convulsions occurred on June 9th at 8 a.m., and five further attacks of convulsions occurred during the following 14 hours. The patient was semi-comatose during the intervals between the convulsions.

The urine had sp. gr. 1·014, was very acid, and contained a trace of albumin. There was marked tenderness of the calves of the legs during this period. The temperature remained between 100° and 101° F. for 36 hours and then fell to 99° F., where it remained for 24 hours, afterwards becoming normal.

The treatment consisted in large doses of alkalis (in the form of sodium citrate, 60 grs.; sodium bicarbonate, 30 grs.; water to 1 oz.) given every four hours by the mouth; also normal saline containing 2 drs. of sodium bicarbonate to the pint was given rectally in amounts of 15 oz. every six hours.

Throughout the period during which the convulsions occurred chloral (10 grs.) and potassium bromide (30 grs.) were given every four hours. The urine remained very acid for three days, in spite of the large doses of alkali that were administered.

After the convulsions had ceased potassium bromide, in doses of 15 grs., was given three times a day for four days.

The patient made a good recovery, but the albuminuria persisted for four days. After recovery there was some loss of memory for several days.

An examination of this Meta Fuel, which was confirmed by Dr. H. E. Cox, showed that it agreed in its characteristics and reactions with metacetaldehyde. It sublimed, without melting, at 112° C., forming feathery needle-shaped crystals, and, when heated, in a sealed tube at 120° C., yielded ordinary aldehyde. It was insoluble in water, but dissolved in chloroform and carbon tetrachloride. When heated with strong sodium hydroxide solution it was converted into the brownish so-called aldehyde resin.

The presence of paraformaldehyde had at first been suspected, but no indication of a pink coloration could be obtained by Schryver's test. The original substance, when boiled with water and filtered, yielded a solution which gave a faint yellow coloration with Nessler's reagent, whereas formaldehyde would have given a brown precipitate changing to grey.

In view of the fact that relatively large doses of paraldehyde can be taken, and that cases are on record of recovery after a dose of 1 oz. or more, it is remarkable that metacetaldehyde should be so much more active than its isomer. It is possible, however, that traces of the condensing agents used in the preparation of metacetaldehyde may be left in the final product and have some influence on its physiological action, since no particular care would be taken to make an absolutely pure product. The list of substances claimed in the patents for the preparation of metaldehyde fuel is a very long one, and includes such substances as sulphuric acid, hydrochloric acid, zinc chloride, phosgene, etc., so that the range of possible impurities is very wide.

In any case, as this fuel is so widely used, and is frequently left within the reach of children, it is hardly possible to give too wide publicity to its dangerous character.

W. H. WILLCOX.
C. AINSWORTH MITCHELL.

Standing Committee on Uniformity of Analytical Methods.

METALLIC IMPURITIES IN FOOD COLOURING MATERIALS.

THE Standing Committee on Uniformity of Analytical Methods has appointed a Sub-Committee to formulate methods for the determination of Arsenic, Lead, Copper, Tin, Zinc, and other metals in Food Colouring Materials.

The Sub-Committee consists of the following:—Dr. T. Callan, M.Sc., Ph.D., F.I.C. (chairman), Dr. H. Drake Law, D.Sc., F.I.C., and Messrs. T. Macara, F.I.C., W. G. Messenger, B.Sc., A.I.C., J. R. Nicholls, B.Sc., F.I.C., and S. G. Clifford, A.I.C. (Hon. Secretary).

METHODS OF EXPRESSING STRENGTHS OF COMMERCIAL CAUSTIC SODA AND SODA ASH.

It has been brought to the notice of the Committee, appointed by the Society, to deal with Uniformity of Methods of Analysis, that a certain amount of confusion exists with regard to the expression of results of analysis of commercial caustic soda and sodium carbonate (Soda ash).

Nearly a century ago, when the atomic weight of sodium was believed to be 24, it became customary to express the alkalinity of both these substances as per cent., in terms of Na_2O titrated by standard acid of such a strength (then considered to be normal) that 1 litre would neutralise 54 grms. of sodium carbonate. This method of expressing results is still largely used under the title of "English" or "Newcastle" degrees, in spite of the fact that the atomic weight of sodium is now known to be 23. Two errors are thus introduced: (1) the acid used is too strong in the proportion of 54/53, and (2) the molecular weight of Na_2O is taken as 64 instead of 62; hence the figures so obtained are 1·013 times the true percentages.

Another form of expressing the results has at times been used to some extent in this country and also in the United States, under the title of "Liverpool" or "New York and Liverpool" (N.Y. & L.) degrees, which gives figures even less accurate. There appear to be various interpretations of these degrees, but in any case they are based on the same incorrect view of the atomic weight of sodium. One view is that these degrees are the same as the English, except that the decimal fractions are ignored. Thus, if the English degrees is 69·5, this is called 70 degrees N.Y. & L., and if 69·49, it is returned as 69° N.Y. & L. Similarly, if the English degrees is 72·49, this is called 72 degrees N.Y. & L., so that the commercial range 70–72 N.Y. & L. on this basis is equivalent to a range of 69·5–72·49 English degrees, which again is equivalent to 68·6–71·5 per cent. real sodium oxide.

Another interpretation of the Liverpool degrees, given by Lunge (*Sulphuric Acid & Alkali*, 3rd edition, 1909, Vol. II, Part I, p. 109), is that they are obtained by increasing the percentage of real Na_2O by multiplying by 54/53, and he also adds that "some Lancashire chemists add to each per cent. real Na_2O another 1/31 to get commercial degrees."

The terms "per cent." and "degrees" are at present used indiscriminately for the percentage of Na_2O, and the confusion is rendered even worse by the fact that on the Continent various other "degrees" are in use.

The Committee has had the advantage of consultation with representatives of the Association of British Chemical Manufacturers on the subject, when it was agreed that the present method of expression was unscientific, but that overriding commercial considerations prevented any sudden alteration being made. It has also been agreed, on the suggestion of the Association of British Chemical Manufacturers, to recommend that, in future, certificates of analysis of caustic soda shall be worded as follows:—

"We find the sample of caustic soda .... drums to contain of real alkali, Na_2O, as indicated by the burette .... per cent., equivalent to "English Test," as per Lunge's tables .... per cent."

Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods.

PHYSICAL CONSTANTS.

The Sub-Committee makes the following recommendations:—

Oils before testing should be clear at 15·5° C., and, if necessary, should be filtered through dry filter paper in a covered funnel; where this is necessary it should be stated on the certificate.

Specific Gravities should be determined at 15·5° C., water at 15·5° C. being taken as unity. The results should be calculated to the nearest 0 or 5 in the 4th decimal place.

Refractive Indices should be determined at 20° C. for the D line, and the reading to the 4th decimal place should be given.

Exceptions:—On essential oils with melting points above 20° C., determinations should be made at suitable higher temperatures.

Optical Rotation should be determined at 20° C. and expressed as that given by a column of liquid 100 mm. long for the D line.

Temperatures, if different from those prescribed above, should be stated on the certificate. The Committee does not recommend the use of corrections in any of the above determinations, as these are different for various oils.

(*Signed*) John Allan (Chairman), C. T. Bennett, S. W. Bradley, E. Theodore Brewis, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, C. Edward Sage, M. S. Salamon, W. H. Simmons, T. Tusting Cocking (Honorary Secretary).

August, 1927.

Notes from the Reports of Public Analysts.

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

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE SECOND QUARTER, 1927.

DURING the second quarter of the year 1420 samples were examined, of which 1217 were analysed under the Sale of Foods and Drugs Acts, 1154 being bought informally (47 adulterated) and 63 formally (14 adulterated).

MILK.—Sixty formal samples (12 adulterated) and 598 informal samples (40 adulterated) were examined. Of 384 samples taken from 24 different farmers, 47 were below the limits for fat or solids-not-fat. Road-borne samples were distinctly worse than those taken at railway stations.

BUTTER.—Boric acid was not present in 85 per cent. of the 184 samples examined; the remainder contained 0·1 per cent., with the exception of one sample, which contained 0·2 per cent.

TABLE VINEGAR.—An informal sample contained 6 per cent. of acetic acid and a trace of colouring matter. The vendor stated that it had been made in France from alcohol. The sample was labelled "Finest Table Vinegar," and was therefore condemned, since, by long usage in England, table vinegar should be a superior form of malt vinegar.

GROUND GINGER.—Two samples from one vendor were adulterated with about 3 per cent. of chalk and about 2 per cent. of plaster of Paris. It may have been obtained by grinding a heavily faced root ginger. The tin from which the inspector was served bore the ambiguous label: "Fine ground ginger. Warranted ground from the finest and specially selected qualities." The qualities may have been "specially selected" because of their cheapness. The vendor had no warranty and was fined £2.

DYES.—Nine samples of dyes the use of which is prohibited by the Food Regulations were examined. One sample each of gamboge and naphthol yellow and two samples of Victoria yellow were of the correct composition. Two samples of Victoria yellow and three of aurantia were not correct, one of them containing 79 per cent. of barium sulphate.

PERSPIRATION DEODORISERS.—Ten samples of toilet articles for the prevention or deodorisation of perspiration were submitted by the Medical Officer of Health. One of them was an alcoholic solution containing a little sodium bicarbonate and two others contained aluminium chloride and glycerin. In one case 1s. 6d. was charged for a bottle containing about an ounce. The chief constituents in a powder were, talc and zinc oxide or carbonate; alum, magnesia and chalk also being present. One sample of paste differed little from zinc ointment, and 1s. 3d. was charged for about half-an-ounce. Another paste was about twice the strength of zinc ointment, and 2s. 6d. was charged for it, the amount being

about an ounce. A stick of wax contained about 20 per cent. of oxide of zinc with some perborate, and a cream contained about 5 per cent. of oxide of zinc with moisture, wax and rice starch; 1s. 3d. was charged for an ounce of it. In most cases the articles were perfumed and daintily packed, but the prices were excessive, and in some cases, at any rate, their value for the purposes indicated was problematical.

EGG SUBSTITUTE POWDER.—Egg substitute powders are coloured baking powders, and are only a partial substitute for eggs, as they do not contain fat or albumin. Dried egg is rarely present in such powders, though some contain small masses of dyed starch which might be mistaken for egg. Six informal samples yielded from 2·6 to 9·8 per cent. of carbon dioxide on the addition of water. A formal sample of the powder giving the lowest yield of gas gave 2·5 per cent. of carbon dioxide and was certified as adulterated.

A number of baking experiments were made to ascertain if the power of an egg substitute powder to produce lightness, was proportional to the amount of carbon dioxide yielded on the addition of water. Directions on packets recommended one or two heaped-up teaspoonsfuls of egg substitute powders to a pound of flour. One heaped-up teaspoonful was found to weigh about $\frac{1}{4}$ oz., and this amount was mixed with half a pound of flour. Water ($\frac{1}{4}$ pint) was then added, rapidly mixed, transferred to a tin and baked at about 200° C., for about one hour.

Flour alone was mixed with water and baked under the same conditions to give, by comparison, the amount of expansion produced by the egg substitute powder. When cold, the volumes of the loaves were determined.

In one experiment the flour alone gave a cake measuring 390 c.c. in volume. An egg substitute powder used in the proportion of $\frac{1}{4}$ oz. to $\frac{1}{2}$ lb. of flour gave a loaf with a volume of 510 c.c., or an expansion of 31 per cent. A local make of egg substitute powder baked at the same time measured 710 c.c., or an expansion of 82 per cent., as compared with the loaf made from plain flour only. Each of these powders was sold at the rate of about $1\frac{1}{4}$d. per ounce. Another powder sold at a penny per ounce gave an expansion of 44 per cent.

At the prosecution (see "Legal Notes," p. 536) I gave evidence of these facts, and that the standard for baking powder was 6 per cent., and asked the magistrates to fix a standard of 6 per cent. of carbonic acid gas to be liberated by water, for egg substitute powder.

The manufacturer, in evidence, stated that he made two qualities of egg substitute powder, and that the article in question was the cheaper one, but that he had had no complaints as to its strength. My analysis of the powder was not disputed.

The magistrates dismissed the case on the grounds that scientific evidence alone was not sufficient to enable them to fix a standard. In a case of this kind it is not easy to suggest what other evidence could be given. Both users of egg substitute powder and vendors of it would be ignorant as to the amount of carbonic acid gas that should be present, and it would be difficult to obtain evidence from rival manufacturers of egg substitute powders.

J. F. LIVERSEEGE.

Legal Notes.

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

APPLE MATTER IN RASPBERRY JAM: A QUESTION OF WARRANTY.

On June 13 a firm of jam manufacturers was summoned at Bow Street Police Court for having given to a firm of grocers a false warranty in respect of raspberry jam, which was found upon analysis to contain foreign ingredients, *viz.* at least 10 per cent. of apple matter.

Mr. Hawkes, for the Holborn Borough Council, stated that in February a summons against the firm of grocers had been dismissed upon proof of a warranty, which was as follows:—"These goods are guaranteed pure in accordance with the Food and Drugs Act." The present summons was therefore issued against the manufacturers, and it had been adjourned to enable the third sample to be submitted to the Government Laboratory. The Government Analyst's certificate had now been received and agreed with the certificate of the Borough Analyst, but was more detailed.

During the war, and up to the end of 1921, a Food Order was in force which permitted the addition of fruit juice to jam without disclosure, but this Order was revoked in December, 1921, and the submission of the prosecution was that since that date any addition to jam other than the specified fruit and sugar was not justified, and that the sale of such goods was to the prejudice of the purchaser, just as it was before the war.

Mr. J. Kear Colwell, Public Analyst for Holborn, gave evidence that the sample of jam analysed by him contained at least 10 per cent. of apple matter.

In cross-examination by Sir Travers Humphreys, he said that he found certain apple cells and obtained reactions associated with apple in jam. His results were consistent with pectin derived from the apple having been used, but apple cells were certainly not pectin. The pectin he had found might possibly have been derived from raspberries, but the apple cells could not. He agreed that concentrated pectin from apple might have been added, as it was put into jam for the purpose of making it set.

Sir Travers Humphreys asked that this answer might be taken down, because it was the whole of his case. He suggested that commercial raspberry jam consisted of raspberries, sugar and foreign pectin in some form. It had been held that the word "quality" in the Food and Drugs Act meant commercial quality, and so it had been held that glucose was a legitimate addition to marmalade.

Mr. Kear Colwell did not agree that foreign pectin was a legitimate addition to raspberry jam unless notice of its presence was given. In his view raspberry jam meant a mixture of sugar and raspberries; the pectin must be derived from the raspberry itself. The addition of foreign pectin caused the jam to set sooner, so that less boiling was required, and a larger quantity of jam was therefore obtained from a given quantity of fruit.

Mr. Andrew More, F.I.C., Analyst in the Government Laboratory, produced his certificate of the analysis of a sample of the jam, which showed that it contained 0·49 per cent. of pectin and a few apple cells. He estimated that 100 lbs. of this jam would contain: raspberry fruit, 20 lbs.; fruit juice or pectin equivalent to apples, not less than 24 lbs.; and sugar, 65 lbs. He said that if fresh fruit was

used, it was not necessary to employ pectin in preparing raspberries for jam, but that it would be impossible to use old pulped raspberries for jam without the addition of pectin. He had estimated the amount of raspberry fruit in the jam partly from the insoluble solids and partly from the number of raspberry seeds. The amount of insoluble solids in fresh raspberries varied from 6 to 9 per cent.; he had never known it as low as 4 per cent. For the purpose of the estimate he had taken it at 8·5 per cent.; if it was taken as 6 per cent., it would give 29 lbs. of raspberries instead of 20 lbs.

Sir Travers Humphreys said that he was going to suggest 4 per cent., which would correspond to 40 lbs. of raspberries.

At the adjourned hearing, on June 21st, Sir Travers Humphreys opened the case for the defence. The warranty in this case, he said, was a warranty that the goods were guaranteed pure in accordance with Sec. 6 of the Food and Drugs Act. The word "quality" in the section was the one applicable to this case. Immense importance attached to the proviso, which was a recognition that certain articles were given names which did not indicate the precise ingredients of which they consisted. Jam might be anything. Raspberry jam might contain other things besides raspberries and sugar, and if the added ingredients were not injurious to health—and apple pectin was just as wholesome as raspberry pectin—it was deemed to be of the quality demanded. Quality meant only commercial quality. That was what the judges said in the case of *Smith* v. *Wisden*. There the contention was that orange marmalade should consist of oranges and sugar and nothing else, and it was found by the magistrates that glucose was added to prevent crystallisation. The magistrates convicted, but it was held by the High Court that there was no evidence upon which they could properly act. There was no legal standard for marmalade, and that was precisely the evidence here. In this case the addition of pectin helped to set the jam. The proposition that raspberry jam ought to consist of raspberries and sugar and nothing else was destroyed by the evidence of the independent witness, the Government Analyst, who had said that pectin was used by 90 per cent. of manufacturers in making raspberry jam. This witness had said: "We cannot tell from our analysis whether apple juice or apple pectin was used, but it is some derivative of apple." He had also said that it was impossible to state exactly how much fruit had been used in the manufacture of this jam, owing to the natural variation in the quality of the fruit. An estimate might be stated, but the Court would not convict anyone of a criminal offence upon an estimate or guess of that sort. The manufacturers of this jam used 50 lbs. of raspberries and 84 lbs. of sugar, and added, on an average, 15 lbs. of pectin to make the jam commercially good. No one could say what proportion of raspberries had been used, for the reason that the first pots filled contained the majority of the seeds, and the last pots very few seeds.

Mr. T. Macara, F.I.C., said that he had had 20 years' experience in the manufacture of jam. Commercially, raspberry jam was almost invariably made with the addition of some other fruit juice, to give the necessary consistence. The witness quoted recipes from various cookery books, to the effect that red or white currant juice should be added to raspberry jam. In those days it was believed that red currant juice had a better jellifying effect than apple juice, but in recent years that idea had been altered. It was not possible to say, with any degree of accuracy, from the figures in the report of the Government Analyst what proportion of raspberries had been used in making the jam.

In cross-examination the witness said that it was not possible to make a jam commercially without adding pectin—"You make a mess," he said, "but you don't make jam." The addition of foreign pectin did not reduce the time the jam

had to be boiled, and he did not agree that it resulted in economy in production. In re-examination, Mr. Macara said that 10 per cent. of pectin (*i.e.* pectinous juice) would not be detected by any ordinary person, and in his opinion it was a reasonable amount to add.

Replying to the Magistrate, the witness said that possibly apple pectin might give an apple flavour, but that it was improbable that it would be noticed. He was not aware of any way of making jam set other than by the addition of pectin.

At the final hearing, on July 15, evidence was given by the defendants' works manager to the effect that the jam had been made from 84 lbs. of sugar, 12 to 15 lbs. of pectin, and 50 lbs. of raspberry, which produced from 124 to 125 lbs. of jam. Some of the pectin used by the firm was bought in concentrated form, but more was manufactured by cooking apples and expressing and filtering the juice. The presence of a few apple cells in the jam indicated that the filtration was not perfect. In his opinion, raspberry jam could not be made without the addition of pectin so that it would remain sufficiently firm to travel. From 30 to 50 lbs. of apples were used to get the 12 or 15 lbs. of apple juice.

Sir Travers Humphreys submitted that the question of fact to be determined was whether apple pectin was an alternative ingredient in raspberry jam. The answer, he suggested, was to be found in the evidence of the Government Analyst, who had stated that 90 per cent. of jam manufacturers probably used it. As it had been shown that it was the practice of the trade and was not injurious to health, he asked the Court to hold that raspberry jam, when sold commercially, *i.e.* so that it would travel, was properly described as raspberry jam when it contained a reasonable percentage of apple pectin. The amount, 10 per cent., required to give consistence to the jam was a reasonable amount. The defendants, when giving their warranty, had reason to believe the statements therein to be true, and Counsel asked the Magistrate to hold that they were, in fact, true. This was raspberry jam, as that term had been understood in this country since 1902. If that were so, the question of disclosure on the label was of no importance.

The Magistrate said that he was inclined to think that an offence had been made out. In his opinion there had been a sale to the prejudice of the purchaser, who was entitled to know what he was buying. If something sold as raspberry jam consisted of raspberries with the addition of a considerable proportion of apple juice, he ought to be told so; otherwise the article was sold to his prejudice. Although evidence had been given that there was no object in adding juice except to give consistence to the jam, yet there was also evidence that it reduced the expense, and there was some evidence that, if added in sufficient quantity, it altered the flavour. It was a significant fact that a large proportion of the manufacturers who sold jam with an admixture of apple juice disclosed it on their labels, and the evidence was that other manufacturers did not like to do this because the public did not like it. He was of opinion that an offence had been committed, and fined the defendants £20, with 15 guineas costs.

Notice of appeal was given.

RASPBERRY JAM, WITH DECLARATION OF ADDED FRUIT JUICE.

A TRADESMAN was summoned at Loughgall for selling raspberry jam not of the nature, substance and quality demanded. The pot had a label to the effect that it was "improved" with the juice of other fruits. The case had been adjourned in May for an independent analysis by the Government Laboratory, and the certificate produced at the adjourned hearing stated that the following composition:—"Water, 34·78; total soluble solids, 64·74; insoluble solids (fruit fibre),

0·48 per cent. Number of raspberry seeds, 2·6 per grm. Iodine test, blue colour; artificial colour present." The report based on these figures was to the effect that the sample had been prepared from sugar, raspberries, and fruit juice products partly or wholly derived from the apple. It was not possible to state exactly how much fruit had been used in the manufacture, but an estimate was that 100 lbs. of jam had been made from approximately 5 lbs. of raspberry fruit, not less than 14 lbs. of fruit juice equivalent to apple, and 62 lbs. of sugar.

The certificate of Mr. J. H. Totten, Public Analyst for Belfast, stated the jam to contain:—Total sugars, 66; raspberry fruit fibre, 0·36; and fruit juice, water, etc., 33·64 per cent. In Mr. Totten's opinion the sample contained 4 per cent. of raspberry fruit and 30 per cent. of added fruit juice, this opinion being based on the fact that raspberry jam contains at least 3 per cent. of raspberry fibre. Raspberry jam ought not to contain more than 10 per cent. of added fruit juice.

An analysis made by Mr. R. T. Thomson, Public Analyst, Glasgow, showed the sample to contain 62·09 per cent. of sugar, 1·95 per cent. of other soluble matters, 0·38 per cent. of seeds, 0·14 per cent. of fibre, and 35·44 per cent. of water.

Counsel for the manufacturers of the jam said that they had not guaranteed to supply raspberry jam, but raspberry jam, *plus* added fruit juice. It was not possible to make a distinction between apple and raspberry juice, and it was not possible to stiffen jam without added juice.

Mr. Totten, replying to the Bench, said that there was no guesswork about his analysis; but he admitted that he could not distinguish between raspberry and other fruit juice. He had analysed other samples of raspberry jam, and found them to be correct.

The Magistrates convicted, and imposed a fine of £3 with £2 18s. costs.

EGG SUBSTITUTE POWDER.

On July 22, a Handsworth grocer was summoned at Birmingham for selling egg substitute powder not of the nature, substance and quality demanded. The City Analyst (Mr. J. F. Liverseege) said that the sample contained 2·5 per cent. of carbonic acid liberated by water, 10·9 per cent. of moisture, and 86·6 per cent. of other constituents. In his opinion, at least 6 per cent. of carbonic acid should be liberated from an egg substitute powder on the addition of water. The amount of moisture was higher than usual, and the excess might have been due to the original constituents. This moisture might have caused some loss of carbonic acid between the manufacture and the retail purchase of the article.

In cross-examination, witness agreed that there was no fixed standard for carbonic acid in the article, but suggested that it was open to the magistrates to fix a standard.

The solicitor for the defence contended that a good deal depended upon the cooking, and that the samples might be all right in the hands of one person, but not of another. He submitted that the defendant had sold what he had been asked for, namely, egg substitute, and that it was sold as received.

The Chairman of the Bench said that the Magistrates were not in a position to standardise the article by giving a decision on the scientific evidence, and they would therefore dismiss the summons.

Ministry of Health.

CONDENSED MILK. DRIED MILK.

THE Minister of Health is about to make Regulations amending the Public Health (Condensed Milk) Regulations, 1923, so far as they relate to the labelling of condensed milk and dried milk. The Regulations for condensed milk will come into operation on the 1st April, 1928, so far as they relate to importation, and in other respects on the 1st July, 1928, and will apply to all condensed milk intended for sale for human consumption in England and Wales. The Regulations for dried milk will come into operation on 1st July, 1928.

Copies of the draft Regulations which have been prepared for this purpose can be purchased under the description "Draft, dated 5th August, 1927, of the Public Health (Condensed Milk) Amendment Regulations, 1927," or "Draft, dated 12th August, of the Public Health (Dried Milk) Amendment Regulations, 1927," from H.M. Stationery Office, Adastral House, Kingsway, W.C.2, either directly or through any bookseller (price 1d.). Any representations on the subject should be addressed to the Secretary to the Ministry at an early date (within 40 days from 15th August in the case of dried milk).

MINISTRY OF HEALTH,
WHITEHALL, S.W.1.
5th and 15th August, 1927.

Government of Canada.

REPORT OF THE DOMINION CHEMIST FOR THE YEAR ENDING MARCH 31, 1926.

Dr. F. T. SHUTT, F.I.C., opens his Report with an account of the branch of the work of the Department of Agriculture which deals directly with the farmer. There are few phases of farm work which do not, at one time or another, call for chemical information or analysis for their rational operation, and the inquiries sent in relate to a host of subjects, among which the following are the most prominent: soils, manures, fertilisers, fodders and feeding stuffs, insecticides and fungicides and water supplies. In recent years there has been an ever increasing response to this offered assistance, and there is ample evidence to show that it is proving a valuable factor towards more rational and profitable methods in Canadian agriculture.

The number of samples examined during the year was 5073, including those sent in by farmers and district representatives, samples in connection with special investigations, and those submitted in the administration of the Meat and Canned Foods Act.

A detailed account is given of the analyses of soils from Prince Edward Island, Quebec, Alberta, and British Columbia. This is followed by a description of the investigational work on fertilisers, including experiments with Ephos (an Egyptian ground rock phosphate), the use of nitrate of soda as a top dressing for hay, and on various commercial fertilisers.

Analyses of Canadian peats and mucks are given, together with experiments as to their use, and a table of the composition of 42 Canadian muds is arranged according to the provinces in which they occur.

The experimental farm work includes the results of experiments on sugar beets for factory purposes, on farm roots, on the influence of early and late sprouting on potatoes, on cereals, silage and forage crops.

INSECTICIDES AND FUNGICIDES.—This work entailed the analysis of a number of brands of calcium arsenate and lead arsenate from both Canadian and American manufacturers, and allied insecticidal and fungicidal preparations.

The outstanding features disclosed by the analysis of the various brands of calcium arsenate may be briefly summarised as follows:—(1) The samples were far from uniform, and in several cases there existed a wide variation in different consignments from the same manufacturer. (2) The total arsenic oxide content of several brands varied from 6 to 10 per cent. below the guarantee. (3) In some instances the water-soluble arsenic greatly exceeded the guarantee.

Calcium arsenate may have a high water-soluble arsenic oxide content, as determined by the official methods of analysis, and still not prove as dangerous to foliage as some arsenates with a low water-soluble arsenic content, determined by the same method.

The wide variance in the samples of calcium arsenate analysed afforded an opportunity to bring to fruition a method for determining the stability of the arsenates when applied to foliage.

Mysterious Roach Powder contained 10·31 per cent. of moisture (volatile at 70° C. *in vacuo*), 82·36 per cent. of boric acid, and 18 parts per millions of arsenic (as metallic arsenic), together with a sweetening agent and an oil.

"*Flit*" (used as control for cockroaches in a Departmental Hospital) was an amber-coloured liquid, consisting essentially of kerosene (sp. gr. 0·8068), with a small quantity of synthetic methyl salicylate.

Fly Salts.—One preparation contained: Superfine sulphur, 25·67; pulverised charcoal, 3·11; and sodium chloride, 70·74 per cent. Another (claimed to protect livestock from insects) consisted of: Common salt, 81·92; finely ground sulphur, 14·27; and calcium oxide, 2·15 per cent.

Analyses are also given of compounds or preparations sold as seed and soil disinfectants and stimulants of growth and germination.

The analytical work undertaken for the Health of Animals Branch, Dept. of Agriculture, comprised 2305 samples, including condensed and evaporated milks, milk powders, evaporated apples, colours and inks, salts and preservatives, spices, lards and edible oils, canned and preserved fruits, tomato products, pickled pork and bacon. The results are summarised in tables.

Government of Madras.

REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1926.

THE Annual Report of the Chemical Examiner (Major C. Newcomb, M.D., F.I.C.) shows a great increase in the number of analyses, *viz.* 4637 as against 4227 in 1925 (ANALYST, 1926, **51**, 409). There were 545 stain cases, with 2231 articles, and 250 cases of human poisoning, being record numbers of each.

HUMAN POISONING CASES.—Poison was detected in 109 of the 250 cases. The poison most commonly found was again opium (25 cases), but mercury (23 cases) and arsenic (20 cases) ran it close. An inorganic poison was found in 46 of the cases.

Oduvan Poisoning.—Three cases of suspected poisoning by a plant known locally as *Oduvan* (Tamil), and of which the botanical name appears to be *Cleistanthus Collinus*, Berth., were investigated. Extracts from the leaves of this plant

are said by W. Dymoch (*Pharmacographica Indica*, pp. 269–270) to give a purple coloration with strong sulphuric acid, discharged on addition of alkaline dichromate, and a blue with nitric acid changing to green. In this laboratory these tests were not found to work, but it was found that an acid ether extract gave a very marked green with strong hydrochloric acid and produced paralysis and death if given subcutaneously to a frog. These tests, of course, cannot be taken to identify the poisonous substance of the plant, but, taken together with the shape, are fairly characteristic of the leaves. In all the three cases leaves were sent amongst the miscellaneous articles. As their shape was that of known oduvan leaves and they gave the above tests, they were reported as probably oduvan leaves. No characteristic reactions were obtained, however, from the viscera which were sent in these cases.

Yellow Oleander.—Dr. Rajagopal Nayudu made some investigations of the test for yellow oleander, a fairly common poison in Madras. In addition to physiological tests, the colour tests commonly used for yellow oleander are the blue colour on boiling with dilute hydrochloric acid, and the cherry red with strong sulphuric acid. Apparently these tests are given by different substances, but which of these, if either, is thevetin, is not clear.

From an evaporated alcoholic extract of the kernels taken up in water and of neutral reaction—(1) Petroleum spirit extracted an oil. On making acid, (2) Ether extracted a poisonous white crystalline substance which gave the cherry red test but not the blue. (3) Chloroform extracted traces of the same substances as ether. (4) Amyl alcohol extracted another poisonous substance which gave the blue coloration with dilute hydrochloric acid, and with strong sulphuric acid a play of colours.

If the kernels are boiled directly with dilute hydrochloric acid, the blue colouring substance can be completely extracted by amyl alcohol, but not by chloroform or ether. This blue substance is poisonous. It is intended to continue this work.

ANIMAL POISONING CASES.—Poison was detected in 18 cases out of 31. Arsenic and yellow oleander were by far the most common poison (8 cases each). In one case *nux vomica* was used, and in one both yellow oleander and datura.

STAIN CASES.—Blood was detected in 443 of the 507 articles examined. During the year 1504 blood stains were sent to the Imperial Serologist, Calcutta, and he reported 1406 of them to be of human blood, 21 the blood of a ruminant animal, 9 both human and ruminant blood, 7 non-mammalian blood, and 8 birds' blood, whilst the origin of 53 of the stains could not be identified. In 35 cases tested for semen it was detected with certainty (spermatozoa) in 9 cases, and was probably present (Florence's test) in 1 case.

IDENTIFICATION OF BONES.—Burnt or partly burnt bones were submitted to determine if they were human, as a murder followed by cremation of the body was suspected. The bones were broken up into too small fragments for it to be determined by their shape whether they were of human origin. They were therefore submitted to the Imperial Serologist, who was able, by serological tests, to decide that they belonged to a ruminant animal.

DETERMINATION OF IODINE IN SOILS.—The experiments on the determination of iodine in soils, etc., mentioned in last year's report, have been continued. The principle of the method finally adopted was: heating the soil with potash to destroy the organic matter, liberating the iodine from the extract of the ignition by means of nitrose (strong sulphuric acid into which nitrous fumes had been passed), separating the iodine by shaking with an immiscible solvent (generally carbon disulphide) and determination of the amount colorimetrically. The method,

although it sounds simple, is full of difficulties, the chief of which is the getting rid of the organic matter without losing iodine at the same time. The amount of potash used and the time and the intensity of the heating require careful regulation. The colorimetric determination is preferable to any method which involves conversion of the iodine into iodate and subsequent liberation of the iodine by the addition of potassium iodide. If this is done, and it is a method commonly used, one is adding a substance containing iodine (KI) from which many other things are liable to liberate the iodine, besides iodate. By reducing the volume of the extract and the amount of carbon disulphide (or other immiscible solvent used), one can detect excessively small quantities of iodine, but their accurate estimation is very difficult. Fellenberg (*Biochem. Zeit.*) uses as little as 0·02, or in some cases even 0·01 c.c., of chloroform (he prefers this to carbon disulphide) as extraction agent, and determines less than a thousandth of a milligram of iodine, but with such small quantities as this it requires a very highly trained eye to get accurate results.

In the method used in this laboratory 2 c.c. of carbon disulphide were generally used, and with this amount down to about 0·01 mgrm. of iodine could be determined. The method, in any case, seems to be only an approximate one, owing to the difficulties in getting all the iodine and none of the organic matter into the final aqueous extract. Analyses of many of the samples of soils were also made by Dr. Norris of Bangalore, Mr. Nath of Coimbatore, and in the laboratory of the Rowett Research Institute of Aberdeen by the kindness of Professor Orr, each using different methods, and the results compared well enough to enable conclusions to be drawn as to the connection between iodine in the soil and the incidence of goitre, but showed fairly large discrepancies for a chemical method.

Purification of Carbon Disulphide.—Two objections to the use of carbon disulphide as the solvent in colorimetric work are (1) its smell, (2) its becoming yellow on keeping. Its smell can be very greatly improved—though hardly to the condition of a "pleasant ethereal odour" it is supposed to have when pure—by shaking it at intervals for some days with cotton-seed oil and then distilling, as suggested by Mr. Hawley, the Public Analyst of Madras. It can be prevented from turning yellow on keeping in the light by putting in the bottle with it some precipitated silver, made by adding excess of dilute hydrochloric acid and some zinc to silver nitrate solution. When required for use a filtration through a dry paper is often necessary to free it from finely divided silver or silver sulphide. For use in micro-iodine determinations it is also necessary to free it from traces of some substance which, to a very small extent, decolorises the iodine. This can easily be done by dissolving a little iodine in it, leaving it an hour or two, and then washing it in the washer as described for chloroform (ANALYST, 1926, **51**, 19), first with a dilute solution of sodium bisulphite and then with water. Having been purified in this way it seems to keep pure for some weeks, at any rate.

TESTS FOR ALCOHOL, ETC., IN CHLOROFORM.—Since the introduction of payments by departments of the Central Government for analyses done in this department there have been very few samples of chloroform to examine. In two cases during the year there was an opportunity of applying the additional tests proposed in the ANALYST (1926, **51**, 19 *et seq*), and these two, which were of different well-known brands, gave figures for their content of alcohol, ethyl chloride, and for the final density which differed in the two samples and corresponded to the figures obtained with previous samples of the respective brands. Some attempts were made to find a more satisfactory test for the presence of water in chloroform, and the red-coloured substance formed by the addition of strong sulphuric acid to a chloroform solution of cholestrol was tried. If the red solution is pipetted

off from the sulphuric acid into a dry tube, its colour is destroyed by the addition of excess of chloroform (once to twice its bulk) owing, it has been stated, to the presence of water in the chloroform. It was found, however, that it is the alcohol in the chloroform which is chiefly responsible for discharging the red colour, and that pure chloroform, even if saturated with water, hardly does so (eight or ten times its bulk being required). The reaction can therefore be applied as a test for the presence of alcohol in chloroform.

Department of Scientific and Industrial Research.

REPORT OF THE FOOD INVESTIGATION BOARD FOR THE YEARS 1925, 1926.

THE Report of the Food Investigation Board* deals with the outstanding results of the years 1925, 1926, and a separate Report of the Director of Food Investigation summarises results under the various sections.

FREEZING OF BEEF.—In pursuance of this enquiry, the work on the water content of muscle and allied problems has secured promising results, but, so far, experimental conditions for beef that produce re-absorption of the water exuding in the ice phase, and avoid alterations of the molecular structure of the muscle have not proved adaptable to commercial practice. Water in a colloid appears to exist in two states, the smaller portion chemically bound to the colloid, and the greater part free, in the sense that it separates as ice on freezing, but no certain way of distinguishing between the two states has as yet been found; the proportion of free water, however, appears to increase with the age of the animal, and at different times after death. The possibilities of partial freezing, *i.e.* freezing just below freezing point, are being investigated on the working hypothesis that with slow freezing within a critical range of temperature $(\theta_1 - \theta_2)$, where θ_1 is the f.pt. of the muscle and θ_2 as yet unknown, the water which separates as ice should be re-absorbed if the conditions of thawing are suitable.

HAMS.—It is established that fluctuations in temperature, and hence of relative humidity, are the main cause of mould growth during transit.

FORMATION OF FAT BY YEAST.—In the study of this subject the changes in the carbohydrate and fat content produced by incubating yeast in oxygenated solutions of simple substances containing 2, 3 or 4 carbon atoms were worked out, and it now seems probable that no fatty aldehyde occurs as an intermediate stage between the hexose molecule and the fatty acid in the path from sugar to fatty acid. The mixture of lipins in yeast appears to be the simplest yet investigated, and only oleic and palmitic acids were identified. Much of the work on the keto fatty acids has been extended (*cf. J. Chem. Soc.*, 1925, **127**, 175; 1926, 2204).

GLYCOGEN AND MAIZE STARCH.—The pure polysaccharide, free from ash or other extraneous compounds, has now been obtained as the result of a troublesome series of operations. By conversion of ordinary glycogen into the corresponding triacetate all mineral compounds were eliminated, this process being the only method which proved effective in removing the last traces of iron, which are otherwise rigidly retained. The hydrolysis of the substituting acetyl groups so as to regenerate pure glycogen was effected by means of an aqueous-alcoholic

* Obtainable from H.M. Stationery Office. Price 2s. 6d. net.

solution of dimethylamine, a granular white powder consisting of pure glycogen being finally obtained. When washed and dried in a vacuum the material had the exact analytical composition required, and showed [α] in water $= +179{\cdot}1°$, a value which may be taken as the standard for glycogen.

A special variety of maize starch was purified in the same way. The triacetyl starch was ash-free and had the correct percentage composition. The difference between this acetate, glycogen triacetate, and rice starch triacetate was shown by the different optical activities.

Solvent.	$[\alpha]_D$ of Glycogen acetate.	$[\alpha]_D$ of Maize starch acetate.	$[\alpha]_D$ of Rice starch triacetate.
Chloroform	+145·7°	+165·70°	+158·5°
Pyridine	140·6	153·1	158·0°
Benzene	123·5	140·3	insol.
Ethyl acetate ..	—	—	160·0°

FRUIT AND VEGETABLES.—The investigation into the keeping properties of fruit grown on some 15 different types of soil is being co-ordinated with the Ministry of Agriculture's Soil Survey. The storage life of apples in relation to respiratory activity and chemical composition, and the relation between the concentration of oxygen and carbon dioxide in the atmosphere, rate of respiration and length of storage life in apples have been studied. The development of internal breakdown in cold-stored apples may be of such long duration in its first stage (with increased rate of production of carbon dioxide) as to give rise to the erroneous belief that it constitutes a distinct disease. Respiration has ceased when the flesh becomes deep brown.

Pectic changes in apples and pears have been studied, and it is shown that the pectic changes observed in apples subjected to fungal invasion bears some relation to the ability of the fungus to utilise pectic substances; thus, with *Cytosporina ludibunda*, pronounced changes occur; with certain strains of *Fusarium*, little change. A microscopical study of pectic changes in the apple shows entire agreement with that conducted on purely chemical lines.

The general scheme of analysis (Archbold) is shown diagrammatically below:—

Systematic Analysis of Apples.

(*Sample*, 10–20 apples,* cut up small and mixed thoroughly.)

Portion 1 (20 grms.) ..	Dried at room temperature to constant weight over P_2O_5, giving *dry weight* (provisional method).
Portion 2 (50 grms.) ..	Dried at 100° C., by Kjeldahl process, giving *nitrogen*.
Portion 3 (30 grms.) ..	Extracted with alcohol; residue weighed, giving *cell-wall material*.
Portion 4 (250 grms.) ..	Frozen and juice expressed; *sugar*, *acid* and *specific gravity* determined.

Note.—If an estimation of mineral content is to be included, a second portion should be dried at 100° C.

FUNGAL ATTACK ON APPLES.—The work on factors affecting the internal resistance of apple to fungal attack has been extended to 8 further fungi. Experiments with various artificially produced strains of *Fusarium* showed that these

* Thirty is the smallest number of apples which give satisfactory results in a single analysis.

strains differ markedly in their rot-forming capacity when apples are inoculated under the skin soon after gathering.

From the experiments with *Fusarium* it is computed that at 3° C., as compared with 12° C., less than half the amount of rotting occurs in more than double the time.

Experiments with *Fusarium* have shown also that the time taken to produce a given amount of rotting in Bramley's Seedling apples is approximately twice that required to produce the same amount of rotting in Cox's Orange Pippin apples.

There are marked differences from season to season in the resistance of apples from the same orchard to fungal attack. From the evidence of experiments conducted on lines similar to those described above it would appear that, in the power of their tissues to resist the growth of parasitic fungi, the apples of the season 1924 were superior to those of 1923, and those of 1925 superior again to those of 1924, and temperature conditions in refrigerated holds of ships carrying fruit have been continued by a further expedition to Australia (ANALYST, 1926, **51**, 80–81; *Food Rept. No.* 27). Trials to test relative efficiency of different storage methods without refrigeration show that some stores are distinctly superior to others, so that an investigation into conditions of temperature, humidity, etc., has become necessary. The work on gas storage of apples has been completed (*Food Investigation Report No.* 30).

PHYSICO-ENGINEERING INVESTIGATIONS.—These have included the development of a thermometer capable of carrying a heavier current than the standard type without undue heating effect; experiments with flow-meters; heat insulators; rate of cooling of large masses, humidity measurements and the mechanical properties of thermal insulators.

D. G. H.

Therapeutic Substances.

STATUTORY RULES AND ORDERS, 1927. No. 486.*

THE THERAPEUTIC SUBSTANCES REGULATIONS, 1927, DATED MAY 31, 1927, MADE BY THE JOINT COMMITTEE CONSTITUTED BY SUBSECTION (1) OF SECTION 4 OF THE THERAPEUTIC SUBSTANCES ACT, 1925. (15 & 16 GEO. 5. c. 60.)

THE Joint Committee, after consultation with the Advisory Committee constituted under Sub-Sec. (2) of Sec. 4, has made the regulations embodied in this Order.

PART I. *Interpretation, &c.*—1 (1, 2 and 3). The Regulations may be cited as the Therapeutic Substances Regulations, and "The Licensing Authority" means the Minister of Health in England, the Scottish Board of Health in Scotland, and the Minister of Home Affairs in Northern Ireland. The Regulations come on August 6, 1927, and the provisions as to labelling (other than those in Part VIII) on Feb. 6, 1928.

(2) For the purpose of the Regulations the millilitre may be used wherever the cubic centimetre is indicated.

PART II. *Licenses for Manufacture of Therapeutic Substances* (3 to 6).—This deals with the conditions and form of licence.

PART III. *Provisions with regard to the names of Therapeutic Substances and to Containers, Labels, &c.*—(7) If any therapeutic substance is advertised or sold as a proprietary medicine or is contained in a medicine so advertised or sold, the name stated in the relative Schedule as being the accepted scientific name or name descriptive of the true nature and origin of the substance (hereinafter referred to as the "proper name" of the substance) shall appear on the label in the manner prescribed in this Part of these Regulations.

* H.M. Stationery Office. Price 9d. net.

(8) There must be effective sterilisation of containers, but the requirement shall not apply to products which are effectively sterilised after being put into the containers. The Licensing Authority may, if they deem necessary, dispense with these requirements or make additional requirements.

(9) Labels must give the proper name of the substance in letters not less conspicuous than the proprietary name, the name and address of the manufacturer, number of the licence, date on which batch was completed, statements as to toxicity or potency (when such tests are required), nature and amount of antiseptic substance (if added), and precautions necessary for preserving the properties to an indicated date. The date of completion is defined in Sub-sec. 2.

(10) Prohibits the sale of the substance after the date recorded on the container as that to which it may be expected to retain its potency or not acquire a toxicity greater than that permitted by the test, but with a proviso that a registered medical practitioner may, in a case of urgency, request the sale of such a product.

PART IV. *Standards of Strength, Quality and Purity and Tests for Determining whether those Standards have been attained :*

(11 and 12) The standards and tests for strength and quality shall be those specified in the Schedules to the Regulations.

(13) Tests for sterility are to be made in the case of (*a*) sera solutions of serum proteins intended for injection; (*b*) certain bacterial vaccines specified in Schedule II.; (*c*) toxins and mixtures of toxins or antigens with serum; (*d*) solutions of insulin; (*e*) dry preparations of insulin intended for therapeutic use; and (*f*) preparations of the posterior lobe of the pituitary body.

(14) Deals with the application of the tests, (15) specifies the amounts of samples, (16) with the method of preparing and using media, and (17 and 18) with the method of testing for bacteria. Certain exceptions to these regulations are specified in (19), and (20) specifies tests for freedom from abnormal toxicity to be applied to each batch of serum.

PART V deals with *Therapeutic Substances Manufactured for Export only.*

PART VI. *Licences for Import of Therapeutic Substances.*

PART VII. *Research Licences.*

PART VIII. *Therapeutic Substances intended for Veterinary Purposes only.*

THE FIRST SCHEDULE gives the forms of application and conditions for the various licences.

THE SECOND SCHEDULE. PART I. VACCINES, TOXINS, ANTIGENS, SERA and ANTITOXINS.

A. Provisions Applicable to the Production of Bacterial Vaccines. (*B*) *Special Provisions Applicable to the Production of Vaccine Lymph* (*Vaccinia*).

PART II. TOXINS AND ANTIGENS.

(A) *Provisions Applicable to the Reagents used in the Schick Test for the Diagnosis of Susceptibility to Diphtheria.*

(B) *Provisions Applicable to Diphtheria Prophylacta.*

(C) *Provisions Applicable to Tuberculins.*

PART III. *Provisions Applicable to the Production of Sera from Living Animals.*

PART IV. *Provisions Applicable to Particular Sera and Antitoxins.*

(A) *Anti-meningococcus Serum.* (B) *Anti-dysentery Serum.* (C) *Diphtheria Antitoxin.* (D) *Tetanus Antitoxin.*

THIRD SCHEDULE. ARSENOBENZENE (COMMONLY KNOWN AS SALVARSAN) AND ITS DERIVATIVES.

PART I. *General Provisions Standard of Preparation and Biological Test.*

PART II. *Special Provisions Applicable to Arsenobenzene.*

1. Arsenobenzene is the dihydrochloride of dioxy-diamino-arsenobenzene. Its proper name is "Arsenobenzene."

2. Arsenobenzene must have the following physical and chemical characteristics:—(1) The substance must be in the condition of a pale yellow to yellow, dry, amorphous powder, freely mobile in contact with glass surfaces, and without odour, except that due to traces of ether.

(2) If 0·5 grm. of the powder is added to 35 c.c. of distilled water, it must dissolve completely within 15 minutes, yielding a clear pale yellow solution, not acid in reaction to Congo-red paper,

and perfectly clear and free from flocculi, hairs, dust and suspended particles of any kind. When 1 c.c. of a 15 per cent. aqueous solution of sodium hydroxide is added to this solution of arsenobenzene, it should cause a preliminary separation of the insoluble arseno-base, which, if the mixture is gently agitated, should redissolve in the excess of alkali to form a clear, bright yellow solution. This solution, when diluted to 250 c.c. with a 0·5 per cent. solution of pure sodium chloride in distilled water, should give a clear light yellow solution.

(3) The dry powder, as taken directly from the sealed ampoules in which it is issued, must contain not less than 30 per cent., or more than 34 per cent. of arsenic, as determined by a method approved by the Licensing Authority.

Test for Stability. The product, as filled into ampoules, shall be kept at a temperature of 56° C. for at least 24 hours, and shall retain its colour, physical properties and solubility, as specified in paragraph 2, substantially unchanged at the end of that period.

PART III. *Special Provisions Applicable to Novarsenobenzene:*

1. Novarsenobenzene is the sodium salt of dioxy-diamino-arsenobenzene-methylene-sulphoxylic acid. Its proper name is "Novarsenobenzene."

2. Novarsenobenzene must have the following physical and chemical characteristics:—(1) The substance must be in the condition of a yellow, dry powder, freely mobile in contact with glass surfaces, and without odour, except such as is due to traces of ether or alcohol.

(2) The substance must be soluble in water, but insoluble in absolute ethyl alcohol and in ether. If 0·6 grm. of the substance is added to 1 c.c. of distilled water, it must dissolve rapidly and completely and form a clear, yellow solution, mobile and free from gelatinous particles or suspended matter of any kind.

(3) A normal solution of sodium carbonate or a 5 per cent. solution of the anhydrous carbonate, added in equal volume to a 10 per cent. aqueous solution of novarsenobenzene, must not produce a precipitate.

(4) Diluted hydrochloric acid (B.P.) added in equal volume to a 10 per cent. aqueous solution of novarsenobenzene must give a yellow precipitate of the free acid from novarsenobenzene. If the mixture is warmed, sulphur dioxide must be evolved, and can be detected by iodate-starch paper.

(5) When a solution of 0·2 grm. of novarsenobenzene in 10 c.c. of water is acidified with phosphoric acid and distilled to about one-half its volume, formaldehyde must be evolved and can be detected in the distillate by adding five drops of a 1 per cent. solution of phenol, and running a layer of sulphuric acid under the mixture, when a red ring is formed at the line of contact.

(6) When 0·1 grm. of novarsenobenzene is rubber with 5 c.c. of a solution of stannous chloride As T (B.P.) and allowed to stand for one hour no brown colour must be produced.

(7) The dry powder, as taken directly from the ampoules in which it is issued, must contain not less than 18 per cent. or more than 21 per cent. of arsenic, as determined by a method approved by the Licensing Authority.

Test for Stability. The product as filled into ampoules shall be kept at a temperature of 56° C. for at least 24 hours and shall retain its colour, physical properties and solubility substantially unchanged at the end of that period.

PART IV. *Special Provisions Applicable to Sulpharsenobenzene.*

1. Sulpharsenobenzene is the sodium salt of dioxy-diamino-arsenobenzene-methylene sulphurous acid. Its proper name is "Sulpharsenobenzene."

2. Sulpharsenobenzene must have the following physical and chemical characteristics:—(1) The substance must be in the condition of a yellow, dry powder, freely mobile in contact with glass surfaces, and without odour, except that due to traces of ether or alcohol.

(2) The substance must be soluble in water but insoluble in alcohol and in ether. If 0·6 grm. of the substance is added to 1 c.c. of distilled water, it must dissolve rapidly and completely, and form a clear, yellow solution, mobile and free from gelatinous particles or suspended matter of any kind.

(3) A normal solution of sodium carbonate or a 5 per cent. solution of the anhydrous carbonate, added in equal volume to a 10 per cent. aqueous solution of sulpharsenobenzene, must not produce a precipitate.

(4) Diluted hydrochloric acid (B.P.) added in equal volume to a 10 per cent. aqueous solution of sulpharsenobenzene must give, after a few minutes, a yellow precipitate of the free acid from sulpharsenobenzene. If the mixture is boiled, sulphur dioxide must be evolved and can be detected by iodate-starch paper.

(5) When a solution of 0·2 grm. of sulpharsenobenzene in 10 c.c. of water is acidified with phosphoric acid and distilled to about one-half its volume, formaldehyde must be evolved and can be detected in the distillate by adding five drops of a 1 per cent. solution of phenol, and running a layer of sulphuric acid under the mixture, when a red ring is formed at the line of contact.

(6) On addition of an equal volume of 1 in 10,000 indigo-carmine solution, a 10 per cent. aqueous solution of sulpharsenobenzene must not reduce the indigo-carmine in 5 minutes at 50° C.

(7) The dry powder, as taken directly from the ampoules in which it is issued, must contain not less than 18 per cent. or more than 21 per cent. of arsenic, as determined by a method approved by the Licensing Authority.

3. The test for maximum toxicity and for therapeutic potency prescribed in paragraph 2 (3) of Part I of this Schedule shall, in the case of sulpharsenobenzene, be carried out by subcutaneous injection into mice or rats.

Test for Stability. 4. The product as filled into ampoules shall be kept at 56° C. for at least 24 hours and shall retain its colour, physical properties and solubility substantially unchanged at the end of that period.

PART V. *Special Provisions Applicable to Derivatives of Arsenobenzene other than those specified in Parts II and III of this Schedule.*

1. In the case of any derivative of arsenobenzene other than those specified in Parts II and III of this Schedule the applicant for a manufacturing or an import licence shall submit to the Licensing Authority with his application a statement of the true chemical nature and composition of the derivative, and a full and detailed account of the chemical tests by which that composition is determined and by which the uniformity of successive batches is secured.

2. The applicant shall also submit with his application the name which he proposes to use for the derivative to which the application relates, and such name, if approved by the Licensing Authority, may be used as the proper name of the derivative.

3. If a licence is granted for the manufacture of such a derivative of arsenobenzene, the licensee shall carry out on each batch of the derivative such, if any, of the chemical tests submitted with the application as are accepted by the Licensing Authority, and any others which the Authority may direct as requisite for determining the composition and securing its uniformity. No batch of the derivative which fails to pass any of the tests so accepted or directed shall be issued.

4. Each batch of such derivative shall further be tested, by biological methods, for toxity and potency, according to the methods prescribed in Part I of this Schedule. In the event of no standard preparation being available for a particular derivative, the tests shall be made in such form and their results interpreted in accordance with such criteria as the Licensing Authority may direct.

FOURTH SCHEDULE. INSULIN:—Proper name. Special conditions of licence. Standard preparation. Unit of standardisation. Quality. Tests. Container. Label.

FIFTH SCHEDULE. PITUITARY (POSTERIOR LOBE) EXTRACT:—Proper name. Standard preparation. Unit of standardisation. Quality. Tests. Container. Label.

United States Department of Agriculture.

FOOD INSPECTION DECISIONS.

THE following revised and amended definitions and standards were adopted by the Food Standards Committee, composed of representatives of the United States Department of Agriculture, the Association of American Dairy, Food and Drug Officials, and the Association of Official Agricultural Chemists, at its meetings, November 29 to December 3, 1926, and March 28 to April 1, 1927.

No. 206. ALIMENTARY PASTES.

1. ALIMENTARY PASTES are the shaped and dried doughs prepared from semolina, from farina, from wheat flour, or from a mixture of any two or of all of these, with or without salt, and with one or more of the following: Water, egg, egg-yolk, milk, a milk product.

An alimentary paste contains not more than thirteen per cent. (13 per cent.) of moisture, as determined by the vacuum method.

2. PLAIN ALIMENTARY PASTES are alimentary pastes made without egg or egg yolk, or so made that the content of the solids of egg and/or of egg-yolk is, upon a moisture-free basis, less than five and one-half per cent. (5·5 per cent.) by weight.

3. EGG ALIMENTARY PASTES are alimentary pastes which contain, upon a moisture-free basis, not less than five and one-half per cent. (5·5 per cent.) by weight of the solids of egg and/or of egg-yolk.

4. NOODLES, EGG NOODLES, are a form of egg alimentary paste which, in the course of its preparation, has been rolled or pressed into sheets or ribbons, with or without subsequent cutting or shaping.

5. WATER NOODLES are a form of plain alimentary paste which, in the course of its preparation, has been rolled or pressed into sheets or ribbons, with or without subsequent cutting or shaping.

6. MACARONI, SPAGHETTI, VERMICELLI, are plain alimentary pastes, distinguished by their characteristic shapes.

7. SEMOLINA MACARONI, SEMOLINA SPAGHETTI, SEMOLINA VERMICELLI, are plain alimentary pastes in the preparation of which semolina is the only farinaceous ingredient used, and are distinguished by their characteristic shapes.

No. 207. SWEETENED CONDENSED MILK.

8. SWEETENED CONDENSED MILK is the product resulting from the evaporation of a considerable portion of the water from milk to which sugar (sucrose) has been added. It contains not less than twenty-eight per cent. (28 per cent.) of total milk solids, and not less than eight per cent. (8 per cent.) of milk fat.

No. 208. RICE.

10. RICE is the hulled, or hulled and polished, grain of *Oryza sativa*.

(*a*) BROWN RICE is the hulled, unpolished grain.

(*b*) POLISHED RICE, "RICE," is the hulled grain from which the bran or pericarp has been removed by scouring and rubbing.

No. 209. COLOURS IN FOOD. (AMENDMENT TO FOOD INSPECTION DECISION 184.)

Food Inspection Decision 184 is hereby amended by adding Fast Green FCF to the list of permitted dyes contained therein. Hereafter the coal-tar dyes which will be accepted for certification, subject to the provisions of Food Inspection Decisions 76, 77, 106, 129, and 159, shall be the following:

Red shades:	80	Ponceau 3 R.
	184	Amaranth.
	773	Erythrosine.
Orange shade:	150	Orange I.
Yellow shades:	10	Naphthol yellow S.
	640	Tartrazine.
	22	Yellow A B.
	61	Yellow O B.
Green shades:	666	Guinea green B.
	670	Light green S F yellowish.
		Fast green FCF (*p*-hydroxy derivative of the sodium salt of alphazurine F. G., C. I. 671).
Blue shade:	1180	Indigo disulpho acid.

The numbers preceding the names refer to the numbers of the colours as listed in the Colour Index, published in 1924, by the Society of Dyers and Colourists of Great Britain.

No. 210. CULTURED BUTTERMILK.

CULTURED BUTTERMILK is the product obtained by souring pasteurised skimmed, or partially skimmed, milk by means of a suitable culture of lactic bacteria. It contains not less than eight and five-tenths per cent. (8·5 per cent.) of milk solids-not-fat.

The foregoing definitions and standards are adopted as a guide for the officials of this department in enforcing the Federal Food and Drugs Act.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Determination of Casein in Milk by an approximately Iso-Electric Precipitation. H. C. Waterman. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 259–263.)—In the following method casein is precipitated from milk within 0·04 P_H of its iso-electric point (P_H=4·7), and the results are obtained in less time and are more consistent than those given by the Official Method 1 of the A.O.A.C. To 20 c.c. of the sample in a 100 c.c. flask add 50 c.c. of a solution containing 250 c.c. *N* acetic acid and 125 c.c. of *M* sodium hydroxide solution per litre, and shake well. Place the flask in water at 50–60° C. for 15 minutes, cool, and filter on a double paper. Return the filtrate to the paper twice, and finally re-filter through a hardened paper. The casein in 10 c.c. of milk is given by the difference between the nitrogen-contents of 10 c.c. of the milk, and of 50 c.c. of the filtrate, multiplied by 6·38. J. G.

Discoloration of Canned Cranberries. F. W. Morse. (*J. Agric. Res.*, 1927, **34**, 889.)—The brown discoloration of cranberries preserved in tin cans is shown to be due to iron, dissolved from the interior of the can, reacting with the natural colouring matter of the fruit, and, to a less extent, with the tannin. The pigment isolated from the American cranberry (*Vaccinium macrocarpum*) differs from that separated by Willstaetter and his students from the European cranberry (*V. vitis idaea*), in that it is only slightly soluble in water.

Characteristics of Some Oils of the Chaulmoogra Group. G. A. Perkins, A. O. Cruz and M. O. Reyes. (*Ind. Eng. Chem.*, 1927, **19**, 942.)—Oils were extracted from the seeds of the following plants :—*Asteriastigma macrocarpa* (Travancore), *Hydnocarpus cauliflora* (Cotobato, P.I.), *H. Ovoidea* (Samar, P.I.) and H. Woodii (Borneo). The *Asteriastigma* seeds resembled those of *H. alcalae*, and the oils were very similar, the first fraction of each giving chaulmoogric acid, instead of hydnocarpic acid, when hydrolysed and recrystallised. The seeds of *H. cauliflora* closely resembled those of *H. Hutchinsonii*. The very low optical rotation of *H. ovoidea* is against its classification, chemically, in the chaulmoogra group. Fractionation of the ethyl esters of the oil from *H. Woodii* showed that it was very similar to the oil of *Taraktogenos Kurzii*.

	Asteriastigma macrocarpa.	*H. cauliflora.*	*H. ovoidea.*	*H. Woodii.*
Sp. gr., 30°/30° C.	0·936	0·946	0·915	0·949
n_D^{30}	1·4709	1·4732	1·4637	1·4755
Solid. pt., °C.	30	25	25	21
Rotation, 100 mm., α_D^{30} ..	36	42	1	49
Iodine value (Hanus) ..	87·6	84	47	96
Saponification value ..	201	201	215	206
Acidity as oleic acid, per cent.	8·2	0·8	5·8	2·5
Solid. pt. of fatty acids, °C.	50	42	40	44

Comparison of Several Processes for the Assay of Podophyllum. L. E. Warren. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 272–280.)—The U.S.P. (X) method for the assay of podophyllum gives higher results than those obtained either by the U.S.P. (IX) or Jenkins methods (*J. Ind. Eng. Chem.*, 1914, **6**, 671). The resulting resin did not conform to the requirements of the U.S.P. (X) with regard to solubility in alcohol, or those of the U.S.P. with regard to ash-content, solubility in ether or chloroform, and laxative properties. Its podophyllotoxin content was less than that of the resin on the market, and it contained an inert material, due probably to potassium citrate carried over in the extraction process. The Jenkins process appears to give satisfactory results. J. G.

Formic Acid in Commercial Acetic Acid. L. Daniel. (*J. Pharm. Chim.*, 1927, **119**, 581–583.)—Formic acid, which was found to be frequently present in commercial acetic acid (2·64 ; 1·68 ; and 0·99 grms. per litre in 3 samples), may be determined by reduction of mercuric chloride and titration of the mercurous salt by means of iodine. If the acid is previously saturated with sodium carbonate the reaction is more sensitive. Acetic acid may be purified from formic acid by distillation over an excess of potassium permanganate.

D. G. H.

Application of the Stahre Reaction to the Accurate Determination of Citric Acid. B. G. Hartmann and F. Hillig. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 264–272.)—The sources of error and sensitiveness of the Stahre reaction for the determination of small amounts of citric acid have been investigated. The solubility of pentabromacetone in the reaction mixture is, to a large extent, avoided in the following suggested method, which gives accurate results with amounts of citric acid of the order of 5 mgrms. To 100 c.c. of solution add 10 c.c. each of dilute sulphuric acid (1:1) and fresh saturated bromine water. After 10 minutes filter the solution, and add 5 c.c. of potassium bromide solution (15 grms. in 40 c.c. of water), and about 0·3 grm. of purified asbestos, to 100 c.c. of the filtrate. Heat the mixture to 48–50° C. for 5 minutes and add at least 15 c.c. of a 5 per cent. solution of potassium permanganate, till the supernatant liquid is brown. Shake, allow the mixture to stand for 10 minutes, cool in ice-water, and add at least 40 c.c. of ice-cold ferrous sulphate solution (20 grms. of salt and 1 c.c. of sulphuric acid in 100 c.c. of water) till the manganese dioxide has dissolved. Shake well, and leave in the refrigerator overnight. Filter the pentabromacetone as quickly as possible on an asbestos pad in a Gooch crucible, and use the filtrate to transfer the last traces of the precipitate. Wash with three portions (20 c.c. each) of ice-cold 1 per cent. sulphuric acid, and of ice-water, and dry in a current of air until a constant weight is obtained to within 0·3 mgrm. Remove the precipitate by three washings with 20 c.c. of alcohol, followed by a similar volume of ether, dry and reweigh. The factor 0·424 gives the citric acid in the anhydrous state, and the correction for the solubility of the precipitate is 1·7 mgrms. for each 100 c.c. of reacting liquids. J. G.

Digitonin, its Properties, Isolation and Quantitative Determination. I. S. Mellanoff. (*Amer. J. Pharm.*, 1927, **99**, 390–401.)—The most successful method for determining digitonin was precipitation of the addition compound formed with 1 mol. of digitonin and 1 mol. of cholesterol. Small amounts of cholesterol (1 per cent. in 90 per cent. alcohol) are added to a hot solution of digitonin in 90 per cent. alcohol until precipitation is complete, the precipitate washed with 90 per cent. alcohol, and the filtrate again treated with cholesterol. Alpha- or beta-naphthol is a cheaper precipitating agent, the former combining in molecular ratio to form an addition product with 8 mols. of water, and the latter with 10 mols. of water. Digitonin cholesterol can be split into its component parts with hot xylene, and the naphthol compound with hot benzene. Digitalin seeds were found to contain an average of 1·4 per cent. digitonin ; digitalin (Merck) 31·1 per cent., and digitonin (Merck) 81·1 per cent. D. G. H.

Determination of Terpin Hydrate in Terpin Hydrate Elixir. A. G. Murray. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 257–259.)—To a convenient volume of the sample add a 20 per cent. solution of common salt till the alcohol content is reduced to about 10 or 15 per cent. by volume. Extract the mixture with four portions (each one quarter of the total volume) of chloroform containing about 6 per cent. of alcohol by volume. Wash each portion of solvent successively with 5 c.c. of the salt solution, and filter through a pad of purified cotton into a tared dish. Remove the solvent in a current of air in the cold, and weigh after 15 minutes. An error of +0·8 per cent. was obtained in a determination by this method. Any essential oil may be removed by a preliminary extraction with petroleum spirit. At 25° C. 1 grm. of terpin hydrate dissolves in 27 c.c. of acetone. J. G.

Biochemical, etc.

Effect of Halogen Salts on Peptic Digestion. W. M. Clifford. (*Biochem. J.*, 1927, **21**, 544–548.)—In a previous paper by Clifford (*Biochem. J.*, 1925, **19**, 218) the effects of certain halogen salts on ptyalin were described, and this investigation has been continued with pepsin. The clotting of milk was chosen as a measure of peptic activity, since it is a definite and easily seen change. It is greatly affected by the addition of halogen salts. The reaction is hastened by the chlorides and bromides of sodium, potassium and ammonium, the ammonium salts having the strongest effect. There is certainly no inhibitory effect exerted by sodium chloride on pepsin in a concentration of approximately 1·5 per cent., though Hamburger and Halpern (*Arch. Int. Med. Chicago*, 1916, **18**, 228) state that a concentration of sodium chloride above 0·25 per cent. inhibits peptic activity. There is an optimum concentration of sodium, potassium and ammonium chlorides and bromides which lies between 0·07 and 0·018 *M*. The iodides and fluorides of sodium, potassium and ammonium, on the whole, retard or inhibit the action of pepsin in coagulating milk. The inhibitory action of ammonium iodide is very weak compared with that of sodium iodide and potassium iodide. This retarding

action is also a function of concentration, since at low concentrations the iodides do not affect the rate, whilst the fluorides actually hasten it. The ammonium radicle favours the coagulation of milk by pepsin. In the presence of magnesium, calcium and barium halides there is a great increase in the rate of coagulation of milk by pepsin. This action is weakest with the magnesium salts. P. H. P.

Factors Involved in the Reaction Changes of Human Saliva. G. W. Clark and K. L. Carter. (*J. Biol. Chem.*, 1927, **73**, 391–404.)—Although the relationship of the reaction of the saliva to deposition of calculus (tartar) on the teeth has been the object of many investigations, the exact chemical and physical processes involved in the formation and deposition of calculus are as yet unexplained. A comparative study of the reaction of saliva in the glands with that freshly taken from the mouth has been made, and also a study of the changes in reaction resulting from the incubation of saliva, in the attempt thereby to simulate, as far as is possible, natural conditions for the action of bacteria and enzymes. The results indicate that the saliva obtained by direct cannulation of the human parotid and sublingual glands is slightly more acid, 0·1 P_H, than freshly taken resting saliva. Although the volume per cent. of carbon dioxide is much higher in paraffin-activated saliva, it varies in much the same manner as in resting saliva. Samples of either resting or paraffin-activated saliva may stand for several hours without much apparent change in carbon dioxide content, as there is an equilibrium between the carbon dioxide escaping and that being formed. The carbon dioxide formation is probably the result of enzymic action. Apparently some ammonia is formed by bacterial action, but most of it is thought to be the result of enzymic action. There is no demonstrable relationship between the P_H value, the volume per cent. of carbon dioxide, and the ammonia content. Apparently the P_H changes in saliva involve other constituents than those studied. Complete analyses must be made of a large number of samples of saliva in order to complete this aspect of the work. P. H. P.

Production of Ozone by Ultra-Violet Rays. J. Dadlez. (*Compt. rend.*, 1927, **185**, 89–91.)—A dose of 1 to 1·5 mgrm. of ozone per cb. m. appears to provoke the first symptoms of mucous irritation in adults, and, since the average quantity of ozone produced by a quartz lamp is in the neighbourhood of 0·05 to 0·3 mgrm. per cb.m., it is not usually necessary to take any precautions unless the space is confined, but accumulation of ozone can readily be prevented by ventilation. D. G. H.

Determination of Urea by Gasometric Measurement of the Carbon Dioxide formed by the Action of Urease. D. D. Van Slyke. (*J. Biol. Chem.*, 1927, **73**, 695–723.)—Urea is changed by the action of urease into ammonium carbonate: $CO(NH_2)_2+2H_2O \rightarrow (NH_4)_2CO_3$. The ammonia has been more commonly determined as a measure of the urea, but an exact estimate can be obtained by determination of the carbon dioxide of the ammonium carbonate. Methods are described for the rapid determination of urea in blood and urine by

the measurement in the manometric blood gas apparatus of the carbon dioxide formed by the action of urease. Preformed carbonic acid and bicarbonate are present in blood and urine, and this carbon dioxide is removed by acidifying and shaking before the urease is added. In analysis of urine, when the carbon dioxide has been removed by phosphoric acid and shaking, sodium hydroxide is added in sufficient amount to form the optimum phosphate buffer mixture for the action of urease. The urease is then added, with sufficient water to dilute the urine sample either 10- or 20-fold. After the urease has acted for 20 minutes samples of the solution may be drawn for carbon dioxide determinations. These, by the technique described, can be easily made in series at the rate of a determination every 4 minutes. The blood urea may be determined by a similar procedure in either whole blood, serum or Folin-Wu filtrate. In the direct analysis of whole blood or plasma the preliminary removal of carbon dioxide is most conveniently effected in the gas apparatus itself. In accuracy there is no difference between determination of the carbon dioxide and that of the ammonia formed by the action of urease, if samples of size best suited for the measurement of each are taken. Micro determinations may be made with very satisfactory accuracy with 0·2 c.c. of blood taken from an ear puncture. P. H. P.

Association of Vitamin *A* with Greenness in Plant Tissue. I. Relative Vitamin *A* Content of Head and Leaf Lettuce. M. Dye, O. C. Medlock and J. W. Crist. (*J. Biol. Chem.*, 1927, **74**, 95–106.)—The question of whether vitamin *A* is associated with the pigment of plants is of considerable importance in horticulture, since many horticultural products are marketed after being bleached to different degrees, either by natural or artificial processes, in order to improve their quality, as determined by appearance, tenderness and palatability. If the destruction of the greenness reduces the amount of vitamin *A* in the plant, and thus decreases its value as a food, then the standards of quality are somewhat superficial. A study of the comparative vitamin *A* content of head and leaf lettuce has been made, and graphs show the results. Leaf lettuce exceeded head lettuce in the promotion of growth in rats that had ceased to gain on a diet deficient in vitamin *A*. The outside, green leaves of head lettuce were far superior to the inside yellow leaves in furnishing vitamin *A*. Indoor-grown leaf lettuce proved as beneficial as outdoor leaf lettuce in the production of growth. Though no certain identity of chlorophyll or any of its primary phases with vitamin *A* in lettuce tissue has been proved, the evidence points plainly towards the probability of some close relationship between the two. This point is discussed, and the results of other workers are considered. P. H. P.

The Antiscorbutic Fraction of Lemon Juice. V. S. S. Zilva. (*Biochem. J.*, 1927, **21**, 689–697.)—Although it might be reasonable to assume that the reducing agency of the antiscorbutic solutions from lemon juice is directly associated with the activity, yet this is not the case ; there are, however, indications that its presence, most probably amongst other substances, in active solutions, may contribute to the stability of the antiscorbutic potency. Decitrated lemon juice

and active fractions derived from that source reduce phenolindophenol to its leuco-compound. In this way the reducing capacity of such solutions can be quantitatively determined. If insufficient of the indicator to destroy the reducing property of such solutions is added, the reduced compound is re-oxidised in the air and is further reduced by the solution. This alternate reduction and oxidation proceeds until the reducing power of the medium is destroyed. The reducing agency, like the antiscorbutic factor, is destroyed in alkaline medium in the presence of air, on aeration of the active solution and on storage. On fractionation of decitrated lemon juice it is found in as high quantities in inactive as in active fractions. If phenol-indophenol is added to decitrated lemon juice until the indicator is no longer reduced and the treated solution is tested *immediately*, no very appreciable loss in the antiscorbutic activity is observed. On heating decitrated lemon juice in a neutral or acid medium in an autoclave at a pressure of one atmosphere for one hour, no very appreciable destruction of the antiscorbutic activity or of the reducing capacity of the solution takes place. On storing, however, both functions deteriorate very much more quickly than in untreated decitrated lemon juice. It is suggested that the stability of the antiscorbutic factor possibly depends on a chain of reactions, which are kept in equilibrium in the living cell. P. H. P.

Colour Reaction of the Japanese Acid Clays with Liver Oils and "Vitamin *A*" on the Market. K. Kobayashi and K. Yamamoto. (*Mem. Facult. Sci. and Eng. Tokyo*, 1927, **4**, 23–24.)—Japanese acid clays, Florida earths and fuller's earth gave bluish-green sediments with codliver and many other liver oils, and with vitamin *A*, oils extracted from cheese, Kazunoko and eels. Japanese clay, if dried at 100–150° C., gives a more intense reaction, and suitable solvents are benzene, carbon tetrachloride and carbon disulphide. The relative content of colouring principle in liver oils may be determined by diluting 1 grm. of sample with 10 c.c. of benzene, and adding this solution, drop by drop. to a series of test tubes, each containing 10 c.c. of benzene, and, after mixing, adding to each 1 grm. of fine clay. The minimum number of drops required to form the blue coloration is compared with the number used for the standard codliver oil. Anhydrous zinc chloride, aluminium chloride, phosphorus pentoxide and phosphoric acid give the same colour reactions as the Japanese clays. D. G. H.

Purification and Properties of Insulin. F. Dickens, E. C. Dodds, W. Lawson and N. F. Maclagan. (*Biochem. J.*, 1927, **21**, 560–571.)—The purification of crude insulin to a degree of activity represented by a unit of approximately 0·1 mgrm. presents few difficulties, yet attempts to exceed this to any great extent usually result in a considerable loss. The methods used for this purpose may be grouped into two main classes: (*a*) precipitation at the isoelectric point, and (*b*) the use of protein precipitants. An investigation was undertaken to determine the reasons which underlie the failure by these methods, and it was found that insulin is completely precipitated with the protein and metaprotein class, following the analytical method of Wasteneys and Borsook (*J. Biol. Chem.*, 1924, **62**, 1).

On this basis a very efficient method of purification has been developed, which depends on the action of salt solutions at the isoelectric point, and which can be used to produce insulin of a very low physiological unit (about 0·02 mgrm.). Three operations are combined, viz., the trichloroacetic acid precipitation, the acid and salt precipitation, and the oxalate precipitation. Similar results are obtained when sodium citrate is used in place of potassium oxalate. The results of various qualitative tests on the purified product are described, and analytical results on specimens of insulin of varying degrees of purity are given. The bearing of these observations on the probable nature and constitution of insulin is discussed.

P. H. P.

Bacteriological.

Production of Acid by Wood-Rotting Fungi. L. P. Curtin. (*Ind. Eng. Chem.*, 1927, **19**, 878–881.)—The reactions of wood-rotting fungi (*Fomes annosus, Lenzites sepiaria, Lentinus lepideus, Polyphorus pilotae, P. sulphureus*) and of certain moulds (*Rhizopus nigricans, Penicillium*) were determined in a nutrient gel containing 1·5 per cent. of agar and 2·5 per cent. of malt syrup. Methyl orange was found to be an excellent indicator for some of the moulds, but was not sensitive enough for the wood-rotting fungi. Congo red was also insensitive. Sodium alizarine sulphonate proved excellent for the fungi, being less toxic than many other indicators and not affected by carbon dioxide which is evolved by fungi. Methyl red, propyl red and neutral red were quickly destroyed by the fungi. Litmus was satisfactory but not so suitable as the alizarine sulphonate, whilst rosolic acid, besides being very toxic, showed a tendency to fade. A study of the results obtained has shown that the acid solution produced by the wood-rotting fungi is of approximately P_H 5. The change of colour of the indicator precedes the visible growth of the fungi. It has not been determined whether the acid liberated is a secretion of the fungus or a degradation product of the nutrient substance.

Toxicological and Forensic.

Toxicity of Zinc. V. G. Heller and A. D. Burke. (*J. Biol. Chem.*, 1927, **74**, 85–93.)—In a previous investigation on the possibility of poisoning from buttermilk which had been stored in zinc-lined containers the authors found (1) what seemed to be contradictory findings concerning the toxicity of zinc, (2) a more general distribution of zinc in animal and plant tissue than might be commonly assumed, and (3) the inadequacy of methods for the separation and quantitative determination of traces of this element in organic matter. The completion of the work has now been simplified by new methods and modifications suggested by recent workers, but certain phases of the problem concerning the probability of zinc contamination and its effect upon the consumer are still untouched. Buttermilk normally contains a small amount of zinc, the amount increasing after contact with zinc containers, and varying according to the duration of contact, acidity of the buttermilk, and the newness of the zinc surface exposed.

Old surfaces are less susceptible to the attack of the weak organic acids present. Biological experiments showed that zinc added to a normal ration either in the form of pure zinc dust, zinc oxide, or certain zinc salts, in amounts as great as ever found in contaminated foods, and such as would prove fatal for a toxic metal, did not interfere with growth, reproduction, and normal functions of the rat through three generations. No pathological conditions were found in the organs of rats given the rations used in this experiment. The total ash content of the organs studied showed no perceptible increase. Tables show that zinc is found normally in the internal organs of rats given growing rations, but only a small increase was observed in the organs of zinc-fed animals. The path of excretion is primarily through the faeces, though the content in the urine is slightly increased in the zinc-fed animals. Large storage in the internal organs was in no case evident.

P. H. P.

Agricultural.

Modification of the Salicylic-Thiosulphate Method for Determining Total Nitrogen in Plants and Soil Extracts. E. R. Ranker. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 230–251.)—The Gunning or salicylic-thiosulphate method for the determination of total nitrogen in plant materials (*A.O.A.C. Methods of Analysis*, 1925, 9) has been found to give low results, especially for amounts of nitrogen less than 10 mgrms., and the following modified method is suggested. The neutral or slightly alkaline sample is placed in an 800 c.c. Kjeldahl flask, any moisture removed on the water-bath in a vacuum, and 35 to 40 c.c. of a solution of 1 grm. of salicylic acid in 80 c.c. of concentrated sulphuric acid added. The mixture is shaken, allowed to stand overnight and gently heated with 5 grms. of sodium thiosulphate for 5 minutes. Anhydrous sodium sulphate (7 to 10 grms.) and a pinch of copper sulphate are also added, and the whole mixture boiled for 1 hour after it has become clear, and then diluted to 400 c.c. and cooled. It is next distilled in the presence of 100 c.c. of a saturated solution of sodium hydroxide and a little paraffin wax and zinc into 0·02 *N* acid, so that 150 to 200 c.c. are collected in 1 hour. The acid is back-titrated with 0·02 *N* alkali, with methyl red as indicator. The accuracy and applicability of the method, and the influence of certain details of manipulation in preventing loss of nitrogen are discussed, and the desirability of suitable accurate qualitative tests for this purpose emphasised. A wide range of materials was employed (culture tobacco, geranium, pea and celery leaves, tomatoes, greenhouse soils, sugar cane, mosses, amino-acids, etc.), and the determinations checked by a modified form of Devarda's method. This, however, gave a lower degree of accuracy. The absence of free water is important, probably because it dilutes the sulphuric and nitric acids and impairs their dehydrating and nitrifying properties, respectively. Their rôles and those of the other reagents are discussed. Neutralisation is best carried out by the addition of a pre-determined quantity of acid or alkali in the absence of an indicator, and frothing is avoided by allowing the acidified mixture to stand overnight. Loss of

nitrogen during any part of the procedure was tested for by means of the diphenylamine and Nessler reagents. Tobacco materials showed the greatest discrepancies on account of the volatility of the nicotine. The technique of the method is largely dependent on the type of material under investigation. J. G.

Inaccuracies of the Devarda Method when Applied to Plant Materials. E. R. Ranker. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 252–256.)—A wide range of plant materials (which included *Aspergillus niger* cultures, sugar-cane, mushroom, pea-seed and tomato extracts, urea, and amino-acids) were examined for nitrate nitrogen by Devarda's method (*A.O.A.C., Methods of Analysis*, 1925, 12). Due allowance was made for all probable errors. The samples were previously rendered free from ammonia by treatment with alkali, and nitrates or nitrites were shown to be absent. In some cases known amounts of potassium nitrate solution were added. In 15 samples out of 24 the method indicated more nitrate nitrogen than was known to be present, and it is suggested that the term " Devarda nitrogen " be used to replace " nitrate nitrogen " when this method is employed. J. G.

Accuracy of the Various Methods of Measuring Concentration of Hydrogen Ions in Soil. C. Olsen and L. Linderström-Lang. (*Compt Rend. Trav. Lab. Carlsberg*, 1927, **17**, 1–27.)—The hydrogen ion concentrations of 93 samples of soils have been determined by means of the hydrogen and quinhydrone electrodes, and colorimetrically by means of Clark and Lubs' indicators. For the colorimetric measurements only, a clear filtered solution was employed, and in the case of the hydrogen electrode, which was taken as the standard, a correction was made for loss of carbon dioxide. The quinhydrone electrode gave results as much as 0·8 too high, but no correction could be applied, as the error was not limited either to any particular range of acidity or to any particular type of soil. The error appeared to be due chiefly to the effects on the electrode of the solid particles of soil. The colorimetric method also showed deviations which varied from +0·4 to −0·3 in a regular fashion. Thus, below P_H 5·0 and above P_H 8·0 the results were about 0·3 too low, whilst from P_H 5·5 to 7·0 they were 0·15 too high. This is due partly to the evolution of carbon dioxide below P_H 8·0, and partly to the " indicator error " due to the effect of humus substances on the colour. The P_H range 5·0 to 8·0 is the " buffer-range " of carbonic acid. Since the latter error is constant for the whole P_H range and for all the indicators used (about −0·35), a correction curve could be plotted which enabled the P_H value to be determined with an accuracy of $\times 0{\cdot}15$. The corrected colorimetric method is therefore recommended, except for highly alkaline "soda-soils " which give very dark filtrates. The moisture content of the soil is important, and the proportion of soil to water recommended is 1:1 by volume. The mixture is kept for 24 hours and stirred frequently before filtration. The degree of accuracy obtainable by this method is considered sufficient for soil investigations. Electrometric methods cannot be used for soils which contain hydrogen sulphide. J. G.

Organic Analysis.

Determination of Carbon Dioxide in Fermenting Mixtures. A. L. Raymond and H. M. Winegarden. (*J. Biol. Chem.*, 1927, **74**, 189–202.)—In connection with a research on enzymic behaviour it was necessary to develop a simple and expeditious method for the determination of the carbon dioxide formed during fermentations. Cain and Maxwell (*J. Ind. Eng. Chem.*, 1919, **11**, 852) for the determination of carbon in steel absorbed the carbon dioxide, formed by combustion, in known volumes of barium hydroxide solution and followed the precipitation of barium carbonate by measurements of the electrical conductivity of the solution. Spoehr and McGee (*Ind. Eng. Chem.*, 1924, **16**, 128) applied this to the determination of carbon dioxide in their studies on plant respiration, and now this general method has been made applicable to studies on fermentation. Full experimental details are given. The carbon dioxide from the fermentation mixtures is liberated by shaking, carried by means of a stream of air (free from carbon dioxide) to the absorption vessels, which contain barium hydroxide, and then the change in resistance of the barium hydroxide solutions is measured. The method is applicable to either aerobic or anaerobic investigations, and its advantages and limitations are pointed out. For biological studies there is difficulty in securing sterility. The specific resistances of barium hydroxide solutions from 0·065 to 0·12 *N* have been determined at 25°, 30° and 37° C., since those found in the literature are almost exclusively at 25° C. and do not agree well. The rate of the evolution of carbon dioxide from aqueous solutions under various conditions has also been examined. P. H. P.

Conductivity Method for the Determination of Carbon Dioxide. L. E. Bayliss. (*Biochem. J.*, 1927, **21**, 662–664.)—A method is described for the determination of the amount of carbonate in a sodium hydroxide and sodium carbonate mixture, by measurement of the conductivity of the solution, since the migration velocity of the CO_3'' ion is considerably smaller than that of the OH' ion, so that the conductivity of a solution of sodium hydroxide falls as it absorbs carbon dioxide. This method is chiefly valuable for the determination of the amount of carbon dioxide absorbed by a caustic soda solution, and it is believed to be the best and quickest method for the rapid absorption and relative measurement of large quantities of this gas. A calibration curve, which can easily be obtained and plotted, is given, showing the conductivities of mixtures, in varying proportions, of solutions of caustic soda and sodium carbonate of equivalent concentration. It is nearly a straight line for carbonate proportions above 0·3. An empirical equation which was derived experimentally is given for calculations. The standard conductivity apparatus is suitable for these measurements, except that, as the equivalent conductivities of the solutions to be used are relatively high, a conductivity cell must be employed which has small electrodes set well apart, so that the actual value of the resistance measured is not less than 10 ohms; trouble may be experienced otherwise, from heating of the solution during measurement, and from the fact that the resistance of the leads to the cell may not be negligible.

P. H. P.

Grape Seed Oil. L. Margaillan. (*Compt. rend.*, 1927, **185**, 306–307.)—Grape-seed oil, when freshly and carefully prepared, is insoluble in alcohol, and may have an acetyl value as low as 4. On the other hand, carelessly prepared oils, or oils which have been exposed, may undergo oxidation or enzymic hydrolysis action, and have acetyl values as high as 25. The acid value, however, remains low. The acetyl value is also increased by " blowing " at 125° C., though to a less extent than for rape oil. Oxidation by blowing is more complex than spontaneous oxidation. The fresh oil bears no resemblance to castor oil. J. G.

Unsaturated, Aliphatic Alcohols of Sperm Oil. E. Andre and M. T. François. (*Compt. rend.*, 1927, **185**, 279–281.)—The unsaturated, aliphatic alcohols of sperm oil consist of a mixture of at least two alcohols, in which oleic alcohol predominates. The other alcohol may be separated in the end-fraction during the distillation of the corresponding mixture of esters under a pressure of 3 mm. The bromine derivative ($C_{22}H_{42}OBr_4$) indicates a doubly ethylenic alcohol. A number of derivatives of oleic alcohol have been prepared,and their properties are described. Among these the β-naphthyl-urethane and allophanate of oleic alcohol (m.pts. 44° to 45° and 129° C., respectively), and the phenylurethane and β-naphthylurethane of its isomer, elaïdic alcohol (m. pts., 55° to 56° and 71° C., respectively) are new. The derivatives of oleic alcohol are difficult to obtain pure on account of the isomeric changes it undergoes during the process. Elaïdic alcohol, however, is stabler (*cf.* ANALYST, 1921, **46**, 197, and 1926, **51**, 644). J. G.

Determination of Allantoic Acid as Xanthylurea. R. Fosse and V. Bossuyt. (*Compt. rend.*, 1927, **185**, 308–310.)—A solution of pure potassium allantoate may be hydrolysed to urea in the presence of sulphuric or hydrochloric acids (0·02 *N* to 0·1 *N*) at 60° C. for 30 minutes. The liquid is then made slightly alkaline with potassium hydroxide, and twice its volume of acetic acid and one-tenth to one-twentieth of the total volume of methyl xanthydrol added. After at least 2 hours the xanthylurea is collected and weighed. The weight, divided by 7, gives the urea produced, and this quantity, multiplied by 1·466, gives the allantoic acid. The error is about –1 per cent. for solutions of about 1 grm. of potassium allantoate in a litre. Allantoic acid was determined in an aqueous extract of the leaves of *Acer pseudoplatanus* by the hydrolysis of 10 c.c. of the extract with 1 c.c. of *N* hydrochloric acid at 60° C. for 30 minutes. The liquid was clarified with basic lead acetate, centrifuged, and the excess of lead removed with hydrogen sulphide. The above method then gave 2·70 grms. of allantoic acid per 1 kilo of dry leaves. J. G.

Inorganic Analysis.

Rapid Determination of Phosphine in Gases. M. Wilmet. (*Compt. rend.*, 1927, **185**, 206–208.)—In the reaction $PH_3+3HgCl_2=P(HgCl)_3+3HCl$, the colour of the precipitate obtained varies from white through yellow to brown,

and the determination of its weight does not give concordant results. On the other hand, it is found that the quantity of liberated acid is proportional to the volume of phosphine present. The gas (100 c.c.) is measured into a flask over water ; an open tube containing an excess of solid mercuric chloride is introduced, and the mixture shaken. The precipitate is filtered off and washed, and the filtrate titrated with sodium hydroxide and methyl orange. The number of c.c. of 0·1 *N* alkali, multiplied by 0·784, gives the volume of phosphine at 15° C. and 760 mm. For percentages below 0·5, a colorimetric determination may be made. The colour of the suspension is matched against a freshly-prepared standard obtained with a gaseous mixture of known phosphine content. W. R. S.

Determination of Lead as Cyanide. S. Grundt. (*Comptes rend.*, 1927, **185**, 72–73.)—Precipitation of lead from a neutral solution by excess of alkaline cyanide, as by the Herz and Neukirch method (*Z. anorg. Chem.*, 1923, **343**), was not found to produce $Pb(CN)_2$, but white lead containing a small quantity of cyanide. A mixture of lead oxycyanide and hydroxide is, in effect, precipitated, and the hydroxide becomes carbonated during washing and drying operations. If $3PbO, H_2O$ is heated at 100° C. in a current of hydrocyanic acid, a product containing 5·97 per cent. of cyanogen is formed after 6 to 7 hours. D. G. H.

Colour Reaction for Magnesium. W. J. Petraschenj. (*Z. anal. Chem.*, 1927, **71**, 291–297.)—The reagent used is a solution of iodine (3 grms.) and potassium iodide (6 grms.) in 100 or 200 c.c. of water ; it is treated with sodium hydroxide solution until just colourless, and immediately added to the cold, neutral magnesium solution free from ammonium salts ; a dark-red precipitate is obtained; 0·0024 grms. of magnesium in 100 c.c. give an immediate precipitate ; more dilute solutions (down to 0·05 *N*) react after some time. The alkaline-earth metals do not react like magnesium, and do not interfere with the test. W. R. S.

Acidity of Japanese Acid Clay (Japanese Fuller's Earth). K. Kobayashi (*Mem. Facult. Sci. and Eng. Tokyo*, 1927, **4**, 1–2.)—Analyses of the chief Japanese acid clays suggest that the clay is a mixture of colloidal hydrated aluminium silicates and an amorphous anhydrous compound of orthosilicic acid, and may be expressed as $Al_2O_3.6SiO_2.xH_2O$, x being greater than 6. The clay is not a true acid, the acid reaction being due to free acid liberated by the adsorption of the clay to the indicator, and the reaction is similar in nature to that with silk and wool fibres. D. G. H.

Reviews.

THERMODYNAMICS AND CHEMISTRY. By F. H. MACDOUGAL, M.A., Ph.D. Second Edition, 1926. Pp. vi.+414. New York: John Wiley & Sons; London: Chapman & Hall. Price 27s. 6d. net.

The brilliant researches of Nernst, Haber and others reveal how great a service thermodynamics may be to the modern chemist in his quest for new and more economic methods of production. Thermodynamical reasoning and the calculations based thereon constitute the mainstay of several important modern industries, such as those involving the fixation of nitrogen, and the hydrogenation of "water gas" in synthesising alcohols. Thermodynamics is therefore rapidly becoming an essential subject in the training of the chemist, and consequently any book which renders it easy for the student to acquire a satisfactory knowledge of the subject will be warmly welcomed. It is probably due to the widespread appreciation of the importance and utility of the subject, and to the comparative scarcity of works dealing with it, that the volume under review, first published in 1921, has now passed to its second edition.

It is felt that Prof. Macdougal sees Thermodynamics through the eyes of the mathematician, rather than through those of the chemist, as he seems to regard the subject as an end in itself, instead of as a means to an end—the end being a fuller knowledge of chemistry resulting in its wider application. The treatment accorded to the subject, both with regard to the phraseology and to the tiresome and persistent use of mathematical symbols, makes it exceedingly difficult to obtain a good grasp of the actual chemical significance of the various aspects of the subject discussed in the volume. The treatment tends to obscure the subject. Instead of one in which thermodynamics is enshrouded in the formalities of mathematics, a volume is required which will enable, and maybe inspire, the student to use thermodynamics as a powerful instrument of research.

The new edition differs from the last one, in that it contains some recent material on electrolytes, and the chapter on the Nernst heat theorem has been re-written. It includes some account of the work of Debye and Hückel on the vexed problem of solutions of electrolytes, in which the author "has endeavoured to give an adequate presentation of their views" relating to chemical equilibrium in solutions and to the subject of electromotive force. After mentioning that Debye and Hückel devised a method to calculate the "mutual electrostatic energy" of an ionic solution, he suddenly introduces an expression connecting this undefined and unexplained "energy" with other factors, among which are the dielectric constant, the gas constant and Avogadro's number. No attempt is made to elucidate, or even to enunciate, the principles upon which this equation is based, for which the reader is referred to the original papers of Debye and Hückel. This is perhaps surprising, in view of the stress which is placed upon Debye and Hückel's

theory. The formula, however, is made "more explicit" by means of more formulae, and then Debye's formula is modified, and finally, *via* more formulae, the formula of Debye and Hückel is brought into line with those based on the activity theory of Lewis and Randall! If the student wishes to know what it is is all about, he would, indeed, be well advised to take the author's advice and refer to the original papers.

In its present form, the reviewer feels that the book will appeal only to those who have a distinct mathematical bias.

HUBERT T. S. BRITTON.

HANDBOOK OF PHOTOMICROGRAPHY. By H. L. HIND and H. B. RANDLES. Second edition. Pp. xii+295, with 76 text illustrations and 44 plates. London: G. Routledge & Sons, Ltd. 1927. Price 16s.

In producing the second edition of this book the authors have taken the opportunity of re-writing several sections, and since workers are no longer dependent upon continental and other foreign makers for appliances of the highest class, owing to the great advances recently made by English manufacturers in the optical and mechanical parts of the microscope, British appliances are described in full, to the almost complete exclusion of foreign makes.

The volume is described in the preface as "an introduction to photomicrography," but this modest description is negatived by the comprehensive nature of the contents, which include instruction suitable for the advanced worker in addition to more elementary details adapted to the requirements of the beginner.

The work is essentially practical in character, and provides necessary details for the manipulation of the microscope, camera, illuminant, condensers, and colour screens, together with methods for low and high power work with transparent and opaque objects illuminated in various ways, and direct colour photomicrography. In addition, some five pages are devoted to the preparation and mounting of microscopic objects, but although the photomicrographer should undoubtedly have some knowledge of such methods it is questionable whether the inclusion of such limited descriptions will prove of much value, since one would naturally turn for information to textbooks devoted entirely to that subject.

The descriptions of apparatus and methods, both microscopical and photographic, are sound and reliable, but certain portions of the text invite criticism. Thus, considering the importance of cover glass correction, the brief reference to this matter on p. 74 is disappointing. The statement that "it is a very difficult matter to make this adjustment" is somewhat misleading, and liable to deter the novice from attempting it. Undoubtedly care and patience are essential in order to acquire the necessary facility, but it is by no means so difficult as the authors suggest, especially when preliminary trials are made with a suitable object.

Undue emphasis appears to be laid upon the necessity for optical flats in the preparation of colour screens, since a large amount of high class work is achieved

with nothing more perfect than lantern slide cover glasses. In Chapter IV, treating of illuminants, the absence of limelight is noticeable, for although this is used to a less extent than formerly, owing to the extended use of electric light, it is still a valuable high power source of illumination and free from some of the disadvantages of electric light.

The advantages of standard magnifications for comparison purposes do not appear to be mentioned, and various illustrations depicted with odd values such as $\times 6\frac{1}{2}$, $\times 56$, $\times 1035$, etc., indicate that but little importance is attached to this matter by the authors. The one example given of a stereo-photomicrograph on Plate 27 is an admirable photograph, but the faulty masking gives rise to non-stereoscopic floating edges when viewed in the stereoscope, and the two prints in the copy of the book before the reviewer are not on the same horizontal level.

On the other hand, several excellent and highly instructive features are provided, particularly the experiments on ordinary and critical illumination described on pages 118 to 126 and 144 to 154. The text throughout is lucid, and the illustrations, both diagrammatic and ordinary, are good and clear, whilst the plates bear reproductions of numerous excellent photomicrographs with magnifications ranging from $\times 1$ to $\times 5000$, extending over a wide range of subject and including some beautiful examples of direct colour photographs and instantaneous photographs of living organisms. The index is comprehensive and accurate, but, owing to its position between the text and the plates, instead of at the end of the book as usual, it is not found with facility.

Much care has been expended upon the production of the volume, since it is practically free from typographic and other errors, and the authors and publishers have combined to produce a thoroughly reliable work admirably adapted to provide sound instruction in the practice of many branches of photomicrography.

T. J. WARD.

LUBRICATION AND LUBRICANTS. A TREATISE ON THE THEORY AND PRACTICE OF LUBRICATION. LEONARD ARCHBUTT and R. MOUNTFORD DEELEY. Fifth edition, revised throughout, greatly enlarged, re-set. London: Charles Griffin & Co., Ltd. 1927. Price 36s. net.

In the fifteen years that have elapsed since the publication of the last revised edition much work has been done: many new ideas have been promulgated; and some approach has been made towards a real knowledge of the nature of friction and the mode of action of lubricants. All that has been done in these directions is embodied in the new edition, so that it differs entirely in many places from the last, and is in so far a new treatise.

In the first chapter a distinction is drawn between "Solid film or boundary," and "Liquid film or viscous" lubrication, and the properties of "oiliness" and "unctuousness" are defined. Chapter II discusses the properties of thin films and surface forces, and a clear account is given of the work of Langmuir on films

of molecular thickness, and the chemical theory of adsorption and, consequently, of friction. Here, too, the experiments of Adam, following Langmuir, and of Miss Pockels and Lord Rayleigh, are described, and a full account is given of the methods of determining the energy of free surfaces, by capillary tubes, by drop weights, and by the very ingenious method of Devaux, utilised by Langmuir and by Adam, using a shallow trough of liquid and a sliding bar. The whole of this chapter is fascinating reading. Chapter III is devoted to solid film friction, and deals with the nature of polished solid surfaces, cohesion, and the laws of friction of adsorbed films, static and kinetic. The chapter is illustrated by the results of a great deal of experimental work—that of Sir William Hardy and Miss Doubleday, for instance, on homologous paraffins and related compounds, which gives the interesting deduction that a hydrocarbon of sufficiently high molecular weight should form a frictionless lubricant; and much experimental work with the Deeley adsorbed film testing machine and the Lanchester Worm-Gear testing machine, some of it done for the Lubrication Committee of the Department of Scientific and Industrial Research. The next two chapters deal with Viscosity and with the Theory and Laws of Viscous Lubrication; and though the proportion of unchanged matter is much higher here, yet the influence of recent investigation is visible all through.

The chapter on sources and properties of lubricants has been brought up to date; and in the next, on physical methods of examination, we find that some of the Tables of Absolute Viscosities of glycerin and water mixtures have been slightly altered, through the substitution of Hehner's pure glycerin for that originally used, and the final table recalculated; and that descriptions of Lidstone's Viscometer and of the Michell cup and ball viscometer have been introduced, and tables of conversion factors for the Redwood, Saybolt, and Engler instruments. Under "Volatility" (and indeed throughout the work wherever applicable) the standard method of the Institution of Petroleum Technologists is described; and tests for "Demulsification" appear for the first time, as does also a paragraph on the heat of adsorption of oils by metal. Chapter VIII, on Chemical Properties and Methods of Examination, contains an interesting discussion of Wells and Southcombe's discovery of the lubricating effect of fatty acids, and an account of results obtained on various lubricants with added acid, in the Deeley and the Lanchester machines. For the most part, as is natural, there is little change in this chapter, methods of analysis given in the last edition having been thoroughly worked out; but oxidation tests, coking tests, and sludge tests for mineral oils have been added.

It is regrettable, in my opinion, that throughout this chapter the words "Estimate" and "Estimation" should have been substituted for "Determine" and "Determination." Why chemists should persist in using a word, which the Oxford Dictionary defines as "forming an approximate notion of the amount, number, or magnitude of anything *without* actual enumeration or measurement," for processes the essence of which is measurement, I have never been able to understand. It appears to me a flagrant misuse of language. The physicist, it seems,

can *determine* surface energy, or volatility, or even the consistence of a grease; but the poor chemist can only *estimate* ash or water (though, incidentally, and no doubt accidentally, he can *determine* caoutchouc) in an oil. On page 385 we are told that the amount of ash should be ascertained; but how can it be ascertained if we are only able to estimate it? And will it cause the public (who use the word estimate in its legitimate sense) to estimate the chemist more highly, if he announces that the figures on his certificates are only estimates?

The chapter on Systematic Chemical and Physical Testing remains almost entirely unaltered, save for the addition of a tentative method of analysis of grease devised by the American Society for Testing Materials; and the remaining mechanical or engineering part of the book (with which the present reviewer has less intimate acquaintance) has been rearranged. Extremely lucid descriptions of Deeley's testing machine, Stanton's Pendulum machine, and Lanchester's Worm-Gear testing machine, and of the use of stream-line filters in the recovery of used oil, are conspicuous additions here.

This is an indispensable book for all who have to do with the use or the examination of lubricants. There is no other work which covers similar ground, and this is not surprising, for the ground is covered so completely and so satisfactorily by the volume under review. The orderly arrangement and clear statement of the last edition are equally gratifying features of the new one, and the care with which the authors have edited their work is shown by the rarity of misprints—I have only detected one, on page 63, where μ is accidentally substituted for N. Nothing but praise can be given to the work, and the authors are to be congratulated on having maintained the high standard of achievement which they had already reached.

J. T. DUNN.

Publications Received.

ATOMS AND MOLECULES. By R. M. CAVEN. London: Blackie & Son. Price 7s. net.

DIE UNIVERSALITÄT DER GRAVITATION IN DEN GRÖSSTEN UND KLEINSTEN SYSTEMEN. By H. KOLLER-AEBY. Basel: Schwabe & Co. Price Fr. 8.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By A. F. HOLLEMAN. London: Chapman & Hall. Price 17s. 6d. net.

THE INDUSTRIAL CHEMISTRY OF THE FATS AND WAXES. By T. P. HILDITCH. London: Baillière, Tindall & Cox. Price 18s. net.

CLINICAL PATHOLOGY AND THE USE OF STAINS. With Price List of Standard Microscopic Stains. London: The British Drug Houses, Ltd.