NOVEMBER, 1925. Vol. L., No. 596

THE ANALYST

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

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, 7th October, 1925. Mr. E. M. Hawkins, Vice-President, was in the chair.

Certificates were read for the first time in favour of Messrs. Alexander Bruce, B.Sc., F.I.C., Felix John Theodore Grigg, M.Sc., A.I.C., Sydney George Clarke, B.Sc., A.I.C., John Hanley, F.I.C., Arthur John Jones, A.I.C., Henry William Lawrence, F.I.C., Fred Mattingley, B.Sc., A.I.C., Bartle Frere Sawbridge, M.A., F.I.C., Harold Jacob Stern, Ph.D., B.Sc., A.I.C., and Major Clive Newcomb, M.D., F.I.C.

A Certificate was read for the second time in favour of Mr. Theodore Rendle.

The following were elected members of the Society:—As Honorary Member: Professor George Gerald Henderson, M.A., D.Sc., F.R.S., F.I.C. As Ordinary Members: Messrs. Lewis Eynon, B.Sc., F.I.C., Jack Rowan Heather, Frederick George Hitchman, and William David Rogers, B.Sc., F.I.C.

The following papers were read:—"Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates: III. 'A New Method for the Separation of Tantalum from Niobium,' IV. 'The Detection and Determination of Tantalum in Niobium Compounds,'" by A. R. Powell and W. R. Schoeller, Ph.D.; "The Determination of Sulphates in Guncotton," by H. B. Dunnicliff, M.A., D.Sc., F.I.C.; and "The Reduction of Chloric Acid and Chlorates by Ferrous Sulphate," by C. O. Harvey, B.Sc., A.R.C.S., A.I.C.

The Reduction of Chloric Acid and Chlorates by Ferrous Sulphate.

By CECIL O. HARVEY, B.Sc., A.R.C.S., A.I.C.

(*Read at the Meeting, October* 7, 1925.)

Many methods and variations of well-known methods have been proposed for the rapid determination of chloric acid and chlorates, but most of these seem to suffer from one fault or another, and, although the method of reduction which forms the nucleus of this communication has proved a source of disappointment to the author, he believes that its publication is amply justified, as it is very easily and rapidly carried out, and furthermore, the results seem to throw some light on the inadequacy of other methods, which have apparently been credited with yielding results of undoubted accuracy.

While carrying out some preliminary experiments on the reaction between chloric and hydriodic acids it was observed that, although a mixture of these two acids did not liberate an appreciable quantity of iodine at laboratory temperature, yet, upon adding a little ferrous sulphate solution, a marked liberation of iodine took place.

It seemed probable that the ferrous sulphate played the part of a catalyst, being alternately oxidised by the chloric acid, and reduced by the hydriodic acid, and experiments were made to determine the completeness of the reaction under varying conditions.

Experimental.—Ten c.c. of an exactly 0·2 *N* (in oxidising power) solution of potassium chlorate were pipetted into a stoppered bottle, 25 c.c. of a solution of ferrous sulphate in diluted sulphuric acid (approximately 0·1 *N* in reducing power and 12 *N* in acidity) added, and lastly 5 grms. of potassium iodide. The mixture was allowed to stand at laboratory temperature, with occasional agitation, for 20 minutes, when 50 c.c. of distilled water were added, and the liberated iodine was titrated in the usual manner with 0·1 *N* sodium thiosulphate solution. A blank experiment was also made in a precisely similar manner, 10 c.c. of distilled water being used in place of the chlorate solution.

Result expressed as percentage purity of the sample of potassium chlorate = 97·5 per cent. of potassium chlorate.

A similar determination, in which the time of standing was increased to 30 minutes, gave 97·3 per cent. of potassium chlorate. As the sample of chlorate was believed to be pure, it was suspected that, under these conditions, the reaction was incapable of proceeding to completion.

For further work one litre of an exactly 0·2 *N* solution of the chlorate was prepared, and an attempt at standardisation by a gravimetric method was made as follows:—

A mixture of 100 c.c. of the chlorate solution, and 50 c.c. of a neutral solution of ferrous sulphate, containing 15 per cent. of $FeSO_4,7H_2O$, was carefully boiled for 15 minutes, when excess of concentrated nitric acid was added, and (after complete solution of the basic ferric salts) the chloride was precipitated and weighed as silver chloride.

Weight of AgCl obtained = 0·4632 grm., which in terms of percentage purity is equivalent to 96·9 per cent. of potassium chlorate.

A repetition of this determination gave 96·6 per cent. of potassium chlorate, and a volumetric determination, carried out in the manner described previously, gave 97·6 per cent.

There is, therefore, reason for suspecting that the neutral reduction of chlorates by means of ferrous sulphate, as described in many analytical treatises, is incomplete. Further reference will be made to this method when the possibilities of the proposed new method have been dealt with.

Work was now resumed on the volumetric method with a view to inducing completeness of reaction, assuming, for the time being, the purity of the sample of chlorate.

It was found that doubling the concentration of the ferrous sulphate (retaining the same degree of acidity) had no beneficial effect, the results obtained being in the region of 97·3 per cent. of potassium chlorate.

Experiments were made to determine the effect of degree of acidity on the reaction, and results were obtained which are in accordance with Enfield's observations (*J. Chem. Soc.*, 1910, T2, 2441). These may be conveniently arranged in tabular form.

In determinations 1 and 2 the ferrous sulphate was omitted.

		Time of standing at 25° C. Minutes.	Result expressed as $KClO_3$. Per Cent.
1.	Ten c.c. chlorate solution + 25 c.c. 12 *N* H_2SO_4 + 5 grms. KI	20	97·7
2.	Do., with 6 *N* acid	20	16·8
3.	Do., with 6 *N* acid solution of 0·1 *N* $FeSO_4$	20	97·7
4.	Do., with 3 *N* acid solution of 0·1 *N* $FeSO_4$	20	97·6

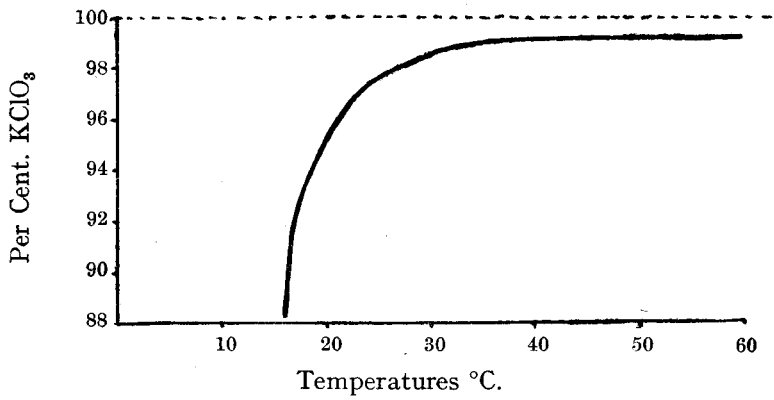
These figures indicate, that, in the presence of ferrous sulphate, nothing is gained by working in very strongly acid solution, and for further work a solution of ferrous sulphate in 3 *N* sulphuric acid (0·1 *N* in reducing power) was adopted.

It was found inadvisable to reduce the time of standing, as a determination in which this time was reduced to five minutes gave only 65 per cent. of potassium chlorate, and furthermore, 20 minutes is the time usually allowed for the completion of the reaction between ferric salts and hydriodic acid.

The other variable factor is temperature, and its importance may be judged by an examination of the results summarised in the table below.

Temperature. ° C.	Completeness of reaction expressed as $KClO_3$ in sample. Per Cent.
16	88·2
25	97·6
35	98·9
45	99·3
50	99·2
60	99·2

These results are represented graphically in the figure, from which the conclusion may be drawn that the reaction cannot be urged further towards completion by working at a temperature higher than 45–50° C.



On the assumption that the original sample of potassium chlorate was quite pure (it was free from chloride and moisture), the conclusion that must inevitably be drawn is that the reaction is incomplete, and that the results fall short of the theoretical figure by about 1 per cent.

Before arriving at a definite conclusion, however, it was necessary to carry out further determinations.

The original sample of potassium chlorate was recrystallised twice from hot water, the first crop of crystals being rejected each time. After being dried at 100° C. for 3 hours the resulting crystals gave, on examination by the new volumetric method, 99·0 per cent. of potassium chlorate, which adds confirmatory evidence of the incompleteness of the reaction.

Some commercial samples of potassium chlorate were examined by the same method, with the following results:—

		Per Cent.
Sample 1.	Crystals	97·8
,, 2.	,, ...	98·5
,, 3.	Powder	98·7
,, 4.	"Santonin" crystals ..	97·8

All these results being lower than one might expect a true result to be, it was decided to determine the percentage purity of one of these samples by an independent method, such as would provide, if possible, a result of undoubted accuracy. Sample 4 was chosen for this determination as being one of the worst.

The method employed was digestion of 0·5 grm. of the sample with excess of hydrochloric acid in a covered crucible on the water bath, the solution being subsequently evaporated to dryness, and the residue dried at a temperature of 120°–130° C. to constant weight.

The loss in weight was found to be 0·1938 grm., which represents the oxygen present as $KClO_3$, and is equivalent to 99·0 per cent. of potassium chlorate.

As a check on this result, the residue in the crucible was assumed to be a mixture of potassium chloride and chlorate, and another calculation on this basis gave 98·9 per cent. of potassium chlorate.

An attempt was also made to determine the perchlorate in the sample by the method of ignition with a large excess of ammonium chloride in a crucible lined with platinum foil, the loss in weight in this case being 0·1980 grm. By deduction of the previous loss in weight one obtains a figure for oxygen present as $KClO_4$, which gives the result 1·8 per cent. of potassium perchlorate.

One cannot, however, rely upon the accuracy of this last figure, though it may be taken as indicating the presence of perchlorate in the sample.

As the result obtained by examination of this sample by the new volumetric method was 97·8 per cent., we have further evidence in support of the conclusion that results obtained by this method fall short of the true value by about 1 per cent., and consequently the original chlorate solution may be taken as a standard 0·2 *N* solution for the purposes of further investigation.

Some experiments in which hydrochloric acid was used in place of sulphuric acid gave inconsistent results, in some cases higher, and in others lower, than those obtained when sulphuric acid was used.

Completeness of Reduction with Ferrous Sulphate.—The results recorded so far have proved that the reduction with ferrous sulphate in acid solution is incomplete, even in the presence of potassium iodide, but further work was carried out which suggests that the new volumetric method gives results more nearly correct than those obtained by reduction with ferrous sulphate under the conditions usually specified.

The low gravimetric results obtained by neutral reduction with ferrous sulphate have already been referred to, and it seemed advisable at this stage to obtain some indications of the completeness of the reduction in the absence of potassium iodide.

Experiments on Reduction in Absence of Potassium Iodide.—A mixture of 10 c.c. of the chlorate solution and 25 c.c. of the acid ferrous sulphate solution was allowed to stand in a tightly stoppered bottle at constant temperature for twenty minutes, when the excess of ferrous sulphate was determined by titration with 0·1 *N* permanganate solution, a "blank" test being also made. The influence

of temperature on the completeness of the reaction is indicated by the following summary of the results obtained.

Temperature. ° C.	Completeness of reaction expressed as per cent. $KClO_3$.
26·5	87·6
35	94·8
45	97·2

A comparison of these results with those obtained by working in the presence of potassium iodide, indicates the beneficial effect which the iodide exerts on the completeness of the reaction.

The following experiment was designed to test the reversibility of the reaction under these conditions.

A determination with permanganate was made at 45° C. in the manner previously described, but before the actual titration the bottle and its contents were cooled to 20° C. and maintained at that temperature for 20 minutes.

The result obtained was 97·4 per cent. of potassium chlorate, which disposes of the possibility of low results being obtained through reversal of the reaction, upon cooling, prior to titration.

Gravimetric and volumetric results so far have indicated that the reaction involving neutral reduction with ferrous sulphate is incomplete (96·8 per cent.), that reduction in acid solution yields higher results (97·3 per cent.), and that the best results are obtained in acid medium in the presence of potassium iodide (99·2 per cent.).

Some experiments were now made to test the accuracy and possibilities of the gravimetric method.

In neutral solution some of the ferric iron is removed from the sphere of action by precipitation, and in acid solution potassium iodide has a similar effect, and also increases the active mass of the ferrous iron. It was therefore thought possible that increasing the concentration of the ferrous sulphate in the neutral reduction might have a beneficial effect, and accordingly a determination was made in which twice as much ferrous sulphate was used as had been used in previous gravimetric determinations. Trouble was experienced, however, in obtaining complete solution of the precipitated basic ferric salts in nitric acid, prolonged heating being necessary, and a very low result was obtained, *viz.* 93·4 per cent. of potassium chlorate.

A gravimetric determination was now made by reduction in acid solution, with the use of a solution of ferrous sulphate in dilute sulphuric acid (0·25 N in reducing power, 6N in acidity).

A mixture of 100 c.c. of the 0·2 N chlorate solution, and 100 c.c. of the acid ferrous sulphate solution was carefully boiled for 20 minutes, and, after boiling with excess of nitric acid, the chloride was estimated as silver chloride. Result: 98·9 per cent. of potassium chlorate.

This result confirms the assertion previously made, that the best results are obtained by reduction in the presence of potassium iodide. This method, of course, cannot be employed when it is desired to make a gravimetric determination,

but the following details of the volumetric method, giving results approximately 1 per cent. below theory, may be given:

VOLUMETRIC METHOD.—*Sulphuric acid—ferrous sulphate solution.*—Approximately 3 *N* in acidity, and 0·1 *N* in reducing power.

Solution of the chlorate.—Should be 0·2 *N* or slightly less in oxidising power.

Put 10 c.c. of the chlorate solution, 25 c.c. of the acid ferrous sulphate solution, and 5 grms. of potassium iodide, into a stoppered bottle having a well-fitting stopper.

Replace the stopper tightly, and stand the bottle in a water bath at a temperature of 45–50° C. for 20 minutes. Cool, remove the stopper, add 50 c.c. of recently boiled water, and titrate the liberated iodine with 0·1 *N* thiosulphate solution.

Make a "blank" determination, using 10 c.c. of water in place of the chlorate solution, in an exactly similar bottle.

It should be noted that in the determination of chlorate occurring as impurity (for instance, in perchloric acid) this method yields sufficiently accurate results if carried out at a temperature of about 20° C., and, for this purpose, the bottles may be placed in the proximity of a steam oven or water-bath.

CONCLUSIONS AND SUMMARY.—(1) That the neutral reduction of chlorates by means of ferrous sulphate is incomplete.

(2) That in acid solution better results are obtained, but that the best results obtainable by this method are given when potassium iodide is present.

The more important results may be summarised in tabular form as follows:

Method.	Temperature of determination. ° C.	Conditions.	Completeness of reaction, expressed as per cent. $KClO_3$. Per Cent.
Volumetric	45	Acid $FeSO_4$ in presence of KI	99·2
Volumetric	45	Acid $FeSO_4$ in absence of KI	97·2
Gravimetric	100	Neutral reduction with $FeSO_4$	96·8
Gravimetric	100	Acid reduction with $FeSO_4$	98·9

The Determination of Sulphates in Guncotton.

BY H. B. DUNNICLIFF, M.A., Sc.D., F.I.C.

(*Read at the Meeting, October* 7, 1925.)

IT has been shown by C. Kullgren (Worden, *Treatise on Cellulose*, 1921, Vol. I., Part iii, p. 1909) that attempts to determine sulphuric esters in guncotton by hydrolysis yield inconsistent results. A method involving the complete destruction of the guncotton by oxidising agents and the determination of the SO_4 as barium sulphate is in common use.

The determination of sulphates by precipitation as barium sulphate has been the subject of a large number of papers, and, in addition to those referred to subsequently, the following are important: Johnston and Adams, *J. Amer. Chem. Soc.*, 1911, **33**, 829; W. A. Turner, *J. Amer. Sci.*, 1914 (iv), **38**, 41; and I. M. Kolthoff and J. van Cittert, *Pharm. Weekblad*, 1923, **60**, 1177.

J. M. Taylor, *J. Soc. Chem. Ind.*, 1923, **42**, 294 T, has shown that uncontaminated precipitation of the barium sulphate is assisted by (1) moderate dilution, (2) the presence of ammonium chloride, (3) distinct acidity, (4) slow addition to the hot solution of moderate excess of hot barium chloride solution, and (5) setting aside for twelve to sixteen hours after boiling. Observance of these details reduces to a minimum the tendency to error due to the adsorption of barium chloride or soluble salts by the barium sulphate.

This investigation was undertaken because it had been observed that, although the process of manufacture was unchanged, the SO_4 content in guncotton was sometimes reported as above the specification limit of 0·10 per cent.

The procedure adopted in the laboratory was as follows: Five grms. of guncotton were mixed with 50 c.c. of A.R. nitric acid (concentrated) and heated gently on a sand bath until solution was effected. After cooling, one grm. of potassium chlorate was added, and the mixture was heated on a sand bath until the residue appeared to be darkening, and then the evaporation to dryness was completed on a water bath. (At this stage the residue was pasty rather than dry.) This residue was treated with 20 c.c. of strong A.R. hydrochloric acid and 0·5 grm. of potassium chlorate, and again evaporated to dryness, as just described. The treatment with hydrochloric acid and potassium chlorate was repeated, and the residue obtained after evaporation treated with 1 c.c. of strong A.R. hydrochloric acid in 100 c.c. of water. The solution was filtered, and the sulphate in the filtrate (which was always of an orange or brown colour) determined as barium sulphate by precipitation with barium chloride.

A blank experiment was made corresponding in every detail with the above procedure except that the guncotton was absent. In this way the sulphate content of the total reagents used was determined and could be deducted from the value obtained for the guncotton under examination. This control was repeated whenever the source of any one or more of the reagents was changed. The values obtained for this "blank" varied between 0·0030 and 0·0038 per cent. The use of potassium chlorate is recommended by Worden (*loc. cit.*, 2300), but the specification test prescribes sodium chlorate.

Determinations of SO_4 in pure sulphuric acid solution by the method given for the determination of SO_4 in guncotton at the end of this communication show that both in the presence of sodium chloride (from sodium chlorate) and of potassium chloride (from potassium chlorate) results of a high degree of accuracy were obtained, though, as found by previous observers (*loc. cit.*), the tendency was for them to be a little high rather than low. In these determinations sodium or potassium sulphate was not found in the aqueous extracts from dried barium

sulphate precipitates, and it is suggested that the high values are due to the adsorption of a trace of barium chloride (C. W. Foulk, *J. Amer. Chem. Soc.* 1896, **18**, 793; D. Balareff, *Zeitsch. anorg. Chem.* 1922, **123**, 69). This would be converted into barium sulphate and weighed as such when converting into barium sulphate the barium sulphide produced during the incineration of the filter paper. The sulphuric acid was determined in a solution of pure sulphuric acid of known concentration. Values found (*a*) in presence of potassium chloride: (0·38 per cent. KCl)—0·1016: 0·1010: 0·1001: 0·1019 grm.; (*b*) in presence of sodium chloride: (0·34 per cent. NaCl)—0·1010: 0·1009: 0·1001: 0·1016 grm. Theory required: 0·1004 grm.

It appears, therefore, that at low concentrations of sodium or potassium chloride, a high degree of accuracy may be attained, but that the tendency is for results obtained with potassium chlorate to be rather higher than those obtained with sodium chlorate (*cf.* Series 4, and Y. Kato and I. Noda, *Mem. Coll. Sci. Eng. Kyōtō*, 1909–1910, **2**, 217; D. Balareff; W. Vaubel, *Zeitsch. öffent. Chem.*, 1914, **20**, 426; 1915, **21**, 1; D. Balareff, *loc cit.*), and the use of sodium chlorate is, therefore, recommended. As the method was carried out (*vide supra*) the oxidation of the guncotton was incomplete. The pasty residue became very dark on being heated to a temperature of 120–130° C. in an air oven. This incomplete action is probably due, in part, to the fact that, at the laboratory in which this work was done, the atmospheric pressure is about 610 mm. The darkening of the residue appears to be desirable, as the treatment assists in the destruction of the highly coloured substances which are not completely attacked by the oxidising agents in a solution which might conceivably consist, in part, of compounds which would give insoluble or sparingly soluble barium derivatives. Further, if there were traces of soluble silica, this treatment would render it insoluble, and it would be eliminated before the treatment with barium chloride solution. It is necessary that the guncotton should be completely destroyed in order to determine the sulphate content accurately. This determination really amounts to the determination of the total sulphur content existing as, or convertible into, soluble sulphates under the conditions of the experiment.

The variations in procedure are noted in the following series of experiments:—

Series 1.—Laboratory procedure was adopted, but the residues were heated to dryness on a sand bath and then in an oven at 120 to 130°C. after each evaporation to dryness, in order to decompose organic matter, and to render insoluble any soluble silica.

(*a*)	Original method, per cent.	...	0·089	0·082
(*b*)	Revised method i,, per cent.	...	0·090	0·090
	Guncotton Sample No.		1	1

Series 2.—Sodium chlorate was used instead of potassium chlorate, and the residues were heated to 120 to 130°C. after each evaporation. The solution

became very dark, and additional nitric acid and sodium chlorate, and hydrochloric acid and sodium chlorate treatments were given (one each).

(*a*)	Original method, per cent.	0·080	0·077	0·090	(0·120)
(*b*)	Revised method ii., per cent.	0·072	0·062	0·065	0·060
	Guncotton sample No.	2	2	3	3

Series 3.—It was thought that the same result would be realised if an extra nitric acid treatment (without sodium chlorate) was inserted between the two hydrochloric acid and sodium chlorate treatments (in this series, only two hydrochloric acid and sodium chlorate treatments were applied, not three as in series 2).

(*a*)	Original method, per cent.	0·100					
(*b*)	Revised method iii., per cent.	0·090	0·095	0·080	0·085	0·090	0·090
	Guncotton sample No. ...	4	4	5	5	6	6

Series 4.—After these various modifications of procedure, the final solution was still slightly coloured. The extra nitric acid and sodium chlorate treatment was applied between the two hydrochloric acid and sodium chlorate treatments. Comparative results were obtained when using potassium chlorate.

(*a*)	Revised method ($KClO_3$), per cent.	0·099	0·099	0·090
(*b*)	Revised method iv. ($NaClO_3$), per cent.	0·090	0·086	0·085
	Guncotton sample No.	11	12	13

It will be observed that the values found when potassium chlorate was used are higher than those obtained with sodium chlorate.

Series 5.—The barium sulphate is often coloured red after the ignition in the crucible. (G. M. Smith, *J. Amer. Chem. Soc.*, 1917, **39**, 1152). This may be due to traces of iron in the guncotton. An attempt was made to find out whether any advantage was gained by precipitating the iron before precipitating the sulphate. This was done by making the liquor ammoniacal before filtration. The filtrate was acidified with hydrochloric acid before precipitating the sulphate.

(*a*)	Method iv. (*b*), without ammonia treatment, per cent.	0·100	0·097
(*b*)	Method iv. (*b*), with ammonia treatment, per cent.	0·100	0·099
	Guncotton sample No.	15	15

Series 6.—A number of determinations were carried out by means of method iv. (*b*) with factory acid which had been redistilled over barium nitrate. The acid fumed strongly and contained 96 per cent. of nitric acid. (Sp. gr., 1·504). It gave a blank—0·0038 per cent. Results obtained with this fuming acid were generally high and very irregular. The solution became darker than is found by the new method with the use of A.R. acid diluted to Sp. gr., 1·400. On repeating the determinations after diluting the nitric acid to 1·400 (=65 per cent. nitric acid), satisfactory results were obtained.

Series 7.—In order to discover if there was an abnormal amount of sulphur in the cotton waste from which the guncotton was made, 500 grms. of a normal sample of cleaned cotton waste were ashed, and the sulphate determined. These results showed that the sulphate was represented by 0·0001 per cent. on the cotton, and 0·00005 per cent. on the guncotton made from it. This indicates that such sulphate as is in the guncotton becomes associated with it during, or after, the process of nitration.

Examination of a large number of analyses did not confirm the observation of Piest (Worden, *loc. cit.*) that high ash is associated with high sulphate content. The sulphates in the portion of the guncotton insoluble in acetone ranged from 0·068 to 0·073 per cent. The sulphate content does not appear to have any direct relationship with the organic matter insoluble in acetone.

As a result of this investigation, the following method is proposed. Modifications of the previous procedure are printed in italics.

THE DETERMINATION OF SULPHATES IN GUNCOTTON.—Heat 5 grms. of the guncotton gently on a water bath with 50 c.c. of concentrated A. R. nitric acid (Sp. gr., 1·400) until dissolved. After cooling, add 1 grm. of A.R. sodium chlorate and evaporate the solution to dryness *on a sand bath, and heat the residue in an air oven at* 120 °*C. for half an hour.* Treat the residue with 20 c.c. of A.R. hydrochloric acid, and 0·5 grm. of sodium chlorate, and again evaporate to dryness *on a sand bath and heat to* 120°*C. in an air oven for half an hour. Heat the residue with* 0·5 *grm. of sodium chlorate and* 20 *c.c. of nitric acid* (*Sp. gr.* 1·400) *and evaporate to dryness on a sand tray. Heat the residue in an oven at* 120°*C. for half an hour* and finally again treat with 0·5 grm. of sodium chlorate, and 20 c.c. of concentrated hydrochloric acid, and evaporate to dryness *on a sand bath.* Dissolve the residue in water *to which* 1 *c.c. of concentrated hydrochloric acid has been added. Boil and filter. Wash the filter with hot water till free from chloride, and add the washings to the filtrate. Now add* 20 *c.c. of a saturated solution of ammonium chloride and* 1 *c.c. of concentrated hydrochloric acid for each* 100 *c.c. of solution and heat the solution to boiling; add slowly, with stirring,* 30 *c.c. of boiling* 10 *per cent. barium chloride solution. Heat to boiling, and then set aside until next day.* (*The final volume of the solution should be about* 400 *c.c.*) *The barium sulphate is determined by the usual gravimetric method.* A blank determination must be made in the absence of guncotton, and an allowance made, when subsequently calculating the percentage of sulphate in the guncotton, for the sulphur value obtained.

This work was done at the Cordite Factory, Aruvankadu, South India, and is published with the permission of the Master General of Supply.

The author desires to acknowledge the valuable assistance of Mr. Daniels in carrying out this work.

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Notes.

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

IMITATION VANILLA ESSENCE.

THE Regulations under the New Zealand Sale of Food and Drugs Act specify that vanilla essence shall be an alcoholic extract of vanilla bean containing not less than 55 per cent. by volume of alcohol. One hundred cubic centimetres of the extract shall contain the soluble matter from not less than 10 grms. of vanilla bean. There must be not less than 0·1 per cent. of natural vanillin present. Sugar or glycerin may be added. It may be coloured with caramel.

The methods of analysis followed in the Dominion Laboratory are those given for vanilla essence in *Food Inspection and Analysis*, by Leach (4th edition).

The essence is usually prepared by extracting the finely cut bean with alcohol of strength 60 to 65 per cent. by volume. It is made in Bond, and the Customs authorities insist on one lb. of bean, at least, being used to the gallon of alcohol. The essence so prepared has certain definite characteristics:—(1) It contains 0·11 to 0·31 per cent. of vanillin. (2) It also contains a considerable amount of extractive matter, consisting, in part, of a reddish brown resin. Although stated to have little or no flavouring properties, this resin is a most important constituent of the essence, as it serves to fix certain delicate flavouring principles other than the vanillin.

The proportion of extractive matter is indicated:—(*a*) By the normal lead number. This is the number of grms. of lead that will enter into combination with the extractive matter in 100 grms. of the essence. The normal lead number varies from 0·40 to 0·75. (*b*) By the ash, which varies from 0·22 to 0·33 grm. per 100 c.c. of essence. (*c*) By the depth of reddish brown colour.

A sample obtained during June, 1924, was found to be of the composition given under A. The composition of an average extract is given for comparison under B.

	A.	B.
Vanillin	0·79	0·15 per cent.
Alcohol by volume	55·0	55·0 ,,
Normal lead number	0·03	0·54 ,,
Ash	0·04	0·22 grms. per 100 c.c.

It was concluded that practically the whole of the vanillin in the sample had been added as synthetic vanillin and that the essence should have been sold as "Imitation."

When informed that legal proceedings would be taken, the manufacturer maintained that the essence was genuine and had been prepared by extracting one pound of Tahiti beans with one gallon of 95 per cent. alcohol. This extract was added to beans which had been steeped in water containing malt, and fermented in such a manner that the amount of vanillin was greatly increased. The essence drawn off then contained about 60 per cent. of alcohol; it was fined with egg white and coloured with caramel.

From experiments made in the Laboratory it was found that the 95 per cent. alcoholic extract differed very materially from that prepared with 60 per cent. alcohol. The difference is shewn in the two following analyses:

	95 per cent.	60 per cent. alcohol.
Vanillin	0·12	0·12 per cent.
Normal lead number	0·15	0·40 ,,
Ash	0·06	0·20 ,,
Colour	light yellow-brown	decided red-brown.

The red-brown resin of the bean, although soluble in 60 per cent. alcohol, is not soluble in 95 per cent. alcohol, but another resinous body is extracted, giving a light yellow brown solution. On diluting this strong alcoholic extract to 60 per cent. this resin is thrown out of solution as a dense cloud, and it requires the addition of egg white or similar coagulant to clear this essence.

The contention that fermented bean was used in the manner described was negatived by the fact that the alcohol, being reduced to 60 per cent., would have extracted the red-brown resin. Experiments proved that this would not have been removed by fining with white of egg.

The fermentation process could not be investigated, as the manufacturer, when pressed, refused to give details. In any case, it is most unlikely that there is any appreciable amount of unaltered coniferin in vanilla beans as sold, and there is the additional objection that coniferin is not hydrolysed by the enzymes of malt.

An exactly similar essence to that sold by the defendant could be prepared by exhausting 1 lb. of Tahiti beans with 95 per cent. alcohol, diluting the solution to an alcoholic strength of 55 per cent., clearing with white-of-egg or by other means, and adding the desired amount of vanillin and sufficient caramel to give the required depth of colour.

With this procedure the Customs official would not be aware that the essence, as sold, was really a very strong imitation essence, as all operations subsequent to the preparation of the 95 per cent. alcoholic extract would be conducted outside the Bond.

When the case came before the Court the defendant pleaded "not guilty," but after lengthy evidence had been given on the above lines by the Department's Analyst, a plea of "guilty" was entered.

As there had been an attempt to mislead, and the Department had been put to considerable expense in investigating the statements made by defendant, the magistrate took a serious view of the case and inflicted a fine of £100 with costs.

J. C. MACLAURIN (*Dominion Analyst*).

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THE DETECTION OF ANNATTO IN MILK.

IN a recent issue of THE ANALYST (1925, 335) there appeared a note by Mr. Harold Lowe on the detection of annatto in milk.

Using 5 c.c. of milk, Lowe claims to be able to detect 0·35 grain per gallon of annatto, and my tests confirm this.

The following modification of Leach's method, which has been in use in this laboratory for a considerable time, appears capable of even greater delicacy,

as when 5 c.c. of milk are taken, 0·25 grain per gallon of dry annatto can be detected. When 25 c.c. of milk are used, as little as 0·03 grain per gallon has been discovered with certainty, and by increasing the quantity of milk, a proportionately smaller amount can be detected. When more than 25 c.c. of milk are taken for the test, a proportionately greater amount of acetic acid is required to coagulate the milk, but never more than 1 c.c., and when made alkaline later on, the volume before filtering should not exceed about 6 c.c. The method is applicable to either fresh or sour milk.

Twenty-five c.c. of milk are coagulated in a conical flask of 100 c.c. capacity by warming to 50° C. and adding 0·2 c.c. of acetic acid (glacial). The whole is then poured into a Buchner funnel (3 in. diameter), in which there is fitted a No. 41 Whatman filter paper. The curd is pressed to free it from water. It is then returned to the original conical flask, shaken vigorously for a minute or so (to disintegrate the curd) with 75 c.c. of ether, and allowed to stand overnight. The ethereal solution, which contains the fat and any annatto present in the milk, is poured into a porcelain basin and evaporated to dryness on the water-bath. Immediately it reaches this stage it is made alkaline by adding 6 c.c. of 0·1 *N* sodium hydroxide solution, *stirred thoroughly*, and transferred to a wet 9 cm. filter paper. When all the liquid has passed through and only fat remains, the filter paper is opened, placed on a clock glass, washed by means of a stream of hot water from a wash-bottle, and allowed to dry in the air.

In the presence of annatto an orange tint is imparted to the filter paper, and its presence is confirmed by adding a drop of stannous chloride solution or citric acid solution (5 per cent.), when a pink colour is developed.

With a view to ascertaining the effect of time and light upon annatto in milk, a series of samples was prepared containing quantities of annatto varying from 0·03 to 0·25 grain per gallon. Six of the samples were placed in diffused sunlight, and six others were placed in the dark. Fifteen months later they were all examined, and it was found that time and light had no effect, and that annatto could be detected as easily as in a fresh sample. The only difficulty was in filtering off the curd, which was in a state of fine division. A Buchner funnel (6in. diameter) with a No. 41 filter paper, was found to be the only effective means of obtaining the curd in a semi-dry condition. (One hundred c.c. of milk required one hour to filter.) By using 25 c.c. of the sample 0·03 grain per gallon of annatto could be detected.

Whether, with these small quantities, any bleaching action goes on or not over so long a period is still to be determined, but with samples containing larger quantities of annatto (0·25—1·39 grains) one can, after three months, say with certainty that the gradation in colour is just as marked as when the samples were fresh.

If any bleaching action does take place, one would anticipate that a corresponding weakness in the chemical reaction would naturally follow.

Speaking generally, therefore, the conclusions to be drawn from these experiments are that, whilst annatto may or may not be bleached, age and sunlight do not prevent a chemical test from being applied successfully, nor is the reaction perceptibly weakened by the exposure.

A. D. GARDINER.

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 interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY AND COUNTY OF KINGSTON-UPON-HULL.

ANNUAL REPORT OF THE PUBLIC ANALYST AND BACTERIOLOGIST FOR 1924.

DURING the year 1924 the number of samples of all kinds examined was 3812, comprising 851 samples of foods and drugs, 2792 bacteriological (pathological) specimens, and 169 other samples. Of the foods and drugs samples, 511 were official (23 adulterated and 21 suspicious), 329 were informal (9 adulterated and 10 suspicious), and 5 were private (1 adulterated). The percentage of adulterated and suspicious samples was 7·6, as compared with 8·5 in 1923 (adulterated samples 3·9, as against 5·4 per cent. in 1923).

MILK.—The total number of samples was 419, of which 19 were suspicious and 14 adulterated, an adulteration percentage of 3·3.

"Dirt" in Milk.—Twelve of the samples contained an unwarranted amount of "dirty" sediment. The following table give the results of the special examinations for sediment in milk from *suspected sources* in 1923 and 1924.

	Total samples.	"Dirty" samples.	Average sediment in "Clean samples." (Parts per 100,000).	Average sediment in all samples. (Parts per 100,000).
1923	44	7	under 1·0	1·4
1924	33	1	0·95	1·0

During the year no samples taken specially for examination for sediment were returned as adulterated, but one sample was classified as "dirty" and of suspicious character (2·5 parts of extraneous sediment per 100,000).

BUTTER AND MARGARINE.—Three of 22 samples of butter contained excessive water (17·3, 21·4 and 22·8 per cent.), and 2 of 12 samples of margarine (17·0 and 16·6 per cent.). No preservatives were detected in the butters, but all the samples of margarine contained boron preservative (0·18 to 0·48 per cent. of boric acid).

CHEESE.—Ten samples of cheese (Cheshire kind) contained from 34 to 45 per cent. of fat, and were free from foreign additons.

FLOUR AND SELF-RAISING FLOUR.—Of 16 samples of flour, 8 contained a persulphate compound, and one of these had also been bleached with nitrogen peroxide, and 5 other samples had been similarly bleached, but not subjected to other treatment. The intensity of the bleaching treatment is not so pronounced as was the case some years ago, but the use of persulphate "improvers" seems to be on the increase.

Six samples of self-raising flour consisted of wheat flour mixed with baking powder; four contained acid tartrate and 2 contained calcium acid phosphate (1·2 and 1·8 per cent.).

BAKING POWDERS.—Fifteen samples contained from 5 to 14 per cent. of available carbon dioxide (average about 8 per cent.).

FARINACEOUS PRODUCTS.—Fifty-nine samples were examined, all of which were returned as genuine, although 2 samples of rice were "polished," and contained 0·3 per cent. of extraneous siliceous matter. It is suggested that, in view of the fact that it is now known that the polishing of rice produces a cereal of inferior food value, the recommendation of a permissible maximum limit of 0·5 per cent. of foreign mineral matter, given in the Local Government Report of 1909, should be withdrawn, and the polishing of rice and other cereals totally prohibited.

All the ten samples bought as "sago" were actually tapioca. The latter is usually supplied when the former is asked for.

DRUGS.—Eighty-six samples were examined of which 1 only (mercury ointment with only 15 per cent. of metallic mercury) was returned as adulterated.

ARNOLD R. TANKARD.

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.

BORIC ACID IN SHRIMPS.

ON August 15 a shrimp dealer of Southport was summoned at Skipton for selling shrimps which contained, in one sample, 0·35 per cent., and in another sample, 0·75 per cent. of boric acid. A greengrocer was also summoned at the same time for selling shrimps containing 1·08 per cent. of boric acid.

For the defence it was urged that new regulations had been made as to the use of preservatives and that the trade was passing through a transition stage. In view of this fact neither case was pressed.

A letter from the Minister of Health to Lieut.-Col. Dalrympe White, M.P. for Southport, was read to the Court. In this letter the Minister regrets that it is impossible to do anything to meet the special case of the shrimp-potters of Southport, since the amount of boric acid used is so high, being nearly 1 per cent., that it would be quite impossible to make a special exception in their favour. He has heard, however, that there is a possibility of research being carried out as to other forms of packing, and hopes that by the time the regulations come into force (Jan. 1, 1927) some alternative method of carrying on their business may have been found.

EXCESS OF PHOSPHORIC ACID IN PRESCRIBED MEDICINE.

ON September 2 a druggist was summoned at Highgate Police Court for selling "a compound drug, to wit, a mixture purporting to be the mist. acid phos. in the formulary of the Middlesex Panel Committee, which was not composed of ingredients in accordance with the demand of the purchaser, but contained an excess of dilute phosphoric acid, contrary to Sec. 7 of the Sale of Food and Drugs Act, 1875."

Mr. H. Glyn-Jones, for the defence, first took exception to the form of the analyst's certificate, but his objection was over-ruled. A certificate of an analysis by Mr. T. Tickle was then put in, which was to the effect that the mixture contained 13·8 minims per half oz., which would confirm the statement of the defendant, viz., that he had been a druggist for over 40 years, and had been brought up on the 1885–1898 British Pharmacopoeia, according to which the mixture would contain 13·8 minims per half oz., instead of the 10 minims required by the B.P. of 1914. The defendant's concentrated acid, when diluted, corresponded with the requirements of the old B.P. instead of that of 1914.

A fine of 20s. with 15s. costs was imposed.

SALE OF BONDON CHEESE AS CREAM CHEESE.

On September 18 a grocer was summoned at Wallasey for selling cream cheese not of the nature, substance and quality of the article demanded.

An agent of the food inspector asked for cream cheese and was supplied with two 3½d. packets labelled "St. Ivel, Bondon."

Mr. Hodgson, the Public Analyst, said that his analysis showed the cheese to contain: Water, 64·6; fat, 6·5; mineral matter, 2·5; proteins, etc., 26·4 per cent. It was not cream cheese, but a soft cheese made from skimmed milk. Genuine cream cheese contained not less than 30 per cent. of fat. The article analysed by him contained 10½ ozs. of water per lb., and the milk used in its manufacture had been deprived of 68·67 per cent. of its fat.

For the defence it was stated that on the previous day the inspector's agent had been told that St. Ivel, Bondon Cheese was not cream cheese. As she had been told this, a second assistant said that he did not think it necessary to repeat the information the next day when cream cheese was again asked for.

The magistrates inflicted a fine of 20s. with £4 4s. costs.

IRON FILINGS IN TEA.

On September 28th a tradesman was summoned by the Hackney Borough Council, at North London Police Court, for exposing for sale tea dust and tea which were unfit for food. About 100 lbs. of tea had been seized from defendant's stall and destroyed by order of the Court. Examination had shown that the tea (which was largely sold to the poorer classes at 1s. per lb.) contained iron filings, metal, and pieces of wire and nails, and evidence was given that particles of metal had been found by means of a magnet in a cup of tea made with this product.

Dr. G. H. Dart, Medical Officer for Hackney, stated that when a magnet was drawn across the top of the tea, particles could be seen moving towards it. With any ordinary infusion of the tea the particles would get through, and would be liable to cause gastritis or gastro-enteritis in the drinker.

For the defence the legal point was raised that if the defendant bought the tea from the wholesaler as fit for human food and sold it as such, not he, but the wholesaler, was liable. The Magistrate, however, held the contrary view.

The wholesale merchant gave evidence that he had sold 120 lb. of tea to the defendant, and that, in his absence, the employee who sent it must have omitted to extract the iron with magnets. Tea from abroad, he said, had iron filings in it which had to be extracted.

The Magistrate (Mr. Bingley) regarded this as a rather serious offence, but was convinced that the defendant had no knowledge of the condition of the tea. On the other hand, it was his duty to protect the public, who did not want to have to go about with magnets in their pockets. Fines amounting to £5, with 3 guineas costs, were imposed.

PAREGORIC WITHOUT OPIUM.

ON September 30 the proprietor of a pharmacy at Carshalton was summoned before the Croydon County Bench for having sold paregoric elixir which contained no tincture of opium, whereas the British Pharmacopoeia required this drug to contain 5 per cent. by volume of tincture of opium.

Defendant, who stated that he was not a qualified pharmacist, said that it was his practice to inscribe on the label "without opium," and that it was by an oversight that he had not done so on this occasion.

The County Inspector said that action had been taken owing to a complaint that the defendant a week before had sold paregoric without opium.

As this was the first offence, the Bench imposed a fine of £5, but warned the defendant that the maximum penalty was £20.

Examination of Milk in the City of London.

THE Report of Dr. W. J. Howarth, the Medical Officer of Health for the City of London for 1924, has a special section on the examination of milk—chemical, bacteriological, and as to presence of dirt.

Chemical Examination.—Of the 244 samples chemically examined by the Public Analyst, Mr. E. A. Pinchin, 9 contained less than 3 per cent. of fat; the highest amount found was 10·4 per cent. The percentage of milk adulteration for both formal and informal samples was 5·7. Special enquiries were made as to samples containing more than 4·2 per cent. of fat. Four had been sampled in course of delivery at railway stations, 2 were from Jersey cows, and 8 were from shop containers, the contents of which had not been properly stirred. All the samples were free from preservatives.

Bacteriological Examination.—Forty-two samples were bacteriologically examined by the City Bacteriologist (Sir F. W. Andrews). No really dirty sample was found. The "traces" noted represented a few blackish or greyish specks in 22 of the samples.

In tests on guinea pigs 12·8 per cent. of the animals developed tubercle, as compared with 2·6 per cent. in 1923 and 9·5 per cent. in 1922. As in previous years, details of samples found to be infected were forwarded to the Medical Officer of Health of the L.C.C., who instituted enquiries at the several farms from which the milks had been derived. The following precautions are taken to avoid danger of contamination during the process of sampling:—On the arrival of the milk train and as soon as the churns have been deposited on the platform, certain churns are selected from which it is proposed to take the samples. The milk in these churns is thoroughly mixed with a clean plunger. A stout new indiarubber band is then twisted round the neck of the sample bottle to form a handle. The bottle is always sterilised by the bacteriologist before use. The stopper is removed

and the bottle lowered into the milk and filled. The bottle is withdrawn from the churn, the stopper immediately replaced and a clean linen cover tied over it. It is then labelled. Six samples are taken at one session.

In order that there shall be no transference of infection or contamination from one churn to another, through the medium of the plunger, this is thoroughly cleansed with hot water and soda before use, and after each sample has been stirred it is washed in running water, and dried with a clean cloth.

Each plunger is only used twice, so that three are required to take the six samples. The cloth on which the plunger is dried is only used once.

Tuberculosis in Milk.—The following comparative table of the results obtained for various authorities in the years 1919 to 1923 is given:

Authority.	1919.			1920.			1921.			1922.			1923.		
	No. of samples examined.	Positive results.	Percentage.	No. of samples examined.	Positive results.	Percentage.	No. of samples examined.	Positive results.	Percentage.	No. of samples examined.	Positive results.	Percentage.	No. of samples examined.	Positive results.	Percentage.
City of London	27	4	14·8	Nil	—	—	29 19 24	7 4 3	24·2 26·3 12·5	42	4	9·5	39	1	2·6
London County Council	943	61	6·5	1294	76	5·9	1808	63	3·48	2284	60	2·6	—	—	—
City of Liverpool	509	30	5·9	1022	73	7·1	809	100	12·4	834	64	7·6	—	—	—
City & County of Newcastle-upon-Tyne	—	—	3·6	—	—	—	—	—	—	—	—	7·0	—	—	—
County Borough of Derby	—	—	—	56	6	10·7	68	10	14·7	70	11	15·7	53	10	18·8

Use of Rat Virus in London.

THE Medical Officer of Health for the City of London in his Report for 1924 (pp. 76–77) mentions that, in spite of the discouragement of its use by the Ministry of Agriculture and representations to the Government by the City Corporation, rat virus is still being largely used in many premises. The experience gained in the City does not bear out the claim that rats and mice die in the open after being poisoned by virus, as complaints have been made of the nuisance of dead rats between match boarding and walls and under floors in premises where virus has been used.

By a general Army Order, dated July 29th, 1919, the use of any vermin-destroying virus preparation is prohibited in all military establishments and camps, the reasons stated for their prohibitions being:—(1) They are apt to produce a rat population which is immune to the action of the virus. (2) There is a certain degree of risk of food contamination, with resultant food-poisoning outbreaks.

Experience in the City has proved that both these reasons are sound. It is regrettable that the civilian population is not afforded the same protection from food poisoning outbreaks as that which the Military Authorities afford to the army by prohibiting the use of virus. It probably kills only 50 to 60 per cent. of the rats and should be condemned for that reason alone.

An Outbreak of Food Poisoning Traced to Flies.

DR. J. PRIESTLEY, Medical Officer of Health for Lambeth, has made a special report upon an outbreak of food-poisoning which occurred in South Lambeth in May, 1925. In each of the 29 cases discovered it was found that the patients (living in 10 different houses) had eaten prepared beef or pork purchased from the same shop.

On inspecting the premises of the retail butcher who supplied this food, it was found that he was accustomed to boil joints of salted beef and of salted pork which were afterwards boned, trimmed and pressed between layers of gelatin, and sold in small portions across the counter. Although the shop itself was clean, the conditions under which the boiling trimming and pressing of the beef were carried out were most unsatisfactory, the boiling being done in a portable copper in a small yard at the back in close proximity to a W.C., to a large and fixed dirty dust receptacle, and to two large dirty refuse cupboards for the fat and trimmings. Large numbers of flies (chiefly of the blue-bottle type) were passing freely from the inside of the cupboards to the dust receptacle, and they also had free access to the meat during the boning, trimming, pressing and cooling operations.

There was no reason, from the evidence available, to suspect that the two attendants employed in the preparation of the meat were "carriers" of germs that would cause the attacks of food poisoning.

Bacteriological examination of remains of the suspected joints, both from the shop and from one or two of the infected houses, showed that the samples were grossly contaminated with ordinary bacteria (perhaps faecal in origin), and with the *Bacillus proteus*, though the specific bacteria of food poisoning (the Gaertner or Salmonella group of bacteria) were not discovered. It may be, however, that they were crowded out by the other commoner germs which were actually found in the meat in large quantities (*viz.* the *B. coli* group and *B. proteus*). Serological (agglutination) tests of patients' blood gave positive (macroscopic) reactions in dilutions of 1 in 25 and 1 in 50, both to the *B. coli* and *B. proteus*. It is difficult to understand how the *B. coli* (or its toxin) could have gained access into the victims' blood as a poison (with consequent serious acute symptoms of food-poisoning and subsequent formation, within the blood, of agglutinins or anti-bodies) unless the intestinal tracts of the affected persons were abnormal, permitting of the passage of the *B. coli* group (or its toxin) through the mucosa, a condition that rarely, if ever, occurs in the case of an intact healthy mucosa. It may be that the exceptionally hot weather at the time of the outbreak (May 13 to May 16, 1925) led to an abnormal growth of the *B. coli* group in the layers of gelatin placed between the layers of pork and beef during pressing, and caused such bacilli to take on virulence and alter their morphology.

In the case of the *B. proteus* that was isolated the matter is different, for this germ has occasionally been found in actual cases of food poisoning.

Flies on the shop premises were caught and bacteriologically examined, and the same germs were found on the suckers, legs and wings as were found (1) in the actual beef and pork that caused the outbreak, and (2) in the coated dirty deposits of putrefactive and fermenting materials (fat, vegetables, meat, etc.) on the insides and outsides of the refuse cupboards and the fixed dustbin or ashpit in the yard at the rear of the shop. The flies also showed, in addition, the presence of *B. staphylococcus*.

The symptoms of the victims were acute gastric and intestinal disturbances, with vomiting, diarrhœa, cramps in the abdomen, fever, together with extreme prostration and a tendency to heart failure and collapse. There was no death among the persons attacked, but a puppy dog that ate some of the meat died.

Report of the Fertilisers and Feeding Stuffs Advisory Committee.*

AN Advisory Committee was appointed by the Minister of Agriculture and Fisheries on December 23, 1924, as recommended in the Report of the Departmental Committee (Part IV. (XXIII.), ANALYST, 1924, **49**, 385) for the purpose of discharging the following functions:—

1. To draw up Schedules for the purpose of prescribing:—
   (*a*) The fertilisers and feeding stuffs to which all the provisions of proposed legislation on the lines of the Report of the Departmental Committee on the Fertilisers and Feeding Stuffs Act, 1906, should apply, and those to which only the civil provisions of such legislation should apply;
   (*b*) Definitions of each of the articles or classes of articles mentioned above;
   (*c*) The statements as to the constituents present, and also as to the absence of certain substances in some instances, which should be given in descriptions and invoices;
   (*d*) Those commodities which should be regarded as "worthless" or "deleterious"; and
2. To recommend the terms in which the valuable constituents should be stated in descriptions and invoices.

The Committee comprised the following:—The Lord Clinton (chairman), Sir E. J. Russell, and Messrs. Haygarth Brown, C. Crowther, J. Garton, C. W. Higgs, A. Holgate, T. Kyle, A. Main, R. L. Norrington, J. W. Pearson, R. R. Robins, J. Speir, G. Stubbs, J. F. Tocher, and T. B. Wood. The following were co-opted as members of the Committee:—Messrs. A. E. Humphries, A. W. Thomson, D. M. Sandral, F. W. F. Arnaud, and E. H. Quibell.

The Report of this Committee, which is dated July 3, 1925, is divided into 5 parts, the first of which is introductory, and the last gives acknowledgment of help.

Part II. deals with the Schedules of Articles to which proposed new legislation should apply. Sections 6 to 14 indicate the principles adopted by the Committee in deciding what articles should come within the scope of the Act, and the methods of procedure adopted in preparing the Schedules. Secs. 15 to 18 contain observations on the Schedules and give the reasons for suggesting a minor modification of the proposals of the Departmental Committee (*loc. cit.*).

This suggestion (Sec. 19) is that provision should be made in the Bill that, if statements as to the percentages of constituents are made, they should have effect as warranties. As a corollary to this, if accepted, local authorities should have power to allow purchasers of such articles to have samples analysed on payment of a fee to be fixed by the local authority, provided that the samples are taken in the prescribed manner (Sec. 20). Further, any voluntary warranty given by a seller should be only in terms of the prescribed method, where such method has been laid down.

Basic Slag (Secs. 22–26).—The question of the value of the "citric-solubility" test is discussed. In view of the divergent scientific opinions, the Committee do not recommend that a statement of the "citric-soluble" phosphoric acid in basic slag should be made compulsory. They suggest that the permanent Advisory Committee, when constituted, should bear this matter in mind with a view to amendment of the Schedule, if and when a more satisfactory means of evaluation is devised.

* Cmd. 2470 H.M. Stationery Office. 36 pages. Price 9d. net.

Compound Fertilisers (Secs. 27 to 32).—The question of classifying the nitrogenous substances is also brought specially to the notice of the permanent Advisory Committee. In the case of potash, an "acid-soluble" method of analysis is recommended. It is not considered desirable to require a statement of the percentage of chlorine.

Fibre in Feeding Cakes (Secs. 33–36).—It is recommended that the percentage of fibre should be required to be stated in the case of cakes prepared from decorticated or partly decorticated seeds and nuts, but not in the case of undecorticated cakes.

Fish Meal (Secs. 37–45).—It was decided to give a general definition to "fish meal" or "fish residue meal," and a more particular one, including maximum limits for oil (6 per cent.) and salt (4 per cent.) to "white fish meal." In every case, however, the seller will be required to state the percentage of oil and salt as well as of protein and phosphoric acid.

Wheat Offals (Secs. 46–49).—It was decided that, although a system of grading wheat offals according to the size of particles would have certain advantages, it was not advisable to recommend such a system at the present time.

Quick Lime, Slaked Lime, Limestone and Chalk (Secs. 50–53).—The recommendation to place these in the second Schedule is conditional. If the requirement of a warranty is likely to prevent the opening of pits or restrict the output of smaller undertakings in rural places, it would be better, for the present, to omit lime and limestone from the schedules. The Committee are of opinion that a statement of the percentage of magnesia would involve ultimate additional cost on the farmers, which would be greater than the information was worth to them.

Shoddy (Secs. 54–57).—This has been included in the Second Schedule without any particulars being prescribed. It would be impossible to apply the principles of the inspection of factories and marking of consignments, and unreasonable to compel a seller to give a warranty as to nitrogen in a consignment drawn, of necessity, from many different sources.

Poultry Mixtures (Secs. 58 to 60).—The ordinary type of poultry mixture, consisting of whole grains and grit, is omitted from the Schedules, on the ground that steps which might discourage the preparation of poultry foods containing grit ought not to be taken. Poultry feeds consisting of meals will come within the definition of the term "compound cakes or meals," and provision against the inclusion of grit in these is made in paragraph (C) of the Fourth Schedule.

Soot (Secs. 61–62).—Apart from the question of cost and other matters, the Committee are of opinion that it is impossible for a seller to state with any reasonable degree of accuracy what percentage of nitrogen the consignment contains, and, consequently, that no such statement should be required of him.

Other Waste Products—fur waste, feather waste, etc. (Secs. 63–64).—These are not in any sense manufactured or prepared as fertilisers. The Committee are not prepared to recommend the making of a warranty a statutory requirement in these cases; they are more suitable for voluntary warranties in transactions between buyer and seller.

Part III. is concerned with the terms in which constituents should be stated. The conclusions are largely based on the proposals of a Sub-Committee, under the Chairmanship of Mr. G. Stubbs.

Nitrogen and "phosphates."—It is recommended that the amounts of nitrogen phosphoric acid and potash should be the statutory requirement, but that a seller

should not be prohibited or discouraged from adding a statement of the equivalents of other units, provided that they are clearly stated to be equivalents.

Lime, Limestone and Chalk.—The seller should be required not only to state, in effect, the percentage purity of the article, but also to give the pure lime (calcium oxide) or its equivalent.

Oil and albuminoids.—It is proposed that the terms be retained, but it is suggested that the word "proteins" should be added in parenthesis after "albuminoids."

Fibre.—It is recognised that "fibre" (or "indigestible fibre") is an arbitrary term, the scope of which can only be determined by prescribed methods of analysis.

Methods of Analysis.—The recommendations are made on the understanding that precise methods of analysis will be prescribed. The meanings intended to be attached to "soluble" and "insoluble phosphoric acid" are, respectively, soluble and insoluble in water. It is recommended that the Permanent Advisory Committee should consider the desirability of prescribing a "water-soluble" method for potash in such substances as muriate of potash, and an "acid-soluble" method for kainit, guano and compound fertilisers.

Part IV. deals with Schedules of "deleterious" and "worthless" ingredients. A statement of the reasons for the decision that it is impracticable to formulate Schedules in the case of fertilisers, and some explanation of the Committee's positive recommendations in the case of feeding stuffs, are to be found in the following extract from the Report of the Sub-Committee (Chairman, Dr. Crowther):

FERTILISERS.

Deleterious ingredients of fertilisers.

The term "deleterious" in this connection may be interpreted as meaning conducing *either* (*a*) to impair the action of the actual fertilising ingredient (or ingredients) contained in the fertiliser *or* (*b*) to lower the fertility of the soil to which the substance is applied, *or* (*c*) to render the crop grown on this soil unsafe to use as food for stock.

With regard to (*a*), we doubt whether sufficient information exists at present to warrant us in scheduling any substance as "deleterious" from this point of view, apart from such effects (*e.g.* reduction of solubility) as would be covered by the ordinary warranties provided in the Act.

As regards (*b*), it is well known that many substances (*e.g.* salts of lead, zinc and copper, borates, &c) when applied to soil in comparatively small doses tend to impair its fertility, but, having regard to the rates at which fertilisers are commonly applied, it is unlikely that, even with a comparatively high concentration of the "deleterious" ingredient, the amount reaching the soil would be such as to exercise an appreciable toxic effect. Moreover, in the case of many of these substances, there is the possibility of an actually beneficial effect if the amount applied falls below a certain proportion, and it would hardly be possible in any case to give a general definition as to the critical dose beyond which detriment might be expected.

With regard to the possibility of deleterious action of the nature indicated under (*c*) above, this possibility cannot be entirely ignored in practice. We may recall the attempt made some years ago to trace the occurrence of arsenic in beer to the superphosphate used in barley growing. The grain or seed of a plant is probably the part of it least likely to acquire abnormal ingredients, deleterious or otherwise, from the soil, but there are greater possibilities in the case of leaves or roots. Here again, however, we are confronted with a paucity of reliable information on the point which makes it impossible for us to prove that the presence of a particular ingredient in a fertiliser would be detrimental from this point of view.

On all three counts, therefore, we are forced to the conclusion that it is not practicable at present to draft a schedule of "deleterious" ingredients of fertilisers.

Worthless ingredients of fertilisers.

Desirable though it may appear to have a schedule of "worthless" ingredients of fertilisers, the matter is beset with such difficulties as to make the drafting of an effective schedule a practical impossibility. The factors that influence plant growth are so complex that we cannot assume a substance to be "worthless" in the strict sense of the term even though it be entirely devoid of the elements of plant food, as it may, nevertheless, have a beneficial effect upon the physical or biological properties of the soil. Even though we take a broader conception of the term

"worthless" as implying material that an intelligent farmer would not knowingly purchase, we are still confronted by the difficulty that the decision of the intelligent farmer might vary considerably under different conditions of soil and cropping.

We are unable, therefore, to recommend any schedules of "worthless" ingredients of fertilisers

Should it be decided that the new Act should contain provisions safeguarding the purchaser of fertilisers against the supply of "deleterious" or "worthless" ingredients, we are obliged to advise, therefore, that such provisions cannot be effectively implemented by schedules.

Feeding Stuffs.

Deleterious ingredients of feeding stuffs.

An ingredient of a feeding stuff may exercise a deleterious effect either by lowering the digestibility of the nutrients proper or by direct toxic or irritant action upon the animal.

Examples of the former mode of action would be afforded, on the one hand, by non-toxic substances with purgative properties (*e.g.* many soluble salts) or, on the other hand, by substances which either re-act chemically with one or other of the nutrients and convert them into less digestible forms (*e.g.* formaldehyde) or interfere in other ways with the effective action of the digestive agents (*e.g.* boric acid).

Substances capable of producing direct toxic effects would, of course, include all poisons and, were a comprehensive schedule of these to be prepared, regard would need to be paid to the fact that some of these may occur as natural ingredients of common feeding stuffs, though in proportions usually well below the minimum toxic dose in the quantities usually fed.

The number of substances that might be classed as "deleterious" from the one or the other point of view is so large that we doubt the practicability of drafting a complete schedule, whilst a less comprehensive schedule designed to include only such substances as we may consider to be at all likely to occur in feeding stuffs might prove a source of continual difficulty through its admittedly incomplete character. We doubt, therefore, whether it is possible to do more than indicate in general terms the classes of ingredients that must be regarded as capable of producing deleterious action, with, possibly, in some cases an indication of the minimum proportion beyond which the ingredients must be regarded as definitely "deleterious" for the purposes of the Act.

Worthless ingredients of feeding stuffs.

In dealing with worthless ingredients in the case of feeding stuffs it is impossible, in practice, to interpret the term "worthless" in its strict sense of "having no value," since this would exclude from the schedule practically every form of natural organic matter with the possible exception of rubber. It would be impossible to prove that even leather was worthless in this sense of the term, and a schedule based upon such a definition could have little, if any, practical value.

In the case of feeding stuffs, however, there is reasonable ground for adopting the wider definition of "worthless" as meaning any substance that an intelligent farmer would not knowingly buy for use as food for live-stock. Using this definition, it would seem to us more practical to draft a schedule applicable to feeding stuffs than in the corresponding case of fertilisers, since the value of a feeding stuff to the animal is less subject to environmental influences than the value of a particular substance for the purposes of crop production. Moreover, by the use of the now commonly accepted Starch Equivalent Method of assessment of the relative nutritive values of feeding materials, it is possible to give a fairly precise numerical significance to such standard of "worthlessness" as may be decided upon.

In seeking such a standard it would seem reasonable to fix upon the material of lowest nutritive value that is at all commonly used as fodder on the farm, and we should regard wheat straw as occupying this position.

In the tables giving the average Composition and Nutritive Values of Feeding Stuffs compiled by Professor T. B. Wood (issued by the Ministry of Agriculture) the Starch Equivalent of average winter wheat straw is given as 11 per cent., implying that 100 lbs. of such straw would have the same general nutritive value as 11 lbs. of starch.

If we accept this as our standard, all materials whose nutritive value is assessed at less than 10 per cent. starch equivalent must be regarded as "worthless," and may be scheduled as such. The scheduling of certain materials (*e.g.* peat moss, sawdust) on this basis would probably not give rise to serious difficulties, but in the case of material of the nature of husks or chaff, which would fall into the schedule, serious difficulties of interpretation might arise, since some of these materials (*e.g.* oat husks) form a natural part of feeding stuffs in everyday use, and it would be practically impossible, except in very flagrant cases, for the analyst to decide between husk which was legitimately present in a feeding stuff and that which may have been added and thus fall clearly into the category of "worthless" materials. Despite this difficulty, we would recommend the inclusion of such materials in the schedule, since such materials form, perhaps more frequently than any others, the ground of complaint, and without them the schedule would lose greatly in practical effectiveness.

No definite recommendation is made as to the condition of fertilisers when sold, but attention is directed to the matter in case it may be possible to find a suitable form of words.

SCHEDULES ACCOMPANYING THE REPORT.

FIRST SCHEDULE.

(Articles to which all the provisions of the proposed Act should apply.)

PART I.—FERTILISERS.

Basic slag.—Amount of phosphoric acid, amount of the article that will pass through sieve. *Basic superphosphate.*—Amount of phosphoric acid. *Bone meal or other product (excluding dissolved or vitriolised bone) obtained by grinding or otherwise treating bone, used for fertilising purposes.*—Nitrogen and phosphoric acid. *Calcium cyanamide.*—Nitrogen. Amount of dicyanodiamide if in excess of 2 per cent. *Compound fertilisers.*—Nitrogen, potash, soluble phosphoric acid and insoluble phosphoric acid respectively. *Dissolved or vitriolised bone.*—Nitrogen, soluble phosphoric acid and insoluble phosphoric acid respectively. *Fish residues, fish waste, etc.*—Nitrogen and phosphoric acid. *Guano, including Peruvian and other raw guanos.*—Nitrogen, phosphoric acid and potash. *Hoofs, hoofs and horns, horns.*—Nitrogen. *Meat and bone residues.*—Nitrogen and phosphoric acid. *Nitrate of lime. Nitrate of soda. Oil seed fertilisers.*—Nitrogen. *Potassium salts used as fertilisers.*—Potash. *Raw phosphate or phosphate rock, ground or unground.*—Phosphoric acid. Amount of article passing through a prescribed sieve. *Sulphate of ammonia.*—Nitrogen and free acid. *Sulphate of ammonia (neutral).*—Nitrogen. *Superphosphate.*—Soluble phosphoric acid.

Amounts are to be stated as percentages of the weight of the article. Nitrogen to be stated in terms of nitrogen; phosphoric acid as phosphoric anhydride (P_2O_5); potash as potassium oxide (K_2O); free acid as sulphuric acid (H_2SO_4).

FIRST SCHEDULE. PART II.—FEEDING STUFFS.

No prescribed particulars:—*Barley meal, bean meal, dari or durra meal, ground oats, locust bean meal, maize meal; Indian meal, pea meal, wheat meal. Coconut or copra cake or meal, cotton cakes or meal (not decorticated), maize germ cake or meal from undecorticated substance or seed, maize gluten feed, oil cakes or meals not otherwise specifically mentioned, palm kernel cake or meal, rape meal or cake, soya cake or meal.*—Amounts of oil and albuminoids (protein) respectively. *Linseed meal.*—Oil. *Compound cakes or meals, cotton cakes or meal from decorticated or partly decorticated cotton seed, maize by-products not otherwise specifically mentioned, oil cakes or meals from decorticated substance or seed from which oil has been removed, rice bran or meal or the by-product in milling shelled rice.*—Amounts of oil, Albuminoids (protein), and fibre respectively. *Dried sugar beet residue, molasses feeds.*—Amounts of sugar and fibre. *Feeding bone flour—feeding meat and bone meal, fish meal.*—Phosphoric acid and albuminoids (protein). *Treacle or molasses.*—Sugar.

SECOND SCHEDULE.

(Articles to which the provisions of the proposed Act, except those relating to the application of a description and sampling on the premises of the seller, should apply.)

PART I.—FERTILISERS.

Calcium hydrate; slaked lime.—Amount of calcium "hydrate" and equivalent of calcium oxide. *Chalk, ground.*—Calcium carbonate and equiv. of calcium oxide. *Dried blood for fertilising purposes.*—Nitrogen. *Limestone, ground.*—Calcium carbonate and equiv. of calcium oxide. Amount that will pass through a prescribed sieve. *Precipitated bone.*—Amount of phosphoric acid. *Quick lime, ground or otherwise.*—Amount of calcium oxide. *Shoddy.*—None.

Calcium carbonate is to be stated in terms of calcium carbonate ($CaCO_3$); calcium hydrate in terms of calcium hydroxide ($Ca(OH)_2$; calcium oxide in terms of calcium oxide (CaO).

PART II.—FEEDING STUFFS.

Clover meal.—Fibre. *Dried brewery and distillery grains.*—Oil and albuminoids (protein). *Dried yeast.*—Albuminoids (protein). *Feeding dried blood.*—Amount of albuminoids (protein). *Malt culms.*—Amounts of albuminoids (protein) and fibre.

Amount of albuminoids (protein) means the amount of nitrogen, other than ammoniacal or nitric nitrogen, if present, multiplied by 6·25.

THIRD SCHEDULE.

This gives the definitions of meanings of names.

United States Department of Agriculture.

FOOD INSPECTION DECISIONS 196 and 197.

THE following revised and amended definitions and standards for sauerkraut and for almond paste and kernel pastes were adopted by the Joint Committee on Definitions and Standards, 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 meeting July 13 to 17, 1925.

196. SAUERKRAUT.

SAUERKRAUT is the clean, sound product, of characteristic acid flavour, obtained by the full fermentation, chiefly lactic, of properly prepared and shredded cabbage in the presence of not less than 2 per cent. nor more than 3 per cent. of salt.

It contains, upon completion of the fermentation, not less than 1·5 per cent. of acid, expressed as lactic acid. Sauerkraut which has neen re-brined in the process of canning or repacking contains not less than 1 per cent. of acid, expressed as lactic acid.

197. ALMOND PASTE AND KERNEL PASTES.

ALMOND PASTE is the plastic product obtained by cooking blanched and ground sweet almonds with blanched and ground bitter almonds, sugar, and water. It contains not more than 14 per cent. of water nor more than 40 per cent. of total sugars expressed as invert sugar.

KERNEL PASTES are the plastic products obtained by cooking, with sugar and water, the blanched and ground kernels of one or more of the following: Apricots, peaches, plums (prunes). They are free from hydrocyanic acid and contain not more than 14 per cent. of water, nor more than 40 per cent. of total sugars expressed as invert sugar. A kernel paste conforms in name to the kind or kinds of kernels employed in its production.

The foregoing definitions and standards are adopted as a guide for the officials of this department in the enforcement of the Federal food and drugs act.

WASHINGTON, *August*, 1925.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Direct Precipitation of Calcium in Cows' Milk. C. S. Rothwell. (*J. Biol. Chem.*, 1925, **65**, 129–133.)—The success of the method of Kramer and Tisdall (*J. Biol. Chem.*, 1921, **47**, 475) for precipitating calcium in blood serum without removal of proteins, suggested the possibility of using a similar technique for milk. A procedure is described by which calcium may be determined accurately in cows' milk by direct precipitation with ammonium oxalate, without removal of protein. The only practical difficulty encountered is from the presence of fat, which gives turbid solutions and indefinite end-points. The fat may be removed

by washing with a mixture of ether and ammonium hydroxide. For fresh milk, boiled or unboiled, direct precipitation gives results as accurate as ashing. As yet, no method for direct precipitation of calcium from human milk has been satisfactory. Protein-free filtrates from human milk show low results, corresponding, in most cases, with those shown by direct precipitation on the same sample. P. H. P.

Colorimetric Determination of Benzoic Acid in Cordials, etc. A. J. Jones. (*Pharm. J.*, 1925, **115**, 144–145.)—A quantity of 10 c.c. of the beverage, mixed with 5 c.c. of 10 per cent. sulphuric acid in a separator, is extracted with 20 c.c. and afterwards with 10 c.c., of a mixture of equal volumes of petroleum spirit and ether. The united extracts are extracted first with 5 c.c. of water containing excess (usually 0·3 c.c.) of 20 per cent. sodium hydroxide solution, and then with 5 c.c. of water alone. The alkaline extract and rinsings are evaporated to dryness in a small basin on a water-bath, and the residue warmed with 5 c.c. of a mixture of 1 vol. of nitric acid (sp. gr. 1·42) with 9 vols. of sulphuric acid (sp. gr. 1·84), care being taken that the attack is complete. The liquid is transferred to a 5 × 7/8th inch test-tube, and the basin rinsed successively with 2 c.c. and 1 c.c. of the acid. The tube, with a thermometer suspended in the acid, is heated rapidly over a naked flame to 155° C., the temperature being maintained at 155° to 160° C. for exactly three minutes, and the tube then allowed to cool to 100° C., and set in cold water. The cold liquid is mixed with 20 c.c. of water, cooled again, and extracted with 15 c.c., and then with 10 c.c., of ether. The ethereal extracts are shaken with a mixture of 8 c.c. of water with 2 c.c. of ammonia solution (sp. gr. 0·880), and afterwards with two quantities of 5 c.c. of water. The ammoniacal extracts are placed in a tube, together with 3 c.c. of concentrated ammonia solution, and 1 grm. of hydroxylamine hydrochloride, and the whole heated to 35° to 40° C. The red colour which develops if benzoic acid is present is compared, after the lapse of 20 minutes, and after adjustment of the volume to 50 c.c., with that similarly obtained from 5·7 mgrms. of benzoic acid, taken as sodium benzoate ; this will correspond with 5 grains of benzoic acid to the pint. T. H. P.

Detection of Small Quantities of Lactic Acid in Fruit Juices. A. Bornträger. (*Zeitsch. anal. Chem.*, 1925, **66**, 430–460.)—It has been sought to extract and identify small quantities of lactic acid in tomato juice. Pure calcium lactate can be readily identified in small amounts by the microscopical appearance of the characteristic small needle crystals, but it must first be separated from other organic acids. Experiments show that extraction with various strengths of alcohol or with ether fail when only 0·02 per cent. is present, but satisfactory results were obtained with 0·1 per cent., or more, on 20 c.c. of the juice in the following manner :—To 20 c.c. of the filtered juice is added a slight excess of calcium chloride, then sufficient freshly-prepared milk of lime to give a strongly alkaline reaction, and the mass is evaporated on the water-bath to a thick paste. The residue is extracted with hot 95 per cent. alcohol and filtered ; the filtrate (10 c.c.)

is evaporated, and the residue extracted with 5 c.c. of hot alcohol of the same strength, and again filtered. To the filtrate, which is now neutral, is added 0·15 c.c. of water, then 5 c.c. of ether, and further quantities of 5 c.c. of ether daily. After three days the characteristic crystals appear and may be separated. H. E. C.

Identification by Chemical Methods of Drugs containing Tannin. A. H. Ware. (*Pharm. J.*, 1925, **115**, 131–135.)—Addition to a solution of quercitrin in 19 per cent. alcohol of pure zinc or magnesium and sufficient concentrated hydrochloric acid to yield a steady stream of hydrogen results in the development of a pink colour, this being more rapid if the liquid is heated. The colour increases in intensity to a deep cerise or red and then gradually fades ; if alkali is added to this colourless solution a purple coloration forms, but if it is added to the deep red solution this becomes green. With the acid and zinc, aromadendrin behaves similarly to quercitrin, except that the red coloration formed is more intense, and is changed to yellow by addition of alkali to make the liquid approximately neutral ; addition of the alkali at the end of the reaction gives no distinctive result.

The following two modifications of the ferric citrate precipitation test (ANALYST, 1924, **49**, 442, 467 ; 1925, 335) are given :—(1) Five c.c. of a fresh aqueous extractive or of a water-diluted commercial extractive are boiled with 10 to 12 drops of 33 per cent. acetic acid solution and 5 c.c. (more if necessary) of 0·25 per cent. aqueous iron ammonium citrate solution, and the liquid cooled, filtered, treated with 1 grm. of ammonium chloride, and again boiled ; a precipitate denotes the presence of pyrogallol-tannin (non-phlobatannin). In the absence of a precipitate, any phlobatannin present may be precipitated by boiling the liquid with slight excess of ammonia solution. Such precipitate may be due to an anthoxanthin or to a mixture of this with phlobatannin, but the presence of the latter may readily be confirmed by the formaldehyde and hydrochloric acid test (*loc. cit.*). By means of these two tests the presence of phlobatannins alone, or pyrogallol-tannins alone, or both together, may be determined. (2) Five c.c. of the extractive are boiled with 1·5 grm. of sodium dihydrogen phosphate and filtered, and the filtrate boiled with the ferric citrate solution. Unless in very small quantity, gallotannins are precipitated partially or completely as violet iron compounds, and ellagitannins as green-black compounds, whereas hamamelitannins give usually deep-brown solutions and only occasionally brown precipitates. Phlobatannins are not precipitated when boiled with ferric citrate solution, and are distinguished better by test (1) and by the formaldehyde reaction. Haematoxylin and the tannin associated with it in logwood give a brown solution when thus tested. A scheme, based on these tests and on that with Mitchell's reagent (ANALYST, 1925, 127), is given for the classification of bodies containing typical pyrogallol-tannins and no phlobatannins, and a table for the identification of 17 kinos is appended. T. H. P.

Nature of the Reaction between Tannin and Carbohydrates. Part I. H. B. Stocks and C. V. Greenwood. (*J. Soc. Leather Trades Chem.*, 1925, **9**, 315.)—A comparative study is described of the action on tannin of gelatin and

tragasol. Tragasol is a galacto-mannan which precipitates tannin from its solutions in a manner very similar to gelatin, for which it might easily be mistaken. On addition of a solution of tannin to a solution of tragasol the solution becomes more viscous ; on further addition, the liquid becomes thin and milky and, on standing, a buff-coloured tenacious clot separates, leaving a clear liquid. On now heating, the whole becomes homogeneous and stiff, but the clot separates out again on cooling, the change being a reversible one. The behaviour is quite different when tannin solution is added to gelatin or albumin solutions. One hundred c.c., each, of 3 per cent. solutions of gelatin, albumin and tragasol were mixed with a solution of 9 grms. of Merck's pure tannic acid in 50 c.c. of water. This proportion had been found the most suitable, the tannin being in excess, and therefore rendering the deposits easy to collect and drain. (If gelatin is in excess both gelatin and tannin are found present in the solution.) A table is given showing that tragasol yields the bulkiest deposit, and that it absorbs practically the same amount of tannin as does gelatin.

The effect of reaction was also studied. Precipitation occurs with both gelatin and tragasol in acid but not in alkaline solution. In the case of gelatin the point at which precipitation occurs is P_H8, but with tragasol it is P_H4. The volume of the precipitate decreased as the acidity increased, but the weight of the dry precipitate remained nearly constant.

The absorption of tannin from solutions of varying concentrations by dry films of tragasol and of gelatin was investigated as follows :—Ten grms. of each film were steeped for 24 hours in 200 c.c. of the tannin solution, the liquor drained off and measured, and the tannin determined by the permanganate method.

Gelatin.			Tragasol.		
Tannin in 200 c.c. of original solution.	Liquid absorbed.	Tannin. absorbed.	Tannin in 200 c.c. of original solution.	Liquid absorbed.	Tannin absorbed.
Grms.	c.c.	Grms.	Grms.	c.c.	Grms.
2·42	60	0·55	2·18	102	1·657
5·08	42	1·04	5·12	42	3·45
8·0	32	1·46	10·00	35	5·07
10·32	26	1·94	26·58	28	8·07
21·02	22	2·52	37·06	25	7·83
31·58	16	2·24			

This experiment confirms earlier work, and shows that in the case of gelatin the liquid is imbibed just like water, there being no combination of the gelatin and tannin, whereas with tragasol there is combination. Combination of tannin with gelatin is only effected if the gelatin is in solution. When gelatin and tragasol are present together in solution the precipitation is practically quantitative, the product being a tragasol-gelatin-tannin complex which, while moist, softens on heating, forming a tough elastic homogeneous product. R. F. I.

Abstractor's Note.—Compare article by Bungenberg de Jong, *J. Amer. Leather Chems. Assoc.*, 1924, p. 14.

Investigation of Chaulmoogra Oil. T. Hashimoto. (*J. Amer. Chem. Soc.*, 1925, **47**, 2325–2333.)—The composition of the last and high boiling-point fraction of the acids of chaulmoogra oil has not hitherto been determined, on account of the ease with which it decomposes when distilled, even at comparatively low pressures. An apparatus is described which enables these acids to be distilled at, or below, 190° C. under a pressure of only 0·05 mm. By applying this to a large volume of the oil the conclusion of Power and Dean that the lighter fractions (85 per cent.) consist entirely of chaulmoogric and hydnocarpic acids was confirmed. The remaining 10 to 15 per cent. of the esters of the acids were distilled without appreciable decomposition, and from them the following substances were isolated : (*a*) Taraktogenic acid, $C_{36}H_{60}O_6$, m. pt. 113·5° C.; iodine value, 42·5 ; (*b*) isogadoleic acid, $C_{20}H_{38}O_2$, m. pt. 65·5–5·66° C.; (*c*) a lactone-like substance, $C_{18}H_{32}O_2$, m. pt. −11·6° C.; (*d*) an acid, possibly arachidic acid ; (*e*) a brown insoluble resin ; (*f*) two unidentified solids. H. E. C.

True and False Santonicas. T. E. Wallis and E. J. Mowat. (*Pharm. J.*, 1925, **115**, 149–156.)—The genuine santonica of commerce may be identified by means of the following characters :—The foliage leaves are linear-lanceolate with a rounded apex and an apiculus, and have a mid-rib with numerous, pinnately-arranged branches connecting it with the two marginal veins which run parallel to the margin at about one-third the distance from it to the mid-rib ; long hairs are absent, but numerous sessile glands occur. The bracts of the flower-head vary in number from 14 to 20, and are most often 16 ; the mid-rib branches freely, and the veinlets are contorted and frequently anastomose, while the number of cotton-like T-shaped hairs is small, and apical marginal hairs are absent. The apices of the corolla lobes are never more than slightly papillose, and bear no trichomes.

Commercial specimens of santonica devoid of santonin may be distinguished from the true drug more particularly by the hairiness of the leaves and by the presence of apical marginal hairs on the bracts of the flower-heads. The botanical source of true wormseed of commerce is *Artemisia Cina* (Berg) Willkomm.

T. H. P.

The Active Constituents of Cape Aloes. H. Kiefer. (*Pharm. J.*, 1925, **115**, 384–386.)—If extract of aloes be prepared according to the Swiss Pharmacopoeia dirctions, the bulk of the active constituents remains in the discarded insoluble residue. By treating Cape aloes with acetone a dark-coloured substance separates, not possessing purgative properties, but producing severe abdominal pain. The acetone extract, on treatment with hot amyl alcohol, yields several fractions, the first containing dark impurities, and the next ones being bright yellow and similar to each other. Aloin can be separated from the second, and the separated fractions are much more active than the aloin itself. They may be fractionated into water-soluble (yielding a powerfully purgative resin by shaking with ethyl acetate) and water-insoluble, which in turn are divided into those soluble in sodium bicarbonate and in sodium carbonate solutions, both yielding resins

similar in properties to the first. All three resins are amorphous substances, insoluble in water, but soluble in an aqueous solution of the water-soluble portion of the aloes after removal of the resins contained in it. They behave, on saponification, differently from the aloes resin examined by Pedersen. The composition of Cape aloes is deduced to be :—(1) Two possibly identical, very active bright yellow resins, soluble as above (about 30 per cent. of each), 60 per cent. ; (2) very active resin, soluble in sodium carbonate solution, 6–8 per cent. ; (3) aloin, slightly active, 5 per cent. ; (4) emodin, slightly active, 1·5 to 1·8 per cent. ; (5) water-soluble substances, inactive, 15 to 20 per cent. ; (6) amorphous substances producing abdominal pains, but not purgative, 5 to 10 per cent. D. G. H.

Picrates of the Opium Alkaloids. C. W. Maplethorpe and N. Evers. (*Pharm. J.*, 1925, **115**, 137–139.)—The following experimental data are given for the monopicrates of the opium alkaloids :—

Picrate of	Melting point (corr.)	Per Cent. solubility at 20° C. in Water.	Absolute alcohol.	Acetone.
Morphine	163 to 165° C.	0·22	0·14	13·86
Codeine	196 to 197°	0·11	0·095	3·89
Thebaine	217° (decomp.)	0·20	0·10	10·1
Narcotine	174°	0·02	0·13	30·0
Papaverine	181–183°	0·007	0·052	1·89
Narceine	195°	0·027	0·01	5·23
		Solubilities at 15° C.		
Cryptopine	161–163°	0·007	0·022	0·162
Gnoscopine	185·5°	0·009	0·04	2·34
Xanthaline	212·5°	0·01	0·022	0·34

T. H. P.

Identification of Cystine by a Colour Reaction. G. Denigès. (*Bull. Soc. Pharm. Bordeaux*, 1924, **62**, 183 ; *J. Pharm. Chim.*, 1925, **117**, 146.)—The following method may be used for the identification of cystine in small portions of renal calculi. A particle is put on a slide with a drop of *N* sodium hydroxide solution, and the liquid carefully evaporated. The residue is mixed with 10 per cent. acetic acid and treated with a trace of 5 per cent. sodium nitroprusside solution, and finally with 1 drop of ammonia solution. The characteristic, although ephemeral, red-violet colour is produced if cystine is present. D. G. H.

Biochemical, Bacteriological, etc.

Elimination of Benzoic Acid and Benzoates from the System. Bordas, François-Dainville and Roussel. (*Comptes Rend.*, 1925, **181**, 304–306.)—A single dose of 2 grms. of sodium benzoate was given to each of a number of persons of different ages, *viz*, 10 of 60 to 68 ; 4 of 52 to 58 ; 1 of 49 ; 1 of 35 ; and 2 under 25. In each case the presence of hippuric acid and of benzoic acid was found in the urine within 3 hours after ingestion of the drug. Elimination was complete after 1 day in the case of 3 subjects ; after 2 days with 3 subjects ; and after 3 days

with 2 subjects. In a second series of experiments a dose of 2 grms. a day was given for 8 days to 7 different subjects. In no case was there complete elimination of benzoic acid 1 day after absorption of the total quantity (16 grms.); in one there was elimination after 2 days ; and in 6 there was elimination after 3 days.

Water-cress and Body Metabolism. S. M. Copeman. (*Pharm. J.*, 1925, **115**, 386–387.)—Sixty mice were inoculated with material from a cancerous tumour ; 20 were fed on ordinary laboratory diet and 40 on oatmeal (insufficient alone) and water-cress. One of each batch died without apparent cause, and all mice in the control batch developed tumours, but only 16 (or 41 per cent.) of the water-cress fed mice, the non-tumourous mice remaining in excellent health. These results have been confirmed by Prof. Gowland Hopkins on rats. An investigation of the chemistry of water-cress reveals the presence of a glucoside as a potassium salt ; this yields, on hydrolysis, first a thiocarbimide which is also present in the plant in less quantity, and finally, in still less quantity in the plant, a naturally occurring base, β-phenyl-ethylamine. This base, prepared synthetically and administered as the hydrochloride, proved innocuous to mice up to 0·25 grm. by mouth, but, if injected subcutaneously, 0·02 grm. was fatal both to mice and guinea pigs. The three vitamins, *A*, *B*, and *C*, are also present in water-cress, together with salts of potassium and iron and a considerable proportion of iodine. D. G. H.

Nitrogen Distribution in Muscle of Shrimp. D. B. Jones, O. Moeller and C. E. F. Gersdorff. (*J. Biol. Chem.*, 1925, **65**, 59–66.)—The distribution of nitrogen and percentages of some of the amino acids in shrimp muscle were determined in order to throw light on the nutritive value of the proteins of this muscle, and to obtain a means of comparing the proteins with those of the scallop. Finely ground muscle of fresh shrimp, *Peneus setiferous* (L.), was extracted at room temperature with 95 per cent. alcohol, and finally with ether. The air-dried extracted muscle consisted of a white, odourless, tasteless, light, coarse powder with the following percentage composition, calculated on an ash-free and moisture-free basis : C 52·93, H 6·33, N 16·88, S 1·55. The Van Slyke method of analysis (*J. Biol. Chem.*, 1915, **22**, 281) gave the following results, expressed as percentages of the total nitrogen : Amide N, 8·13; humin N, 1·29; cystine N, 1·21; arginine N, 19·52; histidine N, 6·07; lysine N, 8·63. These figures, calculated as percentages of the corresponding amino acids in the ash-free and moisture-free muscle, gave the following values:—Cystine, 1·75; arginine, 10·24; histidine, 3·78; lysine, 7·60. By colorimetric methods the following percentages of amino acids were obtained : Cystine, 1·78 ; tryptophane, 1·21 ; tyrosine, 4·88. Aspartic acid (6·98 per cent.) and glutamic acid (15·0 per cent.) were determined gravimetrically. The results are given in a table. The amino acid composition of shrimp muscle is compared with that recorded for scallop muscle. P. H. P.

Micro Method for the Determination of Blood Sugar. E. Komm. (*Chem. Zeit.*, 1925, **49**, 769.)—The principle of the micro-method consists in the reduction of cupric oxide to cuprous oxide. From 0·2–0·4 c.c. of blood is freed

from protein by Folin's method, 2 c.c. of Fehling's solution are added, and its reduction brought about by heating. The cuprous oxide formed is collected by centrifuging, washed and dissolved in 0·3 c.c. of 0·5 per cent. nitric acid ; 0·6 c.c. of concentrated ammonia solution is then added, and the total volume made up to 2 c.c. with water. The solution then has the usual blue colour given by a cupric salt in ammonia, and the amount of copper present can be determined colorimetrically. As a comparison standard, an ammonia solution of a cupric salt is prepared containing 1 mgrm. of copper in 2 c.c., and comparison is made in an Autenrieth-Konigsberger wedge colorimeter. The zero point of the wedge standard solution corresponds to 1 mgrm. of copper or 0·69 mgrm. of glucose, and the amount in the unknown solution can be calculated. Very good results have been obtained by this method. P. H. P.

Temperature Coefficients of Enzymic Activity and Heat Destruction of Pancreatic and Malt Amylases. D. H. Cook. (*J. Biol. Chem.*, 1925, **65**, 135–146.)—The work carried out is described in detail, and the results are discussed. The rates of starch hydrolysis by pancreatic and malt amylases used in the forms of good grades of commercial pancreatin and malt have been determined under certain specified conditions for the temperature range of 20° to 70° C. At temperatures below the point where destruction of the enzyme plays an important rôle the rate of hydrolysis is about doubled for every 10° rise in temperature. The temperature and rate of destruction of these enzymes in water and salt solutions have been determined, and malt amylase is found to be much more stable than pancreatic amylase, the latter being completely destroyed by 15 minutes' heating at 50° C., whilst malt amylase still shows a trace of activity after 30 minutes at 60° C. ; pancreatic amylase is apparently inactivated approximately thirty times as fast at 50° C. as is malt amylase. It is doubtful whether any advantage is to be gained by classing vitamins as enzymes, as has been suggested, since the rates of destruction of these enzymes differ from those found for vitamins *B* and *C* by previous investigators. Results support the view that the heat destruction of the enzyme may be a process of the nature of the coagulation of a protein, probably also accompanied by partial hydrolysis. P. H. P.

Catalytically Active and Inactive Forms of Ferric Oxide. L. A. Welo and O. Baudisch. (*J. Biol. Chem.*, 1925, **65**, 215–227.)—The authors, from their work on biological or chemical reactions in which iron, or some compound of it, plays the part of a catalyst, believe they have discovered the factors which determine whether an iron oxide is, or is not, able to function as a catalyst. It is shown that the catalytic activity depends on the average size of the crystals and on the structure of the crystals composing the material ; the activity may vanish entirely as the structure of the crystals is changed from one form to another. Artificial magnetite (Fe_3O_4, or $FeO.Fe_2O_3$) was used. The oxides were grouped as Lefort's oxide or " mol-oxide " according to their preparation. In the group called a mol-oxide " were placed magnetites made by the precipitation of ferrous hydroxide "lone with no ferric iron present in any form. From magnetite are derived two

distinct oxides, magnetic ferric oxide (oxidised magnetite) and non-magnetic ferric oxide (haematite). Both have the same composition, Fe_2O_3. Three reactions were used as indicators of the catalytic activity of the oxides :—(1) The ordinary blood test ; (2) the influence on bacterial growth ; and (3) the absorption of oxygen. The haemoglobin in blood causes the dissociation of hydrogen peroxide, and the atomic oxygen set free oxidises freshly dissolved benzidine chloride. A pinch of an " active " oxide gives the same blue colour as blood does, but inactive oxides dissociate hydrogen peroxide and set free molecular oxygen which cannot oxidise benzidine; therefore no blue colour is obtained. *Bacterium lepisepticum* will thrive and stay virulent if grown in broth plus blood, or in broth plus a pinch of an " active " oxide. Classification of the oxides by the oxygen absorption test corresponded to that obtained by the blood test and by the test for bacterial growth. The results are tabulated and discussed. The magnetite and the oxidised magnetite of the " mol-oxide " are poor catalysts as compared with the corresponding oxides of Lefort. The effectiveness of the oxides as catalysts should be affected in the same way as the water absorption. Possibly the properties of ferromagnetism and catalytic activity in iron oxides are accompanying properties which are both related to the arrangement of the atoms in space, either directly or indirectly. The ultimate solution awaits a more complete knowledge of the atomic structures of iron and oxygen. P. H. P.

Effect of Bacterial Flora on Biological Test for Vitamin *B*. V. G. Heller, C. H. McElroy and B. Garlock. (*J. Biol. Chem.*, 1925, **65**, 255–264.)—Experiments have been carried out with rats to study the change in the bacterial flora of the intestinal tract and to find whether the bacteria which grow in the intestinal tract of the animals synthesise vitamin *B* and store it within their own bodies. Experimental animals kept under the usual laboratory conditions do not respond as quickly to vitamin-free rations as do those placed upon screens. Animals which have ceased to grow on the experimental ration show an accelerated growth when allowed access to the faeces. The spore-bearing organisms present in the intestinal tract during the early part of the experiment synthesise and store vitamin *B*. Animals having access to their faeces during the early part of the experiment have greater numbers of these organisms, because they re-ingest them. The additional vitamin *B*, synthesised and stored by the spore-bearing organisms, causes continued growth of the animals. Roughage, especially agar-agar, given to animals makes better growth. Extracts of the various forms of roughage used indicate that the substances contain no vitamin, but the added bulk produces a better physical condition in the animal. Tables and charts show the results. P. H. P.

Biochemical Determination of Insulin. F. Wyss. (*Compt. Rend.*, 1925 **181**, 327–328.)—Methods for the determination of insulin are based on its physiological action. The author suggests two methods for the determination of insulin *in vitro* based on the fact that phenols are oxidised by oxygenated water, and that in the presence of insulin this oxidation is retarded or inhibited, except in the

case of polyvalent phenols having two hydroxyl groups in the ortho position. Resorcinol is the phenol used, and the determination is based upon colour changes as the following preliminary test shows:—A solution of insulin known to contain 10 clinical units per c.c. is diluted with water at $P_H = 7{\cdot}5$, so that the solution contains 0·5 unit per c.c. One c.c. of a freshly prepared 0·2 per cent. solution of resorcinol is placed in each of 8 tubes, and 1 c.c. of the insulin solution is added to 7 of them. Increasing quantities (0·25 ; 0·5 ; 0·75 ; 1·25 ; 1·5 ; 1·75 ; 2·0 c.c., etc.) of oxygenated water (1 c.c. = 24 c.c. 0·01 *N* potassium permanganate) are added to the tubes, the contents of each are made up to 5 c.c. with water ($P_H = 7{\cdot}5$), and they are left in boiling water for 20 minutes. At the end of that time the one containing no insulin and the one containing 2 c.c. of oxygenated water are brown, whilst the one containing 1·75 c.c. of oxygenated water is colourless. Thus, under these conditions, 0·5 unit of insulin is neutralised by 2 c.c. of oxygenated water. A second experiment, with 0·25 unit, proves that it is neutralised by 1 c.c. of oxygenated water. In the first method for the determination of an unknown insulin solution, the concentration and quantity of resorcinol, the quantity of oxygenated water neutralising the quarter of a unit, the temperature, the P_H and the time of reaction are invariable factors, and the concentration of insulin in each tube is varied. In the second method the amount of insulin is constant, and the amount of oxygenated water added is the variable factor. P. H. P.

Penetration of Fruits and Vegetables by Bacteria and other Particulate Matter. Resistance of Bacteria, Protozoan Cysts and Helminth Ova to common Disinfection Methods. R. G. Mills, C. L. Bartlett and J. F. Kessel. (*Amer. J. Hyg.*, 1925, **5**, 559–579.)—Under normal growing conditions the interior portions of growing plants are sterile, and bacteria do not penetrate the unbroken skin, although they can gain entrance through injured and decayed portions. Spreading, however, is very limited, although pathenogenic bacteria may live on the surface of fruit and vegetables for 15 days or more. Chlorination destroys them, but is ineffective against cysts and ova ; alcohol acts too slowly to be of practical use, and potassium permanganate is not effective. The best method, and one which will uniformly kill all pathenogenic bacteria, protozoan cysts and helminth eggs, is to dip the material in boiling water for 10 seconds in such a way that the temperature does not fall below 80° C. D. G. H.

Study of a Haemolytic Proteus Bacillus. B. S. Kline. (*Amer. J. Hyg.*, 1925, **5**, 656–661)—A proteus bacillus was isolated from bone marrow 46 hours after death in a case of pernicious anaemia. It grew well in ordinary media, had a fairly characteristic sugar reaction and a marked haemolytic power haemolysis becoming apparent on blood agar plates within 6 hours of inoculation. The blood picture was followed in 18 inoculated rabbits, and a moderate number of nucleated red cells usually appeared in the circulation within 48 hours, together with, in some cases, megaloblasts in moderate number. With repeated increasing doses the rabbits developed siderosis, most marked in the spleen and bone marrow, and the latter was generally found to be hyperplastic. D. G. H.

Domesticated Animals as Sources of Bacilli Pathogenic to Man. **W. G. Savage.** (*Veterinary J.*, 1925, **81**, 435–442.)—Outbreaks of infectious disease of bacterial origin occur which seemingly have no connection with preceding cases. Apart from the development of the organisms from ordinary non-parasitic types, there are three possible explanations :—(1) They may have been passing a parasitic but non-pathogenic existence in human beings ; (2) or a saprophytic existence in soil, water or other medium ; or (3) some of them may be found in animals either as specifically pathogenic or as undetrimental to their host.

The long persistence of such bacilli as those of diphtheria, typhoid fever and paratyphoid fever in human carriers is well known, but there is little or no evidence that the bacteria responsible for many other diseases persist in this way for any material time. With regard to the second possibility, the evidence shows that non-sporing pathogenic types of bacteria do not live long in competition with the natural saprophytes, and the only ones of any practical importance are the resistant *B. tuberculosis*, and possibly *B. pestis* in cases of very recent and gross soil contamination in tropical countries. The others, such as *B. typhosus* or *B. diphtheriae*, are rapidly on their way to extinction in ordinary saprophytic surroundings. The third possibility—that domestic and other animals may serve as a reservoir for bacilli pathogenic to man—has not been exhaustively studied. In some diseases the pathological lesions are closely parallel in man and animals, but in others there are considerable differences, and there are certain cases in which the same organism produces a different type of disease in man and in animals. It has now been proved that a certain proportion of cases of limberneck in chickens is due to infection with *B. botulinus*, the organism of human botulism. Certain outbreaks of forage poisoning in horses have the same etiology (*cf.* ANALYST, **1923**, **48**, 118). A common source of infection in chickens is from canned food spoiled by the growth of *B. botulinus*. The *Salmonella* group of organisms is a fairly common cause of disease in animals, in which they produce a general septicaemia, and are the subsequent probable origin of the bacilli of food poisoning in man (*cf.* ANALYST, 1925, 239, 341). These organisms differ greatly in their pathological effects. *B. paratyphosus* B., for example, while causing paratyphoid fever in man, seems quite harmless to animals. *B. abortus equi*, on the other hand, can set up disease in horses, but seems to be non-pathogenic to man. *B. aertrycke*, a common food-poisoning type for man, is a widespread cause of enteritis in mice, guinea-pigs and other rodents, in parrots and other birds, and is occasionally found in pigs, and also as a cause of calf enteritis. *B. enteritidis*, another human food-poisoning organism, occasionally causes disease in cows and calves, and is a fairly common cause of disease in rats. *B. suipestifer*, which is only very rarely a cause of food-poisoning, is common as a secondary invader in hog cholera, and at times is a primary cause of disease in pigs.

There are numerous examples showing bacilli which are pathogenic to man, but harmless to the lower animals, and *vice-versa*. For instance, *B. typhosus* is pathogenic to man, but causes no disease in animals, and experiments with *B. diphtheriae* have shown that kittens cannot be infected with this organism by way

of the nose and throat, although when injected the bacilli rapidly cause illness and death. Again, the organism causing Malta fever in man (*Micrococcus melitensis*) is often present in large numbers in the milk of goats in Malta and elsewhere. The ordinary type of streptococcus causing mastitis in cows and goats (*Streptococcus mastitis*) is not a cause of human disease. On the other hand, closely allied types of streptococci from human sore throats have been found incapable of setting up mastitis when introduced into goats *via* the teat passage. Experiments by the author and clinical data have indicated that the considerable number of human outbreaks of sore throat derived from cows suffering from mastitis are explainable on the assumption of infection of the cows' udders with streptococci of human origin which have been able to set up mastitis. This hypothesis has been confirmed by experiments in America. As a general conclusion, it appears that the majority of bacteria pathogenic to man or animals must be regarded as organisms which have become highly specialised. They have gained intensive virulence at the price of inability to grow, or even survive, except under restricted and strictly confined conditions. On the other hand, there remain some bacteria with more generalised requirements and a greater adaptability.

Pyorubin, a red Water-soluble Pigment characteristic of *B. pyocyaneus*. P. D. Meader, G. H. Robinson and V. Leonard. (*Amer. J. Hyg.*, 1925, **5**, 682–708.)—Three water-soluble pigments are produced by all typical strains of *B. pyocyaneus*: (*a*) The bright blue pyocyanin, (*b*) the bright red pyorubin, and (*c*) the fluorescent pigment, yellow by transmitted, and green by reflected, light. Of these, (*a*) is specific, and (*b*) characteristic of *B. pyocyaneus*, whilst (*c*) is non-specific. All are produced by oxidation of their leuco bases, and may be reduced to them and reproduced by oxidation. Pyocyanin is the least stable of the three pigments, and pyorubin is the last to undergo change in old cultures, and is also unaffected in colour by acid and alkali changes. It is probable that *B. pyocyaneus* occurs more frequently in nature than has been supposed. Of 44 strains studied culturally, no difference was discovered other than in pigment production or occasional minor variations in times of reaction; neither did agglutination or absorption tests bring out any differences. Whilst typical strains freshly isolated from human lesions invariably produce both pyocyanin and pyorubin, and may be highly virulent (with pronounced selective affinity for the genito-urinary tract of laboratory animals), those isolated from the environment and old laboratory strains may temporarily lose their power to produce any but the fluorescent pigment, and at the same time become non-virulent. D. G. H.

Occurrence of *Linguatula Serrata* in Bovine Lymphatic Glands. A. W. N. Pillers. (*Veterinary J.*, 1925, **81**, 444–447.)—A description is given of several cases in which the parasite *Lingualata serrata* (also known as *Pentastomum denticulata* and *Linguatala denticulatum*) has been found in bovine mesenteric lymphatic glands. Oh reaching the nasal cavities of certain carnivora this parasite becomes adult, and eggs from the nasal discharge or faeces may infect man. Larval pentastoma have been discovered in the sheep, goat, ox, pig, horse, rabbit,

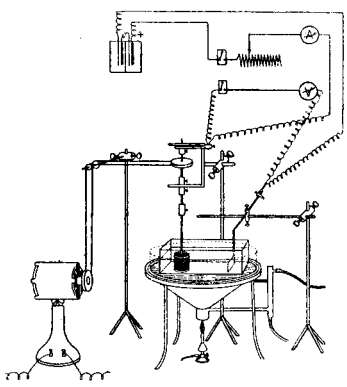
hare, guinea-pig, and rat. In addition to its occurrence in the mesenteric lymphatic glands, it may also be present under the peritoneum, in the liver, and sometimes in the lungs. The lesion is of interest since it may be mistaken for tuberculosis.

An Epidemic of Scarlet Fever spread by Ice Cream. G. H. Ramsey. (*Amer. J. Hyg.*, 1925, **5**, 669–681.)—An epidemic of scarlet fever involving 116 cases was traced to ice cream made by a man suffering from scarlet fever. A detailed investigation was made, including histories and control histories on unaffected persons, and a filtrate prepared from a culture of haemolytic streptococci from the ice cream maker gave typical reactions on Dick-positive individuals. The ice cream was eaten by 81·9 per cent. of the fever cases investigated.

D. G. H.

Toxicological and Forensic.

Determination of Minute Quantities of Lead in Organs. Alteration of Dilute Lead Nitrate Solutions. H. Bernhardt. (*Zeitsch. anal. Chem.*, 1925, **67**, 97–105.)—A modification of the usual method is described, in which the lead peroxide is precipitated electrolytically instead of by treatment with bromine. The operation is conducted in a glass vessel, 20 by 6 by 5 cm., standing in a water-bath. Platinum foil (5·5 by 2 cm.) is used as the cathode, which is made to slide along a glass rod parallel to the long side of the bath. The platinum-iridium anoderotates at 600 to 1000 r.p.m. The solution (250 c.c.) is electrolysed at 70° to 80° C. for $1\frac{1}{2}$ to 2 hours (2·8 to 3·2 V., 0·2 to 0·3 Amp.), after addition of 10 c.c. of 60 per cent. nitric acid. Potential and current density are regulated by a resistance, but chiefly by varying the distance between the electrodes. The anode is dipped into three portions of distilled water, then into a 5 per cent. potassium iodide solution acidulated with a few drops of acetic acid. When the deposit has been converted into the yellow iodide, the anode is immersed for a few seconds in cold 30 per cent. sodium acetate solution, then rinsed twice with distilled water. The three liquids are poured into a conical flask and treated with an excess of 0·001 N thiosulphate solution, which is measured with 0·001 N iodine; Pb = 2I. The thiosulphate solution must be freshly made each day.



Dilute solutions of lead nitrate (1 per cent. and weaker) were found to decrease in strength from 4·4 to 77·3 per cent. after intervals varying from 6 to 600 days. A chemical action of the solution on the glass, resulting in the formation of lead silicate, is assumed to take place. Further, it was found that a gradual demixing of the solutions takes place, in such a manner that a " cream " rises to the upper layer of the solution, especially where unboiled water was used, whilst another enrichment takes place in the bottom layer. A solution containing

2·60 mgrms. of lead per 5 c.c. when fresh, was found to contain, after 41 days :— Upper layer, 2·13 ; middle 1·95 ; and lower layer, 2·76 mgrms. Pb per 5 c.c. It is concluded that part of the lead is present as a colloidal phase. W. R. S.

Stannous and Stannic Hydrides. W. Vaubel and H. von Mairhofen-Aulenbach. (*Chem Zeit.*, 1925, **49**, 827.)—The hydrogen emitted when tin is dissolved in hydrochloric acid has a distinctive odour, burns with a blue flame in Marsh's apparatus, and deposits on porcelain a stain of metallic tin, which has a characteristic odour, is soluble in hydrochloric acid, and forms Prussian blue with ferric chloride and potassium ferricyanide. The gas produces a brown stain on silver nitrate paper, and a brown precipitate in silver nitrate solution. This consists of silver-tin, and has the composition $SnAg_2$, so that the tin hydride producing it would be SnH_2 or Sn_2H_4. Stannous hydride is also formed when silver-tin, $SnAg_2$, is treated with hydrochloric acid. Stannic hydride, SnH_4, is produced when an alloy of magnesium and zinc is decomposed by hydrochloric acid, and, in a not quite pure condition, together with stannous hydride, when zinc and sulphuric acid or dilute sulphuric acid (or the nascent hydrogen liberated from them) act upon precipitated tin.

Stannous hydride has little, if any, toxic action, as has been proved by experiments on men as well as on mice, but, according to Paneth and Joachimoglu, stannic hydride is very poisonous. The so-called " zinc fever " produced by the dissolving of zinc containers soldered with tin must be attributed to the liberated stannic hydride, and some cases of poisoning by food preserved in badly tinned or defective cans are probably due to the liberation of a mixture of stannous and stannic hydrides.

Sulphonal Poisoning. Localisation of Sulphonal and Hæmatoporphyrin. R. Fabre and H. Simonnet. (*J. Pharm. Chim.*, 1925, **117**, 225–227.)—A daily dose of 1 grm. of sulphonal was administered to a rabbit weighing 1·5 kilos., and it was killed after 12 days, when it showed marked signs of intolerance. The pulped organs were boiled with 5 parts of distilled water, cooled to 50–55° C., and submitted at that temperature to the action of pancreatin (1 grm. for 50 grms. of pulp) for 10–12 hours. After boiling, the residue was extracted by centrifuging (or filtering) and treated in acid medium with chloroform, the chloroform evaporated, and the residue recrystallised, where necessary, and identified as sulphonal by the m.pt. (125° C.) and the formation of sulphate and mercaptan. The sulphonal was found to be unaltered by the pancreatin, and an almost theoretical recovery was made from the organs. The only noticeable feature at the autopsy was the red coloration of the bile which under ultra violet rays (George lamp with Wood's screen) showed the fluorescence of haematoporphyrin. This substance, however, was only demonstrated in the bile, urine and in feeble quantity in the spleen. Part of the haematoporphyrin formed during sulphonal poisoning appears to be rapidly eliminated by the kidneys, and too little is present in the blood to detect. The amount of sulphonal in the liver was greater in proportion than that of veronal found after poisoning by compounds of that group. D. G. H.

Toxicity of Compounds of Tungsten and Molybdenum. T. Karantassis (*Bull. Sci. Pharmacol.*, 1924, **31**, 506 and 581 ; *J. Pharm. Chim.*, 1925, **117**, 146.)—Doses fatal in 24 hours for guinea-pigs were. per kilo. of body weight, as follows :—For sodium tungstate ($Na_2WO_4,2H_2O$) ; ingested, 0·55 ; injected subcutaneously, 0·45. For ammonium molybdate ($(NH_4)_6Mo_7O_{24}4H_2O$) : ingested, 1·2, and injected, 0·75 grm. Death appears to be due to asphyxiation. D. G. H.

Toxic Action of Synthetic Methanol. R. Hunt. (*Amer. J. Pharm.*, 1925, **97**, 495–496.)—It has been claimed that synthetic methanol is so pure that, unlike ordinary methyl alcohol, it is harmless. The author's experiments on animals, however, have shown that, although small doses of either methanol or ordinary wood alcohol are not as poisonous as the same amount of ethyl or grain alcohol, yet when the doses are repeated at intervals of 24 hours, the methanol is more harmful, since the animal develops a tolerance to ethyl alcohol. Methanol, on the other hand, has a cumulative effect, a number of small doses having the same effect as the whole quantity given at once. In the case of man a small dose of methyl alcohol is more harmful than a similar dose of ethyl alcohol. The nervous system of man is more seriously affected by methyl alcohol than is that of the lower animals, and single small doses have been known to produce permanent blindness in man. The synthetic methanol is just as poisonous as methyl alcohol from wood.

Cause of Lathyrism. A. P. Anderson, A. Howard and J. L. Simonsen. (*Indian J. Med. Res.*, 1925, **12**, 613 ; *Lancet*, 1925, **209**, 613.)—The disorder, characterised by a spastic spinal paralysis, and commonly termed *lathyrism*, is usually ascribed to chronic poisoning by an alkaloid in the seeds of the pulse, *Lathyrus sativus* (*cf.* Hughes, ANALYST, 1895, **20**, 169). Various analyses of these seeds and feeding experiments on animals have given conflicting results, and it is now shown that the lathyrus crop (*khesari*) is always contaminated with leguminous weeds. The author's experiments with botanically pure lathyrus seeds have shown that they contain no alkaloid and are without deleterious effects on animals. A vetch, known in India as *atka*, produced in animals symptoms closely resembling those of lathyrism in human beings, whereas other weeds occurring in *khesari* fields proved harmless. Chemical analysis showed that *atka* seeds contain a substance termed viciarin, closely allied to amygdalin, and also a glucoside, vicin, which on hydrolysis yields a sugar and a base, divicine, which is an oxy-amino derivative of pyrimidine. Divicine is toxic to animals in doses of 0·4 to 0·5 mgrm. per grm. of body weight, and is looked upon as the poisonous substance in *atka* responsible for the disease. The contaminating weed can be eliminated by sowing *khesari* in lines a foot apart, and removing the *atka* seedlings in the early stages of growth.

Poisoning by *Veratrum album* L., through confusion with *Asparagus officinalis*. J. Maheu and P. Chéramy. (*J. Pharm. Chim.*, 1925, **117**, 185–195.)—A case of poisoning (with recovery in 10 days) with an extract of 50 grms.

per litre of " asparagus " root was examined, and it was found that *Veratrum album* had in fact been used. The macroscopic and microscopic features of this root and of *Asparagus officinalis* are described with diagrams, and, whilst in many points they are similar (both belong to the Liliaceae), there are differences such as the presence of starch and raphides in the piliferous layer in asparagus ; the *Veratrum rhizome* possesses more and better developed scales, and the roots of *Asparagus* are more brittle. *Veratrum album* may also be confused with Galenga (*Alpinia officinalis*) and with cumin, and suggestions for identification of the drugs or powders are given. Symptoms of poisoning are : painful respiration, slow pulse, vomiting, increased saliva, a difficulty in walking and standing, trembling, convulsions, and death. The most important alkaloids present are jervine, pseudo-jervine, rubijervine, veratialbine and veratrine, and dilute sulphuric acid (or, better, Dragendorff's reagent), will show their distribution in the drug, with a pink coloration in the outer cortex. D. G. H.

Organic Analysis.

Determination of Tartaric Acid. K. Täufel and C. Wagner. (*Zeitsch. anal. Chem.*, 1925, **67**, 16–20.)—The solution should contain about 7·5 grms. of tartaric acid per litre. Five c.c. are carefully mixed with 5 c.c. of *N* dichromate solution and 15 c.c. of strong sulphuric acid. The hot mixture is kept for 15 minutes on a boiling water-bath. After cooling, 200 c.c. of water and 10 c.c. of *N* potassium iodide solution are added, and the liberated iodine is titrated with 0·1 *N* thiosulphate solution. According to $C_4H_6O_6 + 5O = 4CO_2 + 3H_2O$, the oxidimetric equivalent weight of tartaric acid is 15·005 grms. per litre. Under the above conditions the action of the acid on the dichromate is negligible ; a blank test may be made with 5 c.c. of water, 5 of the dichromate solution, and 15 of the sulphuric acid. The proper excess of dichromate for reliable oxidation is 100 per cent., as ensured by the directions given. The same process provides a means for determining sucrose, salicylic and phthalic acids, and β-naphthol. W. R. S.

Volumetric Determination of certain Unsaturated Constituents of Oils and Fats. H. P. Kaufmann. (*Chem. Zeit.*, 1925, **49**, 768.)—A brief outline of the principles of a new method of analysing oils and fats is given, in which the reagent used for the titration is a solution of a thiocyanogen compound in glacial acetic acid. The amount of thiocyanogen added to an unsaturated oil or fatty acid does not correspond to the iodine value ; there may be partial or complete absorption, or none at all. The behaviour of linolic acid and its triglyceride is the most interesting, the thiocyanogen radicle being only absorbed at one double bond. Hence by determining the iodine value and the thiocyanogen value of an oil it is possible to obtain, from the difference between the two values, the amounts of the respective unsaturated constituents present. Details of the procedure are to be published.

Approximate Determination of Arachidonic Acid. L. G. Wesson. (*J. Biol. Chem.*, 1925, **65**, 235–250.)—The following method is used for the comparative determination of arachidonic acid in the tissues :—From 50 to 100 grms. of the tissue (macerated) are dehydrated in the cold during 24 hours with 95 per cent. alcohol, in three portions, and then extracted with U.S.P. ether during 3 days, with 6 changes of solvent. The combined extracts are diluted with an equal volume of half saturated sodium chloride solution containing 20 c.c. of 10 per cent. hydrochloric acid per litre. A suitable filter funnel is described. After extraction of the aqueous layer by ether, the combined ether layers are washed, evaporated under reduced pressure to a smaller volume, transferred to a tared flask, and evaporated under reduced pressure to dryness. The residue of ether-soluble material is weighed and dissolved in absolute ether. Bromine vapour, carried by a current of dry carbon dioxide, is projected on to the surface of the ice-cold ethereal solution until the liquid is coloured a deep red, and then the solution and precipitated bromo-arachidonyl compounds are left for 2 days in a cool place. The precipitate is centrifuged from the solution in a small, tared centrifuge tube, washed with ether and alcohol until the washings are colourless, left overnight with concentrated hydrochloric acid at 40° C., then washed with water, alcohol and ether, and dried to constant weight at 100° C. The precipitate is apparently octobromoarachidic acid, and the weight of arachidonic acid is calculated from its weight by the theoretical factor 0·3225. The " ratio " is the ratio of arachidonic acid to substances soluble in ether. Tests of the procedure and tables of results are given. By this method a considerable increase in the arachidonic acid content of the tissues of rats was detected during periods of active fat metabolism, but probable sub-normal glucose metabolism. The increase was proportionately larger in the liver than in the other rat tissues. In rats deprived of fats and ether-soluble substances and in rats suffering from a deficiency of vitamin *A* in their diets, no considerable change in the arachidonic acid content was noted. The acid was present in all dog tissues examined. Possibly arachidonic acid is an intermediate product in the metabolism of, at least, part of the fatty acids which contain fewer than 20 carbon atoms. P. H. P.

Inorganic Analysis.

The Absorption of Oxygen and Liberation of Carbon Monoxide by Alkaline Pyrogallol Solutions. T. J. Drakeley and H. Nicol. (*J. Soc. Chem. Ind.*, 1925, **44**, 457–462 T.)—A study of the various alkaline pyrogallol solutions which have been proposed as absorbents of oxygen shows that they all evolve a greater or less quantity of carbon monoxide when absorbing pure oxygen. The amount varies with the purity of the oxygen ; with air there may be only a trace of carbon monoxide formed, but when 99 per cent. oxygen is being tested there is material error. Shaking is important and tends to reduce the error ; on this account the Orsat pipette is unsuitable for the absorption of oxygen. No pyrogallol solution has been found which is free from this source of error, but

the best available is that of Anderson (which is prepared by adding 15 grms. of pyrogallol to 100 c.c. of solution of potassium hydroxide of sp. gr. 1·55). Four precautions are necessary to ensure reliable results ; the absorbing solution must be in considerable excess, it should not be used after it has absorbed one-tenth of its capacity, it must be vigorously agitated during the absorption, and the oxygen content of the gas should be reduced to about 25 per cent. by suitable dilution with nitrogen. H. E. C.

Elimination of Oxalic Acid in Qualitative Analysis by Bismuth Subnitrate. A. Keschan. (*Zeitsch. anal. Chem.*, 1925, **67**, 81–86.)—The filtrate from the hydrogen sulphide precipitate is evaporated almost to dryness, and again with strong nitric acid to expel as much hydrochloric acid as possible. In absence of iron and chromium, the concentrated solution is treated with the subnitrate (3 grms. of the commercial salt precipitate 0·88 grm. C_2O_4''), diluted with 10 to 15 volumes of water, boiled some minutes, again diluted with an equal bulk of hot water, cooled, and filtered. The bismuth in the filtrate is precipitated with hydrogen sulphide. Iron, if present, is reduced to the ferrous state (see ANALYST, 1925, 200) before the solution is diluted for the first time. Chromium, if present, is precipitated by addition of 1 to 2 c.c. of *N* ammonium phosphate before boiling with the subnitrate. Oxalic and phosphoric acid are eliminated together by the method described. W. R. S.

Volumetric Determination of Mercury. E. Rupp and K. Müller. (*Zeitsch. anal. Chem.*, 1925, **67**, 20–23.)—The finely-powdered cinnabar or other substance to be tested, free from halogen, and equivalent to about 0·3 grm. Hg, is heated till decomposed (about 15 minutes) with 1 grm. of pure potassium nitrate and 5 c.c. of strong sulphuric acid in an inclined boiling tube provided with an ascending 50 cm. tube. When cool, the condenser is rinsed and the mass transferred with 50 c.c. of water into a beaker. Permanganate solution is added, drop by drop, until a coloration is obtained, and this is removed by a minimum of ferrous sulphate (removal of nitrous acid). After addition of a few c.c. of ferric alum solution, the liquid is titrated with 0·1 *N* thiocyanate solution, of which 1 c.c. = 0·01003 grm. Hg. Presence of halogen causes formation of the mercury compounds that do not react quantitatively with thiocyanate. In iodide preparations mercury is determined as follows :—The material is extracted with potassium iodide solution containing a liberal excess of alkali hydroxide. The solution is filtered, if necessary, stirred, and treated with strong formaldehyde solution diluted with water, which precipitates metallic mercury. This is collected on a dense pad of asbestos, washed with water, and treated on the filter with a few c.c. of pure, strong nitric acid. After washing and diluting, the filtrate is treated with permanganate, etc., as above. W. R. S.

Determination of Copper in Iron Pyrites. T. Heczko. (*Zeitsch. anal. Chem.*, 1925, **67**, 35–36.)—The sulphate solution of the ore is precipitated with hydrogen sulphide ; the precipitate is thoroughly washed with hydrogen sulphide water containing 4 per cent. of acetic acid, dried and ignited in a porcelain crucible,

and fused with 10 parts of potassium pyrosulphate. The attack is complete in a few minutes, and results in a sulphate solution ready for electrolysis after acidification with sulphuric acid. W. R. S.

Separation of Copper from Mercury. G. Spacu. (*Zeitsch. anal. Chem.*, 1925, **67**, 27–31.)—The solution is diluted to 150 c.c., boiled, and treated with excess of pyridine, which causes a dark blue coloration. Solid ammonium thiocyanate (8 to 10 times the weight of substance taken) is added while the solution is stirred vigorously. Copper is thrown down as a green, flocculent precipitate; mercury is not affected. After about 1 hour's standing the precipitate is collected, and washed with cold water containing 5 grms. of thiocyanate and 5 c.c. of pyridine per litre. The wet precipitate is dried in a tared porcelain crucible, gradually heated to 150° C., then more strongly without ignition of the gases evolved. Finally, the sulphide is slowly roasted to oxide as usual. The filtrate from the copper precipitate is acidified with hydrochloric acid, and the mercury precipitated with hydrogen sulphide. W. R. S.

Sensitive Tests for Copper. G. Spacu. (*Zeitsch. anal. Chem.*, 1925, **67**, 31–32.)—(1) Very dilute solutions of copper salts, stirred with a solution of alkali thiocyanate and not more than two drops of a freshly-prepared, 2 per cent. alcoholic solution of tolidine, give a blue flocculent precipitate resembling Prussian blue, of the composition $Cu\mathit{Tld}(CNS)_2$. (2) Very dilute, neutral copper solutions, on addition of 2 c.c. of potassium iodide solution, followed by 3 drops of freshly-prepared one per cent. alcoholic benzidine solution, yield, on shaking, a copious dark-blue flocculent precipitate of $Cu\mathit{Bzd}I_2$.—In absence of ferric ions, 0·00002 grm. of copper gives a characteristic precipitate in 10 c.c. by either reaction. W. R. S.

Separation of Palladium from Platinum. F. Krauss and H. Deneke. (*Zeitsch. anal. Chem.*, 1925, **67**, 86–96.)—The following methods were examined critically:—Nitroso-β-naphthol; dimethylglyoxime; acetylene; mercuric cyanide; ammonium chloride; and differential solubility of the precipitated metals in hydrochloric or nitric acid. The last method was found to be unreliable. The three first give very bulky precipitates, and are inconvenient when the amount of palladium exceeds 0·1 grm. The mercuric cyanide method is accurate. The authors favour ammonium chloride in absence of other metals, and recommend the following procedure: The solution, freed from nitric acid, is evaporated to dryness with a slight excess of ammonium chloride; the residue is dissolved in water, and saturated ammonium chloride solution is added. The platinum precipitate is allowed to settle, collected, washed with saturated ammonium chloride solution till the washings are colourless, and again with 96 per cent. alcohol. The precipitate is dissolved in hot water, and the boiling solution reduced with sodium formate; the reduced metal is filtered off, thoroughly washed with dilute hydrochloric acid, and ignited in hydrogen. The filtrate from the platinum precipitate is neutralised with sodium carbonate, boiled with sodium formate, and the precipitated palladium ignited in hydrogen. W. R. S.

Uranium Cacodylate. E. Isnard. (*Bull. Sc. Pharmacol.*, 1925, **32**, 131 ; *Pharm. Chim.*, 1925, **117**, 241.)—When uranium nitrate is treated with excess of sodium cacodylate, uranium cacodylate $[(CH_3)_2AsO_2]_2UO_2$ is formed as an amorphous greenish white precipitate. The salt, which might serve for the determination of uranium, may be separated from iron and aluminium, as these give no precipitate with sodium cacodylate. D. G. H.

Determination of Alkalis in Silicates. O. Cantoni. (*Zeitsch. anal. Chem.*, 1925, **67**, 33–34.)—After the decomposition of the silicate by Berzelius' method (hydrofluoric and sulphuric acids), the following modification of the usual procedure is recommended :—Instead of the partial evaporation of the sulphuric acid, the mass is evaporated to complete dryness, and the residue cautiously heated at a dull red heat until fumes are no longer evolved. The residue is extracted with boiling water and digested on the water-bath, filtered off, and washed thoroughly with boiling water ; slight cloudiness of the filtrate is immaterial. The filtrate is acidified with hydrochloric acid and precipitated with barium chloride followed immediately by ammonia and ammonium carbonate, the liquid being kept vigorously stirred. The determination is concluded in the usual manner. In this method the precipitates and quantities of reagents used are very small. The whole operation can be carried out in 4 to 5 hours in one 50 c.c. platinum crucible. W. R. S.

Detection of Nitric Acid and Nitrates in Sulphuric Acid. J. Wilson. (*J. Soc. Chem. Ind.*, 1925, **44**, 438 T.)—The following test is more sensitive than the well-known brown ring test for nitric acid or soluble nitrates ; it will detect 0·004 per cent. of nitric acid in 100 c.c. of sulphuric acid : A solution or suspension of the material is prepared so as to contain not less than 0·002 per cent. of nitric acid ; to 10 c.c. of this is added 1 drop of a solution of 0·2126 grm. of 1:5-dihydroxyanthraquinone in 250 c.c. of pure sulphuric acid. After the mixture has stood for about 1 minute the colour is compared with that of a like quantity of sulphuric acid containing 1 drop of the indicator ; a colour change from red to yellow indicates the presence of nitric acid. H. E. C.

Physical Methods, Apparatus, etc.

Differential Electro-Titration. D. C. Cox. (*J. Amer. Chem. Soc.*, 1925, **47**, 2138–2143.)—The introduction of this method eliminates the plotting of curves, the use of calomel cells, and errors due to diffusion or drifting. As the potentials to be measured are only relative, the use of a standard cell or the calibration of the bridge wire is unnecessary. The principle is illustrated thus :—Suppose two identical solutions are titrated in the ordinary electrometric way, side by side ; let the one burette be always 0·2 c.c. ahead of the other, then, instead of noting the potentials of the two cells, note only their difference from time to time. When this difference has reached a maximum the end point has been reached. In practice, the solution to be titrated is made up to 200 c.c., and 100 c.c. poured into

each of two beakers, side by side, and connected by a strip of filter paper. A platinum wire electrode dips into each beaker, and these are connected with a potentiometer or millivoltmeter. The titrating liquid is run in from two burettes, the right-hand burette being kept 0·2 c.c. in advance of the left. As the end point is approached the readings increase in value, exhibiting a sudden great rise at the end point, then rapidly dropping almost to zero again. H. E. C.

Study of the Secretion of Silk by means of Ultra-violet Rays. A. Policard and A. Paillot. (*Compt. Rend.*, 1925, **181**, 378–380.)—When a silk-worm about to spin its cocoon is examined with Wood's light (ultra-violet rays of wave length 3650 Å) there is seen a brilliant yellow fluorescence. The cause of this has not been completely ascertained, but examination by this means has shown two phenomena in connection with the secretion of silk. First, there is the secretion of fibroin, a substance giving a white fluorescence and imparting a white appearance to the secreting segment. Secondly, there is the formation of a substance which gives the fibroin its characteristic yellow fluorescence. This substance is not the pigment; the pigment modifies the tint, but does not cause the fluorescence. Sericin itself is not fluorescent. The substance causing the phenomenon exists in the blood; it appears on the 4th or 5th day and disappears after the production of the cocoon; its formation always precedes the secretion of fibroin. H. E. C.

A Cryostat for Temperatures extending to −180° C. J. E. Walters and A. G. Loomis. (*J. Amer. Chem. Soc.*, 1925, **47**, 2302–2306.) –An improved form of the Henning type of cryostat is described, which gives results between 0° and −180° C. with an accuracy of = 0·015°. The distinctive features of the apparatus are safety and simplicity, it being so designed that, in the event of breakage, liquid air or liquid oxygen does not come into contact with any considerable quantity of the hydrocarbon, and so risk an explosion. For the construction it is necessary to consult the original paper. H. E. C.

Erratum: The Höchst Test for Anthracene (ANALYST, 1925, p. 525, line 25). The factor for converting anthraquinone into anthracene should be 0·8558.

Reviews.

PHYSICO-CHEMICAL EVOLUTION. By CH. E. GUYE. Translated by J. R. CLARKE, M.Sc., F.Inst.P. Pp. ix + 172, with 4 diagrams. London: Methuen & Co. Price 6s. net.

This work is a translation of three articles contributed by Professor C. E. Guye to various Swiss scientific journals since 1917. To appreciate the scope of the book it is necessary to realise that the term physical chemistry is taken as including mechanics, astronomy, physics and chemistry, a decidedly unusual application of the term, and one which can scarcely be recommended in general. Nevertheless, from the point of view of Professor Guye's subject matter, the four

sciences are naturally brought into closer apposition than usual, and it may not be without advantage to have this done on occasion.

The fundamental idea which the author takes as his text, more particularly in the first two divisions of the book, is the significance for "physical chemistry" of probability considerations as expressed in the principles of statistical mechanics. The idea is, of course, not novel, but it is probable that the significance of statistical mechanics is relatively little appreciated at the present time, and the author has done an eminently useful service in presenting in simple and intelligible form the qualitative aspect, at any rate, of considerations which are of fundamental importance to the physicist and chemist.

As was to be expected, the author takes the opportunity to demonstrate the statistical basis of the second law of thermodynamics. Possibly his mode of approach may appeal to, and may be preferred by some to the more rigid mode usually associated with pure thermodynamic thinking itself. However this may be, the book serves the very useful function of supplementing in a simple, but at the same time in an authoritative way, even an elementary knowledge of thermodynamics, and it can be warmly recommended to all those whose taste or opportunity is not likely to carry them far in the more formal treatises, but who wish to have at least a general grasp of the philosophic basis of statistical considerations and to appreciate precisely why such considerations must find a place in a theoretical treatment of physico-chemical systems.

The concluding section of the work deals with "Carnot's principle and the physico-chemical evolution of living organisms." This will undoubtedly strike the average reader as being the most novel, and consequently the most debatable, of the problems dealt with. It is a subject which the physicist and chemist would do well to ponder. W. C. M. LEWIS.

THE FATS (MONOGRAPHS ON BIOCHEMISTRY). J. B. LEATHES and H. S. RAPER. 2nd Edition. P. vii. + 242. London: Longmans, Green & Co. 1925. 12s. 6d. net.

The first edition of this important Monograph was published fifteen years ago. Much new work on the physiology of fats has been done during the intervening period, and this edition has consequently been much extended in scope, notwithstanding the fact that, owing to the separate issue of Maclean's monograph in the same series on "Lecithin and Allied Substances; The Lipins," all systematic treatment of these bodies is omitted from Leathes and Raper's work.

This edition comprises 217 pages of text and 20 pages of valuable bibliography, in each case about twice the volume of the first edition. Chapter IV. of the old edition ("The Physiology of Fats") has been expanded into seven very valuable chapters of the greatest interest to the chemist and physiologist. It is a regrettable fact that many chemists, well read in the chemistry of fats, are out of touch with the important physiological problems attaching to these same compounds. The great value of these Monographs to readers of THE ANALYST is their treatment of the particular subject from an angle sometimes unfamiliar and yet important to

the chemist. In over 100 pages the authors discuss the origin and occurrence of fats in nature; the digestion and absorption of fats; the fats in the blood during absorption; their discharge into the blood, and their transfer to the organs of the body; the oxidation of fats; and the part played by fats in cell-life. Much of the matter in these seven chapters is new and is presented in a most interesting manner.

The earlier chapters of the book deal, as in the first edition, with the constitution of the fatty acids of fats, their extraction and estimation, the determination of their physical and chemical properties, and the separation and identification of their constituents. These chapters will repay study by the chemist, as they are replete with suggestive material.

That the formation of fat in the plant and in the animal body is chiefly from the conversion of carbohydrates is now well attested, but the precise mode of the synthesis is not known. The authors marshal the available evidence in a masterly way. The synthesis presumably takes place in two stages, the first being the building up of the fatty acid, and then the union of three molecules of fatty acid with glycerol to form a triglyceride. This latter process may be brought about by the action of lipase, which can cause either hydrolysis or synthesis of fats. It is likely that the higher fatty acids may be produced by the auto-condensation of acetaldehyde to form hydroxy- or unsaturated aldehydes which, by loss of water, reduction and oxidation, form fatty acids. In this way, acetaldehyde is supposed first to condense to aldol (a reaction capable of being brought about by the liver), which by simultaneous oxidation at the -CHO group and reduction at the -CH(OH) group is converted into butyric acid; or the aldol might, more probably, lose water and be converted into crotonaldehyde, this being next reduced to butaldehyde by hydrogen from the initial reaction, in which lactic acid breaks up into acetaldehyde and formic acid. The latter yields hydrogen and carbon dioxide, the butaldehyde being oxidised to butyric acid.

If the aldol condenses further with acetaldehyde, or undergoes auto-condensation before the above change takes place, compounds containing multiples of two carbon atoms would be produced which might be capable of transformation into fatty acids. Those naturally-occurring fatty acids containing six or more carbon atoms have always even numbers of these atoms, suggesting that they are built up two at a time; and this process might well result in the characteristic long straight carbon chains of the fatty acids. By such auto-condensation, straight chain compounds are known to be formed from acetaldehyde and crotonaldehyde. The products of condensation of several molecules of acetaldehyde, by loss of water, would form higher unsaturated aldehydes, and these would be reduced to form more or less completely saturated aldehydes, the final stage being the oxidation of the terminal -CHO group to form the corresponding fatty acid.

Another hypothesis would make pyruvic acid a decomposition product of carbohydrate in the body, from which acid the acetaldehyde of its decomposition would combine with a second molecule of pyruvic acid, when the keto-acid so produced would either lose carbon dioxide with formation of crotonaldehyde, or

by oxidation yield crotonic acid. The crotonaldehyde produced may be supposed to condense with another molecule of pyruvic acid, again yielding a keto-acid which again may lose carbon dioxide or be oxidised and so give an unsaturated aldehyde or acid respectively. By this continued formation of unsaturated aldehydes and condensation with pyruvic acid the long straight chains of even numbers of carbon atoms may be formed. Reduction at the unsaturated linkages and final oxidation of the terminal -CHO group, as before, would complete the process.

Which of the above hypotheses is the correct one awaits final experimental demonstration. The necessary glycerol is, no doubt, produced, according to the evidence, from the glucose of carbohydrates, glyceraldehyde being first formed and then reduced to glycerol.

The authors go on to discuss lucidly the digestion, absorption and oxidation of fats in the living body. The mechanism of the digestion of fats in the small intestine, where the main quantity of fat is normally digested, is fully described. In connection with fat absorption, the discovery of the solvent action of bile has (the authors state) given rise to the modern view that fat is hydrolysed to fatty acids and glycerol in the intestine, and that the fatty acids are partly absorbed as soaps and partly as fatty acids dissolved in bile. Fat appears to be hydrolysed, prior to absorption, so that it may be reconstituted into different glycerides, producing a specific fat, and not merely one like that derived from the food. This hydrolysis of fat certainly prevents the absorption of substances such as petroleum, which cannot supply the body's need for fat.

A careful reading of this book will show that, although much is known, the general laws of fat metabolism cannot yet be deduced from what has been learnt of the condition of the fat in the blood after food containing fat has been ingested.

Fats yield energy by their oxidation in the body, and in a most important chapter the authors lucidly explain Knoop's β-oxidation theory, and show that it is insufficient to explain completely the catabolism of fatty acids. In all probability fat is first transformed into carbohydrate before it is capable of being utilised as fuel in the muscle-contraction mechanism.

This authoritative work presents the chemistry and physiology of the fats in a form suitable for chemists as well as physiologists, and it can be thoroughly recommended. The book is well printed, is commendably free from typographical errors, and the price is reasonable. ARNOLD R. TANKARD.

THE EXTRA PHARMACOPŒIA. Revised by W. H. MARTINDALE, Ph.D., etc., and W. WYNN WESTCOTT, M.B., etc. Eighteenth Edition. Second volume. Pp. xlii. +728. London: H. K. Lewis & Co., Ltd. 1925. Price 20s. net.

The second volume of this well-known work has become as firmly established in the estimation of chemists and medical men as the original work. The editors quite justifiably claim that the auxiliary volume is a means whereby they can

supplement the information contained in the monographs of the first volume, and in this way preserve it from becoming stale before its re-issue. This is what they have done in this instance, as may be seen upon reference to alcohol (mineralised methylated spirit and isopropyl alcohol), insulin, organic antimony compounds, carbon tetrachloride, etc.

The large amount of data available for analytical and bacteriological investigation makes the work valuable to the chemist, inasmuch as it concerns the multifarious substances comprised within the materia medica upon which information is scattered in periodicals and reports not easily accessible. Everything that is germane to such investigations has been recorded by the editors. Their keen efforts to secure the latest results of all important researches is shown by the inclusion of a reference to the work of Dr. Gye and Mr. Barnard.

The new features include a considerable extension of the section on "British Spas and Climatic Health Resorts"; under the "Nutrimenta" is much new experimental evidence concerning the vitamins; the "Recognition of Organic Substances" has been recast in the form of a systematic scheme for the identification of medicinal chemical substances; and the Sections on Radium and Thorium Disintegration Products have been revised. The bacteriological notes constitute one of the most important portions of the volume; they comprise about a hundred pages. Altogether, it is the most complete epitome of the applications of chemistry to the materia medica of to-day. WILLIAM KIRKBY.

A SYSTEM OF PHYSICAL CHEMISTRY. By WILLIAM C. MC. LEWIS, Brunner Professor of Physical Chemistry, Liverpool University. Vol. II. (Fourth edition). Pp. viii. + 489. London: Longmans, Green & Co. 1925. Price 15s.

The value of this textbook as a work of reference has been enhanced by the addition of a chapter on the thermodynamic concept of activity in relation to solutions and on the interionic attraction theories of strong electrolytes. The author has condensed the essential features of the work of G. N. Lewis and Randall on the conceptions of fugacity, activity coefficient, ionic product, etc., into about 20 pages. The interionic attraction theories of Milner and Debye and Hückel have been dealt with by A. A. Noyes in a recent publication, and this is reprinted practically in full. The latter forms a very good summary of the present state of the theory.

The discussion of the Donnan theory of membrane equilibria is extended by an account of the work of Loeb on the behaviour of proteins. In various places also additions have been made of more recent investigations of the applications of thermodynamics to chemistry.

This volume is still one of the best of its kind for honours students, and is of great value as a work of reference. W. E. GARNER.

A COURSE OF METALLURGY FOR ENGINEERS. By F. C. THOMPSON, D.Met., B.Sc. Pp. vii. + 240. London: Witherby. Price 25s. net.

The author states in his preface that "The book was written primarily for engineers, but it is hoped that metallurgical students may find the very general treatment not without interest during the earlier stages of their course."

Reference is also made to the compression of matter into a reasonable compass, yet in some 300 pages of medium 8vo the following are dealt with:—(1) The General Relationship of the Ferrous Metals. (2) Steel: its Composition and Structure. (3) Ingots and Ingot defects. (4) Heat treatment of Steels. (5) The Hot and Cold working of Steel. (6) Tool and Case-hardening Steels. (7) Cast Iron. (8) Brass. (9) Bronze. (10) Aluminium alloys. (11) Bearing Metals.

The book opens with a clearly written description of the general relationship of the ferrous metals, but progress into the realms of steel serves to exemplify the difficulties encountered in the attempt to apply generalisation with compression, and it is in this direction that the author fails to do justice to his matter or himself. Much practical information is embedded in a matrix of loosely written theoretical consideration, and this feature, viewed from the standpoint of the engineer whose knowledge of metallurgy may be but elementary, must inevitably lead to confusion.

The chapters dealing with the heat-treatment of steels fall far below the preceding standard of clarity; they might be re-written with great advantage.

It would seem to the reviewer that any attempt to impart a clear conception of the mechanism of the structural changes in steel, without commencing with the fundamentals *alone*, is destined to failure.

Thus this mixture of theory and practice needs sifting—the theory being taken in simple progressive stages; for example, the early statement that "Martensite differs structurally from Austenite only in that the iron has changed from the γ to the α condition" without any previous reference to either, is predestined to puzzle the innocent reader.

This criticism may be applied in somewhat less degree to the chapter on cast-iron, for here it is of interest to note that the reader is told "It is a curious fact that pipes, etc., required to withstand severe hydraulic pressure often contain as much as 0·20 per cent. sulphur by deliberate intent." Is this desired result due to sulphur alone, or is it that a close-grained iron may often contain this percentage of sulphur without "deliberate intent"?

In his treatment of the non-ferrous metals, having regard to the space allotted, the author has been rather more successful, but, in the light of recent research, the hardening of duralumin is considered to result more from the separation of magnesium silicide than from the precipitation of $CuAl_2$, which latter the author indicates as the main cause of the phenomenon.

The micrographs are of uneven standard of quality, and in some instances could well be replaced by better examples of etching and photography.

It is to be regretted that this feature, together with the lack of clarity of style, mars the presentation of much matter which otherwise could not fail to have intense interest to engineers.

The book contains a useful and extensive bibliography.

GEO. R. THOMPSON.

COMPANION TO THE FIRST EDITION OF CHEMICAL SYNONYMS AND TRADE NAMES. By WILLIAM GARDNER. Pp. 56. London: Crosby, Lockwood & Son. 1925. Price 7s. 6d. net.

This is a supplement to the dictionary of chemical trade terms reviewed last year in THE ANALYST (1924, **49**, 208), and the general remarks then made on its value also apply to this volume. It adds some 2700 definitions to the 14,000 previously given, and, as before, these are arranged in a form easy for reference. A useful feature is that the composition of various reagents, such as that of Kastle and Meyer, is given, and in future editions the list of these might, with advantage, be extended.

The results of a "general knowledge" examination paper based on this book would be instructive. It is questionable whether many chemists would be able to define all of the following:—*trabuk, usco, uspulun, elo, hypotonin, loza, quisqueite,* to mention only a few of the trade terms taken at random from this supplementary volume.

EDITOR.

A Correction.:—THE NATURE OF ENZYME ACTION. In my review of Sir W. Bayliss's book (ANALYST, 1925, 479) the sentence on p. 480, line 6, should read:—"The main sucroclastic enzyme, so far as the brewer is concerned, is naturally maltase."

A. R. LING.

Publications Received.

INORGANIC PHYSICAL CHEMISTRY. By G. H. Cartledge. Boston, U.S.A.: Ginn & Co. Price $4·80.

PRACTICAL PHARMACOGNOSY. By T. E. Wallis. London: J. & A. Churchill. 1925. Price 7s. 6d. net.

HEXOSAMINES AND MICROPROTEINS. (Monographs on Biochemistry). By P. A. Levene. London: Longmans. 1925. Price 10s. 6d. net.

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