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The Influence of Hydrogen Ion Concentration on the Colorimetric Determination of Pyrogallol and Catechol Derivatives

By S. GLASSTONE, M.Sc., Ph.D., F.I.C.

(*Read at the Meeting, December* 3, 1924.)

Mitchell (Analyst, 1923, **48**, 2) has developed a colorimetric method for the quantitative estimation of pyrogallol tannins which depends on the production of a reddish-violet colour on the addition of a reagent containing ferrous sulphate and Rochelle salt to a very dilute solution of the tannin; the intensity of the colour produced appears to be the same for one equivalent of a pyrogallol nucleus independent of its actual state of combination. Mitchell has found this condition to hold good for gallic acid and gallotannin (tannic acid), and the author has been able to confirm his conclusions. Miss Price (*ibid.*, 1924, **49**, 361) has attempted to extend the method to the estimation of catechol derivatives, but the results have been disappointing, perhaps, as she suggested, because of the tendency of the catechol nucleus to form abnormal complex iron salts. It will be seen below, however, that other factors are involved.

The work of Mitchell and of Miss Price has been criticised (Analyst, 1924, **49**, 168) on the grounds that the reaction should have been carried out at a more or less definite hydrogen ion concentration. When one considers the fact that the addition of acid converts the violet colour produced by mixing Mitchell's reagent with a pyrogallol or catechol derivative into a pale greenish-yellow colour, whilst the addition of alkali produces an orange colour, it will be realised that this criticism may have some foundation. It therefore appeared to be of some interest to investigate the limits of hydrogen ion concentration between which it is possible to obtain the violet colour described by Mitchell, and also to determine the conditions under which the maximum colour for any substance could be produced. From the results of the experimental work described below it is seen that different substances have different hydrogen ion limits for the formation of the violet colour, and that, unless precautions are taken

to see that the conditions are such as to be well within the limits of hydrogen ion concentration for each substance, two solutions which contain equivalent amounts of pyrogallol or of catechol nucleus may not give the same intensity of colour. This appears to be the reason for the disappointing results obtained by Miss Price (*loc. cit.*), although it is shown below that her results are not so bad as would appear at first sight. It should be mentioned at the outset that the violet colour given by pyrogallol derivatives is much more intense than that obtained with catechol derivatives; the maximum colour intensities of equivalent solutions of pyrogallol and catechol have been found to be in the ratio of 2:1 (Miss Price, *loc. cit.*, p. 363, gives 8:3 as a result of direct comparison between pyrogallol and catechol, but from her figures for gallic acid and protocatechuic acid the calculated ratio is almost 2:1). It is, therefore, not quite satisfactory to compare derivatives of pyrogallol with those of catechol, and the substances in each series of derivatives should only be compared among themselves.

EXPERIMENTAL.—The object of these experiments was to determine the limits of hydrogen ion concentration between which it was possible to obtain the violet colour by adding the ferrous tartrate reagent to solutions of pyrogallol, gallic acid, tannic acid, catechol and protocatechuic acid. A small quantity (about 0·0002 grm.) of the phenolic derivative was mixed with 2 c.c. of the ferrous tartrate reagent in order to produce a distinct violet colour, and then 10 c.c. of a 10 per cent. solution of ammonium acetate were added to act as a "buffer" and so prevent any large and sudden changes in the hydrogen ion concentration. The violet-coloured solution was diluted and divided into two parts; to one part sulphuric acid was added until the violet colour was only just perceptible, and to the other sodium hydroxide solution until the mixture showed a slight orange tint. The hydrogen ion concentration of each solution was then determined by measuring the potential of a platinised platinum electrode placed in the solution, through which a stream of purified hydrogen was meanwhile made to bubble; the results have been expressed in terms of P_H. All experiments were carried out at room temperatures (about 12°–14° C.). It should be mentioned that, although phenolic bodies are known to interfere with the satisfactory working of the hydrogen electrode, yet in the solutions examined these bodies were present in such small amounts as to exert no appreciable influence on the electrode. The following results were obtained:—

Phenolic Substance.	P_H Limits.
Pyrogallol	6·5 to 10·3
Gallic acid	5·9 to 10·3
Tannic acid	4·1 to 11·1
Catechol	7·0 to 10·3
Protocatechuic acid	6·3 to 10·4

DISCUSSION.—The results show clearly that the latitude permissible in hydrogen ion concentration varies with the substance investigated. If the experiments were carried out under conditions of exact neutrality, that is at P_H 7, catechol would not give the violet colour, pyrogallol would give it slightly, but gallic and tannic acids, and probably protocatechuic acid also, would give it distinctly. Working

in the ordinary way, the ferrous sulphate solution, and also that of the phenolic body, would be acid, the Rochelle salt should be slightly alkaline, and, if tap water were used for purposes of dilution, the resulting mixture would have a P_H of about 7 to 7·5. In the case of pyrogallol derivatives the figures given above, as well as the quantitative results obtained by Mitchell (*loc. cit.*), indicate that these conditions are quite suitable for the production of the maximum violet colour, and so it is found that, even without taking any special precautions, equivalent amounts of pyrogallol, gallic and tannic acid give equal intensities of colour in Mitchell's test. When working with catechol and protocatechuic acid, however, Miss Price did not obtain satisfactory results; this is no doubt due to the fact that catechol requires a larger P_H (about 8) before its maximum colour is produced, whilst protocatechuic acid will give its maximum colour under ordinary conditions, that is with a P_H of 7 to 7·5. It is clear, therefore, that unless special precautions are taken, protocatechuic acid will give a more intense colour than an equivalent amount of catechol when Mitchell's test is applied in the ordinary way. This is actually what Miss Price has found to be the case. It has been found, however, that if the P_H value is so adjusted that catechol gives its maximum colour, it is of the same intensity as that given under maximum conditions by an equivalent amount of protocatechuic acid, and so Mitchell's ferrous tartrate test, with suitable modifications, can also be used for the quantitative estimation of the catechol nucleus. Although Miss Price compared catechol with protocatechuic acid, and catechol with catechin, she did not make any direct comparison of the acid with catechin; such a comparison, however, can be made from Miss Price's results with interesting consequences. For equal intensities of colour

the ratio $\frac{\text{catechol}}{\text{protocatechuic acid}}$ found is approx. 94:100 (Miss Price, *loc. cit.*, p. 362);

and ,, ,, $\frac{\text{catechol}}{\text{catechin}}$,, ,, ,, 100:213 (p. 362);

therefore ,, ,, $\frac{\text{protocatechuic acid}}{\text{catechin}}$ is $100\times100:213\times94=1:2$ (approx.).

The theoretical ratio for these two substances is $\frac{172}{344}=1:2$. The results show that under the conditions of Miss Price's experiments Mitchell's method was quantitative when comparing protocatechuic acid and catechin, although she did not realise this fact. It is fairly evident that at a P_H of 7 to 7·5 catechin produces its maximum colour, as also does protocatechuic acid, but, as catechol only gives its maximum at a larger P_H value, it would appear that, under the conditions of the original experiments, catechol could not be compared with the two derivatives.

We may assume, in general, that the colour changes which result from alterations in the hydrogen ion concentration are due to varying equilibria between three substances A, B and C, viz. $A \rightleftharpoons B \rightleftharpoons C$, where A is yellow in solution, B violet and C orange; decrease of hydrogen ion concentration causes the equilibria to be displaced towards the right. In each group of derivatives, *i.e.* of pyrogallol

or catechol, equivalent amounts of the B form appear to give the same intensity of colour in solution, but the actual position of the equilibrium will not necessarily be the same for each substance at any given hydrogen ion concentration, nor will the colour intensities necessarily be the same for each group. It follows, therefore, that one group may not be comparable with another, and also that the substances in one group are only comparable with one another when the same equilibrium point has been reached, that is when the ratio of B to A is the same in each case; this condition may be realised by varying the hydrogen ion concentration of the mixture of phenolic body and ferrous tartrate reagent.

It has been found that the gradual addition of dilute alkali to the slightly acid mixture of phenolic body and Mitchell's reagent first produces a faint violet colour which becomes reddish-violet and soon reaches a maximum intensity; further addition of alkali causes no alteration in the colour until the orange tint becomes evident. It thus appears that in the reaction $A \rightleftharpoons B$, above a certain P_H value, the equilibrium is displaced almost completely to the right, but that the change from B to C does not become appreciable until there is a much greater increase in the P_H value. It is clear, therefore, that comparisons between different solutions in Mitchell's test are best made under such conditions that each substance is producing its maximum intensity of colour, independent of the actual value of the hydrogen ion concentration in each case. With pyrogallol derivatives it would appear that the ordinary method of making up the test solutions and using tap water for purposes of dilution gives the conditions for maximum intensity of colour, but the present author would recommend the addition of about 5 to 10 c.c. of 10 per cent. ammonium acetate solution to the mixture of 1 c.c. of phenolic body and 2 c.c. of ferrous tartrate reagent before diluting to 100 c.c. for purposes of comparison. The ammonium acetate acts as a buffer, and the resulting solution will always have a P_H of about 7·6, provided, of course, that the reagents do not contain any considerable amount of acid or alkali. Apart from neutralising acidity, the ammonium acetate has been found to have no influence on the colour. In the case of catechol derivatives, although a P_H of 7·6 appears to be sufficient to produce a maximum colour with catechin and protocatechuic acid, it does not do so with catechol itself.* With that substance it has been found that the addition of a little alkali (dilute ammonia solution) to the ammonium acetate, so as to make the P_H about 8, will be sufficient to produce the maximum colour, and this solution may be used for catechol derivatives also. The colour is then somewhat more reddish than that obtained with pyrogallol derivatives.

* Since writing this paper the author has been able to examine, thanks to the kindness of Dr. M. Nierenstein, a number of catechol derivatives; the P_H limits for the formation of the violet or reddish-violet colour have been found to be as follows:

Iso-acacatechin from acacia catechu	6·5 to 8·9
Acacatechin from acacia catechu	6·35 11·4
Gambier catechin from cube gambier	6·3 12·0
Catechin from Chinese rhubarb	6·3 11·9
Catechin from W. Africa cacao bean	6·3 11·8

In accordance with the views expressed in this paper, it has been found that the addition of ammonium acetate alone is invariably sufficient to produce the maximum intensity of colour; in some cases, however, it is necessary to add a little alkali to produce the reddish tint which has been found to be most satisfactory for the comparison of catechol derivatives.

When dealing with a substance for which the conditions for the production of the maximum intensity of colour are not known, two methods are available for discovering these conditions; the first is to determine the P_H at which the violet colour is very faint, and to work at about one unit of P_H above this value; the second, which is much more suitable for actual practice, is to make up a series of mixtures of 1 c.c. of the solution of the phenolic body, 2 c.c. of the ferrous tartrate reagent and 5 c.c. of 10 per cent. ammonium acetate solution, and then to add different amounts of dilute ammonia (about 0·25 *N*) to each mixture. In this way the conditions for the production of the maximum colour can be readily determined. Frequently the addition of ammonia solution will not be necessary at all. If the addition of ammonium acetate alone should produce the orange colour, dilute acid must be added until it disappears and the maximum violet colour is obtained. Solutions made up in this way appear to be comparable with one another independent of the actual hydrogen ion concentration in each case.

CONCLUSION AND SUMMARY.—The limits of hydrogen ion concentration between which certain phenolic bodies yield a violet colour when treated with Mitchell's ferrous tartrate reagent have been determined; they have been found to vary from one substance to another even in the same group. The conditions under which the test may be made quantitative for the estimation of pyrogallol or catechol derivatives have been examined both theoretically and practically, and a modification of Mitchell's original method has been suggested for the determination of these phenolic bodies.

The author desires to express his thanks to Mr. C. A. Mitchell and to Mr. Alan H. Ware, for calling his attention to the problem dealt with in this paper

UNIVERSITY COLLEGE, EXETER.

The Determination of Coconut Oil and Butter Fat in Margarine.

BY G. D. ELSDON, B.Sc., F.I.C., AND PERCY SMITH.

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SOME time ago the authors were engaged in legal proceedings which turned on the amount of butter which was present in a so-called "Margarine blended with butter."

There was some difference of opinion among those engaged in the case as to the amount of butter present in the sample, and as the authors considered that there is a general tendency to over-estimate very small quantities of butter in margarine, and as this opinion was strengthened by the fact that when the formula of Bolton, Revis and Richmond (*vide infra*) was applied to the results obtained by them with their mixtures containing no butter (Table I.) small quantities of butter of the order of 0·5 per cent. were indicated, it was decided to reinvestigate the whole matter. This has been done and the results obtained are given below.

THE CORRECTION OF CRIBB AND RICHARDS.—Since the Polenske and Kirschner processes were first published many more or less useful suggestions have been made with regard to the interpretation of the results obtained by these processes, and the calculation of the amounts of butter, coconut oil and oleo-margarine present in the mixtures examined. Of these suggestions, the first really important one dealt with the Reichert and Polenske processes only, namely, that of Cribb and Richards (ANALYST, 1911, **36**, 327), whose work was extended by Arnaud and Hawley (ANALYST, 1912, **37**, 122). The main point of this work was that in the case of mixtures containing coconut oil and butter fat the Reichert and Polenske figures are not directly proportional to the amount of fat present, or, in other words, that the Reichert and Polenske values obtained by experiment ought to be subject to correction before the amounts of the fats could be calculated by direct proportion. The following formulæ were suggested for the calculation of the true Polenske and Reichert values:

$$P' = P - 0{\cdot}4 - R/10 + T,$$
$$R' = R - 0{\cdot}3 - RC - T,$$

where P′, R′, P and R are the true and observed Polenske and Reichert values, respectively, and RC is the Reichert value theoretically due to the coconut oil present, whilst T is a correction, which is 1·9 when the Polenske value is above 2·5 and becomes less when the Polenske value is below 2·5, in accordance with the curve given by Arnaud and Hawley. This correction is a very important point, and will be dealt with in detail later.

The above work mainly dealt with the determination of coconut oil, but Revis and Bolton (ANALYST, 1911, **36**, 333) and later these authors with Richmond (ANALYST, 1912, **37**, 183) also took up the work particularly in regard to the Kirschner process and the determination of small quantities of butter fat and it is largely to these authors, together with the later work of Cranfield, that we are indebted for our present knowledge of the value of the Kirschner process. As a result of a large amount of work they arrived at the formula

$$\text{Butter fat, per cent.} = \frac{K - (0{\cdot}262P^{0{\cdot}63} + 0{\cdot}09)}{0{\cdot}242},$$

which may be simplified with fairly accurate results, to

$$\text{Butter fat, per cent.} = \frac{K - (0{\cdot}1P + 0{\cdot}24)}{0{\cdot}244},$$

which means that the Kirschner figure is practically proportional to the amount of butter fat present.

These authors also dealt with the relation between the Kirschner and Polenske values for butter fat. This work has been continued by Cranfield (ANALYST, 1915, **40**, 439) and by Richmond (ANALYST, 1919, **44**, 166), who show that

$$P = 0{\cdot}26(K - 14).$$

The last author also gives the relationship between the Reichert-Meissl and Polenske values as follows:

$$0{\cdot}033R - 0{\cdot}6155 = \log 10(P - 0{\cdot}48).$$

In order to test the validity of the correction suggested by Cribb and Richards, the experimental figures given by Bolton, Revis and Richmond (*vide supra*) have been compared with the calculated values,* and the figures so obtained are set out in the following table:—

TABLE I.

Coconut Oil. Per Cent.	Process.	Percentage of Butter Fat. 0 Expt.	0 Calc.	2 Expt.	2 Calc.	5 Expt.	5 Calc.	10 Expt.	10 Calc.
0	Reichert	0·4	—	0·9	1·0	1·7	1·9	3·3	3·4
	Polenske	0·3	—	0·4	0·4	0·4	0·5	0·6	0·6
	Kirschner	0·2	—	0·8	0·7	1·5	1·4	2·7	2·6
5	Reichert	0·9	0·8	1·7	1·4	2·2	2·3	4·1	3·8
	Polenske	0·7	1·1	0·8	1·2	0·7	1·3	0·9	1·4
	Kirschner	0·2	0·3	0·7	0·8	1·3	1·5	2·9	2·7
10	Reichert	1·6	1·2	2·4	1·8	3·4	2·7	4·9	4·2
	Polenske	1·2	1·9	1·2	2·0	1·4	2·1	1·3	2·2
	Kirschner	0·3	0·4	0·9	0·9	1·6	1·6	3·0	2·8
15	Reichert	2·7	1·6	3·2	2·2	4·3	3·1	5·5	4·5
	Polenske	1·7	2·7	1·8	2·8	1·7	2·9	2·0	3·0
	Kirschner	0·4	0·5	0·9	1·0	1·7	1·7	3·0	2·9
25	Reichert	3·9	2·3	4·9	2·9	5·5	3·8	6·5	5·3
	Polenske	2·9	4·2	2·6	4·3	3·0	4·4	2·9	4·5
	Kirschner	0·5	0·7	1·2	1·2	1·9	1·9	3·1	3·1
50	Reichert	6·1	4·2	6·6	4·8	7·7	5·7	9·1	7·0
	Polenske	7·1	8·1	7·2	8·2	6·9	8·3	7·3	8·4
	Kirschner	1·1	1·1	1·6	1·6	2·3	2·3	3·4	3·5
75	Reichert	7·0	6·2	8·3	6·8	9·2	7·7	10·5	9·2
	Polenske	12·4	12·1	11·9	12·2	12·2	12·3	12·3	12·4
	Kirschner	1·5	1·5	1·9	2·0	2·6	2·7	3·7	3·9
100	Reichert	8·1	—	—	—	—	—	—	—
	Polenske	16·0	—	—	—	—	—	—	—
	Kirschner	2·0	—	—	—	—	—	—	—

On examining these figures it will be noticed that the 1·9 correction proposed by Cribb and Richards is only very approximately correct, and even so, only for proportions of coconut oil lying between 25 and 50 per cent. In order that this

* The theoretical values calculated, from the known constants of the constituents of the mixtures used, by simple proportion.

fact may be observed more clearly the differences between the observed and calculated values are set out in the following table:—

TABLE II.

Correction for Reichert and Polenske Values, B., R. & R.

Add to observed values.

Coconut oil. Per Cent.	Reichert Value. Percentage of Butter. 0	2	5	10	Coconut oil. Per Cent.	Polenske Value. Percentage of Butter. 0	2	5	10
0	0·0	0·1	0·2	0·1	0	0·0	0·0	0·1	0·0
5	−0·1	−0·3	0·1	−0·3	5	0·4	0·4	0·6	0·5
10	−0·4	−0·6	−0·7	−0·7	10	0·7	0·8	0·7	0·9
15	−1·1	−1·0	−1·2	−1·0	15	1·0	1·0	1·2	1·0
25	−1·6	−2·0	−1·7	−1·2	25	1·3	1·7	1·4	1·6
50	−1·9	−1·8	−2·0	−2·1	50	1·0	1·0	1·4	1·1
75	−0·8	−1·5	−1·5	−1·3	75	−0·3	0·3	0·1	0·1

Some time ago the authors commenced a detailed study of the Blichfeldt process (*J. Soc. Chem. Ind.*, 1910, **29**, 792) and its modifications (*ibid.*, 1919, **38**, 150T; ANALYST, 1920, **45**, 2) and for this purpose prepared a large number of mixtures of oleo-margarine, coconut oil and butter. Although, for various reasons which will be mentioned later, the study of the Blichfeldt process was not continued, the series of mixtures was examined by the Reichert-Polenske–Kirschner process. The figures obtained are given in Table III. opposite, together with the values calculated from the quantities of the various constituents present. The determinations described as "soluble" will be dealt with later. Each value has been determined in duplicate, and in every case where the first two determinations have not agreed they have been repeated until complete concordance has been obtained. In some cases as many as eight different determinations have been made on one value in order to remove all possibility of doubt as to the true figure, but in no case has the original disagreement exceeded 0·3 c.c. It follows, therefore, that, whatever value this work may have, at least no pains have been spared to make it as reliable as possible.

It is, perhaps, somewhat unfortunate that the margarine base for these mixtures had a somewhat higher Polenske value than usual, but this fact will scarcely influence the results which have been obtained, as will be seen from a study of the figures themselves.

The differences between the observed and the calculated values are tabulated below. It will be seen that, although they bear a general relationship to those obtained from the figures of Bolton, Revis and Richmond, yet the differences are not inconsiderable, and it is submitted that these latest figures show less variation among themselves than those of the others mentioned. As an example, one might point to the variations in the Reichert corrections obtained by Bolton, Revis and Richmond for mixtures containing 25 per cent. of coconut oil. With no butter,

TABLE III.

Coconut oil. Per Cent.	Process.	Percentage of Butter Fat. 0 Expt.	0 Calc.	2 Expt.	2 Calc.	4 Expt.	4 Calc.	6 Expt.	6 Calc.	8 Expt.	8 Calc.	10 Expt.	10 Calc.
0	Reichert	0·2	0·2	0·7	0·8	1·2	1·4	1·8	1·9	2·4	2·5	2·9	3·1
	Polenske	0·7	0·7	0·8	0·7	0·9	0·8	1·0	0·9	1·1	0·9	1·2	0·9
	Kirschner	0·2	0·2	0·7	0·7	1·2	1·2	1·7	1·7	2·2	2·2	2·8	2·7
	Soluble	0·2	0·2	0·7	0·7	0·8	1·2	1·4	1·7	1·9	2·2	2·2	2·7
5	Reichert	0·9	0·6	1·5	1·2	2·0	1·7	2·7	2·3	3·2	2·9	3·8	3·5
	Polenske	1·2	1·6	1·2	1·6	1·6	1·7	1·8	1·7	2·0	1·8	2·2	1·8
	Kirschner	0·3	0·3	0·7	0·8	1·2	1·3	1·7	1·8	2·2	2·3	2·6	2·8
	Soluble	0·1	0·2	0·4	0·8	1·0	1·3	1·7	1·8	2·3	2·3	2·9	2·8
10	Reichert	1·6	1·0	2·0	1·5	2·7	2·1	3·3	2·7	3·8	3·3	4·2	3·9
	Polenske	1·6	2·4	1·8	2·4	1·9	2·4	2·1	2·5	2·3	2·5	2·4	2·6
	Kirschner	0·4	0·4	0·8	0·9	1·3	1·4	1·9	1·9	2·4	2·5	2·9	2·9
	Soluble	0·5	0·3	0·8	0·8	1·5	1·3	2·2	1·8	2·9	2·3	3·3	2·8
15	Reichert	2·3	1·4	2·7	1·9	3·4	2·5	4·0	3·1	4·4	3·7	4·9	4·3
	Polenske	2·2	3·2	2·4	3·3	2·6	3·3	2·8	3·3	3·0	3·4	3·2	3·4
	Kirschner	0·5	0·5	0·9	0·9	1·4	1·5	1·9	2·0	2·5	2·5	3·1	3·0
	Soluble	0·8	0·4	1·1	0·9	1·9	1·4	2·6	1·9	3·1	2·4	3·7	2·9
20	Reichert	2·9	1·7	3·3	2·3	3·9	2·9	4·5	3·5	5·0	4·0	5·5	4·6
	Polenske	2·4	4·0	2·5	4·0	2·8	4·1	3·0	4·1	3·2	4·2	3·3	4·2
	Kirschner	0·6	0·5	1·0	1·0	1·5	1·5	2·0	2·0	2·7	2·5	3·3	3·1
	Soluble	1·1	0·4	1·6	0·9	2·2	1·4	2·9	1·9	3·6	2·4	4·2	3·0
30	Reichert	4·0	2·5	4·4	3·1	5·0	3·6	5·5	4·2	6·2	4·7	6·7	5·3
	Polenske	3·6	5·6	3·7	5·7	3·9	5·7	4·1	5·8	4·4	5·8	4·5	5·9
	Kirschner	0·8	0·7	1·3	1·2	1·8	1·7	2·3	2·2	2·8	2·7	3·3	3·2
	Soluble	1·2	0·5	1·8	1·0	2·4	1·5	3·1	2·0	3·9	2·5	4·2	3·0
40	Reichert	4·5	3·2	5·1	3·8	5·5	4·4	6·0	4·9	6·4	5·5	6·9	6·1
	Polenske	4·8	7·2	5·2	7·3	5·4	7·3	5·6	7·4	5·7	7·4	5·9	7·5
	Kirschner	1·0	0·8	1·5	1·3	2·0	1·8	2·5	2·3	3·1	2·8	3·5	3·3
	Soluble	1·2	0·6	1·8	1·1	2·5	1·6	3·2	2·1	4·0	2·6	4·7	3·1
50	Reichert	5·1	4·0	5·7	4·5	6·2	5·1	6·6	5·7	7·2	6·3	7·4	6·9
	Polenske	6·7	8·9	6·8	8·9	7·0	9·0	7·1	9·0	7·3	9·1	7·4	9·1
	Kirschner	1·2	1·0	1·5	1·5	2·0	2·0	2·5	2·5	3·1	3·0	3·7	3·5
	Soluble	1·3	0·7	2·1	1·2	2·6	1·7	3·0	2·2	3·7	2·7	3·9	3·2
60	Reichert	5·5	4·7	6·0	5·3	6·3	5·9	6·6	6·4	7·0	7·0	7·5	7·6
	Polenske	9·4	10·5	9·6	10·6	9·8	10·6	10·0	10·7	10·2	10·7	10·3	10·8
	Kirschner	1·3	1·1	1·7	1·6	2·2	2·1	2·7	2·6	3·3	3·1	3·7	3·6
	Soluble	1·1	0·8	1·6	1·3	2·0	1·8	2·3	2·3	2·8	2·8	3·4	3·3
70	Reichert	6·2	5·5	6·6	6·1	7·2	6·7	7·6	7·2	8·1	7·8	8·6	8·3
	Polenske	12·3	12·2	12·2	12·2	12·3	12·3	12·4	12·3	12·6	12·4	12·8	12·4
	Kirschner	1·3	1·2	1·7	1·7	2·2	2·2	2·7	2·7	3·2	3·2	3·8	3·7
	Soluble	1·4	0·9	1·8	1·4	2·5	1·9	2·9	2·4	3·5	2·9	3·9	3·4
80	Reichert	6·9	6·2	7·4	6·8	7·9	7·4	8·4	7·9	8·8	8·5	9·3	9·0
	Polenske	14·1	13·8	14·4	13·8	14·5	13·9	14·6	13·9	14·7	14·0	14·8	14·0
	Kirschner	1·4	1·4	1·8	1·9	2·3	2·4	2·9	2·9	3·4	3·4	3·8	3·9
	Soluble	1·4	1·0	1·9	1·5	2·5	2·0	3·0	2·5	3·5	3·0	4·1	3·5
90	Reichert	7·3	6·9	7·7	7·5	8·3	8·0	8·7	8·6	9·2	9·2	9·7	9·8
	Polenske	15·6	15·5	15·7	15·5	15·8	15·5	16·0	15·6	16·0	15·6	16·4	15·6
	Kirschner	1·5	1·5	2·1	2·0	2·6	2·5	2·8	3·0	3·2	3·5	3·7	4·1
	Soluble	1·4	1·1	1·9	1·6	2·5	2·1	3·1	2·6	3·6	3·1	4·3	3·7

Butter:—R = 29·0; P = 2·6; K = 24·8. Coconut oil:—R = 7·7; P = 17·1; K = 1·7; Soluble 1·2.

their correction is 1·6, with 2 per cent. of butter the correction is 2·0, with 5 per cent. of butter it falls to 1·7, and with 10 per cent. of butter it again falls to 1·2, whereas no such variations are observed in the case of the mixtures with 15 per cent. of coconut oil. In the case of the similar mixtures prepared by the authors no such fluctuations have been observed, and it would therefore appear that the figures based on these have a somewhat greater claim to accuracy than the former. It will be seen that the greatest corrections are required when the Polenske value varies between 2·5 and 9·0; Bolton, Revis and Richmond have only two mixtures which come within these limits, and even these are almost at the two extremes. It seems quite probable that had these workers made other mixtures with 30, 40 and 60 per cent. of coconut oil they might have obtained different results.

TABLE IV.

Corrections for Reichert and Polenske values, E. & S.

Add to observed values.

Coconut oil.	Reichert Value. Percentage of Butter.						Coconut oil	Polenske Value. Percentage of Butter.					
Per Cent.	0	2	4	6	8	10	Per Cent.	0	2	4	6	8	10
0	—	+0·1	+0·2	+0·1	+0·1	+0·2	0	—	−0·1	−0·1	−0·1	−0·2	−0·3
5	−0·3	−0·3	−0·3	−0·4	−0·3	−0·3	5	+ 0·4	+0·4	+ 0·1	−0·1	−0·2	−0·4
10	−0·6	−0·5	−0·6	−0·6	−0·5	−0·3	10	0·8	0·6	0·5	0·4	0·2	0·2
15	−0·9	−0·8	−0·9	−0·9	−0·7	−0·6	15	1·0	0·9	0·7	0·5	0·4	0·2
20	−1·2	−1·0	−1·0	−1·0	−1·0	−0·9	20	1·6	1·5	1·3	1·1	1·0	0·9
30	−1·5	−1·3	−1·4	−1·3	−1·5	−1·4	30	2·0	2·0	1·8	1·7	1·4	1·4
40	−1·3	−1·3	−1·1	−1·1	−0·9	−0·8	40	2·4	2·1	1·9	1·8	1·7	1·6
50	−1·1	−1·2	−1·1	−0·9	−0·9	−0·5	50	2·2	2·1	2·0	1·9	1·8	1·7
60	−0·8	−0·7	−0·4	−0·2	0·0	+ 0·1	60	1·1	1·0	0·8	0·7	0·5	0·5
70	−0·7	−0·5	−0·5	−0·4	−0·3	−0·3	70	−0·1	0·0	0·0	−0·1	−0·2	−0·4
80	−0·7	−0·6	−0·5	−0·5	−0·3	−0·3	80	−0·3	−0·6	−0·6	−0·7	−0·7	−0·8
90	−0·4	−0·2	−0·3	−0·1	0·0	+ 0·1	90	−0·1	−0·2	−0·3	−0·4	−0·4	−0·8

It will be noticed that the total volatile acids (the sum of the Reichert and Polenske values) do not vary much from the calculated values. This will be seen by adding together the Polenske and Reichert values and comparing them with the sum of the calculated values. It follows, therefore, that the variations observed are due, not to any great variation in the total amount of volatile acids distilled, but to the varying solubility of the Polenske acids in the acids contained in the Reichert distillate, as we are not concerned with the solubility of acids in water but their solubility in an aqueous solution of other acids.

CALCULATION OF AMOUNT OF COCONUT OIL.—The calculation of the percentage of coconut oil from the observed Reichert and Polenske values is, therefore complicated by the fact that these values are not strictly proportional to the amount of coconut oil present, but it is submitted that if a suitable correction be

taken from Table IV., on the lines first suggested by Cribb and Richards, the corrected Reichert and Polenske values then become proportional to the amount of butter and coconut oil present, and that the calculation of the amount is merely based on proportion and does not involve any complicated formula. It will be seen that the correction varies not only with the amount of coconut oil present but also with the amount of butter, so that in determining the amount of coconut oil present in a mixture by the Polenske process it is first necessary to determine the amount of butter by the Kirschner process.

As it is now most unusual for mixtures of fat to contain more than 10 per cent. of butter fat, it has not been considered worth while to continue these mixtures above 10 per cent. of butter. The authors agree with Bolton, Revis and Richmond that the Kirschner value is directly proportional to the amount of butter present; the calculated and observed values of this figure nearly always agreeing to 0·1 which is not outside the possible experimental error. The percentage of butter fat may be calculated (as a first approximation) from the Kirschner value in the following way:—

$$\text{Per cent. butter fat} = \frac{K - 0{\cdot}2 - P/10}{23{\cdot}5},$$

where K is the observed Kirschner value, P is the observed Polenske value, and 23·5 the average Kirschner value for butter fat. It will be seen from a study of Table III. that the term P/10 is not accurate, and that it should vary both with the Polenske value and with the Kirschner value. To give these two points their full mathematical significance would, however, be to attempt to carry the interpretation of the results beyond the experimental accuracy of the process, and the following simple equations will give the percentage of butter fat with a near approach to accuracy.

Polenske Values.	Equation.
Less than 2	$\frac{K - 0{\cdot}3}{0{\cdot}235}$
2·0— 4·5	$\frac{K - P/6 - 0{\cdot}2}{0{\cdot}235}$
5·0— 7·0	$\frac{K - P/6 - 0{\cdot}1}{0{\cdot}235}$
7·0— 9·0	$\frac{K - P/7 - 0{\cdot}1}{0{\cdot}235}$
9·0—10·0	$\frac{K - P/8 - 0{\cdot}1}{0{\cdot}235}$
10·0—12·0	$\frac{K - P/10 - 0{\cdot}1}{0{\cdot}235}$
12·0—17·0	$\frac{K - P/10}{0{\cdot}235}$

TABLE V.

Corrections for Observed Reichert and Polenske Values.

POLENSKE VALUES.				REICHERT VALUES.			
	Correction to be added.			*	Correction to be subtracted.		
Observed	Percentage of butter.			Coconut	Percentage of butter.		
value.	0	5	10	oil.	0	5	10
				Per Cent.			
1·0	0·4	−0·1	−0·2	0	0·0	0·1	0·2
1·5	0·7	0·0	−0·2	5	0·3	0·3	0·3
2·0	0·9	0·5	−0·2	10	0·6	0·5	0·3
2·5	1·5	0·6	0·2	15	0·9	0·9	0·6
3·5	2·0	1·5	0·9	20	1·2	1·0	0·9
5·0	2·4	1·8	1·5	30	1·5	1·4	1·4
7·0	2·2	2·0	1·7	40	1·3	1·1	0·8
8·0	1·7	1·6	1·3	50	1·1	1·0	0·5
9·0	1·2	1·2	0·9	60	0·6	0·4	0·0
10·5	0·5	0·7	0·5	70	0·7	0·5	0·3
12·0	0·0	0·0	−0·3	80	0·7	0·5	0·3
14·0	−0·2	−0·6	−0·6	90	0·4	0·2	0·0
16·0	−0·1	−0·3	−0·7	100	0·0	—	—

* Calculated from corrected Polenske value.

The amount of coconut oil may be calculated from the corrected Polenske value as follows:—

$$\text{Coconut oil, per cent.} = \frac{(P' - 0{\cdot}2 - 0{\cdot}03B) \times 100}{17{\cdot}6}$$

where P′ is the corrected Polenske value, 17·6 is the average Polenske value of coconut oil, and B the percentage of butter deduced from the Kirschner value. The value 0·2 which is subtracted is to allow for the Polenske value of the non-coconut base; this figure should, of course, alter with the amount of the base present, being slightly lower in the case of a higher Polenske and slightly higher, say 0·3, where the Polenske value is lower, showing little coconut oil to be present.

The amount of coconut oil present having been thus calculated, the correction for the Reichert value may be found from the table, and the corrected figure then used to determine the percentage of butter fat in the following way:—

$$\text{Butter fat, per cent.} = \frac{(R' - 0{\cdot}065C - 0{\cdot}2) \times 100}{28{\cdot}4}.$$

where R′ is the corrected Reichert value, C is the percentage of coconut oil calculated from the previous equation, and 28·4 is the average Reichert figure for butter fat. This figure can then be compared with the amount of butter calculated from the Kirschner value.

These corrections will possibly not be applicable to mixtures containing palm-kernel oil and other oils of the same family. The authors are at present carrying out experiments along these lines and hope to publish their results in the immediate future. The matter, of course, has already been dealt with by Bolton, Revis and Richmond (*vide supra*), but the figures which they give require extending. It would seem advisable that, in all cases where very small quantities of butter fat are being looked for, mixtures should be made which give identical figures in the

same apparatus as the sample in question. By this method most of the complicated factors will be cut out. It is hoped that the present work and that about to be published will give some assistance in the preparation of such mixtures.

THE BLICHFELDT PROCESS.—This process was first described in 1910 (*J. Soc. Chem. Ind.*, 1910, **29**, 792); further details were published in 1919 (*ibid*, 1919, **38**, 150T), and a modification has been described by Gilmour (ANALYST, 1920, **45**, 2). The authors have examined the original process of Blichfeldt, but they do not consider that it holds out sufficient advantages over the Reichert-Polenske-Kirschner process to justify the giving up of the latter which is now recognised as a standard process.

The method of Gilmour is ingenious and certainly, at first sight, appears to contain novel and important suggestions; it is hoped to discuss this process in full at a later date, as a modified method is now being worked out in this laboratory.

The writers have tried some experiments in the form of a modification of the Blichfeldt process. The Blichfeldt process deals with the whole of the volatile acids. It appeared possible that it might be useful to separate by means of the silver salts, the soluble and insoluble volatile acids separately, in place of dealing with them together, as is done in the Blichfeldt process. This was tried, but it was found that practically the whole of the silver salts of the Polenske fatty acids were insoluble in water, and that no useful purpose would be served by attempting their separation. The separation of the silver salts of the Reichert acids, however, is practically the Kirschner process and, as the method of Blichfeldt does not require the second distillation, it was thought that it might be a greater convenience to follow the procedure of Blichfeldt rather than that of Kirschner. This was done in the following method:—

Thirty-five c.c. of 0·1 *N* silver nitrate solution are added to the neutralised Reichert distillate, the whole transferred to a 220 c.c. flask, diluted to the mark with water and allowed to stand for one hour. After this time 200 c.c. are filtered off and titrated with 0·1 *N* ammonium thiocyanate, with iron alum as indicator. To the number of c.c. used in the titration one-tenth is added and also the value obtained in a blank experiment (usually about 0·2), and this value is subtracted from the original 35 c.c. This figure is then subjected to a further correction of one-tenth, so that it may be compared directly with the Reichert value. This final figure represents the amount of acids present of which the silver salts are insoluble under the conditions thus obtained; the soluble figure is found by subtracting this from the Reichert value. The value so obtained is the value referred to as "Soluble" in Table III.

It will be seen at once that the figures are not as good as those obtained by the Kirschner process. For small additions of butter they are not quite so responsive, and, further, there are greater differences between the observed and calculated figures than those shown by the Kirschner process. This modification of the Blichfeldt process may, however, be useful to those who object to the second distillation of the Kirschner process; it has the advantage over the Blichfeldt process

that the figure can be obtained as an extension of the Reichert-Polenske process, and also there is, of course, a considerable saving in time. A somewhat similar method has been published by van der Laan since this work was done, but his results are apparently not so good as those obtained above (*cf. J. Soc. Chem. Ind.*, 1923, **42**, 287A).

DISCUSSION.

Mr. A. MORE remarked that the author had started off to prepare certain mixtures, but did not give any evidence of the extent of variation in the results which would be obtained from mixtures of coconut oil, palm-kernel oil, neutral fat, and butter fat, which contained the same proportions of the constituents, but differed in the analytical constituents of these constituents. There appeared to be no formula that would cover all possible mixtures. In the application of a formula one could not assume that the mixture being analysed contained coconut fat, and a worker must be prepared to meet possibilities. It was true that, in the case of certain mixtures, Mr. Elsdon had made out that the Government Laboratory figures were abnormal. Various formulæ for determining butter had been devised from time to time. The Reichert or Kirschner values of the constituents, especially of the butter fat, were bound to have a great influence on the results, and in calculating the quantity of butter fat in a mixture by means of a formula devised for average fats it was necessary to consider the range of the results due to the use of butters of varying composition. "One or two per cent. depending on the butter fat used in the mixture" was the form adopted in his certificate to indicate this variation. On the face of it Mr. Elsdon's process seemed elaborate.

Dr. BERNARD DYER said that he considered that a discussion as to whether there was 1 per cent. or 2 per cent. of butter in margarine was of little moment to the man in the street, though it might be of interest as a legal disputation.

Mr. G. D. ELSDON, referring to the number of samples, said that, of the data previously worked out, there were no samples of the section between 25 and 50 per cent., and that it was between those figures that the greatest correction was required. In the 30 to 40 per cent. section the correction was large, and if only for that reason, the extended table would be useful. They all realised, of course, that there was no such thing as a standard butter; one must assume average figures. If one was going to assume the presence of between 1 and 2 per cent. of butter fat in a mixture, one of these figures was a long way from an average. Taking an average Kirschner value of 24 for the 2 per cent. figure, the 1 per cent. figure would require a Kirscher value of 12, which would be almost impossibly low.

The Fat of Goats' Butter.

BY H. DROOP RICHMOND, F.I.C.

IN their note published in the ANALYST (1924, **49**, 509), Messrs. Knowles and Urquhart give a few results of the composition of goats' butter, and on this base arguments, first showing that the sale of goats' butter as "butter" is possible, and second, that by the use of accepted methods, and especially by the use of

formulæ given in my *Dairy Chemistry*, goats' butter might be condemned as adulterated with coconut oil.

The figures given by these authors for the percentage of coconut oil, as calculated by the formula given by me, are hopelessly wrong, and are due to misquoting the formula as I give it on p. 249 of *Dairy Chemistry* (*cf.* ANALYST, **1919, 44,** 167). I wrote the formulæ as

"$C = \frac{P - P'}{14{\cdot}4} \times 100.$

C = percentage of coconut oil.

P = Polenske figure.

P′ = mean Polenske figure from the table (calculated for a figure) equal to the Reichert-Wollny figure found + half the Polenske figure found."

The authors leave out the words in brackets, materially altering the sense.

An illustration with their No. 1 sample will show the difference.

R.-W.=27·66; Polenske 8·65.

I calculate thus P′=mean Polenske figure for $(27{\cdot}66 + \frac{8{\cdot}65}{2} =) 31{\cdot}98 = 3{\cdot}2$,

$$\frac{8{\cdot}65 - 3{\cdot}2}{14{\cdot}4} \times 100 = 37{\cdot}8.$$

They have evidently calculated

P′=mean Polenske figure for $27{\cdot}66 = 2{\cdot}52 + \frac{8{\cdot}65}{2} = 6{\cdot}84$,

$$\frac{8{\cdot}65 - 6{\cdot}84}{14{\cdot}4} \times 100 = 12{\cdot}65.$$

In the table below I give in the first column the actual apparent percentage of coconut oil given by my formula $C = \frac{P - P'}{14{\cdot}4} \times 100$. Second, the Reichert-Wollny figure which would be given by this percentage of coconut oil, third, the remainder of the Reichert-Wollny figure which is due to the butter present, and fourth, the calculated Reichert-Wollny figure of the original butters.

	Per Cent. Coconut oil.	R.-W. value of this.	R.-W. value due to butter.	R.-W. value of the original butter.
1.	37·8	3·0	24·66	39·5
2.	33·6	2·7	22·38	33·7
3.	31·8	2·54	25·23	37·0
4.	27·7	2·22	25·00	34·6
5.	40·2	3·2	22·76	37·8
6.	20·3	1·62	22·85	28·6
7.	33·2	2·66	23·41	35·0
8.	15·1	1·21	25·68	30·3
9.	36·5	2·92	23·95	37·7

It is seen that, in the case of seven out of nine samples, the calculated Reichert-Wollny figures are so absurdly high as to indicate to the analyst that he is not dealing with an ordinary mixture of butter and coconut oil, but with some abnormal product to which the formula is not applicable. The iodine values calculated for the original butters in a similar manner are very high in relation to the Reichert-Wollny figures calculated. Further, if the analyst turns to the table given by Messrs. Knowles and Urquhart on page 511, and compares the Reichert-Wollny and Kirschner values, it will be seen that the Kirschner figures are extraordinarily low for the Reichert-Wollny figures for butter.

It is to be regretted that the authors of this note have devoted so much of their paper to drawing attention to the fact that goats' butter might be condemned as containing coconut oil if sold as butter, and so little to the sufficiently marked difference between genuine goats' butter and adulterated cows' butter which might form the basis of a method of distinguishing them.

I may add that I wrote my formulæ in *Dairy Chemistry* with the full knowledge that they would not apply to the fat of mammals other than the cows, including goats' butter, and I have no reason to think that this very rare article of commerce need cause any great modification of existing methods of detecting adulteration. As Messrs. Knowles and Urquhart have quoted so much from my *Dairy Chemistry*, I would like to quote from p. 1: "The expressions 'milk,' 'butter,' etc., must be taken as applying to the products derived from the cow, unless described to the contrary,"

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.

ANALYTICAL NOTES ON TWO SAMPLES OF OLD BUTTER.*

Two samples of tinned butter, at least twenty years old, which had been kept continuously in the offices of the Dairy Commissioner, Ottawa, exposed summer and winter to room temperatures, have recently been analysed by the Division of Chemistry of the Dominion Experimental Farms.

Examination on September 16th showed that both tins were in good condition, hermetically sealed and tight. The excellent condition of the labels indicated that the tins had not been exposed to damp air. There was no evidence of "swells" or other damage to the containers.

No. 1, labelled "Pierre de Bacourt, Dorchester Que. Extra Finest Canadian Butter," had been packed dry in a round tin. On opening the tin the butter was found to be soft with no texture; in appearance it was oleaginous and curdled and of a light pale yellow colour. The odour was slightly rancid, but largely

* *Cf.* ANALYST, 1907, **32**, 80.

yeasty and not very unpleasant. The taste was very disagreeable, and the butter was non-edible.

No. 2, labelled "Pure Canadian Butter" (Canadian Government Dairy Station, Calgary, Alta.) had been packed in brine in a rectangular tin, in two 1 pound portions, each wrapped in parchment paper. There was no liquid on opening the tin; the brine, as such, had disappeared. The butter possessed a very strong rancid odour. It was very soft, with a curdled appearance and had no texture. The colour was pale yellow with white spots or patches. It was absolutely non-edible.

ANALYSIS OF BUTTERS.

	No. 1. Per Cent.	No. 2. Per Cent.
Water	14·87	33·60
Fat	79·73	57·24
Curd	1·42	3·08
Ash*	3·96	6·11
	99·98	100·03
* Including salt ..	3·80	5·94

ANALYSIS OF BUTTER FATS.

	No. 1.	No. 2.
Butyro-refractometer reading at 25° C. ..	48·98°	43·44°
Iodine value	30·70	31·62
Reichert-Meissl value	31·10	25·45
Polenske value	2·03	2·75
Acid value	45·32	121·3
Percentage of free acid as oleic	22·45	60·08
Percentage of soluble fatty acids as butyric ..	5·25	4·11
Insoluble fatty acids	84·93	86·92
Saponification value	227·6	225·8

It will be seen that the refractometer readings are in each case decidedly lower than would be obtained with normal butters; this is particularly true of Butter No. 2 which had been packed in brine. The lowering of refractive indices is explained by the abnormal content of free fatty acids.

The iodine numbers are normal. The lower Reichert-Meissl value and the higher Polenske value for the fat of No. 2 would seem to indicate the conversion in this sample of the soluble volatile acids into insoluble volatile acids, due to the presence of a large amount of water. This deduction is further supported by the figures obtained for soluble and insoluble fatty acids.

The acid value in both samples is very high, especially that of No. 2, indicating the effect of hydrolysis of the glycerides consequent upon the large amount of water present. The saponification values are normal.

FRANK T. SHUTT.

DOMINION OF CANADA,
DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY.

LOSS OF STRENGTH OF SPIRIT KEPT IN OPEN BOTTLES.

IN 1916 the defence that deficiency of spirit was due to "the bottle having been left open" was raised in cases when proceedings were taken for selling potable spirit below standard strength (not exceeding 25 degrees under proof according to the legislation of the Union of South Africa).

During the summers of 1916–17 and 1917–18 opportunity was taken to test the point. During the time of the observations the prevailing temperature of the laboratory frequently rose to 33° C. in the daytime, and at night it seldom fell below 8° C.

In the first place two ordinary spirit bottles (about 27 fl. ozs.) were filled to the extent of about four-fifths with spirit 29·3 degrees under proof. One bottle was left uncorked, and the other was corked with a used cork inserted just as it would be if the bottle were in use. The bottles were kept in a cupboard and the spirits were tested after 11, 29 and 67 days. It was found that the spirit in the corked bottle had lost nothing in alcoholic strength when tested after 67 days, in spite of the bottle having been opened and the strength of the spirit determined (by specific gravity) on the 11th and 29th days. The spirit in the open bottle was 30·7 degrees under proof on the 11th day, 31·7 degrees under proof on the 29th day, and 34·05 degrees under proof after 67 days. The loss from the open bottle was, therefore, 4·75 degrees of proof in 67 days, or one degree of proof in about 14 days, or about 0·07 degree of proof per day.

At the beginning of the summer of 1917–18 four ordinary spirit bottles were filled to the extent of about four-fifths with spirit (brandy) 23·6 degrees under proof. Two of the bottles were left open and two were corked with used corks. An open bottle and a corked bottle were placed on a shelf on the north wall (exposed to the sun) of the laboratory and an open bottle and a corked bottle were placed on a shelf on the south wall (shaded from the sun) of the laboratory. All the bottles were shaded from direct sunlight. Specific gravity determinations of the spirits were made at intervals of 2 or 3 days for a total period of 93 days (30th October, 1917, to 31st January, 1918). On each occasion only such quantity of spirit was taken from the bottle as was required for the determination and the quantity was returned to the bottle immediately. No loss of strength was suffered by the spirits in the corked bottles in spite of their having been opened 38 times before the final determination on the 93rd day. The following table shows the progressive loss of strength of the spirits in the open bottles, the prevailing temperatures being of the order already stated; the figures represent degrees under proof:

Day.	North Wall.	South Wall.	Day.	North Wall.	South Wall.	Day.	North Wall.	South Wall.
0	23·6	23·6	34	27·3	26·6	64	28·9	27·9
4	24·3	24·1	36	27·4	26·6	66	29·1	28·2
6	24·9	24·4	38	27·6	26·7	69	29·25	28·2
8	25·0	24·6	41	27·7	26·85	71	29·35	28·25
10	25·25	24·9	43	27·8	26·95	73	29·6	28·45
13	25·5	25·2	45	27·9	26·95	76	29·8	28·6
15	25·7	25·4	48	28·0	27·1	78	29·9	28·7
17	25·8	25·5	50	28·2	27·3	80	30·25	28·8
20	25·9	25·6	52	28·25	27·4	83	30·45	28·8
22	26·0	25·8	55	28·45	27·5	85	30·7	28·9
24	26·2	25·9	57	28·6	27·6	87	31·05	29·1
27	26·5	26·1	59	28·6	27·7	90	31·25	29·35
29	26·95	26·4	62	28·8	27·8	93	31·6	29·45
31	27·1	26·5						

The results show that the spirit kept in the open bottle at the warmer (north wall) of the two places lost 8 degrees of proof in 93 days which is equivalent to a loss of one degree of proof in between 11 and 12 days, or to a loss of about 0·09 degree of proof per day. The spirit kept at the cooler (south wall) place lost 5·85 degrees of proof in 93 days, which is equivalent to a loss of one degree of proof in about 16 days, or to a loss of about 0·06 degree of proof per day.

In spite of the higher prevailing temperature at which the observations were made it is noteworthy that the losses sustained were appreciably lower than those recorded by H. Lowe (ANALYST, 1924, **49**, 135). The rather higher loss (0·15 degree of proof per day) found by Lowe is probably to be attributed to stronger diffusion by air convection current over the surface of the spirit in spite of the loose cardboard cover, and, in a measure, to the greater surface exposed in a flask than in a bottle.

J. McCRAE.
J. HAWKEN.

GOVERNMENT CHEMICAL LABORATORIES,
JOHANNESBURG, TRANSVAAL.

PREPARATION OF NESSLER'S SOLUTION.

THE sensitiveness of Nessler's solution varies considerably, and usually it increases with age. By the use of the following directions a solution which is very sensitive immediately after preparation can be made.

Dissolve 17·5 grms. of potassium iodide in 100 c.c. of water; next dissolve 15 grms. (a slight excess) of mercuric chloride in 300 c.c. of water, and mix the two solutions. Wash thoroughly by decantation the heavy precipitate that forms, and dissolve it in a solution of 17·5 grms. of potassium iodide in 100 c.c. of water, add a few drops of mercuric chloride solution till a red precipitate, insoluble on shaking, is produced, and dilute to about 500 c.c. Cool the beaker in ice water, and mix the liquid with so much of a 50 per cent. sodium hydroxide solution (previously diluted with 200 c.c. of water and cooled in ice water) as is equal to 105 grms. of sodium hydroxide. Cool well during mixing, and make up to 1 litre. The solution is left to settle and the clear portion decanted for use.

H. DROOP RICHMOND.

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 OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1924.

OF the 1296 samples submitted during the quarter, 1113 were analysed under the Sale of Food and Drugs Acts, 1011 being bought informally (38 adulterated), and 102 being bought under the provisions of the Act (4 adulterated).

MILK. The total number of samples examined was 556, of which 454 were informal samples. Thirty-four of the informal and 4 of the formal samples were adulterated.

CREAM.—Three of 15 informal samples of cream contained boric acid (0·21 to 0·32 per cent.) without a declaratory label; the vendors were cautioned.

Four of the 19 informal samples of preserved cream did not comply with the regulations. One sample, in addition to the declaratory label, was marked "Thick Rich Cream—and Devonshire Clotted Cream Daily." The "and" was very small, so that the statement about Devonshire cream, apparently referred to the contents of the receptacle. Such a label may be legal, but it is certainly misleading.

CHEESE.—Two sample of *cream cheese* contained 70·6 and 72·5 per cent. of fat respectively; about 95 per cent. of the dry solids was fat. A sample of *milk cheese* contained 17·8 per cent. of fat (about 49 per cent. of the dry solids).

FLOUR.—Four of the 28 samples of flour and 4 of the 10 samples of self-raising flour contained persulphate or peroxide. Pending the report of the Government Committee, they were passed as genuine.

JAM.—A complaint that a bramble and apple jam contained an excess of seeds was found to be due to an accumulation of a large proportion of the seeds in the upper part of the jam.

ZINC OINTMENT.—One of 4 informal samples, while containing the right proportion of zinc oxide, had not been prepared with benzoated lard, although marked "B.P."

HEALTH DEPARTMENT.—Of the 62 samples examined, 28 were milk. One of the 16 samples taken under the Rag Flock Act contained 80 parts of soluble chlorine per 100,000 (limit 30 parts); it contained wood shavings, straw and grass. The vendor was cautioned.

J. F. LIVERSEEGE.

Legal Notes.

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

FALSE TRADE DESCRIPTION.

ALLARD *v.* SELFRIDGE AND CO., LTD.

AN appeal was heard in the High Court on November 10th, 1924, from a decision of Mr. Mead, the Marlborough Street Magistrate, who had dismissed an information against Messrs. Selfridge and Co. for selling goods to which a false trade description had been applied. The facts, which were not in dispute, were that the respondents had sold as silk some stockings which were made of artificial silk. Their buyer had bought these from a merchant in a small way of business, and had not applied any tests which would have shown that they were not silk. The Magistrate had held that the buyer had acted innocently and in good faith, and that the defendants, who were responsible for their buyer, had the benefit of her innocence, this being, in his view, in accordance with the finding in *Christie, Manson and Woods* v. *Cooper* (1900; 2 Q.B. 522).

Section 2 (2) of the Merchandise Marks Act, 1887, provides that:—

> Every person who sells . . . any goods . . . to which any false trade description is applied . . . shall, unless he proves—
>
> (*a*) that, having taken all reasonable precautions against committing an offience against this Act, he had at the time of the commission of the alleged offence no reason to suspect the genuineness of the . . . trade description; and
>
> (*b*) that on demand made by or on behalf of the prosecutor, he gave all the information in his power with respect to the persons from whom he obtained such goods or things; or
>
> (*c*) that otherwise he had acted innocently;
>
> be guilty of an offence against this Act.

Sir Duncan Kerly, K.C., for the appellant, said that, putting his argument in algebraical form, it should be a defence to prove either $a+b$ or c, but that the defendant could not prove $a+b-x$ and say that that was "c." In his contention c was intended to cover pure accident, such as the seller affixing a wrong lable or putting his hand into the wrong box. He submitted that the Magistrate was wrong in his decision for the following reasons:—(1) He had put the onus in the wrong place, deciding that the prosecution must show an intent to defraud; (2) he had thought that c must be complied with when there was no intent to defraud; (3) he had thought that even if the defence fall short of $a+b$, it was possible to prove c in a case to which $a+b$ were applicable and were relied upon for the defence; (4) because the Act threw on the seller the onus of giving a true description subject only to the defences of the section.

Mr. Hawke, K.C., for the respondent, contended that it was an answer to a charge under this section for the defendant to prove that he acted innocently, otherwise than by proving $a+b$. The Magistrate, in holding that the buyer had acted innocently, had found that there was no *mens rea*.

The Lord Chief Justice, in giving judgment, said that the Magistrate had decided the case upon the view that *mens rea* for the purpose of this statute meant an intent to defraud. The scheme of the Act was that once the forbidden act was proved, the offence was complete unless the accused proved one of a number of defences. These were of a twofold nature. He might prove (*a*) and (*b*) which were joined by the conjunction "and," or he might prove (*c*), and the words of (*c*) were not "that he has acted innocently," but "that otherwise he has acted innocently." The dichotomy was complete. But if, in seeking to prove (*a*) and (*b*) he failed to prove them apart, he could not have recourse to (*c*); to hold otherwise would involve two consequences, which were absurd—(1) that (*a*) and (*b*) were inserted merely as an illustration; (2) that the word "otherwise" must be omitted. In other words, if a seller sought to excuse himself on the ground that he had no reason to suspect the genuineness of the trade description, he must base that defence on having taken all reasonable precautions. What was done was an attempt to prove that not having taken all reasonable precautions, the respondents had no reason to suspect the genuineness of the trade description, which seemed to be nonsense.

The judgments in the case of *Christie, Manson and Woods* v. *Cooper* ought to be read strictly in conjunction with the facts of that case, and not extended. There the sellers were not putting forward an untrue trade mark as a true mark; although they could not erase it physically, they were doing their utmost to make it of no effect. A comparison of the decision in that case with that in *Stone* v. *Burn* (1911; 1 K.B., 927) seemed to make clear the reasons for the decision.

In the present case the magistrate seemed to have fallen into two errors. Apparently he had overlooked the word "otherwise" in the Sections 2 (2), and he seemed to have thought that a defence could be established by proving a part of

what came under (*a*). Secondly, he seemed to have thought that *mens rea* for the purpose of this statute meant an intention to cheat and defraud. It meant an intention to infringe the Act of Parliament. It was not necessary to inquire into what was meant by (*c*). Where the words "acted innocently" were qualified by the word "otherwise" a defence could not be established by proving a portion of (*a*). The appeal must be allowed, and the case remitted to the Magistrate to convict.

Mr. Justice Shearman and Mr. Justice Salter gave judgments to the same effect.

METHYLATED SPIRIT AS CHERRY BRANDY.

ON November 29th a Stepney tradesman, described as a watchmaker and mineral water manufacturer, was charged at the instance of the Board of Customs and Excise at Old Street Police Court with having prepared beverages named "Kummel" and "Cherry brandy" from methylated spirit, and also, not being an authorised methylator, with being in possession of methylated spirits obtained from a person not authorised to supply them. The firm that supplied him was also summoned for selling methylated spirits without authority or license, and the wholesale retailers were summoned for selling methylated spirits other than mineralised methylated spirits.

Counsel for the firm of licensed methylators said that they had received orders for "methylated finish," and that for some unknown reason pure spirit had been supplied. The firm was fined £40 with eight guineas costs, and one of its directors was fined £20 with four guineas costs for aiding and abetting in the sale.

The tradesman, on whose premises bottles of "Cherry brandy" and "Kummel," made up for the holidays, had been found, was fined £160 with nine guineas costs, and the Magistrate (Mr. Clarke Hall) said that he was sorry he had no power to recommend him for deportation.

IMPEDING AN INSPECTOR.

ON December 31 a pharmacist was summoned, at Old Street Police Court, by the Bethnal Green Borough Council for having obstructed one of their inspectors under the Food and Drugs Acts in the course of his duties, and also for impeding the inspector in the course of his duties under the Acts.

Evidence was given that the inspector had, through his agent, obtained a bottle of medicine to be tested as to the accuracy of the dispensing of the prescription. This had been divided in the usual way, and no complaint as to the sample was alleged. On leaving the dispensary, the inspector went to another shop, giving his agent a prescription on the way. The defendant then entered the same shop and, according to the evidence of the inspector's agent, there was a whispered conversation between the two pharmacists. The inspector spoke to the defendant as he left the shop and said that, in his opinion, he had gone there with the object of giving a warning, and that he should report the matter to the medical officer and to the Insurance Commissioners.

Mr. Glyn Jones, for the defence, contended that a warning was not an obstruction or an impediment, and submitted that intentional misconduct, of which there was no evidence, was essential for the offence.

The Magistrate (Mr. Clarke Hall) considered that the defendant's action was both impeding and obstructing, within the meaning of Act. It was the inspector's

duty to take samples, and he had gone to the shop to take them under such circumstances as those under which an ordinary customer would be supplied. Any action on the part of another person that would prevent that was, in his opinion, impeding the inspector in the course of his duties. Although he had no doubt that he was right, he was prepared to state a case, if required. If he were wrong, all the good, not only of the Food and Drugs Acts, but also of other Acts, would be destroyed. He would not inflict any penalty.

The summons for obstruction was withdrawn, and the defendant was ordered to pay five guineas costs on the other charge—impeding the inspector.

MIXING OF SAMPLES.

ON December 3rd a shop-keeper was summoned at Woolwich for having sold camphorated oil which contained mineral oil and was deficient in camphor. Evidence was given by an agent of the inspector that she had purchased two bottles of the preparation and had handed them to the inspector. The inspector said that, as the bottles were small, he had mixed their contents for the purpose of sampling.

The solicitor for the defence contended that the contents of the two bottles, which were sent out by different manufacturers and were differently described, should not have been mixed.

The Magistrate (Mr. Ratcliffe Cousins) agreed that this should not have been done, and dismissed the case with 2 guineas costs against the Borough Council.

Department of Scientific and Industrial Research.

REPORT OF THE FOOD INVESTIGATION BOARD FOR THE YEAR 1923.*

THE most important event of the year was the scientific expedition to Australia to study the conditions of apple transport to this country, particularly the ventilation and temperature of ships' holds, and the effect upon rate of ripening, formation of "brown heart," etc. The detailed results of the work are being published in separate reports, but it may be noted that four ships, representative of different systems of refrigeration, were fitted with distant-reading thermometers, electrical carbon dioxide indicators, and sampling tubes for gas analysis, and one of the most striking facts revealed was the extent to which accidental ventilation may occur in the ships' holds. Details are given of the work carried out during the year by the several Committees, represented by Sections I. to VII.

SECTION I. THEORY OF FREEZING.—The work on eggs has been continued, and it has been found that the yolk may be preserved without change, either by not allowing the temperature to fall below $-6°$ C., as the irreversible change in consistence appears to be due to change in the nature of the coagulation and to occur between a temperature of $-6°$ C. and some lower limit, or by hurrying over this critical interval sufficiently rapidly. In order to begin to elucidate these complicated changes a study was made of the way water is held by simpler colloid systems such as gelatine.

SECTION II. FISH PRESERVATION COMMITTEE.—The preservative action of ice containing small quantities of disinfectant was not very satisfactory in its results,

* Copies of the Report can be obtained from H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 3s. net.

owing to the disinfectant impregnating the flesh. The difference found between the autolysis of mutton and beef rapidly frozen in brine and in air, was found to be similar in the case of cod, and due to the fact that in the fluid set free in the case of the slowly frozen muscle (or the "drip") chemical changes occur more rapidly than in the remaining tissue.

SECTION III. MEAT COMMITTEE.—Work has been continued on the succinic acid and carbohydrate metabolism of muscle. The presence of a factor in the pancreas (destroyed at 37° C.) that inhibits the formation of lactic acid in chopped muscle has been proved. The first series of studies on the growth of *Staphylococcus aureus* in meat extract has been completed, and problems connected with eggs, such as loss of weight on storage, and handling, have been investigated.

SECTION IV. ENGINEERING COMMITTEE.—The Australian Expedition necessitated the construction of a series of special instruments, and particular attention was devoted to the design of direct reading wet and dry hygrometers, micrometer hair hygrometers, absorption apparatus for the determination of carbon dioxide, apparatus for observing the ripening process in apples, temperature-measuring instruments, waterproof junction box, and a mercury in steel recording thermometer. Among the materials tested for thermal conductivity may be mentioned a hard form of expanded rubber with a surface resembling ebonite and a cellular interior. Work on the moisture content of materials in equilibrium with air of various humidities demonstrated the very slight capacity of slag wool for absorbing water vapour. When used as a heat insulator, however, this material may become coated with ice owing to the penetration of warm humid air into the insulation, which may occur in any granular or fibrous material.

SECTION V. FRUIT AND VEGETABLE COMMITTEE.—The work of this Committee is now very wide and varied, and it is only possible to indicate its scope. Great importance is attached to the commercial cold storage trials and general conclusions on three seasons' trials are now available. The knowledge gained on the Australian Expedition is being used in the continued investigation of the conditions of temperature and humidity in cold stores for this country. Work at the Low Temperature Research Station at Cambridge includes the study of temperature and metabolic balance in living plant tissues, respiration of apples, oxidases, and the physiology of fungal infection. At the Imperial College the following apple problems have been studied: acidity and nitrogen content in relation to storage life, concentration of sugars and the pectin content during storage and parasitism. The work on the chemistry of the cell wall has also been continued.

SECTION VI. OILS AND FATS COMMITTEE.—The examination of the series of glycerol methyl esters has been completed, so that the constitution of any mixed glyceride can now be determined, and a paper suggesting corrections in the published chemistry of the dichlorhydrins of glycerol is in preparation. Glycerol has been found to show little tendency to form either β- or γ-glucosides, and Fischer's glyceryl glucoside has been shown to be the butyleneoxide form. An investigation into the constitution of glycogen has been started. In the course of the continued work on the formation of fat by yeasts, directly extracted fat was found to contain the growth factor, and since the yeast was grown in the absence of direct sunlight it appears probable that the direct synthesis of the vitamin is being dealt with.

SECTION VII. CANNED FOOD COMMITTEE.—Work at Cambridge indicates that the determination of such final products of degradation as volatile organic bases, total acid radicles and amino acids gives some measure of the extent of ageing of fish under ordinary conditions of storage.

The Report is illustrated by numerous plates, charts and graphs. D. G. H.

New South Wales.

DEPARTMENT OF PUBLIC HEALTH.

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1923.

THE system for the control of the sale of food and drugs in New South Wales differs materially from that in force in Great Britain, practically the whole of the chemical work being carried out in the Government Laboratory. The Public Analysts in this State look to the general public for their practice, whilst analysts in the employ of the Government are not allowed to undertake private practice.

During the year 18,197 samples were analysed, of which number 16,183 were submitted under the regulations of the Pure Food Act, 1908, and 2014 in connection with the public services of the State.

MILK.—Of the food samples, 12,906 were milks from the metropolitan area, and 2496 were milks from country districts. In Sydney and suburbs 3·6 per cent. of the milk samples were adulterated, and of the country milks 9·1 per cent. did not comply with the standard. With the exception of 30 samples that contained formalin and 3 samples coloured with annatto, the adulterations were deficiencies in fat and in solids-not-fat. The percentage of adulteration in food and drugs other than milk was 29·4.

BRINE.—Fifty-two samples of brine, intended for use in salting meat, were examined, and 17 of these were condemned as unfit for the purpose. The figures obtained for the amounts of dissolved organic matter did not furnish a true indication of the degree of impurity, and the best practical test was found to be that of odour, which apparently varied with the age of the sample. It seems reasonable to demand that only brine not previously in use should be used for salting brine, or, if this is impracticable, that no brine should be allowed to remain in use for more than a day.

BUTTER.—A number of New Zealand butters failed to reach the standard for milk fat prescribed in this State. The deficiency was not great, and may be accounted for by the fact that the New Zealand standard requires only 80 per cent. of fat, as compared with 82 per cent. demanded by New South Wales.

Three samples of butter preservative composed of a mixture of borax and boric acid, contained 20, 50 and 120 parts per million of arsenic, respectively.

COFFEE.—One sample of coffee essence was over 50 per cent. deficient in caffeine. In connection with the general standard for coffee, a suggestion has been put forward to alter the regulation, which at present permits the use only of the seed of *Coffea Arabica* or *Coffea Liberica*, to include other genuine beans, particularly the *Robusta* bean. In order to ascertain whether this bean would conform with the requirements of the present standard as regards composition, samples were procured and analyses made. Six samples of the green bean were found to possess a fat content ranging from 9·5 to 10·8 per cent. (average 10·2 per cent.), and a caffeine content varying between 1·7 and 1·9 per cent. (average 1·78 per cent.). Eight samples of the roasted bean (5 whole and 3 ground) had a fat content of from 10·2 to 11·7 per cent. (average 10·8 per cent.), and a caffeine content ranging from 1·8 to 2·1 per cent. (average 1·9 per cent.). As a result of this examination it is apparent that, in comparison with published analyses of other varieties of the coffee bean, the *Robusta* bean has a high caffeine content, while its composition generally conforms to the N.S.W. standard for genuine coffee.

TEA.—Three samples of tea contained small quantities of arsenic, and a number of samples labelled "Golden Tips" contained only very small amounts, or, in some cases, no "golden tips."

GELATIN.—Three samples of powdered gelatin each contained 1/50 grain of arsenic per lb. The N.S.W. standard does not allow any metallic contamination of gelatin.

SAUSAGES.—Twenty-five samples were adulterated by the excessive use of the permitted preservative. Three samples of Devon sausage contained an excess of salt petre, and one sample of meat had been illegally preserved with formalin.

DRUGS.—Fourteen samples of acetyl salicylic acid tablets contained free salicylic acid, which is contrary to the B.P.

Artificial Carlsbad salts were found to consist of sodium sulphate instead of a mixture of salts.

A "non-poisonous" chlorodyne did not contain morphine (as prescribed by the Codex), but the presence of chloroform rendered the statement false and misleading.

CRIMINAL INVESTIGATION.—The Police submitted 135 exhibits in connection with criminal investigations. These included foods for examination as to the presence of poisonous or harmful ingredients, some of which gave negative results on analysis, whilst in other cases strychnine, arsenic, caustic soda, and ground glass, respectively, were found to be present. Ten samples of pills and medicines used for abortifacient purposes were examined, and exhibits were also submitted in connection with incendiary outbreaks, counterfeit coining, opium smoking, cocaine selling, illegal sale of spirituous liquors, laying of poison baits, sheep stealing (alteration of brands), quack medicine selling, etc.

Forty-four exhibits of human viscera were examined in connection with coroners' inquests. The poisons responsible for death consisted of cyanide, strychnine, arsenic, veronal, morphine, and opium. In one case the death of a child was due to the consumption of alophen pills, the viscera being found to contain phenolphthalein, aloin, and traces of strychnine and atropine. In another case, a woman's death was caused by the mistaken use of arsenic for baking powder, due to the fact that the arsenic was put in a tin labelled "baking powder" and with no other distinguishing mark.

THOMAS COOKSEY
(Government Analyst).

Toxicology and Forensic Chemistry.

Two lectures that contain much of interest to chemists in general were given last year, and have now been reprinted. The first, by Dr. H. Wilson Hake, F.I.C., was delivered at Westminster Hospital on September 30th under the title of "On Some Problems in Toxicology"; the other, by Sir William Willcox, M.D., F.I.C., was an address on "The Influence of Chemical Research on Medicine and Forensic Chemistry," to a joint meeting of the Manchester and District Section of the Institute of Chemistry and other Manchester Scientific Societies, on November 7th.*

Dr. Hake gives a comprehensive summary of the rise of toxicology, as a branch of science which only dates back to the time of Majendie (1783–1855) and of Orfila

* Issued as a pamphlet by the Institute of Chemistry, Jan. 1925

(1787-1853), Professor of Medical Jurisprudence at Paris. The modern systematisation of the methods of examination is mainly due to Christison, Professor of Medical Jurisprudence (1822), whose "Treatise on Poisons" (1829) was the first work to direct attention to such points as the interval between the administration of a poison and the onset of the symptoms, the comparison of the symptoms with those of disease, the morbid appearances, and what he termed the *moral evidences*.

Christison was of opinion that modern chemical methods would make secret poisoning impossible, but Stevenson, fifty years later (1894) took a different view, pointing out that "many cases of chronic poisoning have been overlooked by medical practitioners, and death certificates signed from normal causes."

Three cases, to mention no others, within the last 20 years afford ample evidence that there is still a risk of mistaken diagnosis in cases of murder—*The Chapman Case* (1903). It was diagnosed that the victim was suffering from some form of intestinal trouble, whereas it was found, after *post mortem* examination, that 25 to 30 grains of tartar emetic were present. The *Seddon Case* (1912). There was a diagnosis of epidemic diarrhoea, but the symptoms were afterwards proved to have been produced by arsenic. *The Armstrong Case* (1922). Heart disease and kidney trouble were diagnosed, and the symptoms were subsequently proved to be due to arsenical poisoning.

It is suggested that insufficient use is made of chemical examination of the urine when the medical practitioner is in doubt as to his diagnosis, and when the possibility of poisoning cannot be excluded.

The lecture includes classified statistics of the poisoning cases for the 20 years ending with 1904, and for the period from 1914 to 1923.

Sir William Willcox, in his address, first deals with the development of chemistry, particularly in its relation to medicine, and gives a brief outline of the various chemical methods that have been devised as means of diagnosis by various diseases, such as micro-chemical processes for the examination of the blood, and gastric analysis after test meals.

In his account of the development of the methods of toxicological analysis he points out how much is owing to the work of Stevenson.

In various cases the application of newly-discovered tests for alkaloidal and other poisons has been of the greatest importance. In 1855 the expert for the Crown in the Palmer case was unable to say that strychnine was present, although there was little doubt that death was due to strychnine poisoning, and the prisoner was convicted. At the present time he would probably have been acquitted unless proof had been brought of the presence of the poison.

In the *Crippen Case* the poisoner had made use of hyoscine, which had previously been stated to be a decomposable alkaloid which no one would be able to detect after the lapse of a few days or weeks. But he had buried the viscera in quick-lime, thereby preserving them, and so probably enabling the hyoscine to be detected. Since that case the work of the lecturer has been checked by other chemists, who have found that it is possible to extract and identify hyoscine from viscera after a period of six months.

The electrolytic Marsh-Berzelius test for arsenic was first used by the lecturer in the Seddon case. For the first time, too, the organs of the body were separately weighed, and the arsenic determined in each, and from the results an estimate of the total arsenic in the body was formed.

In dealing with forensic evidence many valuable hints, based on long experience, are given. Stress is laid on the point that expert evidence should be free from all trace of bias. It is a great advantage for an expert witness to imagine

himself in the position of the judge or cross-examining counsel, and his success as a witness will be much assisted by appreciating the psychological attitude of those who question him; it will also make him more tolerant of the searching questions put to him in cross-examination. Ambiguity and lengthy explanations should be avoided, as well as statements that are not answers to questions.

Referring to questions that may be put from books or reports, the lecturer suggests the wisdom of asking to see the work cited before giving a reply, and he concludes with the following advice, which sums up the whole question of expert evidence: "It is the duty and privilege of the expert witness to assist justice by his experience and advice. It is his duty to ensure that his views are clearly put before the Court and that not one jot or one tittle should be withheld or left in doubt."

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Influence of Glucose and Fructose on the Rate of Hydrolysis of Sucrose by Invertase from Honey. J. M. Nelson and C. T. Sottery. (*J. Biol. Chem.*, 1924, **62**, 139–147.)—Nelson and Cohn (*J. Biol. Chem.*, 1924, **61**, 193) found an increase in the rate of hydrolysis of sucrose by invertase from honey at the beginning of the reaction, which is unusual, since invertase action, when the invertase is obtained from bottom yeast, does not show this effect. Experiments are described which were carried out with the purpose of making a further study of this effect. Tables and curves show the results. Mutarotated glucose, besides retarding the action of a preparation of invertase from honey, when present in higher concentrations, also has an accelerating influence when present in lower concentrations. α-Glucose retards or accelerates, depending upon its concentration, less than the β or mutarotated forms. Mutarotated and β-fructose do not retard or accelerate to the same extent that the glucose does. There is little or no difference between the relative effects of the various forms of fructose. The presence of added glucose tends to eliminate the characteristic initial increase in the rate of hydrolysis of a 10 per cent. sucrose solution by invertase from honey. There appears to be a relationship between the relative concentrations of glucose and sucrose in respect of the extent of the influence of the hexose on the rate of the hydrolysis. P. H. P.

Nutritive Value of the Snail. (*Helix pomatia*, L.) L. Leger. (*Comptes rend.*, 1924, **179**, 1622–1625.)—The part eaten (*a*) includes the well-developed foot, the head, stomach, rectum and oviduct, whilst that discarded (*b*) is chiefly the fat, liver and albuminous glands. The composition at the end of hibernation is as follows, calculated to percentages on the dry basis:—Proteins, (*a*) 79·98, (*b*) 63·25; ether extract, (*a*) 2·12, (*b*) 6·50; mineral matter, (*a*) 8·27, (*b*) 8·37; extractives,

(*a*) 9·63, (*b*) 21·88, including (*b*) reducing and invert sugars 2·74 and glycogen (Frankel-Garnier method) 3·07 per cent. All the glycogen and reducing sugars, the greater part of the nutritive substances, and the most digestible material is found in the discarded portions. D. G. H.

Rancidity and the Kreis Test. T. W. Jones. (*J. Soc. Chem. Ind.*, 1924, **43**, 1258–1259.)—A review of the history of the Kreis test and its various modifications suggests that Powick's modification of the Kreis test of Kerr for the detection of acrolein may be the long-sought specific test for rancidity. In this test 1 drop of 3 per cent. hydrogen peroxide solution is added to 1 or 2 drops of the diluted acrolein solution, followed, after 1 minute, by 5 c.c. of hydrochloric acid (sp. gr. 1·19), and after shaking, by 5 c.c. of an ethereal solution of phloroglucinol, and the mixture again shaken. The hydrochloric acid assumes a deep red colour, and a spectroscopic examination shows a fairly narrow absorption band in the yellow green region. This test is positive with rancid fats, but not with vanillin, eugenol, cinnamic aldehyde and non-rancid cotton seed oil, all of which react with the Kreis reagent, and it is suggested that the substance responsible for the colour may be a product of the decomposition or, rather, the oxidation, of oleic acid, which is likely to prove identical with the acrolein and hydrogen peroxide complex. D. G. H.

The Glycerides of Cacao Butter. K. Amberger and J. Bauch. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, **48**, 371–390.)—An exhaustive investigation into the composition of cacao butter by methods depending on fractional crystallisation from acetone, ether and alcohol (*cf.* ANALYST, 1924, **49**, 283) has shown it to consist of the glycerides of oleic, stearic, and palmitic acids, the acids being present in the following proportions:—Oleic acid, 43–45 per cent.; palmitic acid, 23–25 per cent.; and stearic acid, 31–33 per cent.; no acids of higher molecular weight could be detected. The following proportions of glycerides were found:—Tristearin, 0·02; β-palmito-α-α-distearin, 0·03; oleo-α-β-distearin, 24·92; oleo-β-palmito-stearin, 20·29; and α-palmito-α-β-diolein, 54·74 per cent. A sample of the fat which had been hydrogenated in the presence of palladium had an iodine value of 5·9 and m.pt. 60·5° C., and contained 77 per cent. of palmitic acid with 22·7 per cent. of stearic acid, and the separated glycerides consisted of tristearin, 25; β-palmito-α-α-distearin, 20; and α-palmito-α-β-distearin, 55 per cent. H. E. C.

Characterisation and Evaluation of Ferric Casse in Wines. P. Malzevin and J. C. Essner. (*Ann. Falsificat.*, 1924, **17**, 473–477.)—The following procedure serves for the determination of the proportion of ferrous iron susceptible to oxidation present in wine. A certain volume of the wine is treated with a few c.c. of hydrogen peroxide and with excess of 5 per cent. tannin solution, which is added until no further blackening occurs. This wine is then added gradually from a burette to 5 c.c. of 1 per cent. citric acid solution contained in a porcelain dish; at first a black spot forms and then disappears, and the addition is continued until the black

spot does not disappear, but renders the liquid of similar colour to the added wine. If the volume of wine run in from the burette is n c.c., the quantity of "cassable" iron per hectolitre or the degree of "cassability" of the wine is equal to $38/n$ grms., and the amount of crystallised citric acid to be added to a hectolitre of the wine to preserve it from ferric casse is $\frac{12{\cdot}76 \times 38}{n}$.

In France, citric acid may be added only to the extent of 50 grms. per hectolitre, which corresponds with only 4 grms. of "cassable" iron, an amount often surpassed. In such case the wine may be treated with an amount of tannin equal to four times that of the "cassable" iron present, and then oxygenated, fined, and filtered; the degree of "cassability" is then determined again, and the wine treated with the suitable quantities of tannin and citric acid, as described above. Ferric casse begins to be troublesome when the degree of cassability equals 2, is very active when the value is 4, and is difficult to combat if the value reaches 8 to 9. Red wines may be treated in the above manner, but the titration must be carried out in a good light in order that the end-point may be ascertained. T. H. P.

Determination of Adrenaline in Suprarenal Powders by an application of the Denigès-Grimbert-Leclère Reaction. O. Bailly. (*J. Pharm. Chim.*, **1924, 30,** 404–405.)—One grm. of suprarenal powder and 1 c.c. of N sulphuric acid are shaken up with distilled water, and after 15 minutes made up to 100 c.c., and allowed to remain in contact another 15 minutes before filtering. Two c.c. of the filtrate are added to a solution of 1 grm. of sodium acetate in 8 c.c. of water, shaken, and 3 drops of a 5 per cent. solution of mercuric chloride added. The resulting red colour attains its maximum intensity in 3 minutes, and can be compared with that of a solution containing 0·01 grm. of adrenaline and 1 c.c. of N sulphuric acid in 100 c.c. of water. D. G. H.

Colorimetric Determination of Solutions of Novocaine. P. Chertmy. (*J. Pharm. Chim.*, 1924, **30,** 408–411.)—A type solution and the solution to be examined (say 1 grm. in 200 c.c. of water in each case) are diluted 100 per cent., and to 5 c.c. of each is added, if necessary, 1 drop of 0·1 N iodine solution in order to eliminate any colour due to adrenaline; the solutions are then diazotised by adding 1 c.c. of dilute hydrochloric acid and 3 drops of 10 per cent. sodium nitrite solution. On adding 10 c.c. of 2 per cent. β-naphthol in N sodium hydroxide solution a red colour develops, which is matched in the two solutions by suitable dilution. Novocaine solutions are not appreciably altered if sterilised in slightly alkaline glass ampoules at 100° C., but after sterilisation at 120° C. a good glass should be used; or a 2 per thousand solution of benzoic acid may be added to the novocaine. D. G. H.

Biochemical, Bacteriological, etc.

Fat-Soluble Vitamins. XX. Modified Technique for the Determination of Vitamin A. H. Steenbock, M. T. Nelson and A. Black. (*J. Biol. Chem.*, **1924, 62,** 275–287.)—Absence of growth on suitably constituted rations as used at

present cannot be taken as an indication of the absence of vitamin *A* unless the antirachitic factor is supplied. A method has therefore been devised in which light is used as the antirachitic agent for vitamin *A* determination. A Cooper-Hewitt BY type quartz mercury vapour lamp was used as a source of light for irradiation. To this, rats were exposed at a distance of about 22 inches for 10 minutes daily, 6 days of the week. Charts and tables show the results of the experiments. When vitamin *A* is present in sufficient amounts the amount of antirachitic vitamin can also be determined in foods, provided the inorganic relations are not seriously disturbed. It has been concluded that hog millet, and probably common millet as well, contain considerable quantities of vitamin *A*. Both, however, are deficient in the antirachitic factor, which is responsible for their failure to support growth when supplemented with casein and the ordinary salt mixture. Alfalfa carefully cured in the dark was found very rich in vitamin *A*. Even 0·5 per cent. supported normal growth when the antirachitic factor was supplied in the form of light, otherwise 4·0 per cent. was required. When cured in the sun, exposed to dew and rain, vitamin *A* was destroyed, but an antirachitic activation of certain substances in the alfalfa is suggested. P. H. P.

Critical Study of the Jendrassik Reaction for Water-Soluble Vitamin *B*. **V. E. Levine.** (*J. Biol. Chem.*, 1924, **62**, 157–161.)—The ferric ferricyanide reaction proposed by Jendrassik (*J. Biol. Chem.*, 1923, **57**, 129) is not a specific test for water-soluble vitamin *B*. The method consists in adding acetic acid to the concentrated aqueous solution of the preparation to be tested for vitamin *B* to make a 2 per cent. solution, then adding freshly prepared ferric ferricyanide. In the presence of water-soluble vitamin *B*, a characteristic blue colour is developed, the result of the formation of ferric ferrocyanide or Prussian blue. The ferricyanide in the reagent is reduced to ferrocyanide which further reacts with the ferric chloride. The reagent is added as long as the depth of the colour increases. The tube containing the reaction mixture is stoppered to hinder reoxidation, allowed to stand for 10 minutes, and its contents diluted with 1 to 5 volumes of distilled water, and again observed for colour. A positive test is indicated by the presence of a distinct blue colour, or, after standing for some time, of a blue precipitate; a negative one, according to Jendrassik, by lack of change or the formation of a green colour. The reaction is given by phenols, and may serve as a test for them in the absence of a few positively reacting non-phenolic compounds. The list of substances examined is given. Alkali reacts with phenols to give derivatives or fractions that no longer respond to the ordinary phenol tests. Phenols resemble vitamin *B* with respect to the destructive effect of alkali. The fact that active preparations of water-soluble vitamin *B* do not give a positive Millon or Liebermann reaction is no proof that vitamin *B* is not a phenol, since neither of these two reactions is given by all phenols. The work does not preclude the probability of the presence in the vitamin *B* molecule of one or more phenolic groups. P. H. P.

Vitamin Potency of Cod Liver Oils. A. D. Holmes. (*Ind. Eng. Chem.*, 1924, **16**, 964–965.)—Comparative feeding tests with freshly rendered cod liver oil and that obtained from livers which had rotted for eight months showed that the latter oil possessed less than one-twelfth of the vitamin potency of the fresh oil. The rotting process also altered the physical and chemical characters of the oil; the specific gravity increased from 0·9210 (fresh oil) to 0·9548, the refractive index from 1·4775 to 1·4795, the saponification value from 187·3 to 206·8, and the free fatty acids from 1·3 to 23·3 per cent. The iodine value decreased from 151·4 to 112·9. W. P. S.

Detection of Pollution in Shell-fish. J. W. H. Eyre. (*Public Health*, Dec., 1924; *Lancet*, 1924, II., 973.)—Since disease-producing "intestinal" bacteria rarely occur in shell-fish except in association with a preponderance of *B coli*, a bacteriological examination of a batch of oysters will enable an estimate to be made of their safety. In view of the vexatious delay, from the point of view of the oyster merchant, of the ordinary method of estimating the number of *B. coli*, a "short method" has been devised, by means of which it is possible to form an opinion within 24 hours. The oysters are opened with aseptic precautions, and tubes of bile-salt broth, glucose broth and litmus milk, in suitable dilutions, are inoculated with the liquor and incubated for 24 hours, after which the presence or absence of *B. coli* is ascertained by observation of the usual changes in the culture media. If, for example, acidity and gas are present in the bile-salt broth culture, the inference is drawn that the oyster from which the liquor was derived contained *at least* 50 *B. coli*, and is therefore to be condemned after being tested by the more tedious method of examination.

When a batch of shell-fish is condemned the Company of Fishmongers, which has control over the London fish market, usually takes action, since it is a much more involved process for any action to be taken by the local health authorities.

Anaerobic Bacteria in Meat Foods and their connection with Gastro-intestinal Disturbances. — Brekenfeld. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, **48**, 174–175.)—Although anaerobic bacteria do not produce the paralytic manifestations characteristic of true botulism, it is thought that they are often responsible for the milder types of food poisoning producing gastro-intestinal troubles. This is borne out by investigation of some cases of illness caused by sausages; the bacteria isolated included cocci, *B. subtilis*, and *B. coli*, and certain anaerobes, Frankel's gas bacillus, pararauschbrand (paratyphoid?), and the wart-bacillus (Warzen bacillus). The *B. coli* and other types are common in sausages, and are not likely to occasion sickness, *B. subtilis* is not pathogenic, and it is probable that the gastric symptoms were due to the anaerobes. It is desirable that special attention should be given to the examination of the anaerobic bacteria in the investigation of meat foods which have caused illness. H. E. C.

Determination of Hydrogen Sulphide in Bacterial Cultures and in certain Canned Foods. C. R. Fellers, O. E. Shostrom and E. D. Clark. (*J. Bact.*, 1924, **9**, 235–249; *Chem. Abstr.*, 1924, **18**, 2731.)—The hydrogen sulphide is drawn from the acidified liquid through standard iodine solution by means of a current of air, and any iodine volatilised is caught in a standard solution of sodium thiosulphate. The hydrogen sulphide is then determined by titration of the combined iodine and thiosulphate solutions. From 99 to 100 per cent. of the hydrogen sulphide present is recovered by 15 minutes' aeration. Ordinary bacterial products such as volatile fatty acids, phenols, skatol, indol, etc., and small amounts of ammonia do not affect the results. Of 53 organisms tested, 12 gave positive results with Difco peptone. Armour's and Witte's peptone were not satisfactory for the test.

Bacterial Flora of Salt. Rappin and Grosseron. (*Ann. Chim. anal.*, 1924, **6**, 353–355.)—Refined salt from various sources was found to contain up to 8300 bacteria and 400 mould (spores) per grm. and samples of crude salt from 6000 to 76,000, and even 300,000 bacteria and 100–700 mould (spores), and although the majority of the organisms were saprophytic, toxic cultures were obtained in some cases. Brines of various ages and sources were also found to be badly contaminated, and there is little doubt that the salt may constitute a serious source of danger when added to food products. For food preservation purposes the salt should be free from bacterial contamination and be prepared under strictly aseptic conditions. D. G. H.

Microchemical Test for Nucleic Acid of the Thymonucleic Acid Type. R. Feulgen and H. Rossenbeck. (*Z. physiol. Chem.*, 1924, **135**, 203–248; *Chem. Abstr.*, 1924, **18**, 2725–2726.)—The "nucleal" reaction consists in partial hydrolysis of the preparation on the microscope slide by treatment with *N* hydrochloric acid at 60° C. for 4 minutes, and then for 1 to 3 hours at the ordinary temperature, after which the material is washed with water and immersed in Schiff's reagent (magenta and sulphurous acid). An intense violet coloration, due to the formation of an aldehyde by the hydrolysis, is produced in the case of nucleic acid from animal sources or from higher plants, whereas the pentose-containing nucleic acids of yeast and bacteria do not show the reaction. Any possibility of confusion due to the presence of naturally occurring aldehydes is eliminated by the fact that nucleic acids do not give the reaction before hydrolysis. Moreover, the aldehydic grouping responsible for the reaction cannot be extracted with water. No reaction is obtained with the lowest forms of organisms, including yeasts and trypanosomes, but reactions are produced by infusoria, wheat germs, pus, spermatozoa, and nucleated cells of animals in general. The cell structure remains intact during the test, and the stain can be readily observed in the nucleus.

Detection of Poisonous Gases in Blood. E. Kohn-Abrest. (*Comptes rend.*, 1924, **179**, 903–906.)—A method is described for the detection of alcohol, hydrogen sulphide, hydrocyanic acid, carbon dioxide, and carbon monoxide in

blood, use being made of a modified form of the apparatus previously described. (See Ogier and Kohn-Abrest, *Traité de Chimie toxicologique*, 2nd Edition, Vol. I., 1924.) T. H. P.

Normal Occurrence of Carbon Monoxide in Blood. M. Nicloux. (*Comptes rend.*, 1924, **179**, 1633–1636.)—Contrary to the statement of Buckmaster and Gardner (*Proc. Roy. Soc.* 1909, **81** [B], 515) carbon monoxide is a normal constituent of blood and may be withdrawn from it either by subjecting it to reduced pressure; by means of phosphoric acid, by displacement with nitrogen peroxide, or in the living subject by pure oxygen. It may be recognised as carbon monoxide: By forming with hæmoglobin (1) a compound resistant to decomposition *in vacuo*, and (2) one which shows the two characteristic absorption bands of hæmoglobin-carbon monoxide. It also gives similar results when analysed by means of the micro-eudiometer. The amount of carbon monoxide found in the blood of the ox, pig and horse was about 0·1 c.c. per 100 c.c. of blood. D. G. H.

Method for the Determination of Lipoid Phosphorus in Blood and Plasma. J. C. Whitehorn. (*J. Biol. Chem.*, 1924, **62**, 133-138.)—The method of Bell and Doisy (*J. Biol. Chem.*, 1920, **44**, 55) for determining inorganic phosphates and the procedure of Randles and Knudson (*J. Biol. Chem.*, 1922, **53**, 53) were tried, but could not be satisfactorily utilised for determining the lipoid phosphorus of blood plasma. A method has been devised for this which is not so simple, but which is believed to be more reliable. The chief difficulties encountered were in the control of the digestion process, and these have been overcome without giving up the use of nitric acid. Errors due to local overheating have been avoided by the use of enough sulphuric acid to fill the hemispherical end of the test-tube (1 c.c. of specific gravity 1·84), and the traces of nitric acid remaining after digestion are eliminated by sulphur dioxide liberated from sodium sulphite. The use of so much acid also reduces to relative insignificance the amount of sulphuric acid volatilised during digestion. The intense acidity of the digestion product has necessitated a departure from the process of colour development described by Bell and Doisy or modified by Briggs (*J. Biol. Chem.*, 1922, **53**, 13). With this degree of acidity, 10 minutes in boiling water after the addition of acid molybdate, sodium sulphite and hydroquinone, produces a clear blue colour, the intensity of which, after cooling, is proportional to the quantity of orthophosphoric acid, even when the difference exceeds 33 per cent. A blank determination gives only a faint yellow colour. The blue colour increases slowly for about 24 hours and does not disappear for several weeks. Several unknown solutions can be compared with the same portion of standard in the colorimeter. If the blue solution is diluted with distilled water the intensity of colour varies in inverse proportion to the dilution. Unexpectedly deep colours may therefore be adjusted nearly to the colour of the standard. Examples given show the method to be extremely accurate and reliable. P. H. P.

The Passage of Boric Acid through the Skin by Osmosis. L. Kahlenberg. (*J. Biol. Chem.*, 1924, **62**, 149–156.)—The author has shown, after studying many substances such as lithium chloride, caesium chloride, rubidium chloride, strontium chloride, borax and lithium borate, that boric acid, and this alone, passes through the living skin in perceptible quantities. When salts of boric acid, like borax and lithium borate, are used, no boric radical is found in the urine. The amounts of boric acid found in the urine of a normal person whose feet are soaked in boric acid solution are much the same (a few hundredths of a per cent.) as those observed in patients treated with boric acid compresses for blood-poisoning. In 5 minutes after the feet are immersed in the boric acid solution, boric acid is present in the urine. All the substances tested pass readily through dead human skin and also through other dead animal membranes. Since dead skin and living skin act differently osmotically, one is led to the conclusion that they are chemically different. Similarly, living mucous membranes are chemically different from the living skin. Boric acid given by the mouth to patients suffering from blood poisoning does not quell the infection, but relatively large quantities of it are found in the urine. Sulphuric, hydrochloric and citric acids, when taken by mouth, acidify the urine, whereas when the skin is bathed with them the first two cause an alkaline reaction of urine, whilst citric acid has the opposite effect. Therefore it does not seem so peculiar that boric acid should have quite a different effect when taken internally from that produced when it passes into the system through the living skin. P. H. P.

Toxicological, Forensic, etc.

Effect of Lead on Blood Cells. J. C. Aub, P. Reznikoff and D. E. Smith. (*J. Exptl. Med.*, 1924, **40**, 151–208; *Chem. Abstr.*, 1924, **18**, 2922–2923.)—Previous work has indicated that the anæmia observed in cases of lead poisoning is due to destruction of blood rather than to diminished production of blood. In studying this phenomenon the blood cells were poisoned with lead *in vitro*, and distinct effects were obtained, even when only 0·001 mgrm. of lead was added to approximately 5 billion washed red corpuscles. By the addition of 0·01 mgrm. such a marked resistance to hypotonic salt solution develops that complete hæmolysis does not occur until the cells are exposed to a saline solution of 0·05 per cent., whereas untreated cells are completely hæmolysed in 0·25 to 0·225 per cent. solutions. The reaction is quantitative, and varies with the concentration of lead used. The effects with arsenic are very slight in comparison. The change in hæmolysis does not appear in the blood of all species of animals. In the species in which it does occur, anæmia and stippling of the red cells also tend to develop readily during lead poisoning. *In vitro* cells that have been exposed to lead are more fragile than normal blood cells. It has been found that inorganic phosphate in the same concentration as is normally present in the serum neutralises the same quantity of lead as does the whole serum itself. The addition of inorganic phosphate to red blood cells or to whole blood greatly reduces the action of lead upon the

cells, but cannot eliminate it completely, indicating that there is a simultaneous reaction between the lead and serum and lead and corpuscles when all are present. In agglutination experiments with colloidal iron and arsenic a marked difference was observed between "leaded" and normal cells.

Lead Tetraethyl Poisoning. H. Leffmann. (*Amer. J. Pharm.*, 1924, **96**, 861–863.)—Attention is directed to the occurrence of numerous very severe cases of poisoning caused by exposure to the fumes of lead tetraethyl, which has recently been introduced as a remedy for "knock" with petrol (gasoline).* This has led to drastic regulations being made by various U.S.A. public health authorities, and the petrol companies have accordingly withdrawn the product from sale pending further investigation to determine the limits of safety for its use. Tetraethyl lead, like the other organo-metallic compounds, produces spasm of the glottis when inhaled in admixture in large proportions with air, but when present in minute quantities, as in motor engine exhaust gases, it produces chronic symptoms of lead poisoning.

* According to Jolibois, when the lead tetraethyl is decomposed the rough places in the cylinder, which act catalytically in promoting the spontaneous explosion of the gaseous mixture, become coated with metallic lead, whereby the tendency to explode is reduced.—EDITOR.

Mercury Poisoning from Electric Furnaces. L. Jordan and W. P. Barrows. (*Ind. Eng. Chem.*, 1924, **16**, 898–901.)—Several cases of mercury poisoning occurring amongst men operating high-frequency induction furnaces led to the discovery that mercury vapours escaped from the mercury discharge gaps of the high-frequency converters. The air near the furnaces contained 0·7 mgrm. of mercury per cubic metre, a quantity sufficient to cause mercury poisoning if daily exposure is continued for several months. When a new type of discharge gap having stationary electrodes, mercury-sealed discharge chambers, and operating in an atmosphere of hydrogen, was installed and enclosed in a separate compartment fitted with a forced-draught hood, the escape of mercury vapours from the discharge-gap could not be detected. W. P. S.

Agricultural Analysis.

Copper Sulphate in Agriculture. E. Cerasoli. (*Giorn. Chim. Ind. Appl.*, 1924, **6**, 536–537.)—The proportion of copper sulphate in copper-lime mixtures used as fungicides may be diminished from 8 to 1 per cent. or even less, the efficacy of the treatment depending, not on a high content of copper in the material, but on the thoroughness of the application. The use of such substances in the form of powder is recommended, especially where water is scarce. T. H. P.

Nickel and Cobalt in Arable Land. G. Bertrand and M. Mokragnatz. (*Comptes rend.*, 1924, **179**, 1566–1569.)—Nickel and cobalt were found in all the samples of soil examined which were taken from various parts of France, Germany, Denmark, Italy, Rumania, and Serbia. The proportion of nickel varied between

5·5 and 38·6 mgrms. per kgrm. of dry earth, and that of cobalt between 0·3 and 11·7 mgrms., but the lower limits were exceptional in both cases. Probably the proportion of these metals present varies with the depth from the surface.

D. G. H.

Determination of Manganese in Agricultural Soils. G. Bertrand. (*Bull. Soc. Chim.*, 1924, **35**, 1522–1527.)—The air-dried soil is passed through a 1 mm. sieve, and the proportion of pebbles and fine soil ascertained. A sample of the latter is finely ground in agate, for the following tests. (*a*) *Manganese soluble in dilute acetic acid.*—0·5 grm. is boiled for a short time with 5 to 10 c.c. of one per cent. acetic acid in a boiling-tube. After settling, the clear solution is decanted through a filter; the residue is re-treated 3 to 4 times in the same manner, and the combined filtrates evaporated to dryness in a porcelain dish. The residue is calcined, dissolved in strong hydrochloric acid, and the solution evaporated to fumes with sulphuric acid. The cold mass is dissolved in dilute nitric acid, and the manganese determined colorimetrically. (*b*) *Manganese as humate.* The insoluble residue from (*a*) is extracted several times with ammonia (1 in 10 or 20 water) until the extract is only coloured straw-yellow; the united filtrates are treated as in (*a*). (*c*) *Manganese soluble in strong hydrochloric acid.* The residue from (*b*) [or *a*, if (*b*) is not required] is collected on the filter and the organic matter destroyed by ignition. The residue is digested at gentle heat with hydrochloric acid, and the liquid then evaporated to complete dryness. The residue is moistened with hydrochloric acid, water is added, and the solution is decanted through a filter; the residue is treated once or twice more in the same manner. The combined filtrates are evaporated to fumes with sulphuric acid, etc., as under (*a*). (*d*) *Total manganese.* The finely-ground sample is fused with sodium carbonate in a platinum crucible, the fused mass dissolved in hydrochloric acid, and the silica rendered insoluble by evaporation. The filtrate is evaporated to fumes with sulphuric acid for colorimetric determination. The manganese present in a refractory form is found by difference.

W. R. S.

Poisonous Alkaloid from the Transvaal *Homeria pallida*. M. Rindl. (*Trans. Roy. Soc., S. Africa*, 1923, **11**, 251–256; *Chem. Abstr.*, 1924, **18**, 2909.)—The yellow plant (*Homeria pallida*), both fresh and dried, is poisonous to stock, less than ½ lb. of the dried material being fatal to cattle. Alkaloids are present in all parts of the plant, but cyanogenetic glucosides and saponins are absent from the parts above ground. Alkaloidal reactions are given by the alcoholic extract only. The extraction and all other operations should be conducted in the cold, as far as possible, as these alkaloids are very sensitive to heat. On extracting the slightly ammonical aqueous solution with chloroform, a light yellow transparent varnish, with some crystals, is obtained. This active alkaloidal principle has a slightly bitter taste, is precipitated by the usual reagents, is insoluble in benzene, sparingly soluble in dry ether, and readily soluble in alcohol, acetone, ethyl acetate, chloroform and water. It has a pronounced reducing action. Its effect upon the

heart resembles that of digitalis, and in large doses it is a cardiac poison. It is the only known alkaloid (with the exception of that in the bark of *Erythrophloeum guineënse*), which resembles digitalis in its effects, but is not a glucoside. No crystalline form of the alkaloid and no well defined derivatives have yet been obtained.

Organic Analysis.

Colour Reaction of the Alcoholic Hydroxyl Group. W. Parri. (*Giorn. Farm. Chim.*, 1924, **73**, 109–112; *Chem. Abstr.*, 1924, **18**, 2667.)—A reagent prepared by dissolving 3 grms. of phosphomolybdic acid and 0·3 grm. of ammonium vanadate in 100 c.c. of concentrated sulphuric acid gives colorations when heated with various alcohols, hydroxy acids, polyatomic acids and sugars, and allowed to stand. The most characteristic reaction is the azure blue colour obtained with monatomic alcohols, such as ethyl alcohol, secondary butyl alcohol, and *iso*-amyl alcohol (not methyl alcohol).

Differentiation of Citric from Tartaric Acid. W. Parri. (*Giorn. Chim. Ind. Appl.*, 1924, **6**, 537–538.)—The presence of a small proportion of citric acid in tartaric acid may be detected in the absence of certain other compounds (see preceding abstract), by a reagent prepared by warming 3 grms. of precipitated phosphomolybdic acid (or ammonium phosphomolybdate) and 0·3 grm. of ammonium vanadate in 100 c.c. of concentrated sulphuric acid; a deep blue coloration is formed, this becoming green on heating, but resuming its original colour on cooling. The reaction is disturbed if much sugar is present, owing to browning; also, dextrose or sucrose gives a green coloration. T. H. P.

Determination of Alumina in Chrome Leather. D. Woodroffe. (*J. Soc. Leather Trades Chem.*, 1924, **8**, 581.)—Two methods are given. (1) *With platinum crucible*:—The ash from 5 grms. of leather is fused in a platinum crucible with fusion mixture, extracted with excess of dilute hydrochloric acid, ammonium chloride and slight excess of ammonia solution are added, and the solution boiled till the precipitate flocculates. The aluminium hydroxide thus formed is then filtered off, washed with weak ammonia solution, dried, ignited and weighed.

(2) *Without platinum crucible*: The ash from 5 grms. of leather is fused gently in an iron crucible with 8 to 10 times its weight of pure sodium peroxide (A.R.) and kept fused for 3 minutes. The mass is dissolved in warm distilled water and filtered from the oxides of iron. The filtrate is acidified with hydrochloric acid, boiled with excess of ammonia, and the analysis completed as above. Experiments show the methods to work well on pure materials, but when tested on leather ash by different analysts the results were not quite in agreement, and further work is in progress. It is pointed out that the presence of alumina in chrome leather may be due to the use of alum in the tannage or to the presence of pigments in or on the leather. R. F. I.

New Simplification in the Official Method of Tannin Analysis. A. Jamet. (*J. Soc. Leather Trades Chem.*, 1924, **8**, 613.)—The long time required by the Official Method is a great objection to its use for works control. The various stages of determining non-tans have been specially studied, with the following results:—The time for chroming the hide powder has been reduced from one hour to fifteen minutes. The washing of the chromed hide powder can be reduced from one hour to fifteen minutes, if certain precautions are taken. Mechanical agitation at an increased speed (60–80 revolutions per minute) for chroming or detanning is not indispensable; shaking from time to time gives identical results. The hide powder after detannisation constitutes a perfect filter, provided that it rests on a very fine gauze (brass). A supplementary filtration with washed kaolin through paper therefore becomes superfluous. A special simple apparatus is described by means of which a clear solution of the non-tans can be obtained without a single transference of the hide powder. For evaporation 30 c.c. are taken instead of 50 c.c., thus reducing the time required. Comparative results obtained by this method and by the Official Method on chestnut extract, quebracho extract and oak bark are in close agreement. The total time required is reduced from 8 or 9 to 3 hours. R. F. I.

Fig Tree (Gondang) Wax. A. J. Ultee. (*Pharm. Weekblad*, 1924, 1118–1120.)—Fig tree wax, obtained from the sap of *Ficus variegata*, was shown by Greshoff and Sack (*Rec. Trav. Chim.*, 1901, **20**, 65) to consist of ficoceryl alcohol and ficoceric acid, the alcohol also being present in the free condition. The author has identified the ficoceryl alcohol as β-amyrol, it being present in the combined form as acetate, and the ficoceric acid as impure palmitic acid. Fig tree wax is therefore β-amyrol-palmitate, and can be prepared synthetically by boiling 1 mol. of β-amyrol dissolved in benzene, with 2 mols. of palmitic acid chloride for one hour, and subsequently heating the product in a porcelain dish for two hours on a boiling water bath. The dry residue is extracted with hot alcohol, and the wax crystallises out on cooling (m.pt. 77° C.). W. S. S.

Modified Method of Determining Cellulose in Wood. G. J. Ritter. (*Ind. Eng. Chem.*, 1924, **16**, 947–948.)—The chlorination periods mentioned in a previous paper (ANALYST, 1924, **49**, 196) may be reduced to three minutes without any appreciable difference in the yield of cellulose. Discoloration of the cellulose during drying has been ascribed to the use of permanganate as the bleaching agent and its subsequent incomplete removal, but discoloration also occurs when hydrogen peroxide or sulphur dioxide is used. It is recommended that the cellulose should be digested for two hours with hot water before the final washing; in this way the undesirable gelatinous property of cellulose is eliminated, filtration and washing are facilitated, and the cellulose contains a smaller quantity of substances soluble in hot water. W. P. S.

Determination of Sulphur in Mixtures of Raw or Vulcanised Rubber. V. C. Butironi. (*Giorn. Chim. Ind. Appl.*, 1924, **6**, 535–536.)—The following rapid method yields accurate results. About 20 grms. of pure potassium hydroxide

are melted in a roomy silver crucible the bottom of which projects not more than 0·5 cm. through a hole in an asbestos card, and are then allowed to cool until pasty. The finely ground or rolled sample of rubber (0·2 to 0·5 grm.) is then introduced and immediately mixed in with a silver spatula so that it becomes completely coated with semi-fused potash; by this means any free sulphur on the surface of the sample is fixed. Gentle heating is continued until the destruction of the organic matter is almost complete, after which about 5 grms. of potassium nitrate are added. The subsequent procedure is that usually employed, any iron present in the resulting solution being removed as hydroxide before precipitation of the barium sulphate. T. H. P.

Titration of Aniline and its Homologues. D. O. Jones and H. R. Lee. (*Ind. Eng. Chem.*, 1924, **16**, 948–949.)—The amine is treated, in hydrochloric acid solution, with an excess of nitrite, nitric acid is added to prevent decomposition of the nitrite, and the excess of the nitrite is titrated subsequently. A quantity of the sample (the weight taken should be such that one-tenth of it will require about 40 c.c. of 0·1 *N* nitrite solution) is dissolved in 5 per cent. hydrochloric acid and diluted to 500 c.c.; 50 c.c. of this solution are diluted to 300 c.c., 25 c.c. of concentrated hydrochloric acid are added, the mixture is cooled to 0° C., and 50 c.c. of 0·1 *N* nitrite solution and 10 c.c. of concentrated nitric acid (free from nitrous acid) are added. After thirty minutes the excess of nitrite is titrated with standardised *p*-nitroaniline solution. W. P. S.

Analysis of Dehydrothio-p-toluidine Sulphonic Acid. H. R. Lee and D. O. Jones. (*Ind. Eng. Chem.*, 1924, **16**, 930–931.)—In the method proposed an alkaline solution of the amine is treated with an excess of nitrite, the mixture is then acidified, and the excess of nitrite is titrated with standardised primary amine solution. A quantity of 1·3 grms. of dehydro-thio-*p*-toluidine ammonium sulphonate is dissolved in 200 c.c. of water and 5 c.c. of 10 per cent. sodium hydroxide solution, the mixture is cooled to about 0° C., and pieces of ice are added. Fifty c.c. of 0·1 *N* sodium nitrite solution are then introduced, the mixture is stirred while 25 c.c. of concentrated hydrochloric acid and 10 c.c. of concentrated nitric acid (free from nitrous acid) are added, and, after ten minutes, the excess of nitrous acid is titrated with 0·1 *N* *p*-nitroaniline solution. The end-point is reached when a small drop of the mixture ceases to give a blue coloration immediately with a drop of starch iodide solution. Each c.c. of 0·1 *N* nitrite solution is equivalent to 0·033733 grm. of dehydrothio-*p*-toluidine ammonium sulphonate. The *p*-nitroaniline solution is prepared by dissolving 14 grms. of the substance in 200 c.c. of hot water and 150 c.c. of concentrated hydrochloric acid, filtering the solution after fifteen hours, and diluting the filtrate to 1 litre; it is standardised against pure sulphanilic acid. W. P. S.

The Optical Properties of Some Amino Acids. G. L. Keenan. (*J. Biol. Chem.*, 1924, **62**, 163–172.)—A study of the optical properties of many of the known crystalline amino acids was made by the immersion method commonly

used by crystallographers and mineralogists and more recently successfully applied by Wright (*J. Am. Chem. Soc.*, 1916, **38**, 1647) and Wherry (*U.S. Dept. Agric., Bull.* 679, 1918) to the study of synthetic inorganic and organic crystalline substances. The oily liquids, in which the acids are insoluble, best suited for determining the optical properties by this method were found to be mixtures of mineral oil (Squibb's) with $n=1{\cdot}49$, monochloronaphthalene with $n=1{\cdot}64$, monobromonaphthalene with $n=1{\cdot}66$, and, in a very few cases, methylene iodide with $n=1{\cdot}74$. These oils were mixed in such proportions that each differed in n from the next by 0·005 and their exact n values were determined on a refractometer. Observations were made in yellow light, approximating that of the D line. In addition to the optical determinations, photomicrographs were made of the amino acids to illustrate their crystal habit as ordinarily met in the usual methods of analysis. Reproductions of these are given and the optical properties of each acid.

Determinative Table for the Amino Acids.—The crystalline material is immersed in the liquid indicated and then examined under the microscope with the polariser in place and the diaphragm partly closed. The results shown in the following table were recorded:

Immersion. Liquid. (n)	Remarks.	Amino Acid.
1·515 (n_α)	$n_\beta=1{\cdot}575$ also common	serine
1·535 (n_β)	On plates not extinguishing sharply	leucine
1·565 (n_γ)	Lengthwise on rods	valine
1·575 (n_γ)	,, ,, ,,	alanine
1·605 (n_β)	Fragments show orange and blue bands of colour	glutamic acid
1·615 (n_β)	Fragments remain practically bright with crossed nicols	glycocoll
1·630 (n_γ)	On many fragments with sharp extinction	aspartic acid
1·635 (n_γ)	—— ——	tryptophane
1·675 (n_γ)	$n_\alpha=1{\cdot}600$ also common	phenylalanine
1·680 (n_γ)	Lengthwise on needles	tyrosine
1·700 (n_γ)	Crystals show orange and blue bands	cystine

P. H. P.

Inorganic Analysis.

New Absorbent for Oxygen in Gas Analysis. L. F. Fiesher. (*J. Amer. Chem. Soc.*, 1924, **46**, 2638–2647.)—An alkaline solution of sodium hydrosulphite containing sodium anthraquinone-β-sulphonate is recommended as an absorbent for oxygen; it forms a deep red coloured solution which becomes brown when exhausted. The advantages over pyrogallol are that under no conditions can it give rise to carbon monoxide, and it compares favourably with sodium hyposulphite alone, in that it not only absorbs more rapidly and completely, but its rate of absorption does not diminish until it is quite exhausted. The sodium anthraquinone-β-sulphonate acts solely as a catalyst. For a pipette designed for

shaking, 16 grms. of hydrosulphite ($Na_2S_2O_4$, 86·7 per cent.), 6·6 grms. of sodium hydroxide, and 2 grms. of the sulphonate are dissolved in 100 c.c. of water, and for the bubbling type of pipette the corresponding quantities are 16, 13·3, and 4 grms., respectively. The rate of absorption is just a little less than that of alkaline pyrogallol, but the results are satisfactory. H. E. C.

Gasometric Determinations by means of Combustion with Copper Oxide. J. Svéda. (*Chem. News*, 1925, **130**, 1.)—The determination of combustible gases (methane, hydrogen, carbon monoxide) by burning in contact with copper oxide has hitherto been carried out only in the presence of a current providing an excess of air. The author describes a method by which the oxygen necessary is derived solely from a mixture consisting of three parts of the cupric oxide with one part of ceric oxide, the presence of which prevents the cupric oxide from becoming too compact after repeated use. (It is also said to act as a catalyser in the combustion.) The mixed oxides are contained in a small porous crucible in the eudiometer and can be heated electrically to the desired temperature (280–290° C.). The porous crucible consists essentially of a conical spiral of platinum wire covered with Marquardt paste, which must then be very carefully dried and heated before use. The copper oxide is packed into the porous vessel covered with Marquardt's paste, carefully dried, and the whole placed in a glass tube, 6 mm. in diameter. The platinum leads are fused through the glass, and the tube bent to a U-shape. It is then graduated by etching with hydrofluoric acid and calibrated with mercury. In experiments with pure hydrogen the eudiometer was filled with a definite volume of the gas and transferred to a glass cylinder filled with mercury. The copper-oxide vessel was introduced into the gas and heated to 280–290° C., when a visible contraction took place. The heating was continued for half-an-hour, and the residual gas was dried by the introduction of a bead of metaphosphoric acid or magnesium perchlorate, which was left in it for several hours. Experimental mixtures of pure hydrogen and specially purified nitrogen were treated by this method and shown to give very satisfactory results. In experimenting with carbon monoxide (prepared by the action of sulphuric acid on oxalic acid, and collected over mercury after eliminating air, carbon dioxide and moisture) the same procedure was followed, but the results were quite unsatisfactory. The discrepancy was attributed to differences in the adsorption power of cupric oxide for carbon dioxide and nitrogen. Furthermore, the air occluded by the copper oxide is very difficult to remove. These adsorption errors have been overcome, as will be described in Part II. R. F. I.

Identification of Metals as Double Halogenides with Pyridine, Antipyrine, Pyrazole or Aniline. I. M. Kolthoff and H. Hamer. (*Pharm. Weekblad*, 1924, 1222–1227.)—It has been found that copper, cadmium, zinc and nickel combine with a cyanide and pyridine to give precipitates with the general formula $M.(CNS)_2Py_2$. The sensitiveness of the reaction depends upon the amounts of reagents used, the best proportions being 5 c.c. of metallic solution, 0·5 c.c. of 20 per cent. potassium or ammonium thiocyanate, and 1 c.c. of 10 per cent. pyridine.

This reaction is not specific, as all metals give it, but if a chloride, bromide or iodide be substituted for the thiocyanate, fewer metals are precipitated. In this respect the bromide test is the most sensitive, and 5 mgrms. of zinc or cadmium per litre can be determined. Other weak bases have been substituted for pyridine, but positive results were obtained only with antipyrine and pyrazole. The test, with the use of antipyrine and a thiocyanate can be used to detect 1 per cent. of zinc in the presence of cadmium. By the use of pyrazole and a thiocyanate one mgrm. of copper can be detected, a violet coloration being produced. Microchemically, zinc and cadmium may be detected by the crystalline form of their double halogenide salts when the pyridine and bromide reagents are used. Iron and aluminium interfere with all these tests and must be removed before they are applied. W. S. S.

Copper as a Reducing Agent in the Determination of Iron. J. M. Hendel. (*Ind. Eng. Chem.*, 1924, **16**, 951.)—Boiling ferric sulphate solution may be reduced completely by means of copper gauze immersed in it; 64 sq. cm. of the gauze will reduce 0·150 grm. of iron in fifteen minutes. After reduction, the solution is cooled, aerated for three to five minutes to oxidise cuprous and titanous salts, and the ferrous salt is then titrated with permanganate solution. The acidity of the solution during the reduction process should be 0·1 *N*, and increased to normal before the aeration and titration. The aeration, which should be at the rate of 1 litre of air per five minutes, does not oxidise the ferrous salt. It is advisable to filter the air through cotton wool before use. W. P. S.

Analysis of Germanite (Determination of Germanium, Arsenic, Gallium, and Molybdenum). F. W. Kriesel. (*Chem. Zeit.*, 1924, **48**, 961–963.)—Germanite, discovered in S.W. Africa, is richer in germanium and gallium than any other known mineral. Its composition is: Cu 45·39, Pb 0·66, Zn 2·58, Fe 4·56, Ge 8·70, S 30·65, As 4·13, Ga 0·76, SiO_2 0·226, WO_3 0·184, TiO_2 0·004, Mo 1·282, Mn 0·02, Ni 0·001, Co 0·013, Cd 0·071, CaO 0·122, MgO 0·055, C 0·136, Ag+Au 0·005, total 99·549 per cent. *Determination of germanium.*—Two grms. of finely powdered mineral are digested overnight with nitric and sulphuric acids, and the former evaporated without fuming. The mass is dissolved by warming with 50 c.c. of water, and the solution rinsed into a distillation flask with 150 c.c. of strong hydrochloric acid; any germanium dioxide adhering to the beaker is dissolved in ammonium sulphide and added to the solution. The flask is connected with a spiral cooler, and the latter with a receiver, cooled in ice, and containing 20 c.c. of dilute hydrochloric acid. A slow current of chlorine is passed through the apparatus during the distillation, which is interrupted when two-thirds of the liquid have passed over. About 90 per cent. of the germanium distil with the first 10 c.c. The chlorine is expelled from the apparatus by carbon dioxide, and the distillate treated for half an hour with hydrogen sulphide. A heavy, granular, pure white precipitate of germanium disulphide soon forms; the strong acidity required for its quantitative precipitation is ensured by the above procedure. After settling, the precipitate is collected, dissolved in a little ammonium sulphide,

and the resulting solution (100 c.c.) acidified with 50 c.c. of sulphuric acid (1 : 1) and treated with hydrogen sulphide for 10 minutes. The voluminous precipitate is filtered off and washed three times with 20 per cent. sulphuric acid saturated with hydrogen sulphide, followed by three washings with absolute alcohol. The re-precipitation ensures complete absence of chlorine, which would cause low results by volatilisation. The washed precipitate is rinsed into a platinum basin, the paper rinsed down with ammonia, the liquid evaporated, the residue cautiously moistened with strong nitric acid, again dried, and ignited gently to expel sulphuric acid; these operations are repeated. The ignited residue is moistened with ammonia, dried, and ignited; this treatment is repeated till the weight of the dioxide is constant. It is a heavy, soft powder of snow-white colour. *Arsenic.*—The residual liquid in the distillation flask is acidified with 100 c.c. of strong hydrochloric acid, and distilled in a current of sulphur dioxide to as small a bulk as possible; the distillation is repeated with another 100 c.c. of acid, when all the arsenic will be in the distillate. This is treated, while being cooled, with solid permanganate until the brown colour is permanent; the latter is discharged by sodium hypophosphite, and the arsenic precipitated with hydrogen sulphide. *Gallium.*—Fifty grms. are dissolved, and the nitric acid removed, as before. The mass is dissolved in 300 c.c. of water by warming, and the lead sulphate and germanium dioxide filtered off after cooling. The filtrate, diluted to 500 c.c., is electrolysed for 24 hours at 2 amp. between gauze electrodes. The copper deposit becomes black and spongy (arsenic, molybdenum) towards the end. The electrolyte is filtered into a beaker and evaporated to fumes after addition of 10 c.c. of nitric acid. The mass is taken up in 400 c.c. of water, and the solution precipitated exhaustively with hydrogen sulphide to eliminate the remaining germanium, arsenic, and molybdenum. The precipitate is collected and washed with acidulated water; the washings are caught separately, evaporated to small bulk, strongly acidified, precipitated with hydrogen sulphide, and filtered into the main filtrate (germanium disulphide is soluble in water). The filtrate is boiled for the removal of hydrogen sulphide, the iron oxidised with bromine, and the iron, aluminium, and gallium obtained together by double basic acetate precipitation. The precipitate is dissolved in a minimum of sulphuric acid, the iron reduced by hydrogen sulphide, and the sulphur filtered off. The hydrogen sulphide is boiled off, the liquid cooled and treated with sodium carbonate to faint acid reaction, then boiled a few minutes with excess of a suspension of precipitated cuprous oxide: gallium and aluminium are precipitated. The precipitate is collected and washed with hot water, dissolved in dilute nitric acid, and the solution evaporated to fumes with sulphuric acid. The copper is removed by electrolysis; the electrolyte is again treated with hydrogen sulphide, etc., and the whole cuprous oxide separation repeated to remove the last of the iron, the copper being once more deposited electrolytically. The liquid, which now contains gallium and aluminium, is made faintly ammoniacal and boiled until its reaction is feebly acid. The voluminous precipitate is collected and washed with hot water. The following separation from aluminium is more convenient than the ferrocyanide method;

the precipitate is dissolved in dilute sulphuric acid, the acid is almost completely neutralised with sodium carbonate, and the solution diluted to 500 c.c. after addition of 5 grms. of sodium acetate. A suitable quantity of sodium arsenite is now added (equivalent to twice as much arsenic as the gallium present), and the cold liquid saturated with hydrogen sulphide; gallium is quantitatively precipitated in presence of arsenic. The precipitate must be washed in the cold, otherwise aluminium may be precipitated. The filtrate is tested for quantitative precipitation of the gallium by the ferrocyanide reaction, after being strongly acidified with hydrochloric acid: no precipitate should form. The sulphide precipitate is dissolved in *aqua regia* and the solution evaporated to fumes with sulphuric acid. Any silica is filtered off after dilution and the arsenic precipitated as sulphide. The filtrate is boiled to expel hydrogen sulphide, and the gallium precipitated with ammonia. The precipitate is filtered off, dissolved in nitric acid, and the precipitation repeated (removal of chloride). The precipitate is ignited and weighed as Ga_2O_3. *Molybdenum.*—Twenty-five grms. are digested for some time with 100 c.c. of nitric acid. The solution is diluted, filtered, treated with one grm. of iron as nitrate, neutralised first with strong, then with dilute, sodium carbonate solution to a permanent faint turbidity, diluted to 1500 c.c., and kept hot for 1 to 2 hours. If the quantity of iron is sufficient, the precipitate contains all the arsenic, molybdenum, bismuth, selenium, and tellurium. The precipitate is washed free from copper. A second precipitation, after addition of 0·5 grm. of iron, is carried out in the filtrate. The combined iron precipitates are dissolved in hydrochloric acid, and the solution precipitated exhaustively with hydrogen sulphide. The sulphides are treated with sodium sulphide; the resulting solution is acidified with hydrochloric acid, the precipitate coagulated by warming, collected, and dissolved in hydrochloric acid and potassium chlorate. The chlorine is expelled and the sulphur filtered off; it is burned off at low temperature, the fixed residue treated with hydrochloric acid and chlorate, and the solution added to the bulk. Selenium and tellurium are eliminated by sulphur dioxide. The filtrate contains molybdenum and arsenic; it is evaporated almost to dryness, the residue is taken up with 100 c.c. of strong hydrochloric acid, the solution saturated with sulphur dioxide, and again evaporated as before: arsenic is completely volatilised. The residue is evaporated with 10 c.c. of nitric acid almost to dryness, the mass taken up with hot water and a little nitric acid, and the solution made ammoniacal and filtered. The filtrate is acidified with acetic acid, and the molybdenum precipitated as lead molybdate. W. R. S.

New Organic Reagent for the Detection of Nitrates and Perchlorates. C. S. Marvel and V. du Vigneaud. (*J. Amer. Chem. Soc.*, 1924, **46**, 2661–2663.)—The new reagent is α-phenyl-β-diethylaminoethyl-p-nitrobenzoate, which forms insoluble salts with nitric and perchloric acids. Although it is not quite so sensitive as nitron or a di-(α-naphthylmethyl)-amine, it has the advantage of being specific. When applied in a 30 per cent. solution in dilute hydrochloric acid, nitrates or perchlorates give a white precipitate which is sensitive down

to 0·005 *N* and 0·0025 *N* respectively. Other anions, including nitrites and chlorates, do not interfere, but iodides, oxalates, thiocyanates and dichromates do. H. E. C.

Determination of Phosphorus in Phosphor Bronzes. L. Lindemann. (*Ind. Eng. Chem.*, 1924, **16**, 916.)—The method depends on the complete oxidation of the phosphides, prevention of the hydrolysis of the tin, and precipitation of the phosphoric acid as ammonium phosphomolybdate. About 0·2 grm. of cast phosphor bronze, or 0·5 grm. of malleable bronze, is dissolved in a mixture of 25 c.c. of hydrochloric acid (sp. gr. 1·10) and 5 c.c. of nitric acid; the mixture may be heated slightly at first, but the reaction must not be allowed to proceed too violently. The solution is then heated nearly to boiling for ten minutes to expel chlorine, diluted with 50 c.c. of cold water, 10 c.c. of dilute ammonia (1:1) and 50 c.c. of molybdic acid reagent are added, the precipitate is collected, and the phosphorus estimated alkalimetrically. W. P. S.

Applications of the Method of Electrolysis with the Dropping Mercury Cathode. J. Heyrovsky. (*Compt. rend.*, 1924, **179**, 1267–1268.)—Applications of the dropping mercury cathode described by the author (*Phil. Mag.*, 1923, **45**, 303; abst. *J. Chem. Soc.*, 1923, **124** ii, 119), are given, and it is shown that the method is useful in the investigation of solutions having very low ionic concentrations of the metals. Thus alkaline zincates and plumbates can be examined. It may also be applied to non-aqueous solutions of organic or inorganic substances. The difference between the decomposition potential π_n at the dropping cathode and the normal electrolytic potential E.P., multiplied by a factor F, expresses the affinity of amalgamation A of an equivalent of the metal; this represents the energy set free by the combination of the metal with the mercury. Numerical data are given in the paper. H. E. C.

Electrometric Titration of Hydrazine and its Salts. E. C. Gilbert. (*J. Amer. Chem. Soc.*, 1924, **46**, 2648–2655.)—Although the curve representing the titration of hydrazine with acid in the presence of an indicator such as methyl orange shows only one point of inflexion, indicating a mono-acid base slightly weaker than ammonia, electrometric titration reveals a second point of inflexion. This indicates a di-acid base in which the second stage in the ionisation corresponds with the formation of an unionised base N_2H_5OH or $N_2H_6(OH)_2$. The value of K_2 is less than 1×10^{-12}. Hydrazine may also be titrated electrometrically or stoichiometrically with either iodine or bromate solutions; the results of the two methods agree well. For the electrometric titration a 0·1 *N* calomel cell is used in the ordinary way. H. E. C.

Electrometric Titration of Antimony and Tin by Potassium Dichromate. M. H. Fleysher. (*J. Amer. Chem. Soc.*, 1924, **46**, 2725–2727.)—In the ordinary titration of trivalent antimony or divalent tin by potassium dichromate there is some difficulty with the end-point. This may be overcome by the use of the

electrometric method; an ordinary normal calomel cell and platinum electrode is employed, and there is a well-marked change in voltage of about 100 mv. at the end of the titration. It is advisable to eliminate atmospheric oxidation by replacing the air by carbon dioxide or hydrogen during the titration. Antimonious chloride can be determined in the presence of stannous chloride by the addition of mercuric chloride, which oxidises the tin, but has no other influence on the course of the titration. Arsenious chloride can be estimated in an analogous manner.

H. E. C.

Physical Methods, Apparatus, etc.

The Ultra-Centrifuge, A New Instrument for the Determination of the Size of Particles in Amicroscopic Colloids. T. Svedberg and H. Rinde. (*J. Amer. Chem. Soc.*, 1924, **46**, 2677–2693.)—An instrument has been devised for the measurement of the size and distribution of the particles in amicroscopic colloids about which but little is at present known. It consists essentially of a high speed centrifuge in which special precautions are taken to eliminate vibration and any small changes of temperature which give rise to convection currents. The colloid is centrifuged in this instrument, and the rate of movement of the boundary between the particles and the colourless liquid is observed either by means of a telescope or photographically, then the size of the particles and their distribution is calculated by means of equations developed from Stokes's formula as modified by Svedberg and Nichols. As an example, the size and distribution of the gold particles in gold sols are shown, having radii varying in different sols from 2·3 to 11·6 $\mu\mu$. The determinations give values from 11 to 38 per cent. higher than those given by Zsigmondy's nuclear method. H. E. C.

Method for the Determination of the Distribution of Size of Particles in Emulsions. E. O. Kraemer and A. J. Stamm. (*J. Amer. Chem. Soc.*, 1924, **46**, 2709–2718.)—When an emulsion in which the disperse phase tends to rise under the influence of gravity is placed in a wide vertical tube with an upturned capillary side-tube containing the dispersion medium, as the disperse phase rises there is a corresponding change of density which causes a change in the height of the liquid in the capillary. An instrument based on this principle has been designed, so that by observing the changes in position of the liquid in the capillary tube under suitable conditions the corresponding changes in pressure in the emulsion in the vertical tube, caused by the rising of the particles, can be calculated with the help of the equations which have been elaborated. From these expressions the distribution and the size of the particles can also be calculated. Emulsions of benzene and water, stabilised by potassium oleate and palmitate, have been investigated by this method, and, among other results, some confirmation of the wedge theory of emulsions is afforded by the fact that potassium oleate tends to give an emulsion with larger drops than does potassium palmitate.

H. E. C.

Continuous Conductivity Method of Measuring Small Concentrations of Chlorine in Air. T. B. Hine. (*Ind. Eng. Chem.*, 1924, **16**, 952–953.)—The air containing small amounts of chlorine is scrubbed continuously and rapidly with distilled water which is then allowed to flow through a conductivity cell. The electrical resistance of the cell is a function of the chlorine concentration of the air and serves as a measure of this concentration. A glass scrubber operating on the principle of the Ceco sprayer is recommended; in this apparatus the water falling on the centre of a rapidly revolving horizontal disc is thrown off to the sides in a thin sheet through which the air to be scrubbed must pass. The volume of liquid in the scrubber at any time is small, and there is practically no resistance to gas flow. The apparatus is standardised with air containing known amounts of chlorine. W. P. S.

Economic Anode for rapid Electrolysis. A. Lassieur. (*Bull. Soc. Chim.*, 1924, **35**, 1530–1532.)—The rotating anode consists of a glass rod bent in such a manner that its revolution will rotate the electrolyte. A thin platinum wire (diam. 0·3 mm.) is wound round the rod and communicates at the upper end with the anode terminal. In addition to the small quantity of platinum required, this form of anode presents the advantage of a small conducting surface, on which oxidation reactions are reduced to a minimum. W. R. S.

Reviews.

QUANTITATIVE ORGANIC MICRO-ANALYSIS. By F. PREGL. Second Edition. Translated by E. FYLEMAN. Pp. xv.+190, with 42 illustrations. London: J. & A. Churchill. 1924. Price 12s. 6d. net.

The translator of this volume has rendered a valuable service to British chemists by providing what appears to be the first text-book on this subject in the English language. Although much work of this nature has been carried out in America and in Germany, comparatively little advance in the application of micro-methods has been made in this country, and the publication of this volume should provide a stimulus to the adoption of procedures which are invaluable in many branches of organic investigation. The author was one of the pioneers in the application of micro-methods to quantitative organic analysis and has spent several years in the perfection of the methods described in this volume, these having been thoroughly tested by his colleagues and students and subsequently applied to researches in many branches of organic chemistry.

The subject matter consists of detailed descriptions for the setting up and manipulation of the necessary apparatus and methods for the determination of the usual elements and radicals in organic compounds, together with the micro-electrolytic estimation of copper and the boiling-point determination of molecular weights with the use of 1·5 c.c. of the solvent and 7 to 10 mgrm. of the substance

under examination. The delicacy and utility of the methods advocated will be appreciated when it is realised that a complete and accurate determination of carbon and hydrogen may be carried out with 2 mgrms. of material in about 45 minutes, and that a determination of copper in 20 to 25 grms. of preserved vegetables by the micro-electrolytic method may be completed in a little over one hour, with an accuracy within 1 per cent. of the metal present. Such methods are obviously only possible with a balance of precision, and a modified assay balance constructed by Kuhlmann to the author's specification is described; this is capable of turning to 0·001 mgrm. with a maximum load of 20 grms.

Not only are the manipulations described given with a wealth of essential detail infrequently met with in English books, but the author has also included in several instances the different stages reached in the development of the methods finally adopted. This feature will serve as a valuable example of manipulative evolution to the student, for whom a course of micro-analysis would provide an admirable training, but will be somewhat of a hindrance to the busy analyst. The translator has endeavoured to render his interpretation of Dr. Pregl's work as literal as was consistently possible, and the phrasing is consequently in a few instances somewhat quaint, and, in addition, one notices frequent references to different materials used being "of groat to hempseed size." The text of this volume is practically free from error, but a few references to other parts of the book are incomplete, since the number of the page is omitted, and on page 87 "grains" is printed instead of "grams," and cadmium on page 158 is rendered "cadium."

After studying the text of this excellent work one experiences a feeling of disappointment on turning to the index, for this is by no means on a level with the rest of the book. Many important sections and items in the text are entirely omitted, and, on the other hand, several references are given to pages upon which a substance or piece of apparatus is only incidentally referred to and their inclusion in the index is therefore useless. Thus under the index heading of "Combustion tube," we find on page 42 "connecting it with the neck of the combustion tube"; on page 65 "the rubber stopper at the mouth of the combustion tube" and so on. A further omission from the index is that of many necessary sub-titles, and it is somewhat bewildering to look up one title such as "Hydrogen" and find fifteen references without any indication given of the particular use or determination to which each refers. Such a defect seriously detracts from the value of the book as a whole and should be remedied at the earliest opportunity.

The methods described are in every way excellent, and, after a brief training, the chemist will fully appreciate the great economy of time, space, reagents, and material under examination which are attained by their use. With the exception of the index, the volume is an admirable production, and the author, translator and publishers are to be congratulated upon their success in providing a volume which will be eagerly read, not only by those to whom micro-analysis is an essential, but also by the average chemist who will find much material scattered throughout the book that will be applicable in his own work. T. J. WARD.

A Systematic Course of Qualitative Chemical Analysis of Inorganic and Organic Substances. By Henry W. Schimpf, M.D. Fourth Edition, revised by Alfred I. Cone. Pp. ix.+201. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. Price 8s. 6d. net.

This book was written for American students of pharmacy and consequently, from an English point of view, suffers from bad spelling and queer phrases and a host of other infirmities which we in England have come to consider as inherent in many American publications. In addition, there are several misprints (p. 10, "metadihydrohybenzol" for "metadihydroxybenzol," and p. 172, line 25, "quinine" for "quinidine") and, of course, the few references given are to the U.S. Pharmacopœia.

The opening section of the book deals with general considerations and contains rather scanty accounts of such topics as the Ionic Theory and the Law of Mass Action.

The second part gives, without attempting either to be exhaustive or to depart far from the accepted routine, an account of the ordinary procedure for qualitative inorganic analysis. Each group is treated under four main headings:—(1) The special reactions of the metals in that group; (2) A table of these reactions in the form of a comparison chart; (3) The group separation; (4) Notes on the peculiarities of the group.

These four sections overlap, and hence much unnecessary repetition occurs, so that it is difficult for a student to get a clear view of the main features of group analysis. The acids, both organic and inorganic, are treated in the usual way, *i.e.* a list of the special reactions of each followed by a scheme for their detection.

The final section deals with organic compounds of pharmaceutical value. It opens with a scheme for the detection of carbon, hydrogen, nitrogen, chlorine, phosphorus and sulphur—and omits entirely the sodium fusion method. The major part of the chapter is taken up with the special reactions of compounds such as santonin, strychnine, etc. It may be noted that a new test for quinine is recommended. This test involves the use of Labarraque's solution.

On the whole, although there is nothing very new or very wrong in it, the book offers no great advantages to those studying pharmacy in England, and, an English book is perhaps preferable for those would-be pharmacists who hope to practise in England. Harold Toms.

The Extra Pharmacopœia of Martindale and Westcott. Revised by W. Harrison Martindale, Ph.D., and W. Wynn Westcott, M.B., D.P.H. Eighteenth Edition in two volumes. Volume I. London: H. K. Lewis & Co., Ltd. 1924. Price 27s. 6d. net.

It is only four years since the last edition of this highly esteemed and indispensable compendium of medicines appeared, yet it has increased in bulk by about 50 pages, notwithstanding the numerous excisions that have been made by its revisers. For the chemist, as well as for the physician, the attractiveness of

"Martindale" will remain so long as it continues to be compiled on its present lines, because none of the articles is a mere statement of bald facts. The facts are there for every one to read and apprehend, but they are imbued with the imagination and the constructive spirit of the authors. How to write a preface is a question that chains most writers to the earth. The preface of this volume is an example of what can be done when courage, conviction and knowledge combine to guide the pen.

The monographs to which attention should be directed are many, and they thoroughly represent the rapid advances that are taking place in the field of therapeutics. Chemists will obtain a good idea of the return to favour of some of the metallic compounds. There is, perhaps, not so much importance to be attached, at the moment, to any increase in synthetic organic chemicals produced for medical purposes. On the other hand, many elaborate investigations have been made into the preparation and modes of action and methods of administration of colloidal metals, to which about twenty pages are given in the Extra Pharmacopœia. Basil Valentine seems to be in a fair way to have his belief in the medicinal virtues of antimony justified, if we may judge by the results which are being obtained from its use in protozoal infections. An excellent account of this work has been compressed into about a dozen pages. There is also given much information on the manufacture of the alkali-bismuthyl tartrates and the procedure to be adopted in the administration of them in syphilis; this is a matter in which considerable confusion prevailed, but Drs. Martindale and Westcott have succeeded in clearing up some of the mistakes as to the composition of these compounds.

Among other articles which have a claim for special mention are those on the alkaloidal periodides, the vaccines and antitoxins, potassium iodide and its use in goitre, cod-liver oil and its relation to the newer views on vitamins, and the preparations of chaulmoogra oil and their usefulness in the treatment of leprosy. For the chemist not the least useful feature of this work is the information that can be found as to the identity and composition of proprietary articles with more or less fancy names. A trial of the index for the tracing of these was very satisfactory; in fact, only one blank was drawn, and that was Nizin, which, by the way, was missing from the index of the previous edition.

It is a matter of supererogation to recommend what has already been designated as indispensable. The publishers' part has been accomplished most satisfactorily in every respect. WILLIAM KIRKBY.

THE CONCENTRATION OF SULPHURIC ACID. (Vol. III. Lunge Cumming Series.) By JOHN WILFRID PARKES, M.Sc., A.I.C. Pp. xii.+394. London: Gurney & Jackson. 1924. Price 31s. 6d. net.

The section dealing with this subject in the last edition has been completely revised and issued as a separate volume, and new matter has also been introduced.

The first two chapters give an outline of sulphuric acid concentration processes, and the properties of ordinary concentrated sulphuric acid. This latter chapter is extremely good and contains a large amount of most useful data, a great advantage being that only the most reliable information is given.

The third chapter describes concentration in lead pans, glass, platinum and other vessels. Various cascade plants are discussed, in which vitreosil and different acid-resisting alloys are used, and of these alloys a good description is given; the different types of plant are compared, with data on fuel consumption, etc.

In Chapter IV. concentration by various systems which make use of hot gases is very fully described. The Trepex, Kessler, Perrin, Duron, Gaillard, Gilchrist, and other plants are treated in detail. Much useful information is given as to fuel consumption and the working of the plant, more especially in connection with the Kessler and Gaillard plants.

A useful section taken from the Technical Records of Explosives supply works out in detail, among other things, the heat required for acid concentration.

The performance of the Cottrell and other electrical precipitators is dealt with in a chapter on the Concentration of Sulphuric Acid Vapours. The Calder high-speed scrubber is also an efficient plant, but the chief effect of either this or electrical methods is on suspended particles rather than on acid in the gaseous phase.

Chapter VII. discusses the recovery of acid from waste acid in petroleum refining, nitration processes, and in metal works. A fuller description of recovery from pickling and other acid waste liquors would have been of interest, as would also information on the use of film evaporators which have recently been used for this purpose, constructed in special lead alloys.

Chapters VIII., IX. and X. treat respectively, costs and efficiencies, transport of sulphuric acid, and statistics on its application.

Valuable information can be obtained from the Quinan method of costing used in H.M. Factories, and figures are given showing this in detail. The efficiency of the three general processes in use during the war is of interest, *i.e.*

Cascade	..	85–90 per cent.	Average Efficiency (1914–1918).
Kessler	..	91–93 ,,	,, ,,
Gaillard	..	96–97 ,,	,, ,,

The experience at Gretna, with waste acid from explosives, showed the Gaillard plant to be the most economical in working in all respects save fuel consumption. When dealing with chamber acid the Kessler plant is more flexible and less costly to install, but both were found superior to the Gilchrist plant.

This volume is well written and, like the previous edition, will be recognised as the standard work on the subject of sulphuric acid concentration. ERIC REAVELL.

THE MODERN SOAP AND DETERGENT INDUSTRY, INCLUDING GLYCEROL MANUFACTURE. Vol. I. THEORY AND PRACTICE OF SOAP-MAKING. By GEOFFREY MARTIN, D.Sc., F.I.C. Pp. 367+xii. London: Crosby, Lockwood & Son. 1924. Price 36s. net.

This is described as the first of three volumes which are to form a complete treatise on the Manufacture of Laundry, Toilet, Pharmaceutical, Textile, Abrasive, Scouring, and Powdered Soaps; also Detergent Compositions and Soap Substitutes of all kinds, and "the author hopes to justify the claim that no publication on soap so complete has appeared in any language."

The present volume deals with "the theory of soap, raw materials, calculation of charges, lay-out of soap factories, and the manufacture of ordinary household soaps by the usual processes." It is divided into seven sections, the first, on the Nature of Soap and Detergent action, being largely a reproduction of the very comprehensive article on the Colloidal Chemistry of Soap, by Prof. McBain in the Third Report on Colloid Chemistry, published by H.M. Stationery Office in 1920, while of the three following sections dealing with Raw Materials—Alkali and Alkali Salt; Oils and Fats; and Essential Oils and Perfumes—the two last appear to be abstracted almost verbatim from the author's works dealing with these two subjects, liberally interspersed with copious extracts, unacknowledged, from another text-book on the subject of Soap. In the section on Alkali, the causticisation of soda ash is very well described, but no mention is made of the fact that soap-makers are now taking up the manufacture of cement in order to dispose economically of the calcium carbonate obtained as a waste product. The author gives a very inadequate explanation of the "English" alkali degrees, and his definition of the American degrees as "the percentage of Na_2O present" is entirely wrong. The author's books on *Oils and Fats*, and *Essential Oils and Perfumes*, have already been reviewed in the pages of THE ANALYST (Nov. 1920, p. 432, and Dec. 1921, p. 527), so that it is unnecessary to discuss these sections at length, but it may be pointed out that the defects to which attention was then drawn, have not been remedied in any way in the present volume, and the reviewer would like to protest against the repetition of such statements as that the titre of a fat is "the melting point of the separated fatty acids," that "the refractive index of oils is usually determined at 60° C.," and that the melting point of an essential oil is determined by melting some of the solid oil, sucking it up a glass capillary tube, and attaching this to the bulb of a thermometer immersed in a bath of water, glycerin, or oil, which is then heated until the crystals in the tube melt and rise to the surface, this temperature being regarded as the m.pt. Further, coconut "oleine" and palm kernel "oleine" do not consist "mainly of free fatty acids," although anyone without special knowledge of the industry might think so in view of the final *e*.

These three sections which contain chapters on the analysis of the raw materials and should be of most interest to the analyst, are so full of errors, obsolete methods, and incomplete and misleading statements, as to be worse than useless in inexperienced hands, in spite of the fact that in the preface it is stated: "Very full methods of analysis of the various products are given, which it is hoped will enhance the value of the book to the analytical and works chemist."

The remaining sections, covering only some 173 pages—less than half the volume—are devoted to the manufacture of soap, Section V., from Free Fatty Acids, Section VI., by the Boiling Process, and Section VII., Household and Laundry Soaps. In Section V. it is difficult to understand the statement on p. 4 that "the Twitchell process has made possible the large scale saponification of fats for the production of crude glycerin free from salt," since "saponification glycerin," resulting from the saponification of fats in an autoclave with lime or

magnesia, was on the market long before the introduction of the Twitchell process. The castor seed ferment process is referred to as the "Connstein process," although Sudborough, Watson and Varna have shown that Nicloux's method for the production of the active reagent is the most suitable for oil-splitting on a large scale, and a period of 6–8 hours is much too short for anything approaching complete hydrolysis, usually two to three days being required. Section VI. is very copiously illustrated with various forms of plant used, and proposed for use, in the soap industry, but it is largely made up of abstracts from patents and trade catalogues, without any practical guidance as to their merits, and the whole of this section, as well as the following one, while accurately reproducing what may be termed the text-book methods of making soap, is very scrappy. Section VII., which includes rosined soaps, genuine and filled mottled soaps, cold process soaps, and soaps from waste fats, is, again, largely a compilation of abstracts from official reports, bulletins, patents, and published formulæ, and contains much that is now out of date, which is not surprising in view of the fact that the author has made use of old editions of many works quoted and acknowledged (with dates), much later and more up-to-date editions of which are now available. It is from every point of view a disappointing book. W. H. SIMMONS.

ANTIQUITIES: THEIR RESTORATION AND PRESERVATION. By A. LUCAS, O.B.E., F.I.C. Pp. 135. London: Edward Arnold & Co. 1924. Price 6s. net.

In this little unpretentious book Mr. Lucas embodies some of the results of his long experience in dealing with treasures from the past. Few chemists can have had his opportunities not only of studying the composition of museum exhibits of every kind and ascertaining the effects of time and exposure upon it, but also of applying the knowledge so gained to the task of preserving a marvellous collection of objects unearthed after thousands of years from the forgotten sepulchre of an Egyptian king. Some account of the remarkable chemical questions that were presented in the course of that work would have been welcome, but perhaps this is not yet permissible.

In view of the fact that many, if not most, of the curators of museums have little chemical knowledge, full directions for the preparation and use of the various reagents recommended have been given in very simple terms, and the methods of manipulation described can be followed readily by anyone. Methods of mending, restoring, preserving, and, in some cases, of cleaning every description of antique object likely to be shown in a museum are arranged in a form that is easy for reference. Even such specialised work as the restoration of faded writing and the treatment of old wood and stone is fully described, and, above all, the over-zealous restorer of the antique is taught when to stay his hand.

Apart from its value to a particular class of readers, the book is of general interest to every chemist, and may be profitably consulted by him in dealing with some of the out-of-the-way problems that he is occasionally called upon to solve.

The publishers may be congratulated on their enterprise in making generally available an interesting book in an attractive form. EDITOR.