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Studies in the Titration of Acids and Bases.

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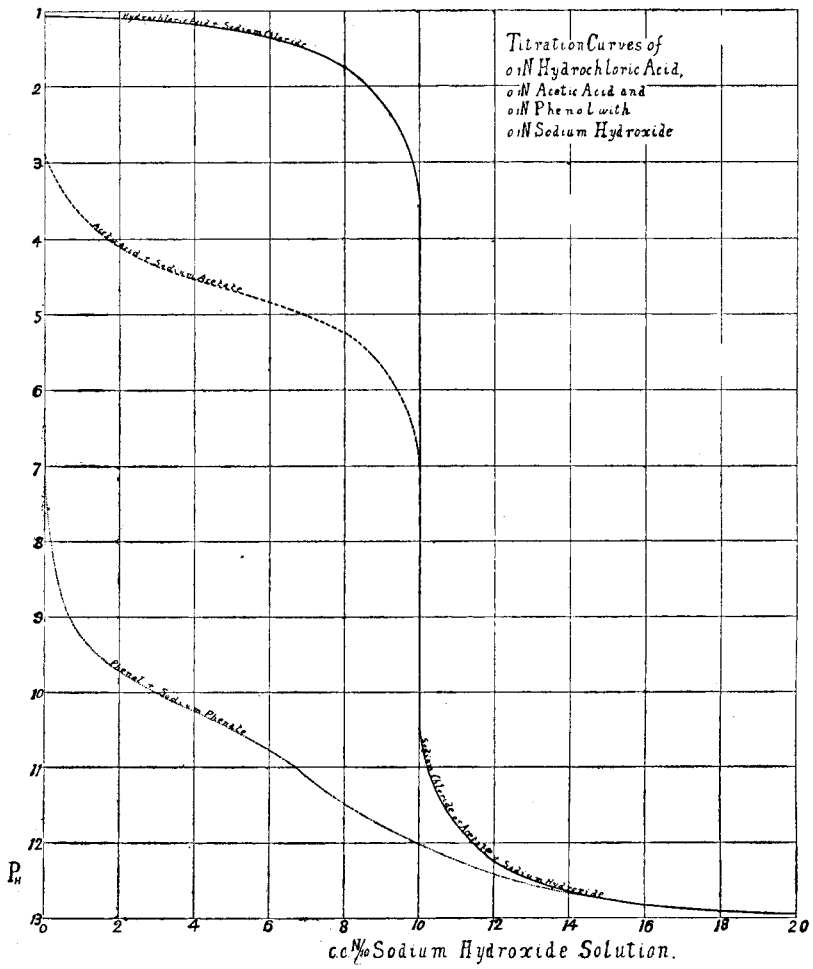
Various new synthetic indicators, such as those of the sulphonephthalein series studied by Clark and Lubs, have found valuable applications in the colorimetric method for determining hydrogen ion concentration (*cf.* Evers, Analyst, **1921, 46,** 393). The application of these indicators to titrations does not appear to have been systematically studied. A number of papers have been published advising the use of this or that new indicator for individual titrations, with the result that to the ordinary analyst the subject appears to be somewhat confused, and consequently he prefers to adhere to the older indicators whose limitations he knows, rather than to risk the use of those whose capabilities he does not know. It has appeared to us that, considering the obvious advantages of these indicators in hydrion measurements, they should also be applicable to titrations, which are, after all, only a particular case of hydrion measurement. We have therefore studied the whole question of the use of indicators in the titration of acids and bases, in order that a clear idea of the value of these new indicators might be obtained.

The Theory of Titrations. In a titration a solution of a substance A is added to a solution of a substance B until the quantity of A added bears a stoichiometric relation to the quantity of B. When this is the case the end-point of the titration is reached.

Now the end-product of a titration has a definite hydrogen ion concentration depending on the degree of hydrolysis of the salt formed by the titration, on the concentration and temperature of the solution. For most practical purposes the last two factors may be neglected, as they are not usually varied sufficiently in

titrations to cause any serious error. The hydrogen ion concentration or P_H* of the end-product is therefore dependent on the nature of the salt formed by the combination of the acid and the base, and our means of determining when the end-point is reached depends on measuring this P_H by the use of indicators which change colour at this P_H. As an example, when ammonia is titrated with hydrochloric acid the end-product is a solution of ammonium chloride. Now owing to the hydrolysis of this salt its solution is not neutral but slightly acid, and has a P_H = about 5·2. Methyl red, which changes colour from P_H = 4·4 – 6·0, is therefore a suitable indicator for this titration.

FIG. 1.



We may represent the course of a titration graphically by means of a curve, plotting the P_H against the volume of titrant added as in Fig. 1. We see that

* Hereafter the hydrogen ion concentration will be referred to as P_H for the sake of brevity, it being remembered that $P_H = -\log [H]$.

when a strong acid is neutralised with a strong base, as in the hydrochloric acid—sodium hydroxide curve, the P_H changes but slowly until the end-point is nearly reached, when a sudden change occurs and the curve becomes almost vertical until the end-point is passed, when it again becomes nearly horizontal. The actual end-point occurs at $P_H = 7$, which lies in the middle of the steep part of the curve. Owing to the steepness of the curve, however, it is unnecessary to confine ourselves to an indicator which changes at $P_H = 7$; any indicator changing between $P_H = 4$ and 10 will give an accurate result. In the case of a moderately weak acid, such as acetic acid, titrated with a strong base, we see that the steep part of the curve is less steep and much shorter. The end-point is now alkaline, viz. at $P_H = 8{\cdot}8$. For convenience we may call the P_H at the end-point the titration exponent or P_T. The indicator used is therefore a matter of importance, and the employment of one whose colour change lies far from $P_H = 8{\cdot}8$ will give inaccurate results. In the same way in the titration of a weak base the end-point is acid.

In the case of bodies with a very weak acid function, such as phenol, we see that there is no steep portion to the curve at all, merely the slightest inflection at the neutralisation point. The end-point is therefore ill-defined, and the substance cannot be titrated with an indicator in the ordinary way.

The possibility of an accurate titration therefore depends on the rate of change of P_H at the end-point, *i.e.* on the steepness of the curve. These titration curves furnish us with a means of determining the P_T of a titration, and this method has been adopted almost exclusively in the work for this paper.

The P_T of the titration lies at the middle of the steep part of the curve. In order to find the P_T of a titration, or whether the substance is titratable or not, a suitable weight of the pure acid or base is dissolved in water,* diluted to about 50 c.c. and titrated with standard hydrochloric acid or carbonate-free sodium hydroxide, with the use of an indicator of the desired range. As soon as the indicator begins to change colour the P_H is determined colorimetrically after each addition of titrant until the change is complete. For making titration curves the compound indicator shown is extremely useful. This indicator changes through the spectrum from P_H 4 to P_H 11 thus:

Colour	Red	Orange	Yellow	Yellow Green	Green	Blue Green	Violet	Deeper Violet
P_H	4	5	6	7	8	9	10	11

This enables a large part of the curve to be roughly sketched out in one titration, and the more important parts can then be determined more accurately with single indicators. From the steepness of the curve at the end-point we can readily judge whether the titration is possible and, if it is possible, with what accuracy it can be carried out. The middle point of the steep part of the curve is taken as the P_T of the titration, and the indicator selected for the titration is the one which is changing colour most rapidly near this point.

* If the substance is not soluble in water it is dissolved in a small amount of alcohol, partly neutralised and then diluted to the required volume with water before completing the titration.

In a satisfactory titration, as carried out in the ordinary way, one drop of standard solution added from a burette should bring about the colour change of the indicator, or, at the most, one drop should change the indicator from its extreme to its neutral colour, and a further drop should change it to its other extreme. It is important then that the indicator should change colour rapidly with change of P_H. Many titrations, however, obviously do not come up to this standard, whatever indicator is used. Such titrations may be made more accurate, and some titrations which are impracticable by the ordinary method may be satisfactorily carried out by titrating to a standard colour of definite P_H. As an example, quinine cannot be satisfactorily titrated in the ordinary way. The P_T, when titrating to the neutral salt, is 5·6, so that it is near the alkaline side of methyl red. By titrating until the colour matches a standard of $P_H = 5·6$, prepared from the usual solutions used for hydrion measurements, the titration may be made reasonably accurate. The following experiment illustrates this point: Anhydrous quinine (0·799 grm.) was dissolved in a small amount of alcohol, about 20 c.c. 0·1 *N* hydrochloric acid were run in, and the liquid diluted with water to about 50 c.c. The titration was continued to methyl red. The first change of the indicator occurred ($P_H = 6·0$) at 22·8 c.c., the neutral colour ($P_H = 5·2$) was reached at 23·8 c.c., and the change was complete ($P_H = 4·4$) at 25·1 c.c.—obviously a very unsatisfactory titration. By preparing 10 c.c. of a standard colour of $P_H = 5·6$ containing a proportionate amount of the indicator—an operation which takes only a few moments if the solutions are ready prepared*—and titrating until the same shade of colour is obtained, the result may be made correct within 0·1 c.c. 0·1 *N* HCl. In the experiment quoted 23·4 c.c. of 0·1 *N* hydrochloric acid were required, as compared with 23·37 c.c. required by theory.

Now if this method of titration is used, obviously an indicator with a short P_H range is not essential, provided that the colour change is marked at the end-point. We shall return to this point later in dealing with mixed indicators. It may be said that for all titrations, except those of strong acids and bases, a knowledge of the P_T and of the shade of colour which the indicator gives at that point will add materially to the accuracy of the titration.

THE CHOICE OF INDICATORS.—For ordinary titrations the range of P_H over which the colour change takes place should be short. Further, the end colours must form a good contrast; for instance, yellow to blue, or yellow to violet indicators are usually more satisfactory, as fine gradations of shade are more easily seen. Other points to be considered are the suitability for use by artificial light and the absence of errors caused by the presence of salts or protein.

ONE OR TWO COLOUR INDICATORS.—In the case of a two-colour indicator the end-point is judged by a *shade* of colour; with a one-colour indicator, by the *depth* of colour. Now in the latter case, of which the best example is phenolphthalein, the first production of colour depends on the amount of indicator added. For instance, a phosphate titration in which 5 drops of 0·2 per cent.

* By using a colour chart such as is given in Clark's *Determination of Hydrogen Ions* no standard solutions are required.

phenolphthalein solution were used required 16·55 c.c. of 0·1 *N* potassium hydroxide solution, but when 10 drops were used it required only 16·4 c.c. This source of error does not exist with a two-colour indicator, since the shade of colour is not dependent on the amount of indicator added. On the other hand, provided that the conditions are standardised, the first appearance of colour of a one-colour indicator is perhaps more certainly judged than the shade of a two-colour indicator. Generally it may be said that, if a large number of routine titrations are being carried out under identical conditions of concentration of indicator, etc., phenolphthalein or, better, phenolthymol-phthalein is a more suitable indicator to use than thymol blue, the corresponding two-colour indicator; but for general use, thymol blue is preferable. The two-colour indicators also have the advantage that the titration can be carried to a definite P_H with greatly increased accuracy. In the selection of the following list of indicators for titrations the above points have been taken into consideration. The list is intended as a suggestion for general use, but the choice between individual indicators is often a matter of individual taste.

TABLE I.

SINGLE INDICATORS.

	P_H range	Colour range
Thymol blue (acid range)	1·2—2·8	Red—Yellow
Bromphenol blue	3·0—4·6	Yellow—Blue
Methyl red	4·4—6·0	Red—Yellow
Phenol red	6·8—8·4	Yellow—Red
Thymol blue (alkaline range)	8·0—9·6	Yellow—Blue

Thymol blue.—The acid range is useful in approximate titrations of very weak bases, or in the titration of strong acids in the presence of weak acids, *e.g.* sulphuric acid in the presence of acetic acid. The alkaline range, generally speaking, takes the place of phenolphthalein, and is to be preferred for most purposes because of its two-colour change and the greater ease with which the colour change is observed in coloured solutions.

Bromphenol blue is of similar range to methyl orange, and will generally replace it. It has a greatly improved colour change.

Methyl red is the best indicator for moderately weak bases.

Phenol red is of value for titrations of acids which are too strong to give accurate results with phenolphthalein or thymol blue.

TABLE II.

MIXED INDICATORS.

	P_H range	Colour change
Methyl-thymol blue	4—10	Red—Yellow—Greenish-blue
Phenol violet	8—10	Yellow—Blue—Violet
Phenol-thymolphthalein	8·3—11	Colourless—Pink—Violet
Thymol violet	9—13	Yellow—Green—Blue—Violet

The use of mixed indicators has, in certain cases, advantages over single indicators; the colour change may be improved and a greater range of shades may be produced, enabling a titration to be carried to a definite P_H with greater certainty. Mixed indicators may also have the effect of providing a warning of the approach of the end-point of the titration, or an indication that the titration has been overshot. It should be said that indicators cannot be mixed indiscriminately; careful attention must be paid to the proportions of the constituents. The mixed indicators mentioned above may now be considered individually.

Methyl-thymol blue.—(Methyl red, 1; Thymol blue, 3) is useful for the titration of strong acids and bases. The neutral colour of the indicator is yellow at $P_H = 6-8$. We have said above that in these titrations indicators changing anywhere between $P_H = 4$—10 may be used. As long as the titration is carried to the yellow colour the correct end-point must be obtained. Excess of alkali gives a blue colour, and excess of acid a red colour.

Phenol violet.—(Phenolphthalein, 1; Thymol blue, 6) is used for the titration of weak acids. It is similar to thymol blue, with the advantage that the alkaline colour is violet, whereas the neutral colour is blue. The over-shooting of a titration is therefore clearly shown, and the useful range is somewhat increased. It is particularly useful in determining saponification values, the change being much more readily seen than that of phenolphthalein.

Phenol-thymolphthalein.—(Phenolphthalein, 1; Thymolphthalein, 6). This may be used instead of phenolphthalein, but the colour, after becoming pink, changes to violet as it becomes more alkaline. It is therefore possible to use it for somewhat weaker acids than is the case with phenolphthalein. The violet colour also provides a warning of the approach of the end-point when coming from the alkaline side. This indicator has the advantages and disadvantages of a one-colour indicator referred to above.

Thymol violet.—(Tropaeolin, 0, 1; Thymolphthalein, 4) is an improvement on other indicators for a very alkaline range for titrating very weak acids. Its range is wide, viz.:—

Colour	Yellow	Yellow-Green	Blue-Green	Blue	Indigo	Violet
P_H	9	10	10·5	11	12	13

In titrations to thymol violet it is usually necessary to work to a definite standard end-colour, but its use makes possible certain titrations which would not otherwise be practicable.

We are of the opinion that all the above indicators have definite advantages over those which they are intended to replace. There are doubtless others of equal value and some which, for certain definite purposes, might be found to give better results, but after considerable experience of their use in the laboratory we can recommend them with confidence.

By means of the titration curve method the titrations of a large number of acids, bases and salts have been investigated, the P_T determined, and the most appropriate indicator selected from the above list. The results are embodied in the following table:

TABLE III. Acids.

Acids	P_T	Indicators	End-Colour	Remarks
Hydrochloric, Hydrobromic, Hydriodic, Sulphuric	7	Methyl-thymol blue Methyl red Bromphenol blue	Yellow Orange Green	
Picric Acid	7	Methyl red	Yellow	
Saccharin	7·1	Phenol red	Orange	
Salicylic Acid	7·2	,,	,,	
Nitric Acid	7·5	,,	,,	
Hippuric Acid	7·5	,,	,,	
Fumaric Acid	7·5	,,	,,	to neutral salt.
Benzoic Acid	7·6	,,	,,	
Formic Acid	7·8	,,	,,	
Lactic Acid	7·8	,,	,,	
Cinnamic Acid	8·0	,,	Red	
Oxalic Acid	8·0	,,	,,	
Acetylsalicylic Acid	8·0	,,	,,	
Tartaric Acid	8·1	,,	,,	
Valeric Acid	8·3	Thymol blue or Phenol violet	Green	
Carbonic Acid	8·4	,, ,,	,,	to bicarbonate
Maleic Acid	8·5	,, ,,	,,	to neutral salt
Malonic Acid	8·5	,, ,,	,,	
Boric Acid with glycerin	8·6	,, ,,	,,	
Acetic Acid	8·8	Thymol blue or Phenol violet	Blue	
Phthalic Acid	8·8	Thymol blue or Phenol violet	Blue	
Succinic Acid	8·8	or Phenol-thymolphthalein	Pink	
Malic Acid	8·8	or Phenol-thymolphthalein	Pink	
Citric Acid	9·5	Phenol violet	Violet	
Oleic Acid	9·5	or Phenol-thymolphthalein	,,	
Diethylbarbituric Acid	10·2	Thymol violet	Green to standard colour	
Phosphoric Acid	4·5	Bromphenol blue	Maximum Blue to acid salt	
or Glycerophosphoric Acid	9·1	Thymol blue or Phenol violet	Blue to normal salt	
Hypophosphorous Acid	5·5	Methyl red	Orange	
Boric Acid without glycerin	11·1	too weak for titration		
Phenol	12	too weak for titration		

Bases.

Base	P_T	Indicator	End-Colour	Remarks
Strong bases	7	Methyl-thymol blue Methyl red Bromphenol blue	Yellow Orange Green	
Nicotine	5·5	Methyl red	Orange	
Homatropine	5·5	,,	,,	
Ammonia, Morphine, Codeine	5·2	,,	,,	
Atropine, Strychnine, Brucine, Ethylmorphine	5·0	,,	,,	

BASES (*continued*)

Salt	P_T	Indicator	Colour	Remarks
Diacetylmorphine, Emetine	4·9	,,	Orange-red	
Cocaine, Pilocarpine	4·7	,,	Red	Direct titration
		Bromphenol blue	Blue (max.)	Back ,,
Piperazine	3·7	,,	Green	
Pyridine	3·6	,,	,,	
Aniline	2·8			Not sharp
Quinine, Cinchonine	3·5 (to acid salt)	,,	Standard colour	
Cinchonidine, Quinidine	5·6 (to neutral salt)	Methyl red	,,	

SALTS.

Salt	P_T	Indicator	Colour	Remarks
Borax	5·2	Methyl red	Orange	
Sodium carbonate to bicarbonate	8·4	Phenol violet or Thymol blue	Yellow	
Sodium phenate	6·5	Phenol red	,,	
Sodium dihydrogen phosphate (to acid salt)	4·5	Methyl red	Red to maximum colour	
Sodium acid phosphate (to normal salt)	9·1	Thymol blue or Phenol violet	Blue to standard colour	
Sodium arsenate	5·5	Methyl red	Orange to standard colour	
Caffeine citrate	9·5	Phenol violet	Violet	
Caffeine hydrobromide	7·2	Phenol red	Orange	
Quinine acid salts (to neutral salt)	5·6	Methyl red	Orange to standard colour	

All the above results were obtained with deci-normal solutions. Titrations with semi-normal or normal solutions are naturally sharper and more accurate.

Of the above-mentioned titrations several call for special notice.

PHOSPHORIC ACID.—Owing to the slow rate of change of P_H at the end-point, titrations of phosphoric acid are very unsatisfactory. The titration may be made either to the acid salt ($P_T = 4·5$) or the normal salt ($P_T = 9·1$). In titrating to $P_T = 4·5$ the difficulty arises that no indicator changes sufficiently at this P_H to give a satisfactory end-point. Accurate results may be obtained by using bromphenol blue when coming from the acid side, and continuing the addition of alkali until the maximum blue colour is attained, which occurs at $P_H = 4·5$. Similarly, when coming from the alkaline side methyl red is used and carried to its maximum red colour. As an example, 25 c.c. of M/15 potassium acid phosphate solution were taken and 10 c.c. 0·1 *N* hydrochloric acid added and titrated with 0·1 *N* potassium hydroxide solution to brom-phenol blue until the maximum violet colour was attained, as shown by comparison with a solution of the indicator of the same strength made alkaline by a few drops of 0·1 *N* potassium hydroxide solution. The number of c.c. required = 10·0. The same volume of phosphate solution was again taken, and 10 c.c. 0·1 *N* potassium hydroxide added. The solution was titrated with 0·1 *N* hydrochloric acid until the red colour of methyl red was no

further increased; 10·0 c.c. were again required, showing that the same end-point had been reached in each case. The P_T when titrating to the normal phosphate is 9·1. The usual indicator used for this titration is phenolphthalein; but, as has been shown above, this does not give accurate results unless the amount is carefully adjusted so that the first appearance of pink colour is at $P_H = 9·1$. By using thymol blue or phenol violet and titrating to the shade of colour corresponding to $P_H = 9·1$, results accurate to one drop of 0·1 *N* acid may easily be obtained; but though this end-point is sharper than that of the acid salt, accurate results cannot be obtained unless this is done. For example, 25 c.c. of potassium hydrogen phosphate solution were titrated to thymol blue. The first colour change occurred after the addition of 16·0 c.c. of 0·1 *N* potassium hydroxide solution, the neutral colour was reached at 16·45 c.c., and the final blue colour at 16·65 c.c. At P_H 9·1 the amount added was 16·5 c.c. Phenolphthalein, under the same conditions when 5 drops of a 0·2 per cent. solution were used, gave 16·55 c.c. and 16·4 c.c. with 10 drops of indicator.

Carbonates.—In the titration of carbonate to bicarbonate the P_T is 8·4. In order that phenolphthalein may change at this P_H a large concentration must be present. By using thymol blue and carrying the titration to a yellow colour, the correct result is obtained. Carbonate and hydroxide together may therefore be estimated by first titrating with thymol blue to yellow, then adding bromphenol blue, and titrating to the neutral colour. The difference between the two titrations gives the carbonate present.

Boric Acid.—In the absence of glycerin or mannitol, boric acid is too weak an acid to give a sharp end-point. The addition of either of these increases the P_H to such an extent that titration is possible.

Oleic Acid.—This is of interest as it concerns the determination of the acid value of oils. The end-point is more alkaline than that of most other acids, and phenol violet taken to full violet will be found the most useful indicator for this titration.

Ammonia.—The chief interest of this titration is its employment for the Kjeldahl method of nitrogen estimation. In this case we have a large volume of liquid containing a low concentration of ammonium chloride and an excess of acid. Usually the liquid contains a fair quantity of dissolved carbon dioxide released from the concentrated sodium hydroxide on addition to the acid in the distillation flask and carried over by the steam. Unless this carbon dioxide is removed the titration is very unsatisfactory. The use of the carbonate-free alkali suggested below reduces this source of trouble and makes a sharper end-point possible.

The Effect of Carbon Dioxide on Titrations.—Unfortunately it is difficult to make and keep standard alkali solutions free from carbonate. The use of baryta is only possible up to 0·2 *N* concentration, and it is not so generally applicable as potassium or sodium hydroxide. The use of alkali which has been carefully freed from carbonate in an apparatus from which carbon dioxide is excluded is not practicable in the ordinary laboratory without considerable trouble, though it was used in the titrations carried out for this paper. Nevertheless,

there is no reason why standard alkali solutions should not be as free from carbonate as possible. If a 1:1 solution of sodium hydroxide is kept in a stock bottle so that the carbonate settles out, the standard alkali prepared from the clear upper layer by dilution with carbon dioxide free water is reasonably free from carbonate.

Carbon dioxide is also introduced into the titration in the distilled water, and the carbon dioxide in the air may have a slight, though not great, effect on the end-point. Carbon dioxide acts as a weak acid; and since the P_H of a solution of carbon dioxide is about 4, it follows that any indicator whose colour-change occurs at a higher P_H is affected by carbon dioxide; and the higher the P_H of the colour-change, the greater will be the error due to carbon dioxide. We can, of course, correct for the carbon dioxide present by means of a factor for each indicator used; but unfortunately a further difficulty arises in that when adding alkali to an acid solution containing carbon dioxide, the indicator, after reaching its alkaline colour, changes slowly back again to its neutral, or even acid, colour. This is caused by the fact that the reaction—$CO_2 + H_2O = H_2CO_3$—is a time reaction. We can avoid this by adding an excess of alkali and titrating back with acid, when the end-point is sharp; but the error due to the carbon dioxide present must of course still be allowed for.

In conclusion, it may be said that the important point in connection with obtaining accurate results by titration is the knowledge first of all of the P_H of the end-point or P_T of the titration. Knowing this, and knowing what indicators are available for this P_T, we may choose the one which suits our particular taste, and the result will be accurate, but the indiscriminate use of phenolphthalein for all weak acids and of methyl orange for weak bases cannot, and does not, give results of such accuracy as may easily be obtained if the right indicator is used.

SUMMARY.—1. A list of indicators for general use in the titration of acids and bases is suggested. 2. The value of mixed indicators is discussed, and several which have been found useful are suggested. 3. By titrating to a definite shade of colour, instead of to the colour-change of the indicator, an increase in the accuracy of titrations results, and certain titrations are made possible which are impracticable by ordinary methods. 4. A list of titrations is given, with the indicators suggested for each.

DISCUSSION.

Mr. F. H. CARR congratulated the writers on making a really practical contribution to analytical chemistry, and said that he believed that we were rapidly approaching the time when the newer indicators would be universally employed. The authors had shown, in a very practical way, how helpful these indicators may be to every chemist. He asked whether they had investigated the behaviour of other acids and bases than those Mr. Evers had mentioned.

Mr. A. E. PARKES said that he agreed with the last speaker; the substance of the paper threatened to revolutionise the ideas of many of those present. He enquired whether the concentration of the solution which was being titrated had any influence on the results. The concentration of a solution was entirely different

from the hydrogen ion concentration; the points at which the curves change might vary with different concentrations. Compared with the old-established indicators, some of these new ones would explain certain difficulties frequently met with, as, for instance, with acetic acid. When titrating strong acetic acid solutions, with phenolphthalein as indicator, results were sometimes obtained as much as 2 per cent. too high. From the authors' diagrams it would be seen why this would occur. The authors had mentioned the trouble likely to occur from carbon dioxide in solution. He had been in the habit of using caustic soda to which 5 per cent. of barium hydroxide solution had been added; it then remained free from carbon dioxide for quite a long time. If this combination were more generally known, it might be found useful in connection with some of these indicators which were sensitive to carbon dioxide.

Dr. J. C. DRUMMOND said that this form of indicator (methyl red) was superior to methyl orange for ammonia, particularly in connection with the titrimetric estimation of very small quantities of ammonia.

Mr. NORMAN EVERS, in reply to Mr. Carr's question, said that only a selection of results had been referred to that evening, but that there were further results in the full paper. With regard to Mr. Parkes' question as to the effect of the concentration of the solution, the difference was in most cases very slight; the titration curve, for example, of $N/200$ hydrochloric acid and $N/200$ sodium hydroxide, differed very little from that of deci-normal solutions. As to the titration of acetic acid, phenolphthalein ought to give accurate results, since the end point of the titration corresponded with the point where phenolphthalein turned pink. As to the use of barium hydroxide for making carbon dioxide free alkali, this was quite a useful method, except that for some purposes the barium hydroxide might be objectionable. The use of a very concentrated sodium hydroxide solution, as suggested in the paper, gave as good results as any.

The Sulphuric Acid Reaction for Liver Oils.

BY J. C. DRUMMOND, D.Sc., F.I.C., AND A. F. WATSON, M.Sc., A.I.C.

(*Read at the Meeting, May* 3, 1922.)

A FEW years ago Dr. O. Rosenheim suggested to one of us the possibility of the dietary unit termed vitamin *A* being a member of the lipochrome class of natural pigments. The researches which followed this suggestion led to a joint paper being published (Rosenheim and Drummond, *Lancet*, 1920, I., 862), in which it was shown that the vitamin could not be identified with the chief members of the lipochrome pigments—xanthophyll and carotene, but that nevertheless there appeared to be some association of growth-promoting powers with the presence of natural fat-soluble yellow colouring matters, an association which had also

been suggested independently by Steenbock and Boutwell (*J. Biol Chem.*, 1920, **41**, 81).

We do not here intend to discuss this aspect of the study we then made, but to refer to certain of our investigations which at the time led us along another path.

In the course of investigating the lipochromes and vitamin content of liver and liver oils and fats we could scarcely fail to turn our interest to the substance which gives rise to the well-known purple colour reaction with sulphuric acid. After a few tests we were led to abandon our original idea that the substance responsible for the colour is, or is closely associated with, the vitamin *A*, for we found a lack of coordination between the intensity of the reaction and the relative figures that we then believed represented the vitamin value of the foods tested. For example, we could obtain at the most a very transient colour reaction with samples of butter then believed to be a highly potent source of vitamin *A*. Nevertheless from other interests we made a number of experiments in order to identify, if possible, the unknown constituent of liver oils which yields the purple colour.

These results were not published in detail at the time because they had not given us a solution of our main problem, but during the last year our interest in this colour reaction has greatly increased owing to the very important observations of Zilva and Miura (*Lancet*, 1921, I., 323). These authors showed that the relative values of average samples of butter and cod-liver oil as sources of vitamin *A* are approximately in the proportion of 1:250. This surprising discovery at once stimulated us to review our results on the substance in liver oil, since it suggested a possible cause of the great difference in the intensity of the colour reactions given by butter and cod-liver oil.

Unfortunately Dr. Rosenheim has been unable to continue his collaboration with us, but he has most kindly placed at our disposal certain of his own notes on the subject.

THE SULPHURIC ACID COLOUR REACTION FOR LIVER OILS.—A considerable number of modifications of this test are to be found in the literature of the subject. The U.S. Pharmacopœia recommends the oil to be dissolved in chloroform and shaken with one drop of sulphuric acid, whilst the German Pharmacopœia advises the employment of carbon disulphide as a medium.

Kadt (*Pharm. Weekblad*, 1920, **57**, 756) states that the reaction is increasingly sensitive in carbon disulphide, carbon tetrachloride, petroleum spirit benzene, and chloroform.

We have found the test to be very sensitive when petroleum spirit (b.pt. 40°-60° C.) is used, and have generally employed this solvent for the oils.

In the majority of standard works on the examination of oils it is stated that the reaction is only given by liver oils, although Thomson and Dunlop (quoted from Lewkowitsch, Vol. I., p. 495, 5th edn.) record having obtained the typical colour reaction with samples of seal oil and porpoise oil of undoubted purity. In the course of our work we have found the substance or substances responsible for the colour in the livers of the following species: Man, horse, ox, pig, cat, monkey, rabbit, guinea-pig, chicken, duck, pigeon, rat, mouse, frog, shark, cod, haddock,

ling, coal-fish, dog-fish, sprat, and skate. It therefore appears probable that the substance is normally a constituent of the liver tissue of animals.

Our next point was to ascertain the origin of this substance. One of the earliest papers is by Salkowski (*Zeitsch. anal. Chem.*, 1887, **26**, 557), who agrees with Bucheim (*Arch. Exp. Path.*, **3**, 118) that Hagen (*Jahrb. Pharm.*, 1885, 182) is wrong in attributing the colour to the action of sulphuric acid on bile constituents.

We have confirmed this opinion (that bile constituents are not responsible) by direct tests on the fresh bile of several of the above species (including cod), as well as on the unsaponifiable fractions prepared from those samples of bile. We found the reaction to be given strongly by many samples of cod-liver oil prepared in our presence by modern methods in which the removal of the gall bladder before steaming is regarded as of primary importance.

Salkowski (*loc. cit*) found that the unsaponifiable fraction of cod-liver oil retains the substance giving the colour test. This fraction is, as he showed, largely composed of cholesterol, which does not give the purple colour, together with pigments of the lipochrome class. His conclusions were that the colour reaction of cod-liver oil is not due to the lipochromes, cholesterol or the fatty acids.

Lewkowitsch (Vol. II., 5th edn.) regards the purple colour as being due to certain of the products of rancidity. It is pointed out (p. 441) that the test indicates the presence of impurities (lipochromes and colouring matter) which have passed from the cellular tissue of the liver into the oil, and that by the improvement in the manufacturing processes the quantity of these bye-products has decreased, so that during later years the better class oils show the reaction less markedly than the liver oils prepared by the old rotting process. He adds (p. 442): "A manufacturer should therefore endeavour to produce a cod-liver oil which does not show the sulphuric acid test at all or very faintly."

We were unable to confirm his view as the result of the examination of a very large number of samples of fish liver oils of which we knew the history.

Further, the livers of freshly killed normal guinea pigs and rats yield an oil which gives the typical colour reaction, and allowing the livers to stand for many hours before extracting the oil, (which is then rancid), does not yield a product giving a more intense colour. Last year one of us (J. C. D.), together with Dr. S. S. Zilva, paid a visit to the chief centres of the Norwegian cod-liver oil industry both in the Lofoten Islands and in Finmarken, and obtained a number of samples of oil from absolutely fresh livers, and in every case the colour reaction was typically given, although varying in intensity with the samples.

From a large number of experiments we have concluded that the substance giving rise to the colour is a normal constituent of the liver of the species we have examined.

As to the chemical nature of this substance, we have, in spite of much work, been unable to obtain any positive information. We have confirmed Salkowski's observations, that it may be wholly transferred to the unsaponifiable fraction of the oils, and that it is not cholesterol. It also appears improbable that it is a lipochrome pigment, since a solution of the unsaponifiable matter decolorised with Norit (a

commercial adsorbent), and presumably free from such colouring matters, still retains its power to yield the typical reaction. Moreover, in the examination of a large number of liver oils, the ability to give the purple colour reaction was frequently strongest in oils which from their colour appeared to contain relatively small amounts of lipochromes.

The substance is very prone to oxidation, which may explain why old samples of liver oils may fail to show the test (Lewkowitsch, Vol. II., p. 442), but it is thermo-stable for several hours at temperatures below 120° C., if protected from oxidation by the passage of a current of carbon dioxide.

It was these facts, few as they are, that led us to draw a parallel with the unidentified dietary factor known as vitamin *A*, and we proceeded to put the matter to the test.

We were at that time investigating the factors that determine the presence of vitamin *A* in certain animal fats, and there were available the body fats and livers of a number of pigs which had been fed on special diets of which some had contained sources of the vitamin *A*, whilst others were deficient in that respect (Drummond, Golding, Zilva, and Coward, *Biochem. J.*, 1920, **14**, 742). We found to our surprise that the liver fat of the pigs fed on diets deficient in vitamin *A*, although containing small amounts of lipochromes, gave no purple colour test with sulphuric acid, whereas not only did the liver fat derived from the other groups fed on a diet rich in vitamin *A* give the reaction, but it was also given faintly by the body fat.

Other miscellaneous material of a similar nature gave results agreeing with this, and we were led to examine the question more carefully.

Closely controlled groups of rats which had been fed on diets containing relatively large amounts of vitamin *A* always showed the presence of the chromogenic substance in the liver, and occasionally, especially when the diets contained a more than usually potent liver oil, the colour reaction was given by the body fat as well. The presence of the chromogenic substance in the body fat of certain species which only appears to be marked when the liver is very rich in that substance probably explains the observations of Thomson and Dunlop on porpoise and seal oil. Vitamin *A* is also frequently stored in body fats in similar cases.

The next step was to investigate whether the potency of a number of sources of vitamin *A* runs parallel with their ability to give the colour reaction. To do this satisfactorily it was necessary to carry out the colour test in such a manner as to render some comparison of the colours possible. So far this task has defied our attempts; and although more recent results make us hopeful of more success soon, only a very rough method is at present available.

The chief disturbing factors are, first, that the colour rapidly fades from blue violet to red violet, and thence to red and brown; and secondly, that the presence of varying amounts of lipochromes cause slight variations in the initial colour itself, since they tend to yield blue or blue-green colorations.

We have tried many methods to overcome these difficulties, but so far with very little success. A rough approximation, which was useful in the examination

of a series of liver oils has, however, been achieved by making a series of dilutions of the oil in petroleum spirit and ascertaining at what dilution the colour reaction is just given on the addition of one drop of sulphuric acid. Naturally, the error is large, even when the tests are carried out as nearly as possible under identical conditions; but the results, inaccurate as they are, have been interesting, and we believe are worth recording. In the examination of the vitamin value of liver oils, in collaboration with Dr. S. Zilva, to which reference has already been made, a method was employed by which comparisons of growth-promoting power could be made in terms of the daily dosage required to cause a certain recovery of growth. As stated elsewhere (ANALYST, 1922, 238) this method is capable, in skilled hands, of greater accuracy than would at first be imagined.

A large number of oils, of which the growth value had been determined by this means, were submitted to the above method of judging the strength of the colour reaction, with the following interesting results:

COLOUR INDEX OF FISH LIVER OILS OF KNOWN ORIGIN.

Daily dose in mgrms., giving approximately the same growth in rats.

	1·5 mgrms.	2 mgrms.	3 mgrms.	5 mgrms.	10 mgrms.	15 mgrms.	20 mgrms.
Colour Indices	20	12	12	8	6	8	5
	25	18	10	8	6	7	5
	30	10	10	10	7	6	4
	—	16	12	4	7	6	4
	—	16	16	16	7	6	8
	—	15	8	10	8	7	2
	—	—	10	8	9	6	2
	—	—	8	8	—	—	2
	—	—	—	—	—	—	2
	—	—	—	—	—	—	3
	—	—	—	—	—	—	3
	—	—	—	—	—	—	5
	—	—	—	—	—	—	3
	—	—	—	—	—	—	3
	—	—	—	—	—	—	—
Averages	25	14	11	9	7	6·5	3·5
	—	—	—	—	—	—	—

The colour index is derived from the dilution at which the colour is just given, and roughly represents the power of the oil to give the test. In spite of the very great source of error in comparing two sets of figures from such very rough tests, it will be seen that there is a general agreement in that oils which give a strong colour test tend to be high in the list of growth-promoting power and vice versa.

To test the value of the method more closely, the vitamin activity of a number of oils which had not been tested on rats was estimated by the rough colorimetric procedure. The figures obtained were found to agree with the results of the subsequent animal-feeding tests very well as a whole, only two cases disagreeing to any great extent.

The following experiment is also interesting in that it demonstrates a parallel destruction of the growth-promoting potency and the power to give the purple colour reaction with sulphuric acid.

A sample of coal fish liver oil of high degree of purity gave a particularly intense purple coloration, and was highly potent as regards growth-promoting powers. A quantity of this oil was heated to 100° C. and a rapid current of air passed through by means of a fine capillary tube. At the end of each hour a sample of oil was withdrawn and tested for vitamin activity by feeding experiments, and for the colour reaction by the dilution method. The table below gives the results of the tests of the fractions.

Fraction	Time of Aeration at 100 C. Hours	Colour Index	Effect on Growth Dose, 10 mgrms.
1	–	20—25	Good
2	1	20	Good
3	2	18	Fair
4	3	15	Slight
5	4	4	None
6	5	0	None*
7	6	0	None*

* Animals fed on these fractions developed xerophthalmia. Several of them died as a result of vitamin *A* deficiency.

The curves illustrating the growth experiments were published in a recent paper in this journal (ANALYST, 1922, 235).

The occurrence of the eye disease termed xerophthalmia, in the rats fed on fractions 6 and 7, is conclusive proof that the vitamin *A* had been destroyed.

It is possible, therefore, that in liver oils there may be an association between the presence of the vitamin *A* and the power to give the typical purple colour reaction, so long used as a test for such oils. From this point to assuming the identity of the two substances responsible is, however, far to go. We have, nevertheless, attempted to throw some light on the matter by investigating the distribution of the two substances in different foodstuffs. We know that vitamin *A* is synthesised by plants, whether terrestrial or marine, which contain photocatalytic pigments (Coward and Drummond, *Biochem. J.*, 1921, **15**, 530), and Jameson, Drummond and Coward (*Biochem. J.*, in the press). Such sources constitute the primary source of this indispensable dietary unit for all animals, land or sea.

We have examined a number of such plants for the presence of the substance producing the purple colour reaction, but with varying success.

In the case of one or two marine algæ (*Ulva*, etc.) we did definitely trace its presence, but we could not detect it in the oil extracted from a marine diatom *Nitzschia*, an organism representative of the ultimate food of all marine animals We have attempted, so far without success, to trace the origin of the chromogenic substance in cod-liver oil. The cod feeds largely on small fish, particularly the caplin, young herring, and on squid, which feed on copepods, amphipods and other

plankton, which in turn thrive on microscopic marine plants (diatoms, etc.). The ultimate food supply, represented by *Nitzschia*, gave no trace of the colour reaction, nor could we detect the chromogenic substance in samples of the mixed plankton (calanus, other copepods, amphipods and decapod larvæ, etc.), which form the food of young fish. Small fish—sprats and young herrings—which live on this food, and which in turn constitute the food of the cod, contain the chromogenic substance in their livers. The diatoms (*Nitzschia*) and the copepods (calanus) contain considerable amounts of a lipochrome pigment closely related to, if not actually identical with, carotene.

The difficulty of examining such material is great owing to these lipochromes which accompany the unsaponifiable matter, and which give rise to colours which tend to mask the purple colour when the latter is faint. Nevertheless, the evidence at present in our hands tends to support the view that the chromogenic substance is derived from the food. For example, the unsaponifiable matter of the liver of a pig that had been fed on a diet devoid of vitamin *A* for several months, gave only a very faint trace of the purple colour reaction, whereas a control animal which had received the same ration together with grass gave the reaction very strongly, although we obtained a doubtful result on testing grass itself.

If the association exists which we believe we have traced, other foodstuffs which contain the vitamin *A* should give the colour reaction. Of the oils and fats, butter is the one considered to be the richest source of vitamin *A* after cod-liver oil. We have usually found butter fat to give the characteristic purple reaction when dissolved in petroleum spirit on the addition of one drop of sulphuric acid, but specimens vary very much in this respect. The fact that they give so very much less marked a reaction is interesting when one recalls Zilva and Miura's observations that cod-liver oil is about 250 times more potent than butter fat (*loc. cit.*). What is to us even more interesting is that the variations in the vitamin *A* value of butters caused by changes in the diet of the cow (Drummond, Coward and Watson, *Biochem. J.*, 1921, **15**, 540) appear to be associated with somewhat parallel variations in the power to yield the colour reaction, although, owing to the feebleness of the latter, it is difficult to make even rough estimations.

To regard the test as specific for liver oils is wrong, for we have repeatedly found body fats and fats from organs other than the liver to yield definitely positive reactions. For example, rats fed on a diet deficient in vitamin *A* for several weeks appear to lose their reserves of the chromogenic substance, for the reaction is given neither by liver nor by body fat. If similar animals be given a small supplement of a potent fish oil (*i.e.* liver oil), the coloration will be shown by the liver fat after about ten or twelve days, and by the body fat after a longer interval. This storage of the chromogenic substance in the body fat explains the findings of Thomson and Dunlop, who obtained positive reactions with porpoise and seal oils. Such blubber oils (whale and seal) also contain vitamin *A*, but usually in low concentration.

SUMMARY.—(1) The substance present in liver oils which is responsible for the well-known purple coloration with sulphuric acid was found in the following

species: Man, horse, ox, pig, cat, monkey, rabbit, guinea pig, chicken, duck, pigeon, rat, mouse, frog, shark, cod, haddock, ling, coal fish, dog fish, sprat, and skate. (2) The substance appears to be a normal constituent of the liver and is not derived from the bile or from products of autolysis or putrefaction. Evidence is presented to show that it is probably derived from the food, although an examination of the stages in the food of the cod did not reveal its ultimate origin with certainty. (3) The chemical nature of the substance has not been ascertained. It forms a low proportion of the unsaponifiable fraction, is not cholesterol, and probably not a member of the lipochrome pigments. It is thermo-stable in the absence of air or oxygen, but is rapidly destroyed by oxidation. (4) The few properties of the substance which are known, as well as the available data regarding its distribution in natural products, show certain resemblances to the unidentified dietary unit known as vitamin *A*; and without assuming the identity of the two factors, it is suggested that the association may be of some significance. (5) The colour test cannot be regarded as specific for liver fats, although they usually give the most intense reactions. The body fat, and fat from other organs of animals, especially if they have been fed on liver oils, may give the reaction.

BIOCHEMICAL LABORATORIES,
THE INSTITUTE OF PHYSIOLOGY,
UNIVERSITY COLLEGE, LONDON.

DISCUSSION.

Mr. F. H. CARR congratulated Dr. Drummond upon introducing at last some real chemistry into the voluminous subject of vitamins. He enquired whether any attempt had been made to concentrate the chromogenic substance in the cod-liver oil; and whether Dr. Drummond had tried feeding cows on cod-liver oil, and, if so, with what effect upon the vitamin value of the milk.

Mr. C. L. CLAREMONT asked what effect the unsaponifiable matter itself had as a vitamin, and if it were possible actually to test that material for the presence of the so-called vitamin. He also enquired if the algæ in the sea were green or red, and what relation their colouring matter had to ordinary chromogenic substances.

Mr. A. E. PARKES asked whether Dr. Drummond had ever tested fish oils for the presence of lecithin or other organic phosphorus compounds. When testing various products (cereals and the like) for lecithin he had found that the alcohol extract frequently gave a violet or purple coloration with sulphuric acid.

Mr. W. PARTRIDGE asked if the sulphuric acid test on cod-liver oil had not been rejected. He remembered (about 20 years ago) some notes were worked out on a modification of Meyer's test; he thought that it was one part of sulphuric acid to two parts of nitric acid. One drop of this was added to 15 drops of oil, and the colorations noted before and after stirring.

Dr. DRUMMOND, in reply, said that both the chromogenic substance and the vitamin passed into the unsaponifiable matter, without serious loss, if one took care to avoid oxidation, and that the vitamin could be further concentrated by removal of the sterol fraction of the unsaponifiable matter. In regard to Mr.

Carr's question; cows were now actually being fed with cod-liver oil, but the results were not yet available for publication. Replying to Mr. Claremont's question on pigments of the algæ, he said that usually the photo-catalytic pigment was green, brown or red; in very deep water all the algæ were red, and most marine algæ contained vitamin *A*. As to Meyer's test; they had employed pure sulphuric acid only for the colour test, but were acquainted with Meyer's paper on the subject, referred to by Mr. Partridge.

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.

SOMERSET COUNTY COUNCIL.

Annual Report of the County Analyst and Bacteriologist for the Year 1921.

The total number of samples analysed under the Food and Drugs Acts during the year was 1080, of which 67 were adulterated.

Milk.—The samples included 569 milks, 46 of which were adulterated and 26 suspicious. The average amount of solids-not-fat (8·52 to 8·83 per cent. in the four quarters of the year) was decidedly lower than the average for the corresponding quarters of 1920. This was probably due to the prolonged drought. Two samples contained boric acid (0·012 and 0·016 per cent.).

Preservatives in Other Samples.—The amounts of boric acid found were as follows: Butter, 0·05 to 0·45 per cent. in 24 out of 30 samples; sausages, 0·03 to 1·2 per cent. (13 out of 19 samples); brawn, 0·05 to 0·26 per cent. (5 out of 15 samples); and potted meat and fish, 0·11 to 0·23 per cent. (5 out of 14 samples).

Seven of 8 non-alcoholic wines contained from 0·05 to 4·8 grains of salicylic acid per pint.

Sago.—A sample contained 1·7 per cent. of rice and 0·3 per cent. of barley, and numerous insect larvæ and cocoons were present. The vendor was prosecuted and fined.

Toxicological Investigation.—A sample of fish meal suspected of causing the death of 50 birds was examined. No poison was found, but from the organs of one of the chickens a bacillus identified as the causative organism of bacillary white diarrhœa was isolated, and the mortality was therefore proved to be due to bacterial infection.

Bacteriological and Public Health Work.—Sixty-seven tuberculin dilutions were made and sent out, and 7318 samples were examined for local authorities, medical men, and departments of the County Council.

Denys R. Wood.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

FOOD INVESTIGATION BOARD.

THE METHODS USED FOR THE INSPECTION OF CANNED FOODS.

PART II.—CANNED MARINE PRODUCTS.*

APART from some canning of herrings and sprats, there is little commercial canning of marine products in this country. The data discussed in the report refer to the tinned marine products entering British ports, including salmon, herrings and sardines, lobsters, crabs, and, to a less extent, cray fish.

METHODS OF CANNING SO FAR AS THEY AFFECT METHODS OF EXAMINATION.—In the case of sardines the fish are steamed for about 20 minutes to cook them; no definite temperature is maintained. They are then packed by hand into the cans, oil or mustard, etc., added, and the edges of the lids and cans crimped together by means of a special machine. The sealed cans are heated in boiling water for 1½ to 2 hours, and in a few factories steam under pressure is used. In canning salmon the can is usually sealed while hot so as to create a vacuum; in the case of 1lb. cans the usual time for "processing" is ninety minutes at 240°F. (155° C.). In some factories the can is sealed cold under vacuum. Cans sealed in this way would have a solder vent, whereas all cans seen by the investigators in this country have been without solder holes. In recent years the use of paper gaskets along the line of junction of can and lid has caused difficulties. If the seam is not perfectly tight this form of gasket will permit the passage of air, although it may still impede the ingress of bacteria. This will account for the occurrence of leaking cans, the contents of which may not be bacterially contaminated from outside.

METHODS OF INSPECTION IN ENGLAND AT THE PORTS OF ENTRY.—As in the case of meat 10 per cent. of consignments are usually examined, and the allowance for rejects based upon this 10 per cent. examination.

Criteria relied upon for the Detection of Unfit Cans.—In general, the methods of examination used in different ports are the same, but there is want of uniformity in interpretation.

Inspection.—Definite holes, marked indentation and other signs of gross ill-usage are at once detected, and extensive rust (which may readily lead to formation of pin-holes) is noted. The most important defect is swelling or "blowing"; contamination with bacteria of the gas-producing type is more frequent with fish products than with meat. A definitely "blown" can is invariably rejected, but the term "blown" is often used incorrectly to describe any tin in which the normally flat surface is at all raised. This spurious appearance of "blowing" is more likely to occur with fish products such as sardines or herrings, which are packed in flat cans of the rectangular or ovoid shape, and may be caused by over-filling the cans. They are readily distinguished from "blown" cans by other methods of inspection, but from the trade point of view are less marketable than normal cans.

A second vent hole does not necessarily indicate an unsound or re-soldered can, but in the case of "sanitary" cans some suspicion must rest upon cans containing a vent-hole when most of the cans in the consignment are free from vents.

Palpation.—The most important use of the "feel" of the can is to distinguish between a "blown" can and one which is bulged but shows no sign of internal pressure.

* Special Report, No. 10. By W. G. Savage, M.D. Pp. 32. H.M. Stationery Office. 1922. Price 1s. 6d. net.

Percussion.—The character of the note yielded by tapping different parts of the surface of the can is of comparatively little value for fish and other marine products. The common view appears to be that cans with minute perforations may give a note different from that produced by sound cans.

Shaking.—Great stress is laid upon the sound produced when a can is shaken. This varies not only with the kind of food canned, but also with the different grades of the same food and with the shape of the can. A definite splash note or a solid thud, however, would be evidence of abnormal changes. The shake test is also of value from the commercial point of view; a loose shake may be an indication of bad packing.

CRITICAL CONSIDERATION OF THE RELIABILITY OF THE METHODS.—Comparisons were made between the findings of expert examiners and the actual physical condition of the fish when the can was opened, as well as with the results of bacteriological and chemical examination.

Fifty samples of canned marine products purchased from shops were all good when judged by the usual physical tests, and all appeared perfectly good when opened. Only 42 per cent. were sterile, the true fish showing a percentage sterility of 51, and the crustacea of only 20. None of the 6 samples of crab was free from living bacteria.

Since bacteria are frequently present in perfectly sound salmon cans their mere presence is insufficient to justify condemnation of a sample otherwise good, and regard has to be paid to the kinds of bacteria present. In two of seven samples with sound contents, but with bacteria present, definitely decomposing bacteria were found, but in the other five samples there were either micrococci or bacilli without any powers of decomposing food (3 samples) or sporing-aerobes allied to *B. subtilis* or *B. mesentericus* with doubtful powers of decomposition. From these and other observation the conclusion is drawn that samples containing bacilli incapable of producing decomposition changes must be regarded as sound and fit for consumption.

Thermophilic bacteria have also been found in perfectly sound shop samples of sardines, but as they are incapable of decomposing proteins, such isolated strains cannot be regarded as prejudicial.

Of the 150 samples which had been examined by the food inspectors, 57 were definitely "blown," all contained gas, and in the majority the contents were obviously unsound.

The other cans were rejected either on account of an abnormal shake and springy condition of the cans, or a combination of both characteristics. Subsequent examination showed that the judgment of the inspectors was correct for 50·6 per cent. of all these samples, but only for a third of those rejected on account of an abnormal shake-sound.

SUGGESTIONS IN REGARD TO PRESENT STANDARDS.—Judgment as to the complete soundness of the contents of cans containing marine products is far more difficult than for cans containing meat. Bacilli causing decomposition have been isolated from fish which appeared quite sound, and the criteria as to fitness are most difficult to assess. The relationship of canned foods to food poisoning does not affect the questions under consideration, for there is no evidence showing that food-poisoning bacilli or their toxins occur more frequently in cans which are physically unsound than in sound cans.

The practical outcome of these comparative tests is that while a "blown" can is clearly a bad can, a can with an abnormal shake-sound or a springy top or bottom is merely a suspicious sample. In view of the various considerations discussed, particularly the difficulties in the way of determining accurately whether the contents are good or bad, it is not considered that there is sufficient

justification to disturb the existing methods of selection, provided these methods are better standardised than they are at present.

A definite link should be established between the Port Health Departments and the Health Departments of Local Authorities on the one hand, and a special central laboratory on the other, so that, in time, the standards of the inspectors could be more closely approximated to the actual results of complete examinations in the laboratory.

Dangerous Drugs.

DANGEROUS DRUGS (PUBLIC ANALYSTS IN SCOTLAND) ORDER, 1922.

Authority, dated 24th January, 1922, granted by the Secretary of State for the Home Department under the Dangerous Drugs Act, 1920 (10 and 11 Geo. 5, c. 46), to Public Analysts in Scotland to be in possession of the drugs to which the Act applies.

In pursuance of the Dangerous Drugs Act, 1920, authority is granted to any person appointed by a local authority in Scotland, with the approval of the Scottish Board of Health, as an analyst for the purposes of the Sale of Food and Drugs Acts, 1875, to 1907, authority to be in possession of the drugs to which the Dangerous Drugs Act, 1920, applies so far as is necessary for the performance of his duties in that capacity.

This authority may be revoked at any time by Order of the Secretary of State.

This Order may be cited as the Dangerous Drugs (Public Analysts in Scotland) Order, 1922.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Fat Obtained from Egyptian Goats' Milk. A. Azadian. (*Bull. Soc. Chim. Belge*, 1922, **31**, 171.)–With the object of establishing analytical standards for Egyptian goats' milk a large number of samples were examined from individual members of the herds which are driven through the towns to be milked at customers' doors, thus feeding on any garbage in the street. The complete milk yield of individual animals was also obtained with notes of ages. Analyses of 104 samples gave in percentages: Total solids 10·65 to 16·55, mean 12·54; fat 2·45 to 7·35, mean 4·04; solids-not-fat 7·6 to 9·95, mean 8·50; and refraction of serum at 30° C. 32·2 to 38·1, mean 35·06. The total milk of groups of goats was mixed, churned, and the butter analysed, six samples giving: Refractive index (Zeiss, n_D^{40}), 41·2 to 41·7 acidity, 1·0 to 6·0; Reichert-Meissl value, 22·4 to 24·4; Polenske value, 3·3 to 4·6; saponification value, 212 to 244; and iodine value (Hübl), 20·7 to 29·0. D. G. H.

Estimation of Carbon Dioxide in Self-Raising Flour. B. R. Jacobs. (*J. Ind. Eng. Chem.*, 1922, **14**, 419–420.)—The apparatus employed consists of a

reaction flask fitted with a stopper carrying inlet and outlet tubes and a tapped funnel; the outlet tube is connected with a tower absorption vessel containing a definite volume of standardised barium hydroxide solution. The tower is filled with glass beads and the top of the tower is connected with an aspirator. Absorption vessels for removing carbon dioxide from air are connected with the inlet tube, and air is drawn through the whole apparatus for twenty minutes. Five grms. of the flour are then introduced into the reaction flask, the air current through the apparatus is adjusted to the rate of about four bubbles a minute, and 100 c.c. of 1 per cent, diastase solution are run into the flask through the tapped funnel. The flask is heated at 70° C. (by means of a water-bath) for ten minutes, then at 100° C. for fifteen minutes, and the contents are finally boiled for a few minutes. The vessel containing the barium hydroxide solution is then disconnected, and the excess of barium hydroxide titrated with 0·1 *N* hydrochloric acid, phenolphthalein being used as the indicator. This estimation gives the amount of available carbon dioxide; if hydrochloric acid is then added to the reaction flask and the operation continued, the quantity of residual carbon dioxide is obtained. W. P. S.

Powdered Cinnamon Bark. C. T. Bennett. (*Pharm. J.*, 1922, **54**, 424.)—The ash limit, 5 per cent., in the B.P. for cinnamon bark is not applicable to the powdered bark. The ether-soluble matter varies from 1·5 to 2·9 per cent., and there is a volatile ether extract varying from 1·9 to 0·2 per cent., the better grades of bark having over 0·5 per cent. The following table shows the results with known samples ground in the laboratory:—

Samples	Total ether extract Per Cent.	Volatile ether extract Per Cent.	Extractive of Tincture (1 in 5) Per Cent.	Ash Per Cent.
1 Large quills	2·52	1·34	1·85	3·8–5·5
2 Small quills	2·22	1·22	1·37	4·0
3 Chips (broken quills)	1·82	0·82	1·72	3·5
4 Chips (practically free from outer bark)	1·76	0·88	1 61	3·6
5 Chips (good quality)	1·36	0·66	1·45	4·7
6 Chips (containing some outer bark) ..	1·82	0·84	1·77	3·5

There is some loss of volatile matter on grinding on the commercial scale, so that the results obtained are usually a little lower than those given above; the lowest figures recorded being 0·94 per cent. total ether extract, with 0·20 per cent. of volatile ether extract. Ether extracts must be made with pure anhydrous ether, and, to prevent loss of essential oil, the ether must be evaporated at a low temperature and the extract dried in a vacuum desiccator. H. E. C.

Estimation of Volatile Mustard Oil in Mustard Flour. E. Luce and A. Doucet. (*J. Pharm. Chim.*, 1922, vii, **25**, 458–464.)—For estimating the volatile mustard oil in mustard flour, the French Codex recommends Dieterich's method, which is based on precipitation of the sulphur of the oil by ammoniacal silver nitrate, with intermediate formation of allylthiourea. The authors find that, in order to obtain exact results in this way (1) the time during which the mustard

flour is macerated with water should be reduced to one hour, without regard to the surrounding temperature; and (2) the action of the ammoniacal silver nitrate should last for either six hours in the cold or one hour in a water-bath at 80–85° C., a reflux condenser being used in the latter case. The percentage of the mustard oil demanded by the Codex, namely 0·7, represents a minimum, mustard flour of good quality often containing nearly one per cent. T. H. P.

Phosphoric Acid in Lemonade. L. R. Wolff. (*Pharm. Weekblad*, 1922, **59**, 622–623.)—Experiments to determine the effect of adding sodium dihydrogen phosphate to human food have shown that in small doses it has a stimulating action, but that in doses exceeding 7 grms. it produces stomach-ache, sleeplessness and diarrhœa (*Klin. Woch.*, Feb. 25, and Mar. 4, 1922). Although the use of phosphoric acid in lemonade is prohibited in Germany, pastilles of sodium dihydrogen phosphate are sold. These are not to be obtained in Holland, where, however, a lemonade syrup of the following composition is prepared: Phosphoric acid, 310 c.c. (=65 grms. H_3PO_4); white sugar, 600 grms.; sodium bicarbonate, 56 grms.; orange essence, 8 c.c.; and water to 2 litres. Fifty grms. of the syrup are diluted with 50 c.c. of water.

Commercial Acetylsalicylic Acid. M. V. del Rosario and P. Valenzuela. (*Philippine J. Sci.*, 1922, **20**, 15–22.)—Eight samples of commercial aspirin of German and American manufacture were found to vary in their crystalline form, colour and odour, while the melting points ranged from 127° to 136° C., and the percentages of ash from 0 to 0·059. No sample showed the melting point 135° C. given by the Pharmacopœia Germanica; the British Pharmacopœia accepts 133° C. With the odourless samples, that is, those free from appreciable dissociation, the melting point was 136° C., but this was obtained also with samples having an aromatic odour related to neither acetic nor salicylic acid. Some of the samples when dissolved in alcohol required more than the theoretical proportion of 0·2 *N* sodium hydroxide for neutralisation, and in other cases more of the alkali was saturated if the neutralised solution was rendered alkaline and boiled under a reflux condenser. The percentages of free acetic and salicylic acids varied from 0·011 to 0·026 and from 0·002 to 0·015 respectively. If well washed, aspirin should be free from sulphate and chlorine ions; and if it is crystallised from a solvent other than water, its melting point will approach that of the pharmacopœias and the tendency to undergo hydrolysis will be minimised. T. H. P.

***Osyris Alba* as Substitute for *Scoparius* N.F. O. A. Farwell.** (*Amer. J. Pharm.*, 1922, **94**, 429.)—This substitute is occasionally found on the American market, but may be distinguished, when in the crude state, by the following characteristics: The dried material is usually pale-brownish or yellowish-green, whilst the branches are without leaves and flowers, but occasionally bear berries. The stems are evenly striated with many ribs, and not five-angled or winged, as in the case of *Scoparius*. The buds are situated at the apex of a rib which forms a keel on the dorsal side of the bud. The wood is white, whilst that of *Scoparius* is yellowish. T. J. W.

Effect of Heat upon *Cocculus Indicus* and Identification of Picrotoxin. D. S. Kabayao. (*Amer. J. Pharm.*, 1922, **94**, 425–428.)—When employed for poisoning fish the berries are roasted until brown and powdered and, on extraction by a modified Stass-Otto method, such material yields white prismatic crystals, producing typical symptoms of picrotoxin poisoning when injected into frogs, but failing to give either the Langley or Fehling reactions. When dried at 104° C., the berries, on extraction, yielded similar crystals which gave positive results with both reagents. Commercial picrotoxin, when heated slightly above its melting point, or dissolved in 20 per cent. sodium hydroxide solution and precipitated by the addition of hydrochloric acid, also exhibited the characteristic toxic properties, but gave no reaction with the above reagents. This result is not due to oxidation, since the same action occurs when picrotoxin is heated in an atmosphere of hydrogen. T. J. W.

Bacteriological, Physiological, etc.

Chemical Composition of Animal Bodies. J. A. Murray. (*J. Agric. Sci.*, 1922, **12**, 103–110.)—The proportion of fat and non-fatty matter in animal bodies varies widely, but can be controlled by food; the percentage of water in the non-fatty matter progressively diminishes with age, whilst, similarly, the amounts of ash and protein are increased. The relations of protein and ash in the non-fatty matter are expressed with fair accuracy by the formula : $P = 0{\cdot}815$ (100–W), $A = 0{\cdot}185$ (100–W) for cattle, and $P = 0{\cdot}83$ (100–W), $A = 0{\cdot}16$ (100–W) in the case of pigs, where P represents protein per cent., A = ash, and W = water per cent. The relation of water to weight is expressed by the formula $w = 90m^{-0.03624}$ where m is the fat-free body weight and w the water in the same. The influence of food is exemplified by the following table, which refers to pigs :

Food	No. of animals	Fasted weight	Fat-free fasted weight	Fat in live weight	Composition of non-fatty matter			
					Ash	Protein	Water	P/A
		lb.	lb.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
Corn alone	5	80·27	47·45	36·69	3·56	17·93	78·51	6·03
Corn and ash	5	130·74	68·25	37·03	4·16	17·39	78·45	4·17
Corn and protein	10	217·94	109·31	48·01	3·54	21·34	75·12	6·07
Corn, ash and protein	5	226·74	118·57	45·55	4·41	21·17	74·42	4·82

These results, calculated for animals of the same size by means of the above formula, show good agreement.

	Corn alone		Corn and ash		Corn and protein		Corn, ash and protein	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Water, per cent.	78·25	78·51	77·21	78·45	75·91	75·12	75·68	74·42
Protein, per cent.	18·12	17·93	18·98	17·39	20·07	21·34	20·26	21·17
Ash, per cent.	3·63	3·56	3·81	4·16	4·02	3·54	4·06	4·41

The ratio of protein to ash is slightly higher in pigs than in sheep and cattle.

H. E. C.

Effect of certain Variations on the Percentage Composition of Milk. W. Taylor and A. D. Husband. (*J. Agric. Sci.*, 1922, **12**, 111–124.)—Experiments on a goat have shown that the percentage composition of milk is determined by its rate of secretion; casein, albumin and globulin, non-protein nitrogen, fat, and ash, vary inversely as the daily volume, whereas lactose varies directly as the volume. The quantity of lactose formed apparently controls the rate of secretion of milk. There is therefore an inverse relation between the amount of the lactose and that of the other constituents, especially the fat percentage. Diet has no direct influence on the composition of the milk, except in respect of non-protein nitrogen, which is not a product of the mammary gland; it has, however, an indirect influence in that it affects the volume secreted. A high protein diet stimulates the rate of secretion. H. E. C.

Unsaturated Fatty Acids of Liver Lecithin. P. A. Levene and H. S. Simms. (*J. Biol. Chem.*, 1922, **51**, 285–294.)—On brominating the fatty acids separated from liver lecithin an octobromide corresponding with octobromoarachidic acid was separated. This was converted into arachidonic acid, which, on reduction, yielded arachidic acid. The soluble brominated compounds yielded oleic acid, which appeared to be the only other unsaturated fatty acid in the lecithin. The iodine values indicated that lecithin extracted from the liver by means of acetone contained arachidonic and oleic acids in the ratio of 1·3:1, whilst in the case of the lecithin extracted with ether the ratio for the two acids was 4·3:1.

Unsaturated Fatty Acids of Egg Lecithin. P. A. Levene and I. P. Rolf. (*J. Biol. Chem.*, 1922, **51**, 507–513.)—Three unsaturated fatty acids—oleic, linolic and arachidonic acids—were isolated from egg lecithin, and identified by the behaviour of their bromides. A comparison of the mixed lecithins of liver with the lecithin of egg yolk shows pronounced differences in the proportions of the individual constituents. Liver lecithin contains a very large proportion of the forms with highly unsaturated fatty acids, whereas in the egg yolk lecithin the proportion of the latter is small. Thus the iodine values of the cadmium chloride salts from liver lecithin varied between 59 and 84, whereas the values in the case of egg lecithins ranged from 30 to 54. Individual samples of egg "lecithin" showed considerable differences. An attempt is being made to develop a method for the fractionation of individual lecithins.

Digestibility of Raw Starches. C. F. Langworthy and H. J. Deuel, jun. (*J. Biol. Chem.*, 1922, **52**, 251–261.)—A continuation of work previously described (*J. Biol. Chem.*, 1920, **42**, 27). The subjects of the experiments were young men provided with a basal ration of oranges, sugar and tea or coffee, supplemented by frozen pudding containing milk, salad oil, sugar, salt, lemon or vanilla extract, and the raw starch under examination. The amount of raw starch supplied to each man per day varied from 59 to 170 grms. Maize, wheat, cassava (*Manihot utilissima*), rice and taro root (*Caladium colocasia* or *Colocasia esculenta*) starches were completely digested. Arrowroot (*Maranta arundinacea*) and tree-fern

(*Cibotium Menziesii*) starches were almost completely digested, a small amount being found in the fæces. Less complete digestion was obtained with commercial arrowroot (*Zamia floridana*) and potato starches, whilst approximately 50 per cent. of canna starch was undigested, although great individual variations in the subjects employed render this figure unreliable. A direct relationship exists between the size of the starch grains and the amount digested, but this is influenced by the quantity of starch taken. A much larger variation exists in the ability of different subjects to digest the large grained starches than can be accounted for by experimental error. T. J. W.

Preparation of Vitamin-Activated Fuller's Earth. A. Seidell. (*Public Health Report*, April, 1922; *Amer. J. Pharm.*, 1922, **94**, 440–442.)—Fresh brewery bottom yeast is diluted with an equal volume of tap water and heated to 90° C. for five minutes, with continuous stirring. After cooling to 50° C., the solid matter is removed by filtration or centrifuging, and English fuller's earth is added to the filtrate in the proportion of 30 grms. per litre, the mixture being rapidly stirred for 30 minutes, after which the suspended matter is filtered off, washed with several changes of water, followed by alcohol, and thoroughly dried. The activated solid prepared by this method contains approximately 1·5 per cent. of nitrogen, and feeding experiments have shown that the vitamin *B* content is about twice as great as the activated fuller's earth prepared from autolysed yeast. T. J. W.

Solubility of the Antiscorbutic Vitamin *C* from Desiccated Orange Juice. E. B. Hart, H. Steenbock and S. Lepkovsky. (*J. Biol. Chem.*, 1922, **52**, 241–250.)—The earlier experiments were made by drying the filtered juice from fresh oranges on filter paper at 20° C., extracting the paper twice for 2 days with the solvent under examination, filtering the extract and evaporating the filtrate on weighed amounts of basal ration, with which rats were then fed. The results obtained showed that vitamin *C* was soluble in 95 per cent. alcohol, but insoluble in acetone, benzene, petroleum spirit (b.pt. 60–90° C.) and chloroform. Later experiments were made with orange juice dried on oatmeal in order to determine the effect both of the solution and the residue upon the rats, and thus determine whether or not the vitamin was destroyed by the procedure adopted. The oatmeal was dried first in a current of air and then over calcium chloride for 6–10 days before extraction with solvents. The desiccation caused some destruction of vitamin, but sufficient remained to induce recovery from scurvy and increased growth of the rats. The vitamin was shown to be soluble in methyl alcohol, and in absolute, 95 per cent., and 80 per cent. ethyl alcohol, but insoluble in butyl alcohol, ethyl ether and ethyl acetate, in addition to the organic liquids given above. In view of its solubilities the vitamin is unlikely to be of a fat or lipin character. T. J. W.

Abstractor's Note.—The authors point out that other workers have shown that vitamin *C* is soluble in water, but that this does not eliminate the effect on solubility of salts and other substances dissolved from the vitamin-containing material. This statement applies also to their own experiments.

Quantitative Estimation of Trypsin. S. Kai. (*J. Biol. Chem.*, 1922, **52**, 133–136.)—A simplified modification of the method described by Gross (ANALYST, 1908, **33**, 130) is given. The results given show that the rate of digestion of casein by trypsin is directly proportional to the amount of enzyme present, and inversely proportional to the amount of casein. An alkaline casein solution is prepared by dissolving 0·1 grm. of pure casein in 15 c.c. of 0·1 *N* sodium hydroxide solution and diluting the solution to 400 c.c. Ten c.c. of this solution are titrated with 0·01 *N* hydrochloric acid until just neutral to phenolphthalein, when a corresponding volume of the acid is added to the remainder and the whole diluted to 500 c.c. An acid sodium acetate solution is made by adding 17·2 c.c. of *N* sodium hydroxide solution to 33·7 c.c. of *N* acetic acid and diluting the mixture to 100 c.c. The standard trypsin contains 0·01 grm. of trypsin in 10 c.c. and is preserved with toluene. Twenty-five c.c. of the casein solution are placed in each of two 50 c.c. flasks and warmed to 40° C. in a thermostat. Into one flask is run 1 c.c. of standard trypsin solution, and into the other 1 c.c. of the solution under examination, the time of addition being noted. The liquids are well mixed, the flasks replaced in the thermostat, and, at intervals of 5 minutes, 2 c.c. of each liquid are removed from each flask and mixed with 1 c.c. of the acid sodium acetate solution. Digestion of the casein to caseoses is complete when no white precipitate of casein or paracasein is obtained, and this will usually require from 15 to 20 minutes with the standard trypsin. Should the unknown solution require 35 minutes to reach this point, its concentration of trypsin will be one-half that of the standard. An excellent series of constants was obtained by multiplying the time of complete digestion by the concentration of trypsin present. T. J. W.

Spectroscopic Detection of Carbon Monoxide in Blood by means of Brewers' Yeast. C. Strzyzenski. (*Comptes Rend. Soc. Biol.*, 1921, **85**, 30; *J. Pharm. Chim.*, 1922, vii, **25**, 478–479.)—In dilute solution, oxyhæmoglobinated blood is reduced by a suspension of yeast, whereas carboxyhæmoglobinated blood undergoes no reduction by yeast. The blood suspected to contain carbon monoxide is well mixed, 0·1 c.c. being then diluted with 10 c.c. of tap water, the liquid ground in a mortar with 0·5 grm. of fresh yeast, and the whole introduced into a conical flask and covered with 1 c.c. of vaseline oil to protect the blood from the action of both atmospheric oxygen and bacteria. The flask is kept at 37–40° C. for 15–20 minutes, and the liquid afterwards centrifuged. Blood thus treated will retain unchanged for some days its original colour and its carboxyhæmoglobin spectrum, if carbon monoxide is present; normal blood, on the other hand, will exhibit a violet tinge and its spectrum only the hæmoglobin band. T. H. P.

Formation of Phenol by Bacteria. F. Sieke. (*Zeitsch. Hyg. u. Infektions krankh.*, 1921, **94**, 214; *Pharm. J.*, 1922, **54**, 491.)—The best medium for the cultivation of phenol-producing bacteria is a solution of 0·3 grm. of tyrosin, 5·0 grms. of asparagin, 5·0 grms. of ammonium lactate, 0·2 grm. of magnesium sulphate, and 2 grms. of potassium phosphate in 1 litre of water. Phenol may be detected

by means of the Berthelot-Lex reaction (blue coloration due to indophenol produced by *p*-aminophenol in alkaline solution in the presence of sodium hypochlorite). *B. coli phenologenes* forms dark red colonies on agar, and strongly ferments dextrose and lactose, while *B. paracoli phenologenes* forms white colonies, and has a slighter fermentative action on lactose. These two types differ from each other, and from non-phenol forming strains of *B. coli* in agglutinating properties. Phenol-producing strains of *B. coli* were found in the intestine of 85 per cent. of all persons examined. The formation of phenol was also demonstrated in three cultures of the bacilus. of fowl cholera, and in two of *B. ozænæ*, Perez (*cf.* Maclaurin, ANALYST, 1922, 294).

Use of the Original Diagnostic Culture for Determining the Virulence of Diphtheria Bacilli. L. C. Havens and H. M. Powell. (*Amer. J. Hygiene*, 1922, **2**, 234–239.)—Original cultures which show the morphological characteristics of diphtheria bacilli, may advantageously be used for the virulence test by the intracutaneous method. Cultures incubated for 12 to 18 hours on Loeffler's serum medium are washed from the medium with 1 or 2 c.c. of sterile salt solution, and further diluted in accordance with the relative number of diphtheria bacilli indicated by the microscopical examination. This eliminates the necessity of isolating pure cultures, and makes it possible to test any desired number of cultures. The method was used to ascertain the influence of the most common contaminating organisms upon the virulence tests. Known numbers of staphylococci or streptococci which had been isolated from the throat were mixed with diphtheria bacilli in a number which had failed to give a positive virulence test, and the mixture was used for the intracutaneous virulence test. For example, in one series of experiments 400,000 diphtheria bacilli in pure culture gave a positive test, whilst 200,000 and 300,000 failed to produce a characteristic lesion. When mixed, however, with an equal number of staphylococci or streptococci, 200,000 diphtheria bacilli gave a positive result in the virulence test, probably owing to destruction of the diphtheria bacilli being retarded, so that they had a longer time in which to produce the toxin.

Colorimetric Estimation of Tyrosine, Tryptophane and Cystine in Proteins. O. Folin and J. M. Looney. (*J. Biol. Chem.*, 1922, **51**, 421–434.)—The development of the following methods and the results obtained in comparison with those yielded by previous methods are given. *Tyrosine and Tryptophane*: Twenty-five c.c. of water and 3·5 grms. of crystallised barium hydroxide are added to 1 grm. of the dried protein, and the mixture is gently boiled under a reflux condenser for 48 hours. Thirty c.c. of 20 per cent. sulphuric acid are then added, and the flask heated for an hour to eliminate any hydrogen sulphide present, after which the contents are cooled, diluted to 100 c.c. and filtered. From 1 to 8 c.c. of the filtrate is transferred to a centrifuge tube, 2 c.c. of Hopkins and Cole's mercuric sulphate reagent added, and the volume made up to 10 c.c. by the addition of 5 per cent. sulphuric acid. After mixing, the solution is allowed to stand for two hours, and is then centrifuged. Five c.c. of the supernatant liquid (containing

the tyrosine) are transferred to a 100 c.c. flask, and 1 c.c. of a standard solution containing 1 mgrm. of tyrosine is run into a similar flask, together with 1 c.c. of the mercuric sulphate reagent and 3 c.c. of 5 per cent. sulphuric acid. To each flask 30 c.c. of water, 20 c.c. of saturated sodium carbonate solution, and 4 c.c. of 5 per cent. sodium cyanide solution are added, followed by 2 c.c. of the phenol reagent (and presumably water to make up the volume to 100 c.c.). After standing for thirty minutes, the colorations produced are compared in a colorimeter. For the tryptophane estimation it is essential that the standard solution containing 1 mgrm. of tryptophane should be treated with the mercuric sulphate reagent in the same manner as the solution under examination. Ten c.c. of water are added to both precipitates, and the tubes shaken, after which 4 c.c. of 5 per cent. sodium cyanide are quickly run in, and the solutions mixed by shaking, the subsequent procedure being as described above for tyrosine. The phenol reagent is prepared by boiling 15 grms. of molybdic oxide and 10 grms. of sodium hydroxide with 200 c.c. of water until free from ammonia, adding 100 grms. of sodium tungstate, 50 c.c. of 85 per cent. phosphoric acid, 100 c.c. of hydrochloric acid and water to make a total volume of 800 c.c. The mixture is boiled for ten hours, a few drops of bromine then added, the excess of bromine boiled off, and the solution diluted to a litre. *Cystine*: From 1 to 5 grms. of the dry protein are gently boiled for twelve hours with 25 c.c. of 20 per cent. sulphuric acid, and the liquid cooled and diluted to 100 c.c. From 1 to 10 c.c. of the liquid and 1 and 3 c.c. of a standard solution containing 0·1 per cent. of cystine and 5 per cent. of sulphuric acid are transferred to separate 100 c.c. flasks. To each flask are added 20 c.c. of saturated sodium carbonate solution and 10 c.c. of 20 per cent. sodium sulphite solution, the solutions left for five minutes and then treated with 3 c.c. of the uric acid reagent of Folin and Denis, and the mixtures allowed to stand for ten minutes. They are then diluted to 100 c.c., and the estimation made with a colorimeter. Some of the results recorded for each amino-acid are in good agreement with those obtained by other methods, but in some cases great discrepancies occur. T. J. W.

Agricultural Analysis.

Classification of Soils on the Basis of Mechanical Analysis. C. L. Whittles. (*J. Agric. Sci.*, 1922, **12**, 166–181.)—For the preparation of soil maps a modification of the triangular coordinate method of classification is proposed. The soil is separated by mechanical methods into three sizes of particles: Coarse (sand), 3 to 0·2 mm. diameter; medium (silt), 0·2 to 0·01 mm.; and fine (clay), below 0·01 mm. From the sides of an equilateral triangle ABC of 100 units side are marked off BP, and along the base AB, AQ, and AR along the side AC, equal to the percentages of coarse, medium, and fine, particles; from P, Q and R are drawn lines parallel to BC, AC and AB respectively; these form a small triangle *pqr*, of which the centre, S, is the required point. Perpendiculars from the centre of the triangle ABC to the sides mark off three equal divisions into which the point S may fall, and these divisions correspond to the principal soil types

A, B and C. Lines from the centre to the vertices subdivide these areas into A_B B_A B_C C_B C_A A_C respectively, and it is shown that well-known types of soil, when plotted in the above manner, fall into these areas. By the employment of an arbitrary colour scale the content of organic matter or the acidity may be indicated on the same map. H. E. C.

Estimation of Humus by means of Chromic Acid. A. Gehring. (*Zeitsch. anal. Chem.*, 1922, **61**, 273–278.)—One to ten grms. of soil are introduced into the distillation apparatus described by Lunge and Berl (*Chemisch-technische Untersuchungsmethoden*, 1910, Vol. I., 472) for the estimation of carbon in iron. Twenty c.c. of water and 30 c.c. of strong sulphuric acid are added, the latter gradually; the liquid is boiled while a current of air free from carbon dioxide is passed through the closed apparatus, to remove the carbon dioxide contained in the soil. The caustic potash bulb is then attached, and 8 grms. of bichromate introduced by momentarily opening the distillation flask. The liquid is gradually heated to boiling, and vigorously boiled for one hour in an air current free from carbon dioxide. The gases are made to pass a heated combustion tube containing copper oxide and lead chromate. The distillation flask should communicate directly with the combustion tube by a very short connection to prevent condensation of any intermediate oxidation products (*e.g.* acetic acid). The results are in close accord with those obtained by elementary analysis. W. R. S.

Citric Solubility of Mineral Phosphates. J. F. Tocher. (*J. Agric. Sci.*, 1922, **12**, 166–181.)—When constant weights of phosphate and of citric acid are employed in the estimation of citric solubility, this solubility increases with increasing dilution; also, when the quantity of citric acid in a given volume of water is increased with a constant weight of phosphate, there is an increase in citric solubility; and if the quantity of citric acid and the volume are kept constant, the solubility decreases as the weight of phosphate taken increases, this decrease being due to the presence of free lime and calcium hydroxide in hydroxyapatite. It is therefore possible to select conditions as to weight of sample and of citric acid and volume so as to obtain any desired result for the citric solubility either of basic slag or mineral phosphate. The official test has no theoretical basis or practical value; the most valuable tests for the practical agricultural value of phosphatic fertilisers would be (1) total phosphate content, (2) degree of fineness of grinding, and (3) freedom from injurious substances. H. E. C.

Removal of Bitter Substances from Lupins. E. Beckmann and F. Lehmann. (*Chem. Zeit.*, 1922, **46**, 473–474.)—The best method of obtaining lupin seeds free from bitter taste and from poisonous alkaloids consists in stirring the sliced or coarsely chopped seeds with water at 40–70° C., repeated changing of the water being necessary. This procedure results in less loss of material than when salts, acids or alkalis are added to the water. For testing the treated lupins, the method of tasting is unsatisfactory, owing to the difficulty of obtaining a small average sample, and may moreover lead to chronic poisoning of the taster. It has

been found, however, that a solution of iodine in potassium iodide solution gives a chocolate-brown precipitate with the aqueous extract of the untreated seeds, the amount of precipitate formed gradually diminishing to zero as the treatment with water proceeds. Attempts to estimate the alkaloids in lupin seeds by precipitation with the iodine reagent have been unsuccessful. T. H. P.

Organic Analysis.

Catalytic Reduction of Organic Compounds by Platinum Oxides. V. Voorhees and R. Adams. (*J. Amer. Chem. Soc.*, 1922, **44**, 1397–1405.)—A mixture of 5 c.c. of chloroplatinic acid solution (containing 1 grm. of platinum) and 20 grms. of sodium nitrate is gradually heated, with stirring, until completely fused and oxides of nitrogen cease to be evolved, the temperature being maintained at about 450° C. After cooling, the mass is dissolved in 50 c.c. of water, filtered, and the brown residue washed until free from nitrates and dried in a desiccator. The platinum oxide thus formed has a greater catalytic activity than metallic platinum, and the following reductions were carried out with an initial hydrogen pressure of 2·75 atmospheres, in most experiments a quantitative yield of the products being obtained: Vanillin to vanillyl alcohol, ethylmethyl ketone to butyl alcohol (secondary), phenol to cyclohexanol, salicyl aldehyde to saligenin, and nicotinic acid hydrochloride to nipocotinic acid hydrochloride. The catalyst may be readily separated from the products by shaking with air at the end of the reaction. T. J. W.

Use of Potassium Bromate in Volumetric Organic Analysis. T. Callan and J. A. R. Henderson. (*J. Soc. Chem. Ind.*, 1922, **41**, 157–164T.)—Titration with potassium bromate solution in the presence of potassium bromide and acid is a suitable method for the estimation of amines, phenols and their derivatives, and certain unsaturated compounds. In the case of amino compounds about 0·5 grm. is dissolved in 200 c.c. of water, and a slight excess of hydrochloric acid; phenols are dissolved in a similar volume of water together with a slight excess of sodium hydroxide, whilst sulphonic and carboxylic acids are dissolved in 200 c.c. of water, and a slight excess of sodium hydroxide is added if necessary. To the solution thus prepared 10 c.c. of 20 per cent. potassium bromide solution and 5 c.c. of concentrated hydrochloric acid are added, the mixture is heated to the required temperature and then titrated with 0·2 *N* potassium bromate solution, starch iodide paper being used as an external indicator. The temperature during the titration has a considerable influence in determining the speed of the reaction and the extent of the bromination. At ordinary temperature, aniline yields tribromoaniline, *o*- and *p*-toluidines absorb 2 atoms of bromine, and *m*-toluidine absorbs 3 atoms of bromine; the end-point being sharp in each case. Dimethylaniline absorbs 1 atom of bromine at 0° to 5° C., 2 atoms at 40° to 50° C., and 3 atoms at 60° to 70° C., and the three stages are defined sharply. With sulphanilic acid, 2 atoms of bromine are absorbed at 30° to 40° C., and the mixture then gives

a faint reaction on starch-iodide paper; a further slight addition of bromate solution produces a turbidity owing to elimination of the sulphonic group, formation of tribromoaniline and precipitation of the latter, and the titration may be continued to the final end-point, when 3 atoms of bromine per molecule are absorbed. Diphenylamine absorbs 4 atoms of bromine at 60° to 70° C.; *p*-nitroaniline may be titrated at the same temperature; *p*-nitrophenol absorbs 2 atoms of bromine at all temperatures between 15° and 70° C., and 1.2.4-dinitrophenol behaves similarly, except that it absorbs 1 atom of bromine. Picric acid is not brominated under any of the above conditions. Thiocarbanilide may be titrated at 25° to 30° C. in acetic acid solution, when it absorbs 4 atoms of bromine. At 20° C. cinnamic acid yields dibromocinnamic acid; substitution begins only at temperatures above 20° C. W. P. S.

Estimation of the Nitro Group in Aromatic Organic Compounds. T. Callan and J. A. R. Henderson. (*J. Soc. Chem. Ind.*, 1922, **41**, 157–161T.)—Further investigation of the reduction of nitro groups in aromatic compounds by means of titanous chloride or titanous sulphate (*cf.* ANALYST, 1920, **45**, 235) shows that the chief sources of error are chlorination and volatilisation of the substance. Chlorination, of course, does not occur when titanous sulphate is employed, and in the case of titanous chloride may be eliminated by using sulphuric acid in place of hydrochloric acid. With volatile substances, such as nitrodichlorobenzene, etc., it is impossible to obtain satisfactory results unless a reflux condenser is used to prevent volatilisation during the reduction. W. P. S.

Estimation of Small Amounts of Lactic Acid. S. W. Clausen. (*J. Biol. Chem.*, 1922, **52**, 263–280.)—The following method is based upon those of Ripper (*Monatsh. Chem.*, 1900, **21**, 1079) and of Meissner and Schneyer (*Biochem. Zeitsch.*, 1915, **48**, 175) and is suitable for quantities of material containing not more than 45 mgrms. of lactic acid : Albumin is removed from the urine, blood, milk, etc., by the addition of tungstic acid and, in the case of blood, the filtrate is evaporated to a small volume under reduced pressure. Phenols are removed, if present, by the addition of a few drops of strong phosphate buffer solution of P_H 7·0 to 2 c.c. of the filtrate and continuous extraction for 15 minutes with ether in a simple apparatus figured and described. To the remaining liquid 1·3 grms. of ammonium sulphate and a few drops of sulphuric acid are added, and a second extraction with ether is made for a period of 30 minutes. Water is added to the ether extract, and dilute sodium hydroxide solution is run in until the reaction is slightly alkaline to phenolphthalein, when the ether is distilled off. The aqueous liquid containing the lactic acid as the sodium salt is mixed with 5 or 10 c.c. of 1 per cent. sulphuric acid in a large test tube connected through a reflux air condenser with two similar tubes arranged in series, each containing 20 c.c. of 0·02 *N* sodium bisulphite solution, and a rapid current of air is drawn through the apparatus, while the reaction tube is heated to 95° C. and 0·005 *N* potassium permanganate solution is run in, drop by drop, until no longer decolorised, when the air current is continued

for a further 10 minutes in order to transfer the whole of the aldehyde formed to the sodium bisulphite solution. For quantities of lactic acid exceeding 10 mgrms. more satisfactory results are obtained by heating the aqueous liquid to 140° C. with 50 per cent. sulphuric acid in the same manner as described above, but omitting the addition of potassium permanganate. The sodium bisulphite solution is titrated to a definite end point with 0·01 or 0·001 *N* iodine solution, sufficient saturated sodium bicarbonate solution is then added to decolorise the solution, and more standard iodine solution is run in to a definite end-point. The second volume of iodine added is equivalent to the aldehyde present, two atoms of the former corresponding with one molecule of the aldehyde. The results obtained with pure solutions of lactic acid indicate between 98·2 and 100·5 per cent. of the acid present, but with biological fluids the values given are probably in error owing to the interference of organic substances which cannot be eliminated. A large number of results are given, obtained during development of the method and in its application to the analysis of urine and blood. T. J. W.

Colour Reactions of Cholesterol. L. Kahlenberg. (*J. Biol. Chem.*, 1922, **52,** 217–225.)—Cholesterol is soluble in anhydrous inorganic halogen compounds, yielding colourless solutions with phosphorus trichloride and oxychloride, stannic chloride, silicon tetrachloride and tetrabromide and carbon tetrabromide. The solution of cholesterol and of lanoline in thionyl chloride is of a red wine colour, changing to brown on standing or heating, the colour not being discharged on the addition of benzene. Colorations are also obtained on dissolving cholesterol in antimony trichloride, titanium tetrachloride and selenium oxychloride, but the reactions are not very characteristic. In arsenic trichloride at 0° C. cholesterol forms a colourless solution which slowly becomes pink and finally cherry-red in colour, especially on warming. If boiled, the solution turns a dirty green shade, which reverts to cherry-red on cooling. Phytosterol dissolved in the same solvent yields a colourless solution which develops no colour, even when boiled, whilst isocholesterol forms a cobalt blue solution; the three sterols may be distinguished by this means. On treatment of these coloured solutions with benzene, toluene, chloroform, water or hydrochloric acid, the liquids become colourless. An attempt to separate the colouring substance formed on dissolving cholesterol in arsenic trichloride was unsuccessful, but showed that on cooling to -10° C. for some hours the solute separates out in colourless crystals. T. J. W.

Evaluation of Gelatin and Glue. R. H. Bogue. (*J. Ind. Eng. Chem.*, 1922, **14,** 435–441.)–The gelatin content of a glue or gelatin, and also the joint-strength of a glue, may be indicated correctly by the melting point. The viscosity at 35° C. of a solution containing 18 per cent. of dry glue or gelatin is well adapted to give an indirect estimation of the differentiation of glues and gelatins in the order of their melting points. This order, in most cases, is the same as the order of viscosity at 60° C., and the order of jelly consistency at 15° C., but for glues in which the viscosity is abnormal to the jelly consistency the viscosity at 35° C. gives a value intermediate between these two properties; it also corresponds with

the true melting point, and gives the gelatin content and the joint-strength of the product. The viscosity is most satisfactorily determined by means of the Mac-Michael viscometer. Tests which are useful in valuing glues for special purposes comprise estimations of the jelly consistency, hydrogen ion concentration, ash, sulphur dioxide, metallic impurities, etc. W. P. S.

Inorganic Analysis.

Oxalic Acid as an Iodimetric Standard. L. Rosenthaler. (*Zeitsch. anal. Chem.*, 1922, **61**, 219–222.)—Oxalic acid (or Sörensen's salt) reacts with iodic acid in the following manner: $5C_2O_4H_2 + 2HIO_3 = 6H_2O + 10CO_2 + I_2$. A 0·016 *N* (*N*/60) potassium iodate solution is equivalent to 0·1 *N* thiosulphate solution, as $HIO_3 + 5HI = 6I + 3H_2O$. A weighed amount of sodium oxalate is heated on the water bath with dilute sulphuric acid and a measured excess of 0·016 *N* potassium iodate solution until the liberated iodine has been volatilised. After cooling, an excess of potassium iodide is added, and the solution titrated with 0·1 *N* thiosulphate solution. The thiosulphate solution having been titrated against a measured volume of cold iodate solution treated with dilute sulphuric acid and excess of iodide, the difference between the two titrations gives the amount of iodate equivalent to the oxalate. W. R. S.

Quantitative Estimation of Minute Amounts of Gaseous Oxygen. H. M. Sheaff. (*J. Biol. Chem.*, 1922, **52**, 35–50.)—An apparatus is described in which small amounts of air or other gas containing oxygen are diluted with hydrogen and treated with excess of pure nitric oxide in the presence of sodium hydroxide solution. The resulting nitrite is estimated colorimetrically by addition of sulphanilic acid and α-naphthylamine in acetic acid solution and comparison with a solution of sodium nitrite, which is standardised by means of an ultimate standard solution containing potassium dichromate and potassium permanganate. Quantities of oxygen of the order of 0·1 c.mm. approximating to a weight of 1×10^{-7} grm. may be estimated with a maximum error of 4 per cent. Extensive details of the methods of preparation and purification of the reagents and gases employed and manipulation of the apparatus are given. T. J. W.

Rapid Estimation of Sulphur. L. Losana. (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 204–206.)—The method proposed is based on the fact that, when a compound containing sulphur is heated with powdered iron in absence of air, the sulphur undergoes such transformation that it is liberated completely as hydrogen sulphide when the resulting mass is subsequently treated with hydrochloric acid. The hydrogen sulphide is absorbed by zinc acetate solution, and the sulphide thus formed titrated with iodine solution.

If the substance contains 0–5 per cent., 5–10 per cent., or more than 10 per cent. of sulphur, the amount taken for analysis is 1 grm., 0·5 grm. or 0·1 grm. respectively. This is mixed, in a hard glass tube, about 4 cm. long, with 2 grms. of pure powdered iron and 0·5 grm. of sodium hydrogen carbonate, the mixture being

covered with a layer, several mm. deep, of the iron, and then heated to incandescence for a few minutes. For the decomposition with acid, use is made of a small round-bottomed flask with a ground stopper sealed to the tube of a reflux condenser, the upper end of the tube being bent over to pass through the cork of a bulbed absorption tube containing about 150 c.c. of 2·5 per cent. zinc acetate solution, rendered slightly acid with acetic acid. A gas delivery tube dipping into a little water in the flask is sealed horizontally through the head of the ground stopper, and ends in a vertical cross-piece to form a T-piece. The latter is connected at the top with a source of carbon dioxide and at the bottom with a rather long rubber tube joined to a tapped funnel. The hard glass tube is allowed to cool somewhat and is dropped, while still hot, into the flask, and thus broken by the cold water. A rapid current of carbon dioxide, washed by permanganate solution and then by water, is passed through the flask, and hydrochloric acid introduced through the funnel. When the reaction slackens, the flask is heated gently; and when evolution of gas ceases, carbon dioxide is passed briskly through the apparatus for about five minutes. The liquid from the absorption bulbs is transferred to a beaker, diluted to 300–400 c.c., mixed with a known volume in excess of standard iodine solution, allowed to settle, and titrated with thiosulphate solution, the sulphur being calculated from the equation, $ZnS + I_2 = ZnI_2 + S$. The content of sulphur in the reagents used is checked by a blank experiment. Tests made on flowers of sulphur and with copper, lead, barium and cobalt sulphates yielded virtually theoretical results. The whole of the operations occupies about 40 minutes. The method is applicable also to organic compounds; but these must first be mixed with copper oxide or lead chromate and heated, in a porcelain crucible if the compound is non-volatile, or in a narrow hard glass tube and covered with a deep layer of the oxidising material if the compound is volatile. T. H. P.

Electro-Volumetric Estimation of Lead. D. A. MacInnes and E. B. Townsend. (*J. Ind. Eng. Chem.*, 1922, **14**, 420–421.)—The lead is deposited electrolytically as peroxide, which is then dissolved in oxalic acid solution, and the excess of the latter titrated with permanganate solution. The metal is dissolved in a mixture of 10 c.c. of concentrated nitric acid and 15 c.c. of water, the solution is placed in a platinum basin, roughened on the inside, and a platinum disc, rotating at about 600 revolutions per minute, is used as the cathode. With a current of about 12 ampères the deposition is usually complete in thirty minutes. The deposited peroxide is washed with a small quantity of water, an excess of 0·1 *N* oxalic acid solution and 5 c.c. of nitric acid are added, and the mixture is heated at 80° C. until all the peroxide has dissolved. The solution is now transferred to a beaker, a small quantity of concentrated sulphuric acid is added to precipitate the lead, and the excess of oxalic acid is titrated with standardised permanganate solution. The accuracy of the method is not affected by hydration of the deposit or by occluded substances unless they are of an oxidising nature. Traces of silver and bismuth, if present, are deposited as peroxides, but most other metals are separated from the lead by the electrolysis. W. P. S.

Iodimetric Estimation of Arsenic and Antimony Sulphides. F. Nikolai. (*Zeitsch. anal. Chem.*, 1922, **61**, 257–272.)—The process is based on the following reactions:—

$$2As_2S_3+4KOH=KAsO_2+3KAsS_2+2H_2O$$
$$KAsO_2+3KAsS_2+10I_2+10H_2O=4KAsO_3+3S_2+20HI$$
$$Sb_2S_3+2KOH=KSbOS+KSbS_2+H_2O$$
$$KSbOS+KSbS_2+5I_2+5H_2O=2KSbO_3+3S+10HI.$$

Hence 10 iodine is equivalent to As_2S_3 or Sb_2S_3. The quantity of iodine required to react with the pentasulphides is the same, as, *e.g.* $As_2S_5+5O=As_2O_5+5S$. The composition of the sulphide precipitate is therefore theoretically immaterial, but free sulphur would cause consumption of iodine, as part of it would react thus: $4S+6KOH=2K_2S+K_2S_2O_3+3H_2O$. A solution of tartar emetic is acidified with oxalic acid and treated with hydrogen sulphide; the precipitate is filtered off, washed free from hydrogen sulphide with hot 5 per cent. sodium chloride solution, and dissolved in a slight excess of sodium hydroxide solution containing 10 c.c. of 3 per cent. gelatin solution. The gelatin prevents oxidation of the alkaline sulphide solution by atmospheric oxygen, which otherwise causes low results (about 1·5 per cent.). The alkaline solution is poured, with stirring, in a thin stream into a measured excess of iodine solution diluted to 0·01 *N* and containing more than enough acetic acid to neutralise the alkali; the excess of iodine is titrated with thiosulphate. The same procedure is applicable to arsenic trisulphide. The titration of the pentasulphides gives slightly high results, because the precipitates are contaminated with small quantities of trisulphide and sulphur, which latter causes consumption of iodine. W. R. S.

Iodimetric Estimation of Arsenic Acid. L. Rosenthaler. (*Zeitsch. anal. Chem.*, 1922, **61**, 222–229.)—In reply to criticisms by Fleury (*Analyst*, 1920, **45**, 389), the original directions (ANALYST, 1906, **31**, 416) are confirmed. The oxidation of hydriodic acid by atmospheric oxygen is negligible for a period of 10 minutes; but if the acidity is lower than 16 per cent. hydrochloric acid (or $33\frac{1}{3}$ per cent. H_2SO_4), the reaction ($H_3AsO_4+5HI=AsI_3+I_2+4H_2O$) involves longer standing, and it is then necessary to add 5 grms. of sodium bicarbonate to expel the air from the flask before adding the iodide. The yellow precipitate produced by the addition of iodide to the strongly acid liquor is arsenic tri-iodide; if formed, it is dissolved by cautious addition of water. W. R. S.

Detection of Tin as Iodide. H. Heller. (*Zeitsch. anal. Chem.*, 1922, **61**, 180–182.)—One c.c. of the solution to be tested is treated with 0·5 c.c. of 5 per cent. potassium iodide solution, and 0·5 c.c. of strong sulphuric acid added through a pipette reaching to the bottom of the test tube. In presence of tin a yellow precipitate is produced at the plane of contact of the two layers. If the quantity of tin is small, the precipitate may be increased by cautious agitation. Careful addition of strong hydrochloric acid causes solution of the precipitate. The original solution should not contain an undue amount of hydrochloric acid. Arsenic

and antimony interfere by the formation of coloured iodides. The above modification of the test, which is as sensitive as the reaction with mercuric chloride, is an improvement on the original directions of Mazuir (*Pharm. Weekblad*, 1920, **57**, 710). W. R. S.

Analysis of Aluminium Alloys and Especially of Duralumin. E. M. da Costa-Vet. (*Chem. Weekblad*, 1922, **19**, 249–251.)—The chief difficulties in the analysis of duralumin (an aluminium alloy containing about 3·5 per cent. of copper, 0·5 per cent. of manganese, and 0·5 per cent. of magnesium) are caused by the magnesium, which cannot be separated from the manganese by most of the published methods. Good results may be obtained by precipitating the manganese and magnesium together as phosphates, weighing the precipitate and then redissolving it, and estimating the manganese by titration with potassium permanganate solution.

Colorimetric Estimation of Magnesium in Small Amounts. F. S. Hammett and E. T. Adams. (*J. Biol. Chem.*, 1922, **52**, 211–215.)—The following method is a modification of one described by Bell and Doisy (ANALYST, 1921, **46**, 13–14) combined with that of Kramer and Tisdall (*J. Biol. Chem.*, 1921, **48**, 223): Five or ten c.c. of the clear liquid from the calcium precipitation in the latter method are treated with 1 c.c. of the ammonium phosphate solution, added drop by drop, and 2 c.c. of ammonium hydroxide, the mixture being allowed to stand overnight. The precipitate is filtered on a Gooch crucible, washed ten times with 5 c.c. portions of 10 per cent. ammonia solution and twice with 90 per cent. alcohol made alkaline with ammonia, and is then dried for a few minutes at 80° C. The contents of the crucible are treated with 10 c.c. of 0·1 *N* hydrochloric acid and allowed to stand one hour at the ordinary temperature, after which the asbestos is separated in a centrifuge. Five c.c. of the supernatant liquid are transferred to a 25 c.c. graduated flask, and 5 c.c. of standard potassium di-hydrogen phosphate solution containing 0·05 mgrm. of phosphorus are added to a similar flask. To each flask 1 c.c. of molybdic solution, 2 c.c. of the hydroquinone solution and, after 5 minutes, 10 c.c. of the carbonate-sulphite solution of Bell and Doisy are added. The contents of each flask are diluted to 25 c.c., allowed to stand from 5 to 10 minutes, and the depth of colour produced compared in a colorimeter. The amount of phosphorus found, multiplied by $0{\cdot}7835 \times 2$, gives the weight of magnesium contained in the liquid taken after the calcium precipitation. The final portion of the calculation is rendered uncertain, since the value varies according to the weight of ash, dilution of the solution and the weight of material used. There is a tendency for the results to be low, but with careful working the error does not exceed 3 per cent.

T. J. W.

Estimation of Bromide in Brines and Mineral Waters. C. C. Meloche and H. H. Willard. (*J. Ind. Eng. Chem.*, 1922, **14**, 422–425.)—A portion of the brine, containing not more than 0·5 grm. of combined bromine, is treated with an excess of potassium permanganate and hydrochloric acid, heated, and the

bromine removed by means of a current of air. The bromine, together with some chlorine, is absorbed in sodium hydroxide solution, reduced to bromide and chloride by means of hydrazine sulphate, the mixture then acidified with nitric acid and treated with silver nitrate. The quantity of bromine present is calculated from the loss in weight of the mixed halides when these are ignited in a current of chlorine. When notable amounts of iodide are present the brine should be rendered distinctly alkaline, treated with an excess of permanganate, and boiled to convert iodide into iodate. The solution is then cooled, acidified, and the estimation carried out as described. If permanganate is present in excess during the whole operation, the iodine remains in the form of iodate and does not interfere.

W. P. S.

Iodimetric Estimation of Hydrosulphurous and Sulphoxylic Acids. F. de Bacho. (*Zeitsch. anal. Chem.*, 1922, **61**, 209–219.)—Interference of atmospheric oxygen is counteracted by titrating in presence of formaldehyde (*cf.* Crowther and Heywood, *J. Soc. Dyers Col.*, **38**, 279), which allows the estimation to be carried out in contact with the air. One grm. of sodium hydrosulphite or sulphoxylate is dissolved in the weighing bottle in 5 c.c. of water and 10 c.c. of pure concentrated formaldehyde solution. After 20 minutes' standing the solution is rinsed into a graduated 500 c.c. flask and treated with 200 c.c. of water free from carbon dioxide, 2 drops of 0·1 per cent. methylorange, and *N* sulphuric acid just sufficient to obtain the pink tinge. The volume is made up with boiled water, and 50 c.c. treated with phenolphthalein and 0·1 *N* alkali free from carbonate to faint pink; the solution is now titrated with 0·1 *N* iodine free from hydriodic acid, and starch: $NaHSO_2+4I+2H_2O = NaHSO_4+4HI$; or $Na_2S_2O_4+4I+3H_2O = NaHSO_4+4HI+NaHSO_3$. Neither bisulphite nor pyrosulphite (metabisulphite) interferes in presence of excess of formaldehyde, neutral sulphite being converted into bisulphite by the above procedure. On the other hand, thiosulphate, which is practically always present, gives high results: $2Na_2S_2O_3+2I = Na_2S_4O_6+2NaI$. The solution, after titration with iodine, is therefore decolorised with a drop of thiosulphate solution and titrated with 0·1 *N* alkali free from carbonate, the acidity found giving the measure of the sulphoxylate or hydrosulphite: $NaHSO_4+4HI+5NaOH = Na_2SO_4+4NaI+5H_2O$. The bisulphite formed in the second equation does not interfere, as it combines with the formaldehyde. The amount of thiosulphate is calculated by multiplying the number of c.c. of 0·1 *N* alkali by 0·8 and subtracting the product from the number of c.c. of 0·1 *N* iodine solution.

W. R. S.

Method of Testing the Degree of Incorporation of Explosives and other Powders. E. P. Perman. (*J. Soc. Chem. Ind.*, 1922, **41**, 155–157T.)—During the preliminary or coarse grinding of ammonium nitrate and trinitrotoluene, ordinary methods of analysis are used on samples taken from different parts of the mill; after this stage, the methods fail to detect improvement in the quality of the powder resulting from further milling, although coarse grains of the separate components may be detected by the naked eye in the 10 grm. samples taken for

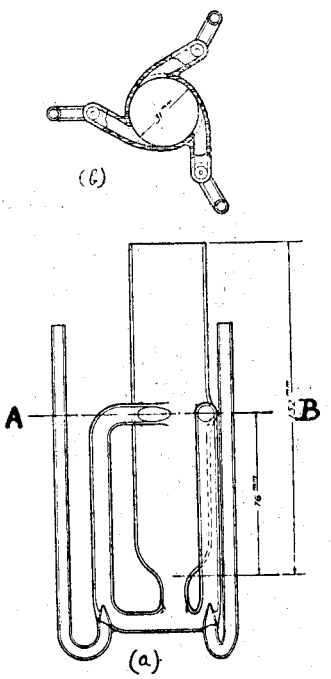
analysis. The author proposes to reduce the amount of the sample until the composition of the powder would be disturbed very seriously by the presence of a single grain of unmixed ammonium nitrate or trinitrotoluene. A sample is taken from the mill and from this about 1 mgrm. is transferred to a light tared platinum capsule and weighed on an assay balance by the method of vibrations to 0·01 mgrm. The capsule is then placed in a funnel containing a loose plug of cotton-wool, and the ammonium nitrate is washed into a 100 c.c. flask with ammonia-free water. The solution is diluted to 100 c.c., 20 c.c. of it are transferred to a flask, and 2 c.c. of Nessler reagent are added; a comparison solution is prepared in another flask by mixing 5 c.c. of ammonium chloride solution (containing 0·01 mgrm. of ammonia per c.c.), 15 c.c. of water and 2 c.c. of Nessler reagent. The colorations of the two solutions are then compared in a Duboscq colorimeter, into which is admitted a uniform and steady source of light, such as the Ediswan "Pointolite" lamp. Six separate estimations should be made on each sample, which may be taken from the mill at intervals of one minute. After about four minutes' milling it will usually be found that the results obtained do not vary by more than 1 per cent. from the mean, and the mixing is as complete as can be measured by this test. W. P. S.

Standardisation of China Clay. J. Strachan. (*Chem. Trade J.*, 1922, **70**, 660–661.)—*Moisture*: China clay with 10 per cent. of moisture is coherent but friable, with 15 per cent. it is distinctly damp, and with 20 per cent. it forms a stiff plastic mass. Although the moisture content could be reduced to 1 or 2 per cent. without risk of calcining the clay, the 12 per cent. basis now frequently adopted in contracts is probably a fair figure, in view of the loss in transport to which very dry clay would be subject. *Grit and sand*: The kaolin particles range in diameter from less than 0·001 to less than 0·01 mm., whereas the sand particles are much coarser and may vary from 0·01 to 0·2 mm. in diameter, the average usually exceeding 0·05 mm. Mica is the chief constituent in most cases, and it causes objectionable shining specks on the surface of highly finished paper. Granules of quartz and other minerals are still more objectionable on account of their hardness, which averages about three times that of the clay. They cause undue wear of the paper machinery and also of type-face and blocks during printing. Clays of good quality for printing papers frequently contain as much as 1 per cent. of sand. It is suggested that a rate of flow of 1·5 mm. per second should be taken as the standard for estimating the grit in commercial samples of china clay in an elutriator. Theoretically, particles of sand with a diameter of 0·04 mm. are floated by water having a velocity of 1·4 mm. per second, but to obtain accurate results the suspension must not exceed 6 to 7 grms. per litre. A soft water free from organic matter should be used at about 20° C. In practice a 25 grm. sample can be separated by successive decantations and washings in a little over an hour, and the sand is then dried and weighed. Mica may be estimated mechanically by spreading the dried sand on an inclined sheet of glass, which is then tapped gently; the grains of sand, quartz, etc., travel down the inclined plane more rapidly than the flat scales of mica. Finally, the separated

fractions may be examined with a petrological microscope under polarised light to determine the nature of the minerals present. The following standards are suggested as the maximum permissible amounts of grit in various grades of clay: China clay for coating, not more than 0·1 per cent.; for fine papers, not more than 0·25 per cent.; and for news paper, not more than 0·5 per cent. Low grades containing from 5 to 10 per cent. of mica should be described commercially as "mica clays."

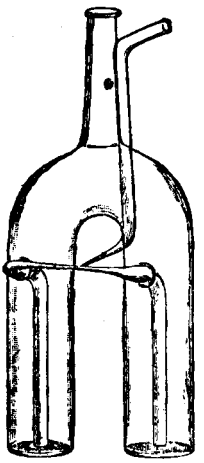
Physical Methods, Apparatus, etc.

Apparatus for Rapid Electrolysis without Rotating Electrodes. G. Edgar and R. B. Purdum. (*J. Amer. Chem. Soc.*, 1922, **44**, 1267–1270.)—The apparatus figured is constructed of Pyrex glass and consists of a cylinder connected at the base with three air-lift tubes which open tangentially into the cylinder midway between the top and base. A cross-section along the line AB is shown at *b*. Electrolysis is carried out by filling the cylinder to the level of the tangential tubes with the solution to be analysed, fitting the open end of the cylinder with a



rubber cork provided with a glass tube and the two electrodes, and connecting the glass tube with an aspirator, thus causing air to enter at the base of each side tube and make the liquid circulate. Owing to rotation of the liquid the air bubbles burst against the wall of the cylinder and no liquid is lost as spray, even when using a rapid current of air. Experimental data are given of copper estimations under varying conditions in which approximately 0·2 grm. of the metal was deposited with a maximum error of 0·1 per cent. T. J. W.

Atomising Apparatus. (*Chem. Zeit.*, 1922, **46,** 570.)—The apparatus shown in the diagram effects the simultaneous atomisation of oily and aqueous, or light and heavy liquids. It consists of an inverted U-tube, on to which is fused a third tube, and which contains the atomiser. The heavy liquid is introduced



by means of a funnel into one limb of the U-tube and the light liquid into the other, and the small tube of the atomiser is connected with a supply of air under pressure. Both liquids will then meet in a fine state of distribution at the point of junction of the U-tube and upper tube.

Prevention of Frothing during Distillation. Klanhardt. (*Chem. Zeit.*, 1922, **46,** 493.)—The frothing of liquids such as solutions of soap or saponin may be prevented by "blowing" the surface with a compressed gas, *e.g.* carbon dioxide. The gas is introduced into the flask through a tube which passes through the cork and extends about half way to the surface of the liquid. Upon the end of this tube is blown a bulb about 2 cm. in diameter, pierced with three openings about 1 mm. in diameter. The apparatus may also be used for distillations with steam.

Estimation of Suspended Impurities in Gases. W. W. Scott. (*J. Ind. Eng. Chem.*, 1922, **14,** 432–433.)—An optical device is described for the detection of dust particles in a gas. A narrow pencil or beam of light from an arc lamp is passed from end to end of a tube, blackened on its inside, and this beam is observed through another tube crossing the first at an angle. The gas under examination enters near the eye-piece of the observation tube and escapes at the other end of it. The beam caused by liquid mist alone appears as a uniform pencil or band of light, whereas dust particles produce a sparkling effect. To estimate sulphuric acid mist in a gas, from 10 to 100 cb. feet of the gas are aspirated through a dry, blue-fibre asbestos filter at the rate of about 5 cb. feet per minute. It is essential that the filter should not become clogged with condensed moisture, and if the gas is supersaturated with moisture, it should be passed first through one or more bottles which act as condensing chambers. The filter is then extracted with water, and the sulphuric acid is estimated in the solution. Portions of the aqueous solution may also be used for the estimation of chlorides and arsenic. W. P. S.

Reviews.

A Course of Practical Organic Chemistry. T. Slater Price, D.Sc., and Douglas F. Twiss, D.Sc. Third Edition. London: Longmans, Green & Co. 1922. Price. 6s. 6d.

This new edition of *A Course of Practical Organic Chemistry* does not differ very markedly from the older edition, but the authors have taken advantage of the opportunity to introduce a brief account of the modified view of the mechanism of the interaction of glycerol and oxalic acid whereby formic acid or allyl alcohol is produced, which is based on the recent work of Chattaway.

On pp. 92–93 is given a description of the preparation of aniline by the reduction of nitrobenzene with tin and hydrochloric acid, which is the one usually described in text-books of practical organic chemistry.

According to this method there are required for the conversion of 50 grms. of nitrobenzene to aniline 90 grms. of granulated tin, 200 c.c. of concentrated hydrochloric acid and 150 grms. of caustic soda, with the result that the bulk of liquid from which the aniline is removed in a current of steam becomes quite large.

As stated in the preface, the primary object of this book is to provide a course of work in organic chemistry for evening students attending technical institutions —a class of students who, as a rule, can devote only a limited amount of time to laboratory work, and then only in comparatively short periods.

It therefore seems to the reviewer that the well-known procedure of reducing nitrobenzene with fine iron filings and a few c.c. of hydrochloric acid would have the double advantage of effecting a considerable saving of time and material, and also of avoiding the working up of a large bulk of liquid by a student who, in carrying out the preparation of aniline, is generally conducting his first "steam distillation."

In the diazotisation of aniline considerable time could be saved by telling the student to add crushed ice to the solution of aniline hydrochloride instead of cooling the solution in water containing ice.

Moreover, it is surely not necessary in preparing a solution of benzene diazonium chloride from aniline to add the nitrite solution "in small quantities (2 to 3 c.c.) about every two minutes" as stated on p. 103. By the simple expedient of delivering it under the surface of the well-stirred reaction liquid all but the last few c.c. of the nitrite solution may be added in a continuous thin stream within one minute.

In the description of the preparation of benzoyl chloride on p. 118 it is stated that the chlorides of phosphorus are the most convenient agents for converting carboxy acids into the corresponding acid chlorides. But now that thionyl chloride is a comparatively cheap commercial article its use would appear to have considerable advantages over that of phosphorus pentachloride, which is recommended in this particular case.

These various suggestions are not made in any spirit of hypercriticism of a very good book, but only in the hope that their adoption would increase the usefulness of the book to the class of students for whom it is primarily written.

Joseph Kenyon.

THE ANALYSIS OF NON-FERROUS ALLOYS. By F. IBBOTSON, D.Met., B.Sc., F.R.C.Sc.I., F.I.C., and L. AITCHISON, D.Met., B.Sc., A.I.C. Second Edition. Pp. ix+246. London: Longmans, Green and Co. 1922. Price 12s. 6d. net.

The first edition of this useful work appeared in 1914. The second edition contains additional text-matter describing chiefly the analysis of aluminium alloys and those of nickel with copper and with chromium and iron. The book may be subdivided into three sections: I. Introductory (46 pages), II. Methods for estimating metals (130 pages), and III. The analysis of commercial alloys (54 pages). Section I. comprises three excellent chapters dealing respectively with apparatus for electrolysis, theoretical considerations on electrolysis, and recent investigations on the influence of acid concentration on the precipitation of metals by hydrogen sulphide. In Section II., a separate chapter is devoted to each important metal, the various methods of estimation being discussed as well as described. It is to be regretted that the authors have not treated manganese in this manner, though the estimation of this commercially important constituent of alloys is described in Section III. On the other hand, bismuth, which is not mentioned at all in Section III., has a long chapter all to itself; while arsenic—hardly more than an occasional impurity—forms the theme of the longest chapter in Section II, and, in addition, is accorded full treatment in Section III. This section is a compilation of thoroughly useful and up-to-date processes for the estimation of single constituents, and the complete analysis of brass, bronze, German silver, white metal alloys, aluminium alloys, nickel-chromium-iron, copper-nickel, and stellite, as well as special alloys containing manganese or phosphorus. What criticism the writer has to offer bears only on minor points. Thus, lead sulphate need not be washed with alcohol, a 0·75 per cent. solution of ammonium sulphate being as effective and cheaper. Under the volumetric estimation of tin, the authors state that two minutes' boiling with one grm. of powdered antimony suffices for the reduction of 0·1 grm. of tin to stannous chloride. The writer does not stand alone in considering the time allowance a very small one, but, not having made any actual tests to determine the time required, he prefers not to commit himself to a more definite expression of opinion. It is rather surprising that the authors do not allude to Dittrich's device for facilitating the filtration of aluminium and ferric hydroxides by mixing the precipitate with filter pulp. The finely-divided oxides obtained by igniting the mixture quickly attain constant weight, and are quite readily soluble in strong hydrochloric acid; a pyrosulphate fusion is thus obviated. Precipitated antimony sulphide is described as being of a "gelatinous consistency," a term which the writer considers unnecessarily harsh when applied to so tractable a precipitate. The authors rightly state that it obstinately retains chlorine, but do not mention that it can be obtained free from chlorine if precipitated from solutions containing tartaric acid.

The pleasure of reading the book is occasionally somewhat marred by peculiarities of style and negligence in the use of certain terms. For instance, "hydrate" and "hydroxide," "kathode" and "cathode" are used interchangeably. We read

expressions such as: "the alloy is opened-out," as well as "opened out"; "most workers dissolve up the precipitate"; "the metal is precipitated as carbonate, weighing up as oxide"; "the salt analyses out to the composition"; "the beaker must be cleaned very thoroughly with a policeman." Laboratory jargon looks decidedly ugly in print. The volume is practically free from misprints; the most noticeable is the formula "CrO" for chromium trioxide (p. 83).

In conclusion, the authors are to be congratulated on the production of this book, a copy of which should be kept in every metallurgical laboratory.

W. R. SCHOELLER.

DER GEBRAUCH VON FARBENINDICATOREN. By I. M. KOLTHOFF. Pp. 144. Berlin: Julius Springer. 1922. Price 45 mks.

Owing to the increasing importance of hydrogen ion determinations in chemical work the subject of indicators has, during the last few years, received an increasing amount of attention. The developments in this field have been so rapid that books on the subject have become quickly out of date. The work under review is an attempt to give a clear idea not only of the uses of indicators for titrations and hydrogen ion measurements, but also a concise account of the theory of the subject. In this it may be said that the author has been successful. The theoretical part is concisely and clearly treated, and in the more practical part much of the author's own valuable work of the subject is included.

In the first and second chapters a description is given of the ionisation theory and its application to the colour change of indicators and to titrations. A considerable portion of the second chapter is taken up with an admirable treatment of the effect of concentration of indicator and of temperature on the range of the colour change.

The third chapter deals with titrations, and a selected list of indicators is given for this purpose. In the reviewer's opinion this list is open to criticism, and is capable of considerable improvement. The inclusion of methyl orange seems unnecessary, and not one of the Clark and Lubs indicators obtains a place, in spite of the manifest superiority of certain of them, *e.g.* bromphenol blue over dimethyl yellow, phenol red over neutral red, and thymol blue over phenolphthalein.

A list of titrations, with the most suitable indicators for each, is also given, but this might be considerably improved in usefulness if the titration exponent of each titration were included. Some titrations are also given which are not practicable under ordinary conditions; for instance, the statement that quinine may be titrated with the use of methyl red, methyl orange or dimethyl yellow is misleading—as a matter of fact quinine can only be satisfactorily titrated with the use of methyl red as indicator and the titration must be carried to a definite shade of colour.

The fourth and fifth chapters describe the colorimetric method of hydrogen ion determination and various practical applications of the method. The tables of standard solutions would be more useful if they were uniformly drawn up;

in their present form they give directions for preparing quantities which vary from 10 c.c. to 200 c.c.

Indicator papers are the subject of the sixth chapter, and much matter of interest is included. The concluding chapter deals with the theories of indicator colour change.

Tables of dissociation constants, indicator ranges, etc., complete the volume. A useful bibliography is given at the end of each chapter. The book is well printed and free from errors, but surely a work of this character deserves something more permanent than a paper cover.

NORMAN EVERS.

A DICTIONARY OF APPLIED CHEMISTRY. Vol. III.: EXPLOSIVES TO K. By SIR EDWARD THORPE, C.B., F.R.S., assisted by Eminent Contributors. Revised and Enlarged Edition. Pp. 735. London: Longmans, Green & Co. 1922. Price 60s. net.

The scale of the enlargement of the new edition of "Thorpe" is shown by the fact that the subject matter of little more than two volumes in the 1912 edition now occupies three full volumes. In spite of the introduction of much new material it is difficult to suggest any parts of the work where space-saving omissions could have been effected without impairing the usefulness of what is perhaps the most valuable treatise of its kind in the world. The only criticism that can be made is that in a few of the articles, such, for instance, as that on Glucosides, some of the information tends to a theoretical character such as one would seek in a text-book on the subject rather than in a Dictionary of Applied Chemistry.

All the articles have been carefully revised and brought up-to-date; many new references are given, even including some quite late in 1921. Among the new articles may be mentioned hardened or hydrogenated oils, interferometer, and gas warfare. The article on hydrogenated oils is by C. A. Mitchell, and is an interesting account of this important development in the fat industry; the most recent patents are noted; also the preparation and purification of the hydrogen and the catalysts; the effect of hydrogenation on the chemical and physical constants of the oils, and the applicability of well-known tests to the products are mentioned. The description of the interferometer, specially in its applications in the technical laboratory, will be of interest to analysts generally.

The article on gas warfare is certainly of historical value, and catalogues the principal substances used by the Germans; whilst its incorporation in the work is necessary for purposes of reference, its utility is perhaps doubtful, from the fact that most people may regret that chemistry should be thus "Applied."

The inclusion of much new matter is particularly noticeable in sections on explosives, coal-gas, glass, glue, and glycerin. The subject of explosives is so fully dealt with that we have practically a text-book of 100 pages describing almost all substances coming under the heading.

The coal-gas section includes the important changes introduced by the Gas

Regulation Act of 1920, also a description of the latest and most approved methods of purification, such as that of Carpenter and Evans. Professor W. E. S. Turner's section on glass is quite a feature of the volume; its many references to English literature on glass technology being a striking evidence of the headway made in this branch of chemical technology in this country during and since the war.

Turning to details of the work, there are very few misprints or errors, but the greatly increased number of substances described both under principal and subordinate headings makes the preparation of an index volume seem most desirable. It is noticeable in this connection that Fehling's solution is not to be found in this volume, nor even an indication that it should be sought under the name of Barreswil in Volume I.

The general impression left upon the reviewers after careful reading is that the volume has been well and carefully revised, brought up-to-date, and fully maintains the high standard of excellence so long associated with the work.

G. R. THOMPSON.
H. E. COX.

COLLOID CHEMISTRY OF THE PROTEINS. By Prof. Dr. WOLFGANG PAULI. Translated by P. C. L. THORNE, M.A., A.I.C. Part I., with 27 Diagrams and Numerous Tables. Pp. xi+140. London: J. & A. Churchill. 1922. 8s. 6d. net.

This little volume is an excellent translation into English (on which the translator must be congratulated) of Professor Pauli's book summarising his investigations on proteins.

Professor Pauli and his collaborators have for years been engaged in studying the behaviour of the proteins from the standpoint of physical chemistry, and as a result, as the translator points out, "by the application of the quantitative methods of physical and colloid chemistry, a consistent theory of the behaviour of proteins, particularly in acid and alkaline solution, has been established."

The albumins receive special attention, as one expects from Pauli, whilst, of the other proteins studied, the discussion on casein deserves special mention, both on account of its importance and its lucidity. Gelatin is practically unmentioned, and there is no mention at all of Loeb's work on the proteins, although the opinions of T. B. Robertson find occasional reference.

The great value of the book lies in its being a summary of investigations involving very careful measurements of hydrogen ion concentrations, protein viscosities, migration velocities (cataphoresis) and electrical conductivities. The importance of the hydrogen ion concentration of the medium in relation to the properties of the protein is well described, and there is an unusually clear exposition on the iso-electric conditions of the proteins.

The typography is excellent. Altogether, the monograph is to be recommended to all colloid chemists, whether they be interested from the biochemical side or the purely physico-chemical side.

WILLIAM CLAYTON.

THE VITAMINS. By H. C. SHERMAN and S. L. SMITH. (American Chemical Society Monograph Series.) Pp. 273. The Chemical Catalog Co., Inc., New York. 1922. Price $4.00.

The difficulties of preparing a readable account of the vitamins are very great, if it is to be suitable both for the medical practitioner and the student who wish to have a general knowledge of the subject, and for the research worker who asks for a review and bibliography of the vast literature concerned with these substances. They appear to have been overcome most successfully, however, by Professor Sherman and his co-worker, whose volume is excellent. This book is a pleasure to read because the subject-matter is adequately treated in a connected manner, and there is an entire absence of that "scrappiness" which so often characterises monographs in which a large field of literature must be reviewed.

The monograph is confined chiefly to a consideration of the vitamins themselves and the existing knowledge regarding their distribution in foods and their chemical and physical properties, and does not discuss in any detail the so-called deficiency diseases. This is perhaps wise, for the latter aspect of the vitamin question has in the past received the greater share of the attention of reviewers, frequently to the exclusion of what must ultimately be the most important point—the evidence which will one day lead to the elucidation of the nature of these remarkable substances.

A full bibliography of over a thousand references is given, which makes one ponder over the task that will face a reviewer of this subject when a second decade has passed after the discovery of vitamins.

We will indeed be indebted to the American Chemical Society if the future monographs on other subjects which are announced are such valuable and readable volumes.

J. C. DRUMMOND.

Publications Received.

VITAMINS AND THE CHOICE OF FOOD. By V. G. PLIMMER and R. H. A. PLIMMER, D.Sc. Pp. vii+164. London: Longmans, Green & Co. 1922. Price 7s. 6d. net.

COAL TAR COLOURS IN THE DECORATIVE INDUSTRIES. By A. CLARKE. Pp. xiii +166. London: Constable & Co. 1922. Price 6s.

NOTES ON QUALITATIVE ANALYSIS (Supplement.) By H. J. H. FENTON, D.Sc., F.R.S. Cambridge University Press. 1922. Price 3s. 6d. net.

MODERN MICROSCOPY. By M. I. CROSS and M. J. COLE. Fifth Edition. Pp. x +315 London: Baillière, Tindall & Cox. 1922. Price 10s. 6d.

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METALLURGICAL AND ANALYTICAL APPLICATIONS OF THE SPECTROGRAPH. Photography of Emission Spectra.) London: Adam Hilger, Ltd. 1922.

Includes a bibliography of papers on quantitative spectrum analysis by means of the quarz spectrograph, and a photogravure of arc spectra of lead and copper.