THE ANALYST

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

The Determination of Phosphoric Acid as Magnesium Ammonium Phosphate.

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(Read at the Meeting, December 2, 1925.)

PRECIPITATION IN THE COLD.—Candless and Burton (*Ind. Eng. Chem.*, 1924, **16**, 1267) have given some results of their experiments in precipitating magnesium ammonium phosphate in the cold with an ammoniacal magnesia mixture, after the solution of the molybdic precipitate in ammonia water had been exactly neutralised to litmus paper, and they state that corallin might be applicable instead of litmus paper.

The results agree very well with one another, and this has astonished me, because, more than twenty years ago, I showed in a prize-essay, proposed by the Academie Royale des Sciences et des Lettres de Danemarc, that the same method, but with the use of rosolic acid, did not give sufficiently exact results.

The results of these experiments are to be found in my dissertation ("Ueber die Bestimmung der Phosphorsäure als Magnesiumammoniumphosphat und als Ammoniumphosphomolybdat," *Memoires de l'Academie Royale des Sciences et des Lettres de Danemarc*, 1905; Publishers: Andr. Fr. Höst & Sön, Copenhagen), and the method of determining phosphoric acid in mineral phosphate, based on them, has been published in this Journal (ANALYST, 1909, **34**, 392).

SUMMARY OF PREVIOUS CONCLUSIONS.—The magnesia mixture used in these experiments contained per litre: $MgCl_2.6H_2O$, 55 grms. (0·27 mole); NH_4Cl, 70 grms. (1·31 mole); NH_3, 25 grms. (1·47 mole).

The results obtained by direct precipitation of phosphoric acid from a cold solution were widely divergent; when the magnesia mixture was added slowly and much ammonium chloride was present they were too low, whilst a rapid addition of magnesia mixture to a strongly ammoniacal solution caused them to be too high.

Precipitation with magnesia mixture after dissolving the precipitated ammonium phosphomolybdate in ammonia, and without neutralising the ammonia, gave too low results, owing to variable amounts of $Mg(NH_4)_4(PO_4)_2$ being formed; If the ammonia was neutralised before the precipitation, the composition of the precipitate was found to vary with the conditions of neutralisation.

The conclusion was therefore drawn that the compound $MgNH_4PO_4$ is never precipitated in the cold in so pure a form that the accompanying reactions can be ignored, and, further, that it depends on the concentrations of the substances in the solution which of other sparingly soluble salts are precipitated at the same time.

INFLUENCE OF P_H VALUE.—As a supplement to these investigations, which were carried out more than twenty years ago, and long before chemists had become aware of the importance of the hydrogen ion concentration for the course of so many chemical reactions, I have now made a series of experiments to ascertain how the P_H value of an ammoniacal solution of phosphomolybdic acid is altered by the admixture of variable quantities of hydrochloric acid.

The experiments have been carried out in the same way as those given in the second table (p. 35) in my essay (*loc. cit.*), with the exception that the intervals now chosen have been a fourth of those then employed, the difference between the added quantity of hydrochloric acid for two consecutive experiments being 1 ml. of 25 per cent. hydrochloric acid for 100 ml. of solution containing about 0·2 grm. of phosphoric anhydride.

II.*a* corresponds then almost with II. in the table mentioned above, and III.*a* with III. in the same table. For 1 mol. of H_3PO_4, 12 of $(NH_4)_2MoO_4$ were present, and the volume was 34·9 ml.

Mole.	Ic.	Id.	IIa.	IIb.	IIc.	IId.	IIIa.
NH_4Cl	31·4	31·4	31·4	30·3	27·4	24·7	22·0
Free HCl	6·9	4·2	1·6	—	—	—	—
,, NH_3	—	—	—	1·1	4·1	6·8	9·4
P_H	6·65	6·8	7·2	8·1	8·7	9·0	9·2
H_3PO_4 found as in the second table (p. 35), grm.			1·0075				0·9919

In the first three experiments the P_H was measured both with bromthymol blue and rosolic acid, with the same results, for II.*b* with phenolphthalein, and for the last three with thymol blue. For II.*a* Biilmann's quinhydrone electrode was also tried, but this method has not given constant results in this case, probably owing to reduction of the molybdic acid. As was to be expected, a decided buffer effect appears, *i.e.* for the P_H values about 7 and 9.

With litmus paper in the solution I found it rather difficult to observe the change of colour, although it seems very much like that of the rosolic acid, but, if different analysts are to work at the same P_H value, it would be advisable to use a comparison liquid consisting of a precisely defined buffer solution, mixed with a fixed quantity of indicator.

According to N. Bjerrum (*Z. anal. Chem.*, 1917, **56**, 86) litmus and rosolic acid present almost the same exponent of titration (P_T), viz. for more closely defined concentrations of the indicators about 6·5, at which P_H value the solutions contain acid and basic forms of the indicators in equal quantities.

Now in experiment No. 5 in the first table (*loc. cit.*), in which so much hydrochloric acid was added that the rosolic acid showed a reddish colour and the P_H, therefore, presumably was between 6·5 and 7·0, I found 1·0110 grm. of H_3PO_4, and in experiment No. II. in the second table (*loc cit.*), in which the P_H, according to my recent determinations, was about 7·2, I found 1·0075 grm., and the method I applied at that time whenever the P_H of the solution at the beginning of the magnesia precipitation was near 7, as were also the values in the experiments in the table (p. 34), (*loc. cit.*) gave too high results.

The agreement was not so close for the experiments in the first table (p. 35), in which I used phenolphthalein as indicator, but this may be explained by the fact that variable quantities of the indicator were applied.

So far as I am aware, it has been fully accepted that the more ammoniacal a phosphoric acid solution, when precipitated with magnesia, the lower the results will be. As the solution subsequently (during the addition of the ammoniacal magnesia mixture) gets more and more basic, I conclude that if the weight of $Mg_2P_2O_7$ corresponds to the added quantity of phosphoric acid, it must be due to the fact that the former part of the magnesium ammonium phosphate has been precipitated with too large, and the latter with a correspondingly too small, content of magnesium. The method, then, is a compensation-method, and, because of this, it will always be very difficult for different chemists to get concordant results. It is obvious that the conditions of precipitation cannot readily be made absolutely the same when the analyses are made by different persons, even if the precipitation every time is begun at the same P_H value; other factors must also be taken into account, *e.g.* the temperature of the solution and the phosphoric acid content, the composition of the magnesia mixture, the rate of adding it, and the amount of shaking or of stirring.

All these points must be taken into consideration when an explanation is required as to the contradictory views of different investigators concerning the reaction necessary for the solution of the molybdic precipitate before the addition of the ammoniacal magnesia solution. Whilst I (as also H. Neubauer, *Inaug. Dissert.*, 1893) have found that a precipitation begun in a nearly neutral solution gives too high results, Candless and Burton (*loc. cit.*) get exact results under like conditions, and R. J. Caro and E. L. Larison (*Ind. Eng. Chem.*, 1925, **17**, 261) obtain too low results.

THE A.O.A.C. METHOD.—The procedure for the magnesia precipitation which has been described in the Report of the Committee on Editing Tentative and Official Methods of Analysis, published in 1916 by the Association of Official Agricultural Chemists, differs from mine in these two items:—

(1) The magnesia mixture applied contains twice the quantity of ammonium chloride and four thirds as much ammonia as that of Wagner (*Z. anal.*

Chem., 1880, **19**, 444), which I have employed. It was, then, to be expected that the American magnesia mixture (if the precipitation is begun at the same P_H value) should give lower results than that of Wagner, especially as the latter part is precipitated in a more ammoniacal solution; according to my experiments (Table, p. 30, *loc. cit.*), corroborated by those of Karaoglanow (*Z. anal. Chem.*, 1918, **57**, 497), an increased ammonium chloride concentration has also the same effect.

(2) As the rate at which I have added the magnesia mixture has been at least twice that of the Association (about one drop per second), it was also to be expected (provided the other conditions of precipitation were the same) that the American method should give lower results than the German method (Wagner, Neubauer) which I then used.

It is questionable whether so slow an addition as that of the American process will prove satisfactory, as it is doubtful whether it will always be observed in a commercial laboratory, where the work is often done at high speed.

INFLUENCE OF AMMONIUM SALTS.—When Candless and Burton, after having washed the magnesium ammonium phosphate on the filter with 2·5 per cent. ammonia solution, finally add 5 ml. of a concentrated solution of ammonium nitrate to the washing medium on the filter, it will be admitted that this may cause some error, the extent of which will vary with the strength of the ammonium nitrate solution and with the quantity of ammonia solution on the filter, the speed of filtration, and the method of adding the ammonium nitrate solution, on which depends whether it has time to mix with the ammonia solution before it gets into contact with the precipitate.

We all know that ammonium salts hinder, to a great extent, the dissociation of ammonium hydroxide and, according to my investigations, the solubility of magnesium ammonium phosphate in ammonia solutions which contain 0·2 mol./litre of ammonium chloride should be something like twice its solubility in pure ammonia solutions of the same concentration. I suppose, therefore, that the above-mentioned procedure may be a concurrent cause of Candless and Burton getting lower results than should be the case according to my investigations.

PRECIPITATION FROM ACID OR NEUTRAL SOLUTION.—Whilst these analysts have experimented with phosphate solution of exactly known contents, Caro and Larison have used a sample of mineral phosphate analysed by the Bureau of Standards, and they have found that it is necessary to precipitate with the ammoniacal magnesia mixture in acid solution in order to get results as high as those of the Bureau. Further, it is stated that the Bureau found 31·38 per cent. of P_2O_5 by a repeated magnesia precipitation, first in ammoniacal, and later in acid solution, whilst the average of 12 results obtained by a single precipitation of the magnesium ammonium phosphate in acid solution is 31·52 per cent.

As these authors found determinable quantities of molybdic acid in the magnesia precipitates which have been precipitated in neutral or acid solutions, these

results must be too high for this reason alone; how great the discrepancy is would have been recognisable if the authors (as I have done) had stated the quantity of magnesium oxide in the precipitates. My own experience leads me to believe that the result should be lower by this method than by that of the Bureau, but I cannot say so definitely, as I am not acquainted with the details of the American second precipitation. Only one thing I look upon as quite certain: when a similar excess of magnesium is present in the acid solution to be precipitated as in the usual single precipitation of phosphoric acid, the results are sure to turn out too high.

I have not felt it my duty, however, to continue further investigations on precipitation from a cold solution, as for many years it has been, and still is, my belief that this method is too readily influenced by slight variations in procedure, for which reason it should not be relied upon too much in commercial laboratories. And as it has been abandoned in England (B. Dyer, "Fertilisers," in *Thorpe's Dictionary of Applied Chemistry*, 1922, Vol. III.) and in Germany ("Verein Deutscher Düngerfabrikanten," *Methoden zur Untersuchung der Kunstdüngemittel*, 1916), I would suggest that American chemists should carry out some experiments by the following method, which I, having thoroughly tested it, look upon as the most reliable and which has given me results approaching the theoretical amounts with an accuracy of about 1:1000.

THE AUTHOR'S METHOD: PREPARATION OF THE REAGENTS.—(a) *Molybdic solution.*—One hundred grms. of pure ammonium molybdate are dissolved in 280 ml. of ammonia (Sp. gr. 0·97), and 300 ml. of this solution are poured, with vigorous shaking, into 700 ml. of nitric acid (Sp. gr. 1·21), and the mixture allowed to stand for twenty-four hours. The ammonia solution may be prepared by mixing 84 ml. of ammonia (Sp. gr. 0·91) with 196 ml. of water, and the nitric acid by mixing the strong acid (Sp. gr., 1·4) with about an equal weight of water.

(b) *Acid Ammonium Nitrate Solution.*—This should contain 40 grms. of ammonium nitrate and 10 grms. of nitric acid per litre. It is prepared by mixing 90 ml. of nitric acid (Sp. gr., 1·4) with about 1500 ml. of water, adding 80 ml. of ammonia (Sp. gr., 0·91), and making up to a volume of 2000 ml.

(c) *Magnesia Solution.*—Fifty grms. of pure magnesium chloride ($MgCl_2$ +$6H_2O$) and 150 grms. of pure ammonium chloride are dissolved in water, and the solution made up to 1000 ml.

METHOD FOR MINERAL PHOSPHATES.—(1) Five grms. of mineral phosphate are placed in a 250 ml. flask, and gently boiled for about half an hour with 25 ml. of nitric acid (Sp. gr. 1·21) and 12·5 ml. of hydrochloric acid (Sp. gr. 1·12). The contents of the flask are then cooled, made up to 250 ml., and filtered.

(2) To 50 ml. of the filtrate contained in a beaker flask (250 ml.) is added the quantity of molybdic solution shown in the equation below (p. 67), the flask placed in a water bath at a temperature of 50° C. for ten minutes, and its contents occasionally stirred. When quite cold (*e.g.* after immersing the beaker flask in cold water for 15 minutes) the contents of the flask are filtered, and the precipitate

washed ten times by decantation with acid ammonium nitrate solution, about 20 ml. being used for each washing. If necessary, the filtrate may be tested for unprecipitated phosphate by adding more molybdic solution, heating to 50° C., and leaving for twelve hours. The detection of calcium, as a test of the washing being sufficient, may be made by adding a little sulphuric acid and alcohol to the extent of twice the volume of the washings.

(3) The washed molybdic precipitate is dissolved in 100 ml. of 2·5 per cent. ammonia solution, filtered, if necessary, through the same filter which held the molybdic precipitate, the filter being washed eight times with about 10 ml. (each time) of the ammonia solution, so that the final volume is about 180 ml.

(4) The beaker flask is covered with a clock-glass, the contents brought just to the boiling-point, the flask removed from the burner, and 30 to 35 ml. of the magnesia solution added, drop by drop, from a burette with a glass cock, the whole being well stirred. The beaker flask is again covered, and so long as the liquid remains very warm it is stirred frequently, and if the precipitate is not compact and crystalline the stirring should be continuous. After standing for at least four hours the solution is filtered on to a platinum crucible packed with spongy platinum, and the precipitate washed with 2·5 per cent. ammonia solution until free from chlorides, and then once with alcohol.

(5) The precipitate is dried and heated gradually over an Argand burner, then ignited strongly, cooled, and weighed.

To this I may add the following explanatory notes:—

(A) *Standard Phosphate.*—In my earlier work on the determination of phosphoric acid I chiefly used sodium ammonium phosphate which I had recrystallised myself and found to be of the right composition. Later, I made use of S. P. L. Sörensen's disodium phosphate (with 2 mols. of water of crystallisation), but it has proved somewhat hygroscopic. On the other hand, a preparation that was a little too aqueous gave off too much water when dried for 24 hours in a thermostat at 20° C. Thus two of my collaborators found only 0·2770 grm. of $Mg_2P_2O_7$ in 0·45 grm. of an old preparation which formerly had given the correct result (0·2814 grm.). A determination of the residue after ignition yielded a result rather more than 1 per cent. too low.

Of the commercial preparations, Kahlbaum's monopotassium phosphate, prepared according to the directions of S. P. L. Sörensen, must therefore be looked upon as the best control-preparation.

(B) *As solvent for mineral phosphates* and *superphosphates* I use Glaser's mixture, of which the above-mentioned quantity is sufficient for dissolving the phosphoric acid. When concentrated sulphuric acid, *aqua regia*, or a greater excess of nitric acid is used, a larger excess of the molybdic solution is necessary for a quantitative precipitation of the phosphoric acid.

For determining the total phosphoric acid in Thomas phosphates I boil 5 grms. of the sample with 40 ml. of hydrochloric acid (Sp. gr., 1·18) for 30 minutes

and then dilute to 250 ml.   Nitric acid and *aqua regia* must not be used, as these solvents oxidise the unsaturated phosphorus coumpounds, and with concentrated sulphuric acid I have not had sufficiently concordant results, probably partly because the precipitated calcium sulphate diminishes the volume of the liquid, and partly because it readily absorbs some phosphoric acid (*vide infra*).

(C) *Silica in the Precipitate.* It is superfluous to render *the silica insoluble* by evaporation with acid, since in the molybdic precipitation one does not use a substantially greater excess of the molybdic solution than necessary for a quantitative precipitation of the phosphoric acid, and only heats to 50° C. for short time. I have had correct results, even when the phosphate solution contained up to 0·17 grm. of silica in the form of sodium silicate, and such large amounts of silica will surely never be found in the extracts of fertilisers subjected to analysis.   In the citric acid extract of 1 grm. of Thomas phosphate the amount of silica found was 0·05 grm., and in the hydrochloric acid separation only a few mgrms. of silica for 1 grm. of substance.

According to some analyses which have not been published, it seems likely that a little phosphoric acid may be volatilised during evaporation with *aqua regia*; also, it is to be feared that the separated silica retains some phosphoric acid, which cannot (or, at any rate, can only with difficulty) be removed by washing on the filter.   Anyway, I have repeatedly had lower results when the silica was made insoluble by evaporation to dryness than when this had not been the case, although the magnesia precipitate did not contain silica.

(D) *The hydrolysis of pyro-phosphoric acid* is completed by heating 50 ml. of the aqueous solution with 2·5 ml. of nitric acid (Sp. gr. 1·4) for 30 minutes in a water bath, even if all the phosphoric acid was originally present in the above-mentioned form.

(E) With regard to *the molybdic precipitation*, the quantity of the molybdic solution of the above-mentioned composition to be used for a complete precipitation of the phosphoric acid may be calculated according to the following equations:

$$\text{I.} \quad x_{\mathrm{I}} = 0\cdot12v + 345p. \qquad \text{II.} \quad x_{\mathrm{II}} = 0\cdot34v + 412p,$$

where x = ml. of molybdic solution, v = ml. of the phosphate solution, and p = grms. of P_2O_5.

Equation I (small excess of the molybdic solution) is applicable to the determination of the total phosphoric acid in mineral phosphates and superphosphates, dissolved as mentioned above, as well as for water-soluble phosphoric acid in superphosphate hydrolysed as mentioned before.

Equation II (great excess of the molybdic solution) is applicable to the determination of total phosphoric acid, as well as of citric-acid-soluble and citrate-soluble phosphoric acid, in Thomas phosphates.

The following examples will illustrate this:

	Equation I.		Equation II. Thomas Phosphates.	
	Mineral Phosphates.	Super-phosphates.	Total.	Citr. soluble.
Volume of the phosphate solution, ml.	50	50	50	100
P_2O_5 grm.	0·4	0·2	0·2	0·16
Molybdic solution, ml.	144	75	100	100

(F)   An acid ammonium nitrate solution *for washing the molybdic precipitate* has been proved to dissolve less of the molybdic precipitate than water, 1 per cent. nitric acid, or neutral ammonium nitrate solution.

(G)   *Determination of phosphoric acid by weighing the molybdic precipitate* has also been tried (*Z. anal. Chem.*,1907, **46**, 370).   The method has also been used in the investigation of fruit-juice (*Ann. Falsificat.*, 1923, **16**, 156).   When only very small quantities of phosphoric acid are to be determined, *e.g.* in organic compounds which have been decomposed with sulphuric acid and nitric acid, I prefer to wash the molybdic precipitate on a small asbestos filter, and to dissolve it in a little dilute ammonia solution which, together with the water applied for the washing, is received in a tared porcelain crucible.   The solution is evaporated, a drop of nitric acid is added, and the dried residue is gently heated until the colour darkens.

As the conditions of the precipitation have some influence on the proportions between the phosphorus and molybdenum in the molybdic precipitate, I do not find the direct molybdic method so exact as the above-mentioned molybdic magnesium method, but it will be found satisfactory, especially for determining small quantities of phosphoric acid and in cases in which the degree of accuracy need not exceed 1:100.

In my opinion N. von Lorenz's gravimetric molybdic method should not be preferred to mine, as a more constant ratio between phosphorus and molybdenum is not obtained by his method; besides, as the molybdic precipitate is very hygroscopic before the ignition, and, as it may contain variable proportions of ammonia according to the composition of the washing liquid, the method contains more sources of error than mine.

I look upon the gravimetric determination of phosphoric acid as phospho-molybdic acid as being safer than the acidimetric methods, because the latter require the ammonia and then the carbonic acid to be boiled off in order to give exact results, and this adds to the difficulty of the examination; and, not only this, it involves the possibility of error if alkali in the glass is dissolved during the boiling.

(H)   As to the other manipulations, I have only to add that the quantity of the 2·5 per cent. ammonia solution, used in dissolving the molybdic precipitate, amounts to about 100 ml., and that of the neutral magnesia solution to about 15 ml. for 0·2 grm. of P_2O_5.   I often add nearly two-thirds of the magnesia solution rather quickly, with continuous stirring, then stop the addition and shake until

the precipitate has become compact and crystalline, after which the rest is added in drops. By this procedure the danger of forming a salt which does not contain sufficient magnesia is avoided; moreover, the precipitate has sufficient time to become compact and crystalline before a noticeable excess of magnesium ions is present, and, as the crystalline forms are the most difficultly soluble, the formation of a salt too rich in magnesium is prevented.

(J) *The Citrate Method.*—I have thoroughly examined the *Citrate Method*, also, and have found it to have the same drawback as the molybdic magnesium method, *i.e.* that by cold magnesia precipitation sufficiently exact results are not obtainable, or, at least only with difficulty, this being especially due to the fact that the rate at which the magnesia mixture is added influences the magnesium content of the precipitate. On the other hand, the same degree of accuracy as with my molybdic magnesia method is obtainable in a warm solution, but care must be taken that a sufficiently great excess of magnesium chloride is present, and that the liquid is allowed to stand for a sufficient time.

As the solution which is to be precipitated by the citrate method must not contain either silica or arsenic acid, nor considerable quantities of sulphates or compounds of ferric iron, aluminium or calcium, this method can only be of use in the case of mineral phosphates and fertilsers for a determination of water-soluble phosphoric acid in superphosphates; in the case of high percentage products it is scarcely possible to work with more than 0·5 grm. of substance if one wishes to avoid determining the calcium absorbed in the magnesium precipitate, and this complicates the method. Hence I never use the citrate method for these determinations.

The following table shows the results obtained by determining the phosphoric acid content by different methods:

WATER-SOLUBLE PHOSPHORIC ACID IN 2 SAMPLES OF SUPERPHOSPHATES.

	A. Per Cent.	B. Per Cent.
I. My molybdic magnesia method	17·25	17·16
II. My citrate method	—	17·23
III. International method[1]	17·06	16·92
IV. Verein Deutscher Dünger-Fabrikanten[2]	17·70	17·86
V. Verband landwirtschaftl. Versuch-stationen[3]	17·45	17·40

The result in II. is too high, and this is certainly due to the calcium phosphate in the magnesia precipitate.

The methods in III. and IV. are molybdic-magnesia methods, but whilst the precipitation with the magnesia mixture in III. was carried out in an ammoniacal

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[1] *Bericht über die Arbeiten der Internat. Kommission für die Analyse der Kunstdünge-u.-Futtermittel*, 5th Internat. Kongress f. Angew. Chemie, Berlin (1903).

[2] *Methoden zur Untersuchung der Kunstdüngemittel*, 3 Aufl. (1903).

[3] *Die landwirthschaftlichen Versuchstationen*, (1893), **42**, 105.

solution (Fresenius, Wagner), that in IV. was carried out in a solution which was neutralised as nearly as possible with hydrochloric acid, and therefore it was to be expected that III. would also give too low and IV. far too high results. Method V. is a citrate method with cold magnesia precipitation, and the result is too high.

CITRIC-ACID-SOLUBLE PHOSPHORIC ACID IN 7 SAMPLES OF THOMAS PHOSPHATES.

	My molybdic magn. method. Per Cent.	Kellner-Böttcher's method.[1] Per Cent.	Magnesia-precipitate including calcium. Per Cent.
I.	14·07	14·42	14·09
II.	13·80	14·16	13·85
III.	12·60	12·82	12·71
IV.	12·03	12·17	11·98
V.	14·13	14·34	—
VI.	11·90	12·22	—
VII.	7·79	8·07	—

This shows that the Kellner-Böttcher method, which is a citrate method, gives far too high results, which is principally due to the presence of considerable amounts of calcium phosphate or ammonium calcium phosphate in the magnesia precipitate. The quantity of iron compounds, introduced into the precipitate through the hydrogen sulphide in the solution, only amounts to some few tenths of a mgrm., and the silica content is also of no great importance. Although it has often been supposed that considerable amounts of silica have been present in the magnesia precipitate, this is merely due to the formation of some $Mg(NH_4)_4(PO_4)_2$, which by ignition is converted into $Mg(PO_3)_2$, which is insoluble in hydrochloric acid; whilst a lower result after reprecipitation is surely due, for the most part, to the calcium in the first precipitate.

TOTAL PHOSPHORIC ACID IN THOMAS PHOSPHATES.—In six different extracts of the same sample (in which the phosphoric acid was determined according to my molybdic-magnesia method (hydrochloric acid being used for three of them and concentrated sulphuric acid as a solvent for the other three) I had the following results (see page 67):—

Hydrochloric acid extract, P_2O_5 per cent., 14·65, 14·67, 14·69.
Sulphuric acid extract, 14·59, 14·78, 14·93.

The variations in the latter method must undoubtedly have been due to the separation of variable quantities of calcium sulphate after the evaporation of more or less sulphuric acid.

On examining the same hydrochloric extract of a sample of Thomas phosphate by my molybdic-magnesia method I found 14·67 per cent. of P_2O_5, and by Märcker's method (*Methoden des Vereins Deutscher Dünger-Fabrikanten*, 1903), 14·70 per cent. However, this close agreement was due to an accidental circumstance, as in the filtrate from the Märcker's magnesia precipitate 0·0038 grm. of

[1] *Methoden zur Untersuchung der Kunstdüngemittel*, 3 Aufl. (1903).

P_2O_5 was found, owing to the fact that the quantity of magnesia mixture pre-scribed for the precipitation is far too low compared with the prescribed quantity of ammonium citrate, but, on the other hand, the magnesia precipitate contained 0·013 grm. of calcium oxide in the state of a calcium phosphate. Compensation methods of this kind should obviously be discarded.

OFFICIAL TESTS OF THE AUTHOR'S METHOD.—In this connection I must not omit to record the following proof of the applicability of my molybdic-magnesia method:—In 1908 this method was authorised by the Danish Board of Trade (for the analysis of fertilisers), and that through all these years it has stood the test, as is shown by the fact that re-determinations carried out by one or several persons have been concordant. One collaborator of mine, who has been doing this work for nearly four months, but had previously never had to determine phosphoric acid, has, in re-determinations of 8 samples of mineral phosphates, only once had a want of agreement so high as 1·2 mgrms. of $Mg_2P_2O_7$ for each grm. of the phosphate; in all other cases the greatest difference was 0·9 mgrm. None of the re-determinations of water-soluble phosphoric acid in 47 samples of superphosphate showed a difference above 1 mgrm., whereas the variations in the determination of citric-acid-soluble phosphoric acid in 22 samples of Thomas phosphate were about twice that amount, half of the samples showing a difference of 1 to 2 mgrms. As all the re-determinations were made with different extracts, so that any lack of homogeneity in the samples and the errors of weight and measure would have their effect, as well as the errors in the method, it must be admitted that the method will give results sufficiently accurate for commercial analysis.

When the results of the analyses of the Thomas phosphate do not accord so well as the other analyses, the explanation is surely to be found in the fact that the citric acid solution has dissolved different quantities of phosphoric acid from the two portions of the same samples.

The same agreement is shown in the determinations of water-soluble phosphoric acid in 8 samples of superphosphates which have recently been examined both in my laboratory and in the laboratory of a Danish superphosphate factory, the results of the one laboratory being wholly unknown to the other. These were:

Stein's laboratory,   17·27, 17·62, and 16·91 per cent.
Factory laboratory,   17·25, 17·57, and 16·99 per cent.

From this factory I have also received the results of the analysis, recently made, of 14 samples of mineral phosphates, which, according to the examinations, made in the laboratory of the factory and in Stein's laboratory, contained from 65 to 87 per cent. of tricalcium phosphate.

The difference between the contents of tricalcium phosphate for the two laboratories was as follows:—0·04 to 0·09 in 4 samples; 0·11 in 1 sample; 0·24 to 0·28 in 2 samples; 0·31 to 0·35 in 5 samples; and 0·41 to 0·49 in 2 samples.

That there is close agreement in the procedures of these two laboratories is clearly shown by the fact that in eight cases the factory, and in six Stein's, laboratory, has obtained the highest results.

In earlier days, too, we obtained none but good results by my molybdic-magnesia method, and I still very much regret that the late Chairman of the International Committee for Analysis of Fertilisers and Feeding-Stuffs, Dr. Ritter von Grueber, did not have time, before his early death, to arrange that my method should be adopted as the only method of analysis for arbitration in interna ional commerce—an application for which he urged me to make in December, 1905.

Lastly, I may state that Z. Karaoglanow (*Z. anal. Chem.*, 1918, **57**, 497), on submitting my method of precipitation to several tests, obtained exactly the same va iations in the results that I have done, in spite of the fact that he altered the conditions of the precipitation still more than I did.

The Determination of Palm Kernel Oil and Butter Fat in Margarine.

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

(Read at the Meeting, November 4, 1925.)

IN a previous paper (ANALYST, 1925, **50**, 53) the authors gave the results of determinations by the Reichert-Polenske-Kirschner process made on a number of mixtures of coconut oil, butter fat and other vegetable oils, and mentioned that similar determinations were being made on palm kernel oil. These have been completed and are now published in the hope that they may be of some value.

A table covering a portion of this ground has already been published by Bolton, Revis and Richmond (ANALYST, 1912, **37**, 188), and the authors' results are in more or less general agreement with those in this table. There are differences, however, and these, together with the wider scope of these later results may render them more useful than the former. The present table (No. I.) is not quite so complete as the previous one by the present authors on coconut oil, as results are only given for mixtures containing two and ten per cent. of butter. It will be observed, however, that the differences introduced for the varying quantities of butter are quite regular, so that this will not be found to be any disadvantage.

TABLE I.

Palm kernel oil. Per Cent.	Process.	Percentage of Butter Fat.								
		0			2			10		
		Expt.	Calc.	Diff.	Expt.	Calc.	Diff.	Expt.	Calc.	Diff.
0	Reichert	0·6								
	Polenske	0·4			See Coconut Oil Table.					
	Kirschner	0·2								
20	Reichert	1·8	1·4	−0·4	2·3	2·0	−0·3	4·6	4·3	−0·3
	Polenske	1·7	2·3	0·6	1·7	2·3	0·6	1·9	2·5	0·6
	Kirschner	0·5	0·4	−0·1	0·9	0·8	−0·1	2·9	2·6	−0·3
40	Reichert	2·6	2·3	−0·3	3·2	2·9	−0·3	5·2	5·2	0·0
	Polenske	3·2	4·1	0·9	3·2	4·1	−0·9	3·5	4·3	0·8
	Kirschner	0·6	0·5	−0·1	1·0	0·9	−0·1	3·0	2·7	−0·3
50	Reichert	3·1	2·7	−0·4	3·6	3·3	−0·3	5·6	5·6	0·0
	Polenske	4·3	5·1	0·8	4·3	5·1	0·8	4·7	5·3	0·6
	Kirschner	0·8	0·6	−0·2	1·1	1·0	−0·1	3·2	2·8	−0·4
60	Reichert	3·5	3·1	−0·4	4·0	3·7	−0·3	6·0	6·0	0·0
	Polenske	5·6	6·0	0·4	5·6	6·0	0·4	6·0	6·2	0·2
	Kirschner	0·9	0·7	−0·2	1·3	1·1	−0·2	3·3	2·9	−0·4
70	Reichert	3·9	3·5	−0·4	4·4	4·1	−0·3	6·5	6·4	−0·1
	Polenske	6·2	6·9	0·7	6·2	6·9	0·7	6·6	7·1	0·5
	Kirschner	0·9	0·8	−0·1	1·3	1·2	−0·1	3·5	3·0	−0·5
80	Reichert	4·3	4·0	−0·3	4·7	4·6	−0·1	6·9	6·9	0·0
	Polenske	7·4	7·8	0·4	7·5	7·8	0·3	7·8	8·0	0·2
	Kirschner	0·9	0·8	−0·1	1·3	1·2	−0·1	3·5	3·0	−0·5
90	Reichert	4·7	4·4	−0·3	5·1	5·0	−0·1	7·3	7·3	0·0
	Polenske	8·6	8·8	0·2	8·6	8·8	0·2	8·9	9·0	0·1
	Kirschner	0·9	0·9	0·0	1·3	1·3	0·0	3·6	3·1	−0·5
100	Reichert	4·8	—	—	—	—	—	—	—	—
	Polenske	9·7	—	—	—	—	—	—	—	—
	Kirschner	1·0	—	—	—	—	—	—	—	—

Butter = Reichert 28·5, Polenske 2·2, Kirschner 22·0.

Many of the differences noticed between these figures and those of Bolton, Revis and Richmond are due to the variations in the analytical characteristics of the constituents of the mixtures, so that the two tables may usefully be read together for purposes of convenience; hence the original table is reprinted herewith, the original figures being rounded off to the first place of decimals.

TABLE II.

(Bolton, Revis and Richmond.)

Palm kernel oil. Per Cent.	Process.	Percentage of Butter Fat.			
		0	2	5	10
	Reichert	0·4	0·9	1·7	3·3
0	Polenske	0·5	—	—	—
	Kirschner	0·2	0·8	1·5	2·7
	Reichert	0·5	1·3	2·1	3·5
5	Polenske	0·7	—	—	—
	Kirschner	0·3	0·8	1·5	2·7
	Reichert	1·0	1·6	2·5	4·0
10	Polenske	1·0	—	—	—
	Kirschner	0·4	0·9	1·5	2·8
	Reichert	1·4	2·0	2·9	4·4
15	Polenske	1·4	—	—	—
	Kirschner	0·4	0·9	1·6	2·8
	Reichert	2·0	2·6	3·6	5·0
25	Polenske	2·0	—	—	—
	Kirschner	0·5	1·0	1·7	2·9
	Reichert	3·5	4·1	4·9	6·2
50	Polenske	4·2	—	—	—
	Kirschner	0·7	1·2	1·9	3·1
	Reichert	4·6	5·2	5·7	7·3
75	Polenske	6·9	—	—	—·
	Kirschner	1·0	1·4	2·1	3·4
	Reichert	5·2	—	—	—
100	Polenske	9·8	—	—	—
	Kirschner	1·1·	—	—	—

The chief difference that will be observed between the palm kernel table and that for coconut oil is the fact that the differences between the observed and calculated values (calculated from the analytical figures of the components of the mixtures by means of simple proportion) are very much less in the case of the former than of the latter. This is shown in the following table:—

TABLE III.

Corrections for Reichert and Polenske values (E. & S.).
Add to observed values.

Palm kernel oil. Per Cent.	Reichert Value. Percentages of Butter Fat.			Palm kernel oil. Per Cent.	Polenske Value. Percentages of Butter Fat.		
	0	2	10		0	2	10
0				0			
20	−0·4	−0·3	−0·3	20	0·6	0·6	0·6
40	−0·3	−0·3	0·0	40	0·9	0·9	0·8
50	−0·4	−0·3	0·0	50	0·8	0·8	0·6
60	−0·4	−0·3	0·0	60	0·4	0·4	0·2
70	−0·4	−0·3	−0·1	70	0·7	0·7	0·5
80	−0·3	−0·1	0·0	80	0·4	0·3	0·2
90	−0·3	0·1	0·0	90	0·2	0·2	0·1

The Reichert corrections are quite constant, being of the order of 0·3 (to be subtracted from the observed reading) when no butter is present, and rising to 0·0 in the case of mixtures containing 10 per cent. of butter. For most palm kernel margarines, therefore, the subtraction of 0·3 from the observed Reichert value will give a figure from which the percentage of its components may be calculated by simple proportion.

In the case of the Polenske value, however, the correction in most cases is greater and is not so uniform, so that the actual figures must be taken from the above table. The actual amount of palm kernel oil present in the mixture may then be calculated from the correct Polenske value by means of simple proportion.

CORRECTION FOR THE KIRSCHNER VALUE.—The differences between the calculated and observed Kirschner values are given in the following table, due account of the algebraic sign being taken in making the correction to be added to the observed value.

TABLE IV.

Correction for Kirschner values (E. & S.).

Add to observed values.

Palm kernel oil. Per Cent.	Percentage of Butter Fat.		
	0	2	10
0			
20	−0·1	−0·1	−0·3
40	−0·1	−0·1	−0·3
50	−0·2	−0·1	−0·4
60	−0·2	−0·2	−0·4
70	−0·1	−0·1	−0·5
80	−0·1	−0·1	−0·5
90	0·0	0·0	−0·5

The corrections here are greater than with coconut oil when the amount of butter is as high as 10 per cent. For all ordinary purposes a correction of 0·1 should be used when the amount of butter is small, this correction rising to 0·4 when the proportion is of the order of 10 per cent. The exact corrections may be taken from the table.*

THE RELATIONSHIP OF THE REICHERT AND POLENSKE VALUES.—On an examination of the Reichert and Polenske values of the mixtures containing no butter fat it will be observed that the Reichert value due to the palm kernel oil is in all cases numerically less than the Polenske value, whilst in the case of coconut oil the Reichert value is the greater until about 40 per cent. of coconut oil is present. This fact at once suggests a method for the approximate determination of the

* The percentage of butter fat present in mixtures may be calculated with a fair approximation to accuracy from the formulæ:—

(Where Polenske is less than 6·5) Per cent. butter fat = $\dfrac{K - 0·2 - P/10}{23·5}$.

(Where Polenske is more than 6·5) Per cent. butter fat = $\dfrac{K - P/10}{23·5}$.

proportion of coconut to palm kernel oil in mixtures without the application of specific tests. The authors are at present engaged in the examination of a series of mixtures of coconut and palm kernel oil with this object in view, and hope to publish their results later.

DISCUSSION.

Mr. RAYMOND ROSS said that it seemed possible to draw many deductions from these figures. It was really the composition of these saturated fatty acids which mainly determined the nature of the non-oleic portion of the fat. If one determined the amount of oleic acid present, one could calculate from the saponification value the molecular weight, of these, and thus obtain the molecular weight of the residual fatty acids other than oleic acid. In his opinion the molecular weight of the residual fatty acids was a more efficient way to discover the composition of the different fats than the Polenske and Kirschner values.

Dr. COX said that he would like to ask the authors: (1) Whether, and, if so, in what way, the formula, which they now proposed, was an improvement on that of Bolton and Revis published a few years ago. (2) Whether the differences due to unavoidable experimental error, which appeared to be equivalent to about 1 per cent., were not in fact greater than those arising from the differences in the formulae.

Mr. E. R. BOLTON, in expressing his satisfaction that the authors agreed with him on this occasion, remarked that the matter was becoming more and more complicated, and he wondered if the attempt to attain an exact figure were not being pressed further than the process really permitted. He referred to a simple method which he used for calculating the proportion of palm kernel and coconut oils from the Reichert-Meissl-Polenske value and the saponification value, after making correction for butter fat as determined by the Kirschner value, and said that, although his results were approximate, they were within a definite margin of error, and he did not think the process could be strained any further.

Mr. E. HINKS said that he presumed the mixtures examined by the authors were composed or not more than one or two specimens of palm kernel and coconut oil, and asked whether the natural variations in the constituent fats, which must be allowed for in unknown mixtures, would affect the results. In the case of coconut oil the authors had previously found that the "total volatile acids" was the sum of the soluble and the insoluble volatile acids; was it the same with palm kernel oil?

Mr. G. D. ELSDON replied that he thought Mr. Raymond Ross's suggestion might be carried out from existing data and would not need any experimental work. Regarding the enquiry as to there being any improvement. The new method, he considered, showed a slight improvement with regard to percentages in the neighbourhood of 2 per cent. in their particular formula; there was no difference so far as limits of error were concerned. If mixtures of unknown fats were obtained, the differences were shown by the figures themselves. He quite agreed with Mr. Bolton that one must not strain these things too far, but it was advisable to determine how far one might do so, and to apply a correction in order to bring these results somewhere near the truth. He questioned whether Mr. Bolton's calculations involving the use of the saponification value were sufficiently near in all cases. He used Whatman No. 5 11 cm. paper and found it to yield perfectly bright filtrates. In reply to Mr. Hinks, he stated that they had worked with more than one sample of oil, and that the differences so introduced were not large; there was a tendency for the total volatile acids to be more or less constant.

The Use of 2:4-Dinitrophenylhydrazine as a Reagent for Aldehydes and Ketones.

By OSCAR L. BRADY, D.Sc., F.I.C., AND GLADYS V. ELSMIE.

(Read at the Meeting, December 2, 1925.)

THE action of 2:4-dinitrophenylhydrazine on aldehydes and ketones has been investigated by Purgotti (*Gazz. Chim. Ital.*, 1894, 24, 564) and by Curtius and Dedichen (*J. prakt. Chem.*, 1894, 50, 266).   Since this compound offers advantages over other reagents for the identification of aldehydes and ketones, it is surprising that it is so seldom used.   The base is very easy to make, is clean and will keep indefinitely even when exposed to air; the dinitrophenylhydrazones, especially those of the aliphatic aldehydes, are finely crystalline, stable, and have sharp melting points; they are sparingly soluble in alcohol and can be easily crystallised ; moreover, the relatively high molecular weight of dinitrophenylhydrazine enables one to obtain a reasonable amount of the derivative from small quantities of aldehyde. The main disadvantages of dinitrophenylhydrazine are its somewhat leisurely action and its sparing solubility in cold alcohol, so that if the base is employed in alcoholic solution, unless a slight excess of aldehyde is used, it tends to crystallise with the hydrazone.   Acetic acid is not a suitable solvent, but, with aldehydes and ketones soluble in water, a solution of the hydrochloride of 2:4-dinitrophenylhydrazine in 2 N hydrochloric acid can be used, the feeble basicity of the dinitrophenylhydrazine enabling it to react even in strongly acid solution, which is a great advantage in certain circumstances.   The hydrochloride is sparingly soluble and is hydrolysed by water or by the addition of sodium acetate to its solution in hydrochloric acid.   A solution of the hydrochloride is a useful qualitative reagent for aldehydes and ketones; it gives a distinct filterable precipitate with 0·003 grm. of acetone or acetaldehyde in 1 c.c. of water; it also gives a precipitate of acetone or acetaldehydedinitrophenylhydrazone, respectively, with one drop of commercial rectified methyl alcohol or with the aqueous solution obtained by shaking 20 c.c. of an ordinary sample of ether with 5 c.c. of water.

A number of 2:4-dinitrophenylhydrazones of the commoner aliphatic aldehydes and ketones have been prepared for reference.   Purgotti (*loc. cit.*) describes the derivatives from formaldehyde, acetaldehyde, *o*- and *m*-nitrobenzaldehydes, *o*- and *p*-hydroxybenzaldehydes, furfuraldehyde, acetone and benzophenone; Curtius and Dedicken (*loc cit.*), those of acetone, benzaldehyde and *o*-hydroxybenzaldehyde; Chattaway and Clemo (*J. Chem. Soc.*, 1923, 123, 3061), those of 2:4-dinitrobenzaldehyde and 2:4:6-trinitrobenzaldehyde.

EXPERIMENTAL: PREPARATION   OF   2:4-DINITROPHENYLHYDRAZINE.—2:4-dinitrochlorobenzene (50 grms.) was dissolved in hot alcohol (750 c.c.) and 50 per cent. hydrazine hydrate (100 c.c.) added in small portions.   A vigorous action occurred, and the 2:4-dinitrophenylhydrazine immediately began to separate;

after cooling, washing with cold alcohol, then with water and air drying, a 92 per cent. yield was obtained of a practically pure product. It may be crystallised from much alcohol; acetic acid is unsatisfactory as it tends to acetylate.

PREPARATION OF 2 : 4-DINITROPHENYLHYDRAZONES. — 2 : 4-Dinitrophenyl-hydrazine(5 grms.) was suspended in alcohol (150 c.c.), and propionaldehyde (2 grms.) added. The mixture was boiled under reflux for an hour; the dini-trophenylhydrazine dissolved slowly, and the solution changed in colour from deep red to orange. On cooling, almost pure propionaldehyde 2:4-dinitrophenyl-hydrazone crystallised, and was recrystallised from alcohol. Other compounds may be prepared in a similar manner, although it may be necessary to dilute the alcoholic solution somewhat in the case of the more soluble derivatives.

2:4-Dinitrophenylhydrazine (4 grms.) was suspended in 2 N hydrochloric acid (25 c.c.), concentrated hydrochloric acid added (20 c.c.), and the hydrochloride formed was dissolved by the addition of 2 N hydrochloric acid (1200 c.c.); to the filtered solution acetaldehyde (2 c.c.) was added, when immediate precipitation of the dinitrophenylhydrazone occurred; after shaking for a few minutes this assumed an easily filterable form; on crystallising from absolute alcohol, acetal-dehyde 2:4-dinitrophenylhydrazone was obtained, melting at 162° C. (Purgotti 147° C.). Other water-soluble aldehydes and ketones may be used in place of acetaldehyde.

n-Propylaldehyde 2:4-dinitrophenylhydrazone crystallises in tangerine-red needles, m.pt., 155° C. (Found: N, 23·6 per cent.; $C_9H_{10}O_4N_4$ requires N, 23·5 per cent.); *n-butylaldehyde 2:4-dinitrophenylhydrazone*, in pale orange plates, m.pt., 122° C. (Found: N, 22·4 per cent.; $C_{10}H_{12}O_4N_4$ requires N, 22·2 per cent.); *iso-butylaldehyde 2:4-dinitrophenylhydrazone*, in long orange needles m.pt., 182° C. (Found: N, 22·6 per cent.; $C_{10}H_{12}O_4N_4$ requires N, 22·2 per cent.); *isovalerylaldehyde 2:4-dinitrophenylhydrazone*, in long orange-red needles, m.pt., 123° C. (Found: N, 21·3 per cent.; $C_{11}H_{14}O_4N_4$ requires N, 21·1 per cent.); *n-capronic aldehyde 2:4-dinitrophenylhydrazone* in long orange-yellow needles, m.pt., 104° C. (Found: N, 19·7 per cent.; $C_{12}H_{16}O_4N_4$ requires N, 20·0 per cent.); *n-heptylaldehyde 2:4-dinitrophenylhydrazone*, in pale orange needles, m.pt., 106° C. (Found: N, 19·0 per cent.; $C_{13}H_{18}O_4N_4$ requires N, 19·0 per cent.); *n-nonylaldehyde 2:4-dinitrophenyl-hydrazone*, in bright yellow plates, m.pt., 96° C. (Found: N, 17·5 per cent., $C_{15}H_{22}O_4N_4$ requires N, 17·4 per cent.); *methyl ethyl ketone 2:4-dinitrophenylhy-drazone*, in orange needles, m.pt., 115° C. (Found: N, 22·3 per cent.; $C_{10}H_{12}O_4N_4$ requires N, 22·2 per cent.).

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Notes.

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

THE VOLATILITY OF SALICYLIC ACID.

In the analysis of certain medicinal products containing salicylates the nature of the substance under examination is often such that it is necessary to extract the liberated salicylic acid with ether or some such solvent. It appears to be generally stated that it is not practicable to evaporate the solvent and actually to weigh the salicylic acid.

Fresenius and Grünhut (*Zeitsch. anal. Chem.*, 1899, 299) state that they were unable to drive off the last traces of solvent (they used a mixture of ether and petroleum spirit), without losing salicylic acid. Prideaux and Bentley (*Pharm. J.*, 1923, 427) appear to have had the same experience.

Allen (*Organic Analysis*), on this point, says cautiously, that "some loss by volatilisation is difficult to avoid."

As it was thought advantageous to be able actually to weigh the acid, before determining it by other methods, the writer made several experiments, both on salicylic acid and sodium salicylate, drying the extracted acid at various temperatures. Methylated ether was used as the solvent, and in each case about 0·5 grm. of salicylic acid was present. The following conclusions were reached:—

(1) Accurate results may be obtained by allowing the ethereal solution to evaporate spontaneously and drying the salicylic acid at room temperature, but about 48 hours are required.

(2) Accurate results may be obtained by spontaneous evaporation and drying the residue for two hours in an oven at 35° C.

(3) Salicylic acid does not volatilise appreciably until temperatures higher than 40° C. are reached. Between 50° and 60° C. volatilisation becomes comparatively rapid.

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A WET METHOD FOR THE DETERMINATION OF SILVER IN LEAD.*

THE following method has been found to give accurate results in cases where no cupellation apparatus was available:—A convenient amount (quantities up to 50 grms. can be used) of the sample is weighed into a beaker and dissolved in nitric acid, the lead nitrate taken up with water, the solution made alkaline with ammonia and acetic acid added until the precipitate is redissolved. A strip of copper foil (about 6½ in. × 1 in.) is made into a flat spiral by rolling round a pencil and afterwards opening out; it is cleaned in nitric acid (sp. gr. 1·2), rinsed and dropped into the solution. This is now boiled gently for about 2 hours, with a cover on the beaker, and is then removed from the plate and allowed to stand until the liquid has cleared sufficiently to allow of filtering. The silver is now completely precipitated, partly as flocks in the liquid, partly as a very fine suspension, and partly adhering to the

* Communication from the Research Department, Woolwich.

copper; the liquid is filtered, an absolutely bright filtrate being essential, and the copper and precipitate washed with hot water, after which the filter is replaced in the original beaker, nitric acid (sp. gr. 1·2) added, and the whole boiled until the copper and silver are completely dissolved and the filter disintegrated. The solution is then filtered through pulp and the pulp washed with hot water. Sodium hydroxide solution is added to the filtrate until a permanent precipitate is formed; this is just redissolved in hydrochloric acid and sufficient excess of the acid added to precipitate all the silver, after which the liquid is boiled for 15 minutes and allowed to stand overnight. The silver chloride is filtered off (a bright filtrate is again essential), washed thoroughly with cold water, the funnel placed in the original flask and the silver chloride dissolved by treating it in the following sequence with ammonia (1:1) ; water; hot nitric acid (1·2 sp. gr.); water; ammonia (1:1), and the filter washed with hot water. The solution is cooled and neutralised with ammonia or nitric acid as required (a small piece of litmus paper having been placed in the flask); 10 c.c. excess of 1:1 ammonia are added, and the whole made up to about 200 c.c. with cold water. Excess of standard potassium cyanide is now added, followed by two or three crystals of potassium iodide, and the solution is back-titrated with standard silver nitrate solution as in the case of nickel. The potassium cyanide solution would be standardised for each test by running into the exactly titrated liquid approximately the same amount of cyanide as already used and retitrating with silver nitrate.

The following results were obtained with synthetic mixtures:—

Lead taken. Grms.	$AgNO_3$ added. c.c.	= Ag added. Per Cent.	$AgNO_3$ for titration. c.c.	$AgNO_3$ recovered. c.c.	= Ag recovered. Per Cent.
50	—	—	0·26	—	—
50	2·00	0·0147	2·10	1·84	0·0135
50	5·00	0·0368	5·03	4·77	0·0351
50	10·00	0·0736	10·15	9·89	0·0728

The following results were obtained by precipitating the silver chloride direct in the nitric acid solution with sodium chloride.

Lead taken. Grms.	$AgNO_3$ added. c.c.	= Ag added. Per Cent.	$AgNO_3$ for titration. c.c.	$AgNO_3$ recovered. c.c.	= Ag recovered. Per Cent.
50	—	—	0·4	—	—
50	2·0	0·0147	2·7	2·3	0·0169
50	4·0	0·0294	4·0	3·6	0·0265
50	6·0	0·0442	6·3	5·9	0·0431
50	8·0	0·0589	8·2	7·8	0·0574
50	10·0	0·0736	10·1	9·7	0·0710

The following results were obtained with samples of lead alloyed with known amounts of silver.

Weight of sample taken. Grms.	Silver present. Per Cent.	Silver found. Per Cent.
50	0·050	0·049
50	0·050	0·050
41	0·050	0·050
10	0·500	0·499

The solution of silver used for titration contained 3·681 grms. of silver per 1000 c.c.

B. S. EVANS.

THE VOLUMETRIC DETERMINATION OF SULPHATES BY MEANS OF BARIUM CHLORIDE AND POTASSIUM STEARATE.

As I was unable to be present at the reading of my paper, I should like to make the following reply to some of the points raised in the discussion:—

The salts remaining in solution when the end-point is reached are neutral, and, as varying concentrations of the solutions gave varying deviations from the normal titrations, it might be supposed that addition of neutral salts would tend to produce the same effect. This actually is the case, and the presence of 1 per cent. of sodium chloride depresses the barium chloride titration by about 0·05 c.c. in 10 c.c., and the end-point is reached somewhat more slowly.

The effect of potassium chloride is still greater, but, on standing for some time, the solution changes colour to the "alkaline" side and the new end-point approaches that of a solution free from neutral salts. It will be observed (Table C in my paper) that a solution as weak as 0·05 N has a slightly lower barium chloride titration than a solution of sodium sulphate of corresponding strength.

Potassium nitrate has the reverse effect, and the addition of 1 per cent. of this salt to a solution of sodium sulphate slightly increases the barium chloride titration instead of decreasing it.

In the experiments mentioned in my paper the concentration of neutral salts was too low to have an appreciable effect on the titrations, but with these salts present in quantities as high as those mentioned above, concordant results are only obtained so long as the standard made for comparison is approximately of the same composition, and, if neutral salts are present in sufficient quantity to "salt out" the potassium stearate, the method fails.

With regard to phosphates: the alkali phosphates are salts of a weak acid, and tri-sodium phosphate is strongly alkaline to the indicator. Indeed, di-sodium hydrogen phosphate (ordinary sodium phosphate) is slightly alkaline.

In a neutral solution containing phosphates in addition to sulphates, the addition of a little of the potassium stearate solution produces no colour change, and the method fails.

It appears to be possible to remove the phosphate, but it is doubtful whether the procedure has much advantage in speed over the gravimetric method.

A solution containing, say, sodium sulphate and sodium phosphate, is heated to boiling, and a solution of aluminium chloride is added in excess of that required to precipitate the whole of the phosphates. The indicator is then added, and the boiling solution, which has a distinctly acid reaction, is gradually neutralised with dilute sodium hydroxide solution until the red colour just disappears and a pale yellow colour results. This liquid, on cooling, turns greenish yellow, but on treatment in the same way as in Method 3 for the determination of sulphates in alum, the filtrate, the first portions of which are rejected, is bright yellow, and a test with magnesia mixture shows only minute traces of phosphates.

In four determinations 20 c.c. of 0·1 N sodium sulphate were diluted to 50 c.c. and sodium phosphate was added, in amounts varying from 0·1 to 0·5 grm. The quantity of aluminium chloride added was unknown, but it was observed that unless it was added in appreciable excess over the amount required for the complete precipitation of the phosphates, the latter were not completely removed.

The neutralised solution was made up to 100 c.c. in each case, and 50 c.c. of the filtrates titrated and compared with that from a standard made up of 10 c.c. of 0·1 N sodium sulphate solution and about 0·2 grm. of sodium chloride diluted to 50 c.c. with water.

The results were slightly low, as in the case of the determination of sulphates in alum, being respectively 0·1, 0·05, 0·05, and 0·1 c.c. less than the standard.

ERRATA IN THE PAPER:—

Table I., p. 592.　*For* "15·12" *read* "15·0."

Tables V. and VIII.　*For* "Total Alkalinity" *read* "Total Hardness minus Alkalinity."

Table X., Method I.　*For* "0·2 N" *read* "0·02 N."

P. 600 (6).　*For* "0·01 N" *read* "0·1 N."

H. ATKINSON.

PUBLIC HEALTH DEPARTMENT, CAIRO.

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.

THE USE OF GLAZED EARTHENWARE CONTAINERS.

THE Public Analyst for Durham (Mr. C. J. H. Stock), in a report to the Durham County Council (November, 18, 1925), stated that samples were obtained at the request of one of the Ministry of Health inspectors, with the object of ascertaining whether food packed in glazed earthenware containers was contaminated by particles of glaze from the containers. The outcome of the examination of these samples is given in the following table:—

Containing glaze.	Containing glass.	Containing glaze and glass.	Free from glaze and glass.	Total.
6 samples.	1 sample.	3 samples.	8 samples.	18 samples.

"The whole of the samples comprised jam and marmalade, and the results of the investigation are very much as was anticipated, with the exception of the 3 samples which were found to contain particles of both glaze and of glass, although in these cases a possible explanation might be that these jams had been repacked in earthenware containers after having been put up in glass jars which, through some cause or another, had been broken.

"The number of particles of glaze noted ranged from 1 up to 4, and of glass from 1 up to 3, and the measurements varied from 1/17th × 1/80th of an inch down to 1/166th × 1/400th of an inch. It is to be inferred from this inquiry that there is no reason to suppose that jams packed in earthenware are necessarily free from undesirable particles."

The Local Government Committee reported that the Clerk had communicated with the manufacturers and had received letters from them generally admitting the seriousness of the presence of these particles, and stating that they were doing all they could to prevent recurrence (*cf.* ANALYST, 1925, **50**, 393).

Legal Notes.

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

PROSECUTIONS FOR ARSENIC IN APPLES.

ON November 25, 1925, a firm of fruiterers was summoned at Hampstead for selling 2 lbs. of apples which, on analysis, had been found to contain 15 parts of arsenic per million (= 1/10th grain per lb.).

Samples of apples had been purchased from various shops in the district, owing to a specific case of illness which had been reported as due to eating apples. All the samples of English apples were found to be free from arsenic.

Mr. G. Corner, for the defence, said that it would be no use calling his clients, who could only say that if they had known that arsenic was on the apples they certainly would not have bought or sold them. He mentioned that, in America, the codlin moth laid its eggs three times a year, and that, in consequence, three spray-ings of fruit trees were needed. This moth did not occur in England, and so here it was only necessary to spray the trees during blossom time.*

The defendants, who pleaded guilty to a technical offence, were fined 20s., with £2 12s. 6d. costs.

In a similar case brought against another Hampstead fruiterer, 1/30th grain of arsenic per lb. had been found on the apples. A fine of the same amount was inflicted.

Three further cases were heard at Marylebone Police Court on December 8th. The purchases were made at five different shops, at the instance of the Hampstead Borough Council, and quantities of arsenic ranging from 1/10th to 1/30th of a grain per lb. were found.

Mr. S. Turner, prosecuting, said that in five instances out of a total of 17, arsenic was discovered in excess of one-hundredth of a grain per lb. All the contaminated samples were Jonathan apples from the United States; other samples of English apples were free from arsenic.

Dr. H. E. Cox, Public Analyst for Hampstead, said that the arsenic was almost entirely confined to the surface of the skin, particularly round the stalk and calyx. He attributed the presence of the amount of arsenic to the spraying of the apples at a later period than usual. Washing the apples would remove from 70 to 80 per cent. of the arsenic, but not the whole of it, since some remained in combination with the proteins of the apple skin.

The Magistrate (Mr. Hay Halkett) said that in his opinion this was an un-fortunate accident which might have happened to traders all over the country. He dismissed the first summons on payment of 20 guineas costs, and the other two summonses on payment of 3 guineas and 10 guineas costs.

On January 22, 1926, two more cases were heard at the Marylebone Police Court. In the first of these the arsenic in the apples was 1/35 grain, and in the second 1/30th grain per lb.

The Medical Officer of Health in his evidence said that experiments made by the Public Analyst had shown that washing would not remove the whole of the lead arsenate from the apples.

The Magistrate (Mr. Bingley) said that, as it was not disputed that these apples might be part of the same consignment as those in the former cases, he

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* This statement is incorrect.—EDITOR.

would dismiss the summonses under the Probation of Offenders Act, on payment of 3 guineas costs in the first, and 2 guineas costs in the second case. This must not be taken as a precedent, and if he had more of these cases he would have to deal with them in a different way.

LEMON CHEESE: A DEFECTIVE CERTIFICATE.

ON December 11th, 1925, a wholesale firm was summoned at Birkenhead for having sold as lemon cheese a product containing 42 per cent. of starch and added water.

Mr. N. S. Pain, for the Corporation, said that the Public Analyst (Mr. Davies) had found about 57 per cent. of the four ingredients—sugar, butter, eggs, and lemon—in the sample, whilst the Government Analyst (to whom the reserve sample had been submitted) had found only 49 to 50 per cent., and Mr. Melling had found 64 per cent. of "lemon cheese solids." Mr. Pain was proceeding to quote from several cookery books as to what lemon cheese was, when successful objection was taken to this by Mr. Harrison (for the defence) on the ground that quotations from books without calling the authors as witnesses was inadmissible. Mr. Pain submitted that the product in question was already lemon cheese without the additional ingredients—glucose, starch and water—and the very presence of colouring matter suggested that an inferior product was being coloured to look like lemon cheese.

Mr. Harrison objected to any reference to the colour being made, since it was not mentioned in the certificate of the Public Analyst.

The Inspector, giving evidence of purchase, stated that he had expected to get a substance composed solely of sugar, butter, eggs and lemon. In cross-examination he admitted that jams frequently contained glucose, and that he was not aware of any convictions for the sale of such jams.

Mr. Davies said that lemon cheese was composed of the four ingredients that had been mentioned. The proportions varied with the individual taste, but, speaking generally, lemon cheese was composed approximately of 50 per cent. of sugar, 25 per cent. of egg, 15 per cent. of butter, and 10 per cent. of lemon. No water was necessary.

Mr. Harrison objected to this evidence, which he regarded as an attempt to alter the certificate. In the certificate it was stated that lemon cheese was understood to consist of eggs, butter, sugar, and lemon, and that, although most manufacturers added some starch and water, the amounts contained in the sample were, in his (the Analyst's) opinion, excessive. This was an admission that it was quite right and proper that there should be certain quantities of starch and water. The Analyst was not entitled to go behind his certificate and say that there should be no water. In his (Mr. Harrison's) submission the Analyst's certificate was bad in law, and the case should be dismissed, and he quoted previous cases in support of his contention.

Mr. Pain admitted the force of this technical argument, but asked the Bench to fix a standard for lemon cheese as a future protection for the public. Mr. Harrison, however, said that he had intended to call many experts to prove that the article sold was genuine, and asked the Bench not to prejudice the matter by making any comment. His clients had not done anything wrong, and he asked that the case should be dismissed.

The Bench declined to give any opinion on the subject of a standard. They dismissed the case, but refused costs to the defendants.

Department of Scientific and Industrial Research.

FOOD INVESTIGATION BOARD.

Special Report No. 23.

FUNCTIONAL DISEASES OF APPLES IN COLD STORAGE.*

APPLE SCALD, AND CERTAIN SPOTTING DISEASES NOT DUE TO FUNGI.— "Scald" consists in browning of the fruit unaccompanied by softening or browning of the flesh tissues, and is controlled to some extent by efficient ventilation during storage, and largely by impregnating wrappers with mineral oil, or placing oiled straw, etc., among the fruit.

INTERNAL BREAKDOWN.—This includes "internal browning," "soft scald," "flesh collapse," "Jonathan scald," "Jonathan breakdown," and "physiological decay." Premature browning of the tissues is particularly a disease of cold storage, and may be controlled (1) by only storing mature but not over-ripe fruit, and (2) by keeping the storage temperature rather above 32° or 34° C. It should be noted, however, that the same sort of apples from different localities show differences in susceptibility to breakdown, *e.g.* percentage of internal breakdown at the end of February were as follows for localities of the Okanagan valley: Okanagan centre, 5·0; from Summerland, 5·5; from Kelowna, 32·2; from Salmon Arm, 46·6; and from Vernon, 73·8. Stiemer Pippins in New Zealand showed 52 and 5 per cent. breakdown, respectively, from different localities. Investigations of climatic conditions as affecting the question of internal breakdown have been made by Stubenrauch ("Fruit Handling, Precooling and Storage Investigation," *Ice and Refrigeration*, 1912, **40**, 34), Ballard, Magness and Hawkins ("Internal Browning of the Yellow Newtown Apple," *U.S. Dept. Agric. Bull.*, **1004**, 1922), and Winkle ("A Study of the Internal Browning of the Yellow Newtown Apple," *J. Agric. Res.*, 1923, **24**, 169).

BROWN HEART (*cf.* ANALYST, 1923, **48**, 490).—Since this disease is caused by concentration of carbon dioxide in the atmosphere, in the presence of oxygen, conditions favouring its development are not likely to occur, except where storage chambers have relatively gas-proof walls and no ventilation, such as may be found in ships' holds. Carbon dioxide should not be allowed to rise above 8 to 10 per cent. in the storage atmosphere.

FROST INJURY.—With *slight* injury are seen mealiness and no browning, with *moderate* injury, diffuse browning, localised or general, mealiness after thawing, and the whole appearance may resemble internal breakdown. With *severe* injury all or most of the fruit is dead, often waterlogged and translucent after thawing, browning spreading slowly in the waterlogged parts. The injury appears to depend upon the formation of ice in the tissue, the extent of injury being in proportion to the amount of ice. When freezing has not been severe the whole flesh is not involved in the subsequent injury and browning. The latter is often not detectable without cutting the fruit, and it is sometimes seen that the vascular bundles only are browned and waterlogged.

D. G. H.

Meteorological Office, Air Ministry.

ADVISORY COMMITTEE ON ATMOSPHERIC POLLUTION.

REPORT ON OBSERVATIONS IN THE YEAR ENDING MARCH 31ST, 1925.*

THE STANDARD GAUGE (for collection of deposited matter).—Complete records have been made by 44 stations, and maps are included to shew the positions of instruments, where these have not been published in previous reports. The annual mean monthly deposits have this year been grouped as A, B, C, and D, according to the different values selected for the type of deposit, class A being in each case the lowest and class D the highest. Highest and lowest deposits for summer (S) and winter (W) expressed as metric tons per hundred square kilometres were as follows:—*Tar*: (S) Newcastle, City Road, 164; Birmingham, S.W., 15; (W) Newcastle, City Road, 387; Leeds, Headingley, 9. *Carbonaceous matter*: (S) Newcastle, City Road, 3953; Leeds, Headingley, 243; (W) Newcastle, City Road, 4053; Leeds, ·Headingley, 187. *Insoluble ash*: (S) Liverpool, 6018; Marple, 189; (W) Newcastle, City Road, 8403; Marple, 178. *Volatile matter*: (S) Wakefield, 4134; Birmingham, S.W., 301; (W) Wakefield, 4334; Birmingham, S.W., 397. *Soluble ash*: (S) Wakefield, 4514; Marple, 695; (W) Wakefield, 4480; Marple, 497. *Total deposit*: (S) Blackburn, Tech. Coll., 13,957; Leeds, Headingley, 1892; (W) Newcastle, City Road, 16,741; Marple, 1523. *Rainfall* in mm.: (S) Blackburn, 792; Huddersfield, Cooper Bridge, 265; (W) Rochdale, 690; London, Finsbury Park, 260.

It may be observed that the least chlorine is recorded for the station furthest from the sea (Birmingham). A study of the figures for sulphur deposits raises the question either of sulphur travelling further than other impurities or of the ratio of sulphur to soot in the air increasing on reduction of smoke by burning smokeless fuels.

AUTOMATIC FILTER. No new instruments were installed during the year. The curves shown for Blackburn, Stoke-on-Trent and Westminster are on the same principle as in previous reports. Curves are included showing the incidence of thick smoke haze on the different days of the week (winter) as a percentage of the number of days, and indicate a general tendency to clearer days on Saturday and Sunday. In order to study the effect of wind on impurity the mean wind velocity was plotted against the mean suspended impurity at Westminster, and the variation of concentration of impurity was found to vary inversely as the first power of the velocity of the wind, and not as some higher power. When the wind drops below 1 metre per second in winter a smoke haze or fog is almost invariable in London.

THE JET DUST COUNTER.—Certain records of interest were taken, such as that on a voyage across the Atlantic where, with a haze ahead, a strong west wind and sunshine, the record showed the presence of very hygroscopic crystals, but it is doubtful whether they existed in the air as drops or as crystals. Records in Madrid showed on one day the following numbers of dust particles at 8.20 a.m., 420; at noon, 550; at 3.30 p.m., 149; at 7.20, 2500; and at 10.40, between 750 and 1000. Records taken near the sea coast at Vila Real de Santa Antonio were almost identical with those taken 3 years previously. During a fog at Cheam (11–12 miles S.W. of London), 70–80,000 particles of suspended solid matter settled per sq. cm. per minute, a dust record at the same time showing 15–16,000

particles per c.c. In London, on a day with 27,000 particles per c.c., settlement was at the rate of 1,200 particles per sq. cm. per minute. This is, however, a low figure. In the London fog of December 11th, 1924, the number of particles at noon were 27,000 per c.c. of diameter from 2 microns down. At Cheam on the same day there was much more water in the fog and about half as much impurity.

SPECIAL RESEARCHES.—Visibility research, and experiments with the vapour pressure hygrometer were unavoidably suspended, but it was hoped to resume them this winter. A list of some 15 questions affecting atmospheric pollution and awaiting investigation or further investigation is given.

D. G. H.

Connecticut Agricultural Experiment Station.

REPORT ON FOOD PRODUCTS AND DRUG PRODUCTS FOR 1924.

THE total number of food and drugs samples examined during the year 1924 was 2045, of which 340 were adulterated, below standard, or otherwise illegal.

CARBONATED BEVERAGES.—The use of saccharin as a sweetening agent in non-alcoholic drinks is illegal in the State. Only 3 of 172 samples examined were found to contain saccharin, whereas in 1923 it was present in 16 per cent. of the samples.

COCOA, ETC.—Cocoa is defined as chocolate from which a portion of the fat has been removed, and, on a moisture-free and fat-free basis, should not contain more than 8 per cent. of ash, not more than 0·4 per cent. of ash insoluble in acid, and not more than 7 per cent. of crude fibre. The term "breakfast cocoa" designates cocoa containing not less than 22 per cent. of fat. Cocoas treated with alkali by the so-called Dutch process are labelled to show that the mineral constituents are increased by 1 to 3 per cent. The ash in such products is likely to exceed 8 per cent., and did exceed it in all cases, with one exception. The range in ash for all the samples of this type of cocoa was from 7·63 to 12·25 per cent.

DIABETIC AND OTHER SPECIAL FOODS.—A table of analyses of 82 special foods is given. Materials of low nutritive value are being increasingly used for the preparation of foods intended for low calorie diets. *Cellu flour* and *Cellulose flour* from corn cobs are materials of this type, They contain but little nitrogen and fat and inconsiderable amounts of available carbohydrates, by far the greater proportion belonging to the undetermined nitrogen-free extract. *Hoyt's Special Gluten Flakes* and *Protein Cereal* contain 75 to 80 per cent. of protein and 3 to 6 per cent. of available carbohydrate. Two chocolate confections for diabetic patients contained about 30 per cent. of starch and sugar.

EGGS.—Of 12 samples submitted as "fresh" eggs, 8 were classed as not fresh but edible. The 4 samples passed as fresh had air spaces generally less than 1 inch in diameter, yolks not appreciably settled in the shell, and ammoniacal nitrogen ranging from 0·8 to 1·2 mgrms. per 100 grms. Those classed as not fresh but edible, had air spaces larger than 1 inch in diameter, yolks settled in the shell, whites watery, and ammoniacal nitrogen varying from 1·9 to 3·7 mgrms. per 100 grms. of egg.

"GRAHAM" AND "ENTIRE WHEAT" FLOURS.—There appears to be no uniform opinion as to the distinction between these two types of flour. Dr. S. Graham recommended abstinence from meat and the use of bread made from unbolted wheat meal as a remedy for alcoholism. This unbolted meal became known as

"Graham" flour, and such flour, evidently, should have the same composition as the wheat from which it was ground.   Owing to the coarseness of this product, attempts were made to decorticate the wheat, removing only the indigestible parts of the grain, and to grind the remainder without bolting.   This flour was called "whole meal flour" or "entire wheat flour."   Since the introduction of the roller process for milling flour it is probable that many of the "Graham" and "entire wheat" flours of trade, are recombinations of various fractions obtained in the process of commercial milling.   The following table gives analyses of some of the 12 samples of these flours examined, together with those of wheat grain and wheat mill products:

Samples.	Moisture. Per Cent.	Ash. Per Cent.	Nitrogen. Per Cent.	Protein (N × 5·7). Per Cent.	Fibre. Per Cent.	N-free extract. Per Cent.	Fat. Per Cent.	P/A.
Graham Flour. 1	11·09	2·40	2·42	13·79	2·36	67·22	3·14	5·7
2	11·14	1·98	2·30	13·11	2·48	68·45	2·84	6·6
3	11·26	1·44	2·50	14·25	1·03	69·30	2·72	9·9
Entire Wheat Flour	12·49	1·72	2·05	11·69	2·14	69·46	2·50	6·8
	9·95	1·45	2·30	13·11	1·31	72·38	1·80	9·0
	10·30	0·81	2·10	11·97	0·28	74·86	1·78	14·8
Grain and Mill Products.								
Wheat grain*	10·20	1·90	1·98	11·29	2·20	—	2·10	6·0
Wheat bran†	10·10	6·30	2·56	14·59	9·50	—	4·40	2·3
First patent flour‡	9·70	0·38	2·00	11·40	—	—	—	30·0
Straight flour‡	10·00	0·48	2·10	11·74	—	—	—	24·5
First clear flour‡	9·77	0·64	2·30	13·11	—	—	—	20·5

* Based on 858 analyses.   † Based on 7742 analyses.   ‡ Conn. Exp. Sta. Bull., 255 (1923).

A comparison of the ratios of protein to ash (last column) shows that the ratio for the whole wheat grain is 6, although, according to some analyses, it may slightly exceed 10; for bran it is about 2·5; and for the various grades of commercial flours the range is about 15 to 30, the values less than 20 being for low-grade flours. In general, the ratios of commercial Graham flours do not exceed 10·0, and there are no consistent differences in this respect between Graham flours and entire wheat flours.

ICE CREAM.—Only 5 samples were found to contain less than the legal minimum of 8 per cent. of fat, and one of these was sold under a label which declared not less than 4 per cent. of fat.

HAMBURG STEAK.—Twenty-two of 62 samples examined contained sulphites, the use of which is illegal under State Regulation 51.

FOODS EXAMINED FOR POISONS, ETC.—Forty-two samples were examined. Copper, arsenic and lead in quantity were found in a sample of cakes.   Three samples of wild cherry wine contained 1, 4·7 and 5·4 mgrms. of hydrocyanic acid, respectively, in 100 c.c.

DRUGS.—Medicaments dispensed by physicians were brought within the scope of the State food and drug law about 10 years ago.   Ninety-two samples of pills and tablets, chiefly obtained from the stocks of dispensing physicians, have been examined.   In more than half, the variation in dosage between the lightest and heaviest tablets was within 10 per cent. of the declared dosage, and in nearly

seven-eighths of the samples the variation did not exceed 20 per cent. In general, tablets or pills in which the average quantity of medicament equalled the quantity claimed, and in which the variation between the heaviest and lightest units did not exceed 10 per cent. were passed as satisfactory. Somewhat more tolerance was shown in the few instances in which the quantity of medicament was very small, or in which it could not be determined with the exactness desired.

Six samples varied from the claim by considerable amounts, *viz. acetasal,* which contained 2·5 per cent. of caffeine instead of 2·5 per cent. of caffeine citrate; sodium salicylate, 2 (both below amount claimed); migraine tablets (deficient in sodium salicylate, other ingredients correct); and strychnine sulphate, 2 (excess of medicament).

TOILET PREPARATIONS.—Six samples were examined, chiefly in accordance with Sec. 2679 of the General Statutes, which prohibits the use of wood alcohol in the compounding of any toilet lotion. One hair tonic contained 23 mgrms. of arsenic per 100 c.c., and a "Dandruff Exterminator" was a dilute alkaline, alcoholic solution containing 93 mgrms. of arsenic per 100 c.c., with a salicylate and glycerin. In view of the statements in medical literature (*e.g.* Cushny, *Pharmacology and Therapeutics,* p. 595, 602; Sollmann, *Manual of Pharmacology,* pp. 737, 742; Peterson, Haines and Webster, *Legal Medicine and Toxicology,* p. 218; Kober and Hayhurst, *Industrial Health),* there appears to be no doubt that the indiscriminate use of arsenic in toilet lotions and hair tonics is attended with danger.

"BEAUTY CLAY."—A preparation sold as *Boncilla Clasmic Pack* consisted essentially of perfumed clay (iron aluminium silicate), glycerin and water, with a little calcium carbonate. The composition is typical of so-called "beauty clays."

The Methylated Spirits Regulations, 1925.

THE material articles of the Regulations* on methylated spirits, dated December 7, 1925, which came into force on February 1, 1926, include the following:—

3.—(1) It is hereby prescribed that the substance and combination of substances to be mixed with spirits for the purpose of making the following different kinds of methylated spirits, and the proportions in which such substance and combinations of substances shall respectively be used, shall be as follows:—

In the case of industrial methylated spirits, to every 95 parts by volume of spirits five parts by volume of wood naphtha.

In the case of industrial methylated spirits (pyridinised), to every 95 parts by volume of spirits five parts by volume of wood naphtha, and also one-half of one part of crude pyridine to every 100 parts of the volume of the mixture.

In the case of mineralised methylated spirits, to every 90 parts by volume of spirits 9½ parts by volume of wood naphtha and one-half of one part of crude pyridine, and to every 100 gallons of the mixture three-eighths of one gallon of mineral naphtha or petroleum oil and not less than one-fortieth of an ounce by weight of powdered aniline dye (methyl violet).

(2) Essential oil or other flavouring matter must not, without the express sanction of the Commissioners, be added to or mixed with methylated spirits.

Other sections deal with the possession and sale of methylated spirits other than mineralised methylated spirits, or industrial methylated spirits for use in an art or manufacture under the special authority of the Commissioners, and for the conditions under which industrial methylated spirits may be in the possession of a druggist or for sale as received, or as a constituent of an antiseptic or lotion or

* Obtainable from H.M. Stationery Office, Adastral House, Kingsway, W.C. 2. Price 3d. net.

other preparation prescribed for external use which is not capable of being used as a beverage, for medical and surgical purposes other than internal use as a medicine, and for veterinary purposes. A form of account is scheduled to be kept by persons authorised by the Commissioners to receive and supply industrial methylated spirits for medical, surgical or veterinary purposes in accordance with the Regulations.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Use of Sodium Nitrite in Curing Meats. W. L. Lewis, R. S. Vose and C. D. Lowry. (*Ind. Eng. Chem.*, 1925, **17**, 1243–1245.)—It appears to be established that the potassium nitrate added in curing meat must first be reduced to nitrite, probably by bacteria, before becoming available for the formation of nitrosohaemoglobin, the colouring principle giving the desirable redness to the cured meat (*cf.* Haldane, ANALYST, 1925, **50**, 520). Comparative experiments on a large scale showed that small amounts of sodium nitrite produce the same effect, and that successful results are obtained when the potassium nitrate is replaced by one-tenth its amount of sodium nitrite. In the case of a nitrite pickle, the nitrite content decreases slowly, whilst in a nitrate pickle it increases and may eventually exceed the amount of nitrite present initially in a nitrite pickle. Nitrite-cured hams contained 45 parts of sodium nitrite per million, and nitrate-cured hams 35 to 50 parts per million. W. P. S.

Oils of the Chaulmoogra Group. E. André. (*Compt. Rend.*, 1925, **181**, 1089–1091.)—Each of the many kinds of oil of the chaulmoogra group which are of therapeutic value in leprosy is optically active, but this activity is not entirely due to the chaulmoogric and hydnocarpic acids. Treatment with solvents enables separation to be made of liquid and solid glycerides, both of which are strongly dextro-rotatory ; it is thought that some other derivative of cyclopentene is also present. The following table shows the varieties and botanical sources of commercial chaulmoogra oil :

| Source.	Sp. gr. at 32° C.	Refractive Index at 29° C.		M.P. °C.	Sap. value.	Iodine value. (Hanus).
Taraktogenos Kurzii	0·9425	—	+48°0′	33/39	210·4	96·1
Hydnocarpus anthelmintica	0·9447(29°)	1·4755	+58°10′	26/29	191·0	90·0
ditto.	0·9427	1·4742	+48°0′	25/26	187·3	88·3
Hydnocarpus Wightiana	0·9330	1·4780	+61°40′	28/32	197·2	103·0
Hydnocarpus alpina	0·9346	1·4764	+57°0′	20·5	201·0	95·0
Asteriastigma macrocarpa	0·9217	1·4725†	+44°0′	37/39	189·4	82·8
Oncoba echinata	0·9286	1·4740*	+56°10′	41	184·5	98·0
Carpotroche Brasiliensis	0·9499	1·4755*	+53°40′	21/23	183·7	106·1

† at 25°.   * at 31°.

H. E. C.

Standard Alkaline Copper Solution (Fehling Reagent). M. G. Pegurier. (*Ann. Chim. anal.*, 1925, **10**, 289–291.)—The various solutions, such as Fehling's solution, which have been used for sugar determinations, are not true standards, for various reasons, and, therefore, results with them are not comparable. A liquid is needed which could be preserved and the theoretical " titer " of which, when finished, would be identical with that of the official (French) formulary (10 c.c. = 0·05 grm. of glucose). The author describes a reagent consisting of three solutions A, B and C, which, when mixed in the proportions indicated, give a fresh, not diluted Fehling solution:—A. *Tartaric acid* (33⅓ per cent.) *solution*: 150 grms. of the acid are dissolved in about 300 c.c. of hot distilled water, cooled, made up to 450 c.c., and filtered. B. *Cupric solution*: 52·50 grms. of purified crystallised copper sulphate are dissolved in 200 c.c. of warm water, the solution cooled, 10 drops of pure sulphuric acid added, and the whole made up to 250 c.c. C. *Sodium hydroxide solution* of the French Codex (399·6 grms. per litre). These three solutions should be mixed, when required, in the following order and amounts: Solution A, 45 c.c.; solution B, 25 c.c.; soda lixivium C, sufficient to make the whole up to 150 c.c. This Fehling solution should be kept in a well stoppered bottle and away from the light, and its " titer " will then remain almost unchanged for several months. The following table shows the amounts of copper and dextrose, equivalents of the principal modifications of Fehling reagent :—

	Author.	" Titer " of copper sulphate per litre. Grms.	Dextrose equivalent per 10 c.c. Grm.
Alkaline copper tartrate solution	Barreswill	34·64	0·05
Potassium-cupro liquid	Fehling	34·63	0·05
Potassium-ammonium cupric tartrate solution	Pavy	4·158	0·005
Tartaric-cupro liquid	Violette	36·46	0·05
Potassium-cupro solution	Pasteur	40·00	0·05
Tartaric-cupro solution (in 2 liquids C and T)	Denigès	17·50	0·025
Tartaric-cupro solution (in 3 liquids, C, T, and 5 per cent. potassium ferrocyanide)	Causse-Bonnans	17·50	0·0205 = (0·025 × 0·82)
Standard copper solution	Codex français	34·641	0·05
Potassium-cupro solution	Italian Pharmacopoeia	34·639	0·05
Solution of cupric potassium tartrate	British Pharmacopoeia	34·64	0·05
Standard solution of alkaline cupric tartrate	American Pharmacopoeia	34·67	0·05
Cupro-sodium solution (in 3 officinal solutions: A. B and C)	Pegurier	35·00	0·05

P. H. P.

Action of Salts of Mercury on the Veronals. P. Fleury. *(J. Pharm. Chim.*, 1925, **117**, 465–476.)—The action of mercuric sulphate and chloride was studied upon the following acids of the general composition

$$R\diagdown \underset{R'\diagup}{\overset{CO-NH}{\underset{CO-NH}{\overset{|}{C}}}}\diagup CO$$
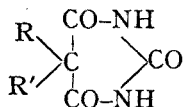
where R and R' are the same or different :—Veronal, gardenal or lucinal, soneryl, isopropylallyl, and diallylbarbituric acids. Mercuric sulphate gives, with aqueous solutions of the acids, immediate precipitates in the cold, gelatinous and readily soluble in dilute hydrochloric acid. If the solution used is made up of 70 grms. of the crystallised mercuric sulphate and 45 c.c. of sulphuric acid (sp. gr. 1·84) in a litre of water, the reaction is sensitive for 1 part in 10,000 or 80,000, according to the acid used. Mercuric chloride only forms precipitates with the allyl derivatives, and the reaction is sensitive for 1 part in 125,000 of diallyl acid, and 1 in 66,600 of isopropylallyl derivative. Most of the precipitates formed with mercuric salts will allow of the quantitative isolation of the dialcoylbarbituric acids, and in some cases the mercury may be indirectly determined.   D. G. H.

Cotarnine Hydrochloride. D. B. Dott. *(Pharm. J.*, 1925, **115**, 757.)— The cotarnine alkaloid base loses water when heated on a water bath, darkens in colour and remains as a fused translucent mass, and the hydrochloride from this product contains less hydrochloric acid than would be required by cotarnine hydrochloride. Owing to the decomposition, the original content of water of hydration cannot thus be determined. The alkaloid may be converted directly into hydrochloride, which is then rendered anhydrous, and the proportion of hydrochloric acid is determined as silver chloride. The constitution of the alkaloid appears to be best represented as $C_{12}H_{15}NO_4,3H_2O$, and that of the hydrochloride as $(C_{12}H_{13}NO_3HCl)_2,5H_2O$.   D. G. H.

Method for the Determination of Iodine in Thyroid Gland. F. A. Pickworth. *(Biochem. J.*, 1925, **19**, 768–772.)—The known methods for the determination of iodine are criticised, and a new method is described which depends upon the destruction of organic matter by fusion with alkali and oxidation of the resulting iodide to iodate with permanganate solution ; excess of the permanganate is removed with animal charcoal, and, after addition of iodide, the liberated iodine is titrated with thiosulphate. The finely powdered dry thyroid (0·25 grm.) is mixed with 10 c.c. of 50 per cent. sodium hydroxide in a nickel crucible of 150 c.c. capacity. The crucible is covered with a lid having a hole $\frac{1}{8}$ inch in the centre, and is slowly heated till the water is evaporated, then more strongly in a furnace below red heat, but hot enough to give a clear fusion product in an hour, and finally over a large free flame to a dull red heat, at which it is maintained for $\frac{1}{2}$ to 1 minute. After it has cooled, 70 c.c. of water are added, and it is placed on a warm plate, and the contents dissolved by gentle stirring. The solution is transferred to a 250 c.c. Erlenmeyer flask, 3 drops of 10 per cent. sodium sulphite solution added,

the liquid acidified with 50 per cent. sulphuric acid and cooled, and 5 c.c. of approximately 0·1 N permanganate solution added. After 3 minutes a suspension of charcoal is added, and, when decolorisation is complete, the whole is filtered, the residue washed with water, and a crystal of potassium iodide is added to the filtrate, which is then immediately titrated with freshly prepared 0·01 N thiosulphate, starch being added towards the end of the titration. Each 1 c.c. of thiosulphate × 85 gives the mgrms. of iodine in 100 grms. of dried gland when 0·25 grm. is taken for analysis. Precautions are given, and the results of test experiments with experimental mixtures described. Considerable latitude is allowable in the amount of reagents and other factors of the method. Duplicate experiments give results which are correct to one drop of titrating solution and obtained at different times. Over 100 human thyroid glands have been analysed by the method, and the results obtained have ranged from 5 to 520 mgrms. per 100 grms. of dried tissue ; and 0·4 to 52·5 mgrm. per whole gland. P. H. P.

Biochemical, Bacteriological, etc.

Delicate Colour Reaction for the Presence of Vitamin A. O. Rosenheim and J. C. Drummond. (*Biochem. J.*, 1925, **19**, 753–756.)—In the course of work on the activation of cholesterol by ultra-violet light Drummond, Rosenheim and Coward (*J. Soc. Chem. Ind.*, 1925, **44**, 123) found that arsenic chloride gives with cod-liver oil a brilliant ultramarine blue colour reaction. Like the sulphuric acid test (ANALYST, 1922, **47**, 341) it appears to be characteristic of vitamin A. One c.c. of pure arsenic chloride is added from a 1 c.c. pipette to one drop of cod-liver oil in a test-tube and shaken. The oil dissolves to form a blue solution which assumes a purple tint in a few seconds and gradually fades. The reaction is characterised by a well-defined absorption band (λ550–590), which persists for about 5 minutes. A 1 per cent. solution in petroleum spirit of a highly growth-promoting Newfoundland cod-liver oil was found to react intensely with 1 c.c. of arsenic chloride in amounts of 0·05 c.c. (0·5 mgrm.) of oil. The limit was reached with 5 c.mm. (=0·05 mgrm.), measured with a Wright's capillary pipette. A suitable colour standard for the arsenic chloride reaction is a mixture of 100 c.c. of crystal violet solution, 1 : 10,000, with 50 c.c. of methylene blue solution of the same strength (both in alcohol). The colour produced by 20 mgrms. of the New-foundland oil (= 1 drop from a pointed glass rod of 3 mm. diameter) with 1 c.c. of arsenic chloride matched the standard dye solution diluted in the proportion 3 : 2. There seems to be a close relationship between the chromogenic substance and vitamin A. Over thirty oils and fats have shown complete agreement between the colour intensity and the growth-promoting activity as tested by experiments on animals. This reaction makes it possible to differentiate vitamin A and vitamin D. Cod-liver oil (and other liver fats) yielded precisely similar blue colour reactions with a number of heterogeneous reagents, known to give, like arsenic chloride, a red colour with cholesterol. These reagents are dimethyl sulphate, trichloroacetic acid, acetyl chloride and benzoyl chloride (the last two only in the

presence of zinc chloride). They react with cholesterol only when heated and give a permanent red colour (absorption band in green), but with cod-liver oil they react at room temperature, and the blue colour produced (absorption band in yellow) fades within 5 to 10 minutes. The reaction with trichloroacetic acid is carried out by letting one drop of oil fall on a few crystals of the acid, or by adding 1 c.c. of a saturated, fresh chloroform solution of trichloroacetic acid to one drop of oil. The colour (slightly more purple than in the test describ.d above) formed is discharged by alcohol, ether, ethyl acetate, acetic anhydride, glacial acetic acid, and 90 per cent. formic acid, but not by benzene, toluene, petroleum spirit or chloroform. If further work on this reaction confirms the tact that the colour intensity is proportional to the growth-promoting power, it will be feasible to replace, to a large extent, experiments on animals for the evaluation of the vitamin A content of oils by a chemical test.   P. H. P.

Effect of Storage on the Antirachitic Factor of Cod Liver Oil, when mixed with Ground Grains. E. B. Hart, H. Steenbock, and S. Lepkovsky. (*J. Biol. Chem.*, 1925, **65**, 571–578.)—Owing to its potent antirachitic properties, cod-liver oil is often mixed with infant foods and poultry feeds. This practice has raised the question of the permanence of the antirachitic properties of such mixtures after several months of storage. Accumulating evidence indicates that vitamin D is a fairly stable substance as compared with vitamin A. The authors have re-investigated the stability of the vitamin D of cod-liver oil when stored with a grain mixture. Experiments were carried out on baby chicks which were fed on a ration rich in vitamin A but poor in vitamin D. It is shown that cod-liver oil mixed with ground grains and stored in galvanised iron cans at room temperature retained its calcifying power for at least 6 months. In some experiments the oil was stored separately and added to the ration just before use. The ash content of the alcohol-extracted bones was determined. Photomicrographs are shown of the proximal ends of the tibiae of chicks receiving rachitic rations which had been fortified with cod-liver oil and stored, and of those receiving fresh cod-liver oil. The results are tabulated.   P. H. P.

Effect of High Temperatures on the Accessory Food Factor Content of Cod-Liver Oil. H. W. Southgate. (*Biochem. J.*, 1925, **19**, 733–736.)—Experiments have been carried out to determine the effect of heat alone for varying periods on the vitamin content of cod-liver oil. A figure shows the effect on the growth curve of rats, and a table gives the relative calcification effects produced by the samples. When cod-liver oil is slowly heated out of contact with air to 300° C. the anti-rachitic and growth-promoting factors contained in it appear to be completely destroyed. If it is slowly heated to 200° C. and maintained at this temperature for some hours these two factors slowly disappear *pari passu*. Oxidation from external sources is unnecessary for the destruction of these factors at these temperatures. If oxygen is excluded, the chemical compound (or compounds) representing these factors is fairly stable to heat.   P. H. P.

Presence of Glutathione in the Corpuscles of Mammalian Blood.

H. F. Holden. (*Biochem. J.*, 1925, **19**, 727–728.)—Glutathione has been identified as a constituent of the red corpuscles of sheep's blood. It appears to exist in the corpuscles of many animals in the reduced form. It is apparently the chief optically-active constituent of de-proteinised blood other than glucose, and as such is responsible for the effects recorded by Winter and Smith (*J. Physiol.*, 1922, **57**, 100) and others, and quoted as evidence in favour of the presence of an unstable modification of glucose. Probably it accounts for much of the " neutral " sulphur of blood. The yield of 0·05 grm. per litre obtained may be considerably below the actual concentration, due to loss from the methods of precipitation. Both cysteine and reduced glutathione can convert methaemoglobin into oxyhaemoglobin, and can reduce the latter to haemoglobin *in vitro*. This may explain the rapid conversion of methaemoglobin into oxyhaemoglobin in the animal body.   P. H. P.

Isolation of a New Substance from Blood and its bearing on Present Methods for the Determination of Uric Acid.   G. Hunter and B. A. Eagles.

(*J. Biol. Chem.*, 1925, **65**, 623–642.)—As a result of some recent work in France, a new non-protein substance of the empirical formula $C_6H_{11}N_2O_3$, believed to be a simple pyrimidine nucleoside, has been isolated from pig's blood, and evidence has been obtained of its presence in the blood of other animals. It is commonly present in human whole blood to the extent of 10 to 12 mgrms. per 100 c.c., and, as it is confined entirely to the corpuscles, it is there in approximately twice these concentrations. The amount in blood varies over a wide range, even in the same individual. A description is given of the method of isolation and properties of the pure substance. It gives a blue colour with the phosphotungstic and arseno-phosphotungstic acid uric acid reagents in the presence of either sodium carbonate or sodium cyanide. The use of sodium carbonate makes its presence in human blood more conspicuous, as the reagent, with this alkali, is less sensitive towards uric acid. The behaviour of the new substance has been quantitatively studied with the old and new uric acid reagents. The discrepancies between the direct method of Benedict and the precipitation method of Folin and Wu for the determination of uric acid in human blood are due to the fact that this new substance adds to the values obtained for uric acid by the direct method. The substance now isolated is that mainly responsible for the direct " uric acid " values recently obtained in animal bloods by Bulmer, Eagles and Hunter, and is separable from uric acid in blood filtrates by the precipitation method of Folin and Wu. Full details are given of the work carried out, with tables and charts of the results.

P. H. P.

Reaction of Potassium Ferricyanide with the Blood Pigment.   M. Nicloux and J. Roche.

(*Comptes Rend.*, 1925. **181**, 823–826.)—By measuring the carbon monoxide and oxygen evolved when a definite amount of alkali ferricyanide solution acts on excess of carboxyhaemoglobin and oxyhaemoglobin respectively, it is confirmed that the formula of methaemoglobin is *HbO*, so that this pigment contains one-half of the oxygen of oxyhaemoglobin.   T. H. P.

Factors Influencing the Action of Pancreatic Lipase. B. S. Platt and E. R. Dawson. (*Biochem. J.*, 1925, **19**, 860–874.)—In the course of a determination of the action of pancreatic lipase on certain esters, it was necessary to find a convenient method of preparing the enzyme in an active and pure condition, and to investigate the influence of certain factors with a view to obtaining the optimal conditions of action. The enzyme was prepared by the method of Umeda (*Biochem. J.*, 1915, **9**, 38). Lipase can be determined by titration of the acid formed from ethyl butyrate, when the reaction is carried out in a phosphate buffer medium. The substances present in the reacting mixture determine the optimum P_H for pancreatic lipase action. With a purified pancreas powder containing lipase, the optimum P_H in phosphate and in phosphate-borax buffer solutions was 7·0, and in borax and boric acid buffer solutions there was an optimal zone about P_H 8·4. Lipase of a glycerol extract of pig's pancreas in phosphate buffer mixtures, acting on ethyl butyrate showed maximum activity at P_H 7·8, but no definite P_H optimum. In the complete absence of activators the hydrolysis of ethyl butyrate is not promoted by lipase, even with favourable hydrogen ion concentration of the medium. Increasing concentrations of phosphates and bile salts act similarly on lipase activity. The buffer value of the solutions and a specific influence of a chemical nature on the enzyme seem to determine the form of the curve obtained by plotting activity values against increasing salt concentrations. Phosphates should be present in a system of activators intended for complete activation of pancreatic lipase. The protein structure which has been ascribed to lipase is characteristic of the substances associated with it rather than of the enzyme itself. Changing the accompanying protein alters its ester-hydrolysing properties. The apparent destruction of lipase by trypsin is due, partly, to the removal, by hydrolysis, of activating proteins. Formaldehyde has no appreciable effect on pancreatic lipase action in concentrations of less than 0·2 per cent.   P. H. P.

Further Investigation of the Chemical Properties of Insulin. D. A. Scott. (*J. Biol. Chem.*, 1925, **65**, 601–616.)—Insulin of known potency has been subjected to the action of various reagents. Benzoyl chloride and carbon disulphide rendered insulin inactive in an alkaline solution. Formaldehyde and nitrous acid greatly decreased the activity. Attempts to reactivate the insulin by acid hydrolysis and oxidation were unsuccessful. Insulin was destroyed by other reducing agents, such as nascent hydrogen, sulphur dioxide and calcium bisulphite. A very pure insulin product has been prepared from pancreatic glands of the ox. The essential steps in this preparation are :—(1) Extraction with hydrochloric acid alcohol, (2) precipitation of the concentrated extract with ammonium sulphate, (3) solution of the precipitate and reprecipitation in warm alcohol, (4) fractional precipitation at different acidities, (5) precipitation with trichloroacetic acid. The resulting, almost snow-white, product had a nitrogen content of 0·006 mgrm. per unit of activity. The physiological assay showed 25,000 units of insulin per grm. of powder. Carbon, hydrogen and ash values have also been determined on this purified insulin product, and the chemical tests on it showed

characteristic protein reactions. Colour reactions for tryptophane were faint, phosphorus was not present, and the Molisch and orcein tests were negative. The distribution of nitrogen and of the tyrosine, tryptophane and amino nitrogen has been determined in a purified sample. From a consideration of the following points :—(1) The action of trypsin on insulin, (2) the action of specific reagents, (3) the preparation, (4) the chemical tests, (5) the combustion analysis, (6) the distribution of nitrogen—the similarity between insulin and a protein is apparent. Possibly this purified product contains two or more proteins having very similar physical properties.   P. H. P.

Determination of Small Quantities of Bismuth in Urine. C. A. Hill. (*Lancet*, 1925, **209**, 1281.)—Three portions of 5, 20 and 50 c.c. of urine are measured into 100 c.c. beakers, the last two being evaporated on asbestos board to 5 c.c. 5 c.c. of concentrated nitric acid are added to each, the mixture evaporated to dryness, and the residue heated so that the organic matter is oxidised but not charred. The evaporations with nitric acid are repeated in each case till the ash is white. The cool residue should dissolve as a clear solution in 2 drops of nitric acid and 25 c.c. of water. This solution is placed in a Nessler cylinder, 0·3 grm. of urea is dissolved in it and then 0·5 grm. of phenazone. Solution is hastened by agitation, and then potassium iodide is added in about 50 mgrm. portions till the maximum colour is obtained when one more portion is added. The colour is matched with a solution made up in a similar manner and containing a known volume of a standard solution of bismuth nitrate. This solution is prepared by dissolving 0·62 grm. of bismuth carbonate (B.P.) in 10 c.c. of nitric acid, diluting to 1 litre, and then diluting 10 c.c. of this to 1 litre. The best results are obtained when the colour in the test solution matches the colour produced by 10 c.c. of the above (0·05 mgrm. Bi) diluted to 50 c.c. after the addition of 1 drop nitric acid. R. F. I.

Electrolytic Method for Investigating the Circulation of Gold in the Animal Organism. S. Lomholt. (*Comptes Rend.*, 1925, **181**, 821–823.)— The following procedure serves to determine the distribution, throughout the body, of gold administered intravenously in soluble form in cases of tuberculosis. The organic matter is burnt away in presence of fuming nitric acid, and the ash dissolved in diluted *aqua regia*. The solution is heated to boiling, rendered feebly alkaline with ammonia, treated with 0·75 grm. of potassium cyanide, diluted to 75 c.c., and electrolysed at 4 volts by means of weighed platinum cathodes (2 sq. cm. and 0·07 grm.), which are afterwards again weighed ; care must be taken to avoid the formation of platinum black. Control experiments give good results. Tests made on three rabbits show that the kidneys take up about 6 per cent. of the gold introduced, the liver about one-half as much as one kidney, and the lungs and heart only insignificant amounts. After a week the blood contains only a minute quantity, whereas the intestines—especially the large intestine—and their contents show considerable, although variable amounts. The remainder of the body contains little gold. About two-thirds of the metal are eliminated in the urine, and the remainder in the faeces.   T. H. P.

Effects of Zirconium, Titanium and Manganese Salts on Nutrition.
Richet, Gardner and Goodbody. (*Comptes Rend.*, 1925, **181**, 1105.)—Dogs
were fed for 146 days on diets containing citrates of zirconium, titanium and
manganese (0·1 grm. per 1 kilo. body-weight), and also on similar diets without
addition of these salts. Observations were made of the change in body-weight,
and the following conclusions were drawn :—Zirconium, titanium, or manganese
do not have any toxic effect. Titanium appears to have a slightly favourable
action : zirconium more so. In cases where manganese was administered every
day the results were unfavourable, but when administered every four days they
were very favourable.   R. F. I.

Researches on the Fermentation of Dried Tobacco. I. Methods for
Separating Nicotine and Ammonia. A. Fodor and A. Reifenberg.
(*Biochem. J.*, 1925, **19**, 827–829.)—The authors have carried out experiments to
separate the nicotine from the other volatile nitrogen-containing bases contained
in extracts or expressed juices from tobacco leaves and to determine them. They
obtained a mixture of nicotine and ammonia by direct steam-distillation of tobacco
leaves. This was made weakly acid with sulphuric acid, and by means of a solution
of mercuric iodide in potassium iodide (3 grms. per 100 c.c. of water) the nicotine
was precipitated. The wax-like, crystalline precipitate was left overnight and
washed by decantation, and its nitrogen then determined by the Kjeldahl method.
The ammonia was distilled from the filtrate, but an excess of potassium iodide was
added before making the liquid alkaline, to prevent the formation of a Nessler
precipitate and the consequent loss of ammonia. If the total titration value of
the volatile nicotine and ammonia is known, and then, after precipitation of the
nicotine, the ammonia content of the filtrate is determined, the difference between
the two titration values gives the nicotine content. Satisfactory results were
obtained by this method. Since some other volatile bases may pass over also
from the tobacco leaves, the value for the ammonia will generally be more correctly
expressed as the value for volatile non-nicotine bases.   P. H. P.

Effect of Dehydration on the Bacterial Flora of Eggs. G. G. De Bord.
(*J. Agric. Res.*, 1925, **31**, 155–164.)—The total number of viable bacteria in de-
hydrated egg varies with the quality of the raw egg, but is, in general, greater
in that dried on a vacuum drum than that prepared by the spray process. By this
process the total counts vary from 350 in a good egg to over a million in
" spots " ; these numbers are reckoned on a basis of 1 grm. of the liquid egg.
In eggs dried on a vacuum drum the numbers vary from 45,000 to over
2 millions. The numbers depend not only on the initial count, but also on the
time and temperature of storage. In good eggs after 10 months' storage at
37° C. and 20° C. there was a diminution, whereas, in bad samples there was
sometimes an increase and sometimes a decrease. The characteristic smell
of doubtful eggs is almost lost in the drying process.   H. E. C.

Toxicological and Forensic.

Pyrotannic Acid Method for the Determination of Carbon Monoxide in Blood and in Air. R. R. Sayers and W. P. Yant. (*U.S. Bureau of Mines, Tech. Paper*, 373, 1925.)—The method is based on Wetzel's test, in which when normal blood diluted 1 : 4 is shaken with an equal volume of 1 per cent. tannic acid solution and allowed to stand 24 hours, it gives a grey suspension, whereas blood containing carboxy-haemoglobin remains carmine red. This reaction is sensitive, and the colour, when once formed, changes very slowly. For the application to blood 5 c.c. or more are drawn and kept from clotting by the addition of 0·05 grm. of potassium citrate per 10 c.c. One half of this is diluted to 10 parts with water, the other is saturated with carbon monoxide and then diluted 1 : 10. To each is added 1 c.c. of a mixture of fresh 2 per cent. pyrogallic acid solution and 2 per cent. tannic acid solution, and the tubes are immediately sealed to serve as standards. The full colour is developed in 30 minutes and is permanent for 1 or 2 weeks. Standards are similarly made from dilutions of blood saturated with carbon monoxide, in 10 per cent. steps, from *nil* to complete saturation. For the application, a few drops of blood are drawn from the finger of the suspected victim, 0·1 c.c. is pipetted and diluted to 2 c.c., the reagent is added, and the colour compared with the foregoing standards. The same principle is applied to the examination of air by shaking therewith normal blood and determining the carbon monoxide colorimetrically ; instructions are given for the necessary calculations.   H. E. C.

Cases of Poisoning by Sodium Silicofluoride. Lührig. (*Chem. Zeit.,* 1925, 49, 805–806.)—Two fatal cases of poisoning by sodium silicofluoride, commonly sold as an insect powder, are recorded. In one of these a man took half a spoonful of the salt in mistake for sodium carbonate, and death took place within 10 hours. Fluorine was determined in parts of various organs of the body after evaporation with 1 grm. of sodium carbonate and 0·5 grm. of calcium hydroxide (as milk of lime), and ignition of the residue. The ash was extracted with hot water, most of the carbonate in the extract decomposed with sulphuric acid, the still alkaline liquid added to the original ash, and the whole evaporated and gently ignited. The final ash was mixed with about 7 grms. of finely ground quartz powder, and heated for several hours with anhydrous sulphuric acid at about 180° C., the resulting hydrogen silicofluoride being conducted into dilute sodium hydroxide solution by means of a current of dry air. The alkaline solution was neutralised, while boiling, with hydrochloric acid (phenolphthalein as indicator), and the amount of fluorine determined by Greef's method (*Zeitsch. Nahr. Genussm.*, 49, 31) by means of ferric chloride and ammonium thiocyanate in the solution after saturation with sodium chloride. The following amounts, as sodium silicofluoride, were found:—Stomach, stomach contents and alimentary tract, 144 mgrms. from 248 grms. ; small intestine and contents, 48 mgrms. from 680

grms.; large intestine and contents, 488 mgrms. from 417 grms.; kidneys, 5·1 mgrms. from 290 grms.; urine, traces in ash from 23 grms.; and liver, 42·4 mgrms. from 1205 grms. No fluorine was detected in the ash from 10 grms. of the blood.

Deciphering Chemically Bleached Writing by means of Dyes. R. Mellet and A. Bischoff. (*Comptes Rend.*, 1925, **181**, 868–869.)—Writing in ink is usually bleached by the application of oxidising agents, followed by one or more washings with acids. The surface of the paper appears to be protected for a short time against the action of the oxidising agent by the ink pigment, so that there is a difference of superficial oxidation of the paper thus protected and that on which there are no ink characters. This difference should be shown by a difference in the degree of adsorption of dyes by the protected and unprotected surface, but, in practice, owing to the pronounced adsorption of dye by the mineral matter of the paper, the colour appears to be uniformly fixed over the whole surface of the paper. If, however, paper with bleached writing upon it is stained with a fluorescent dye (*e.g.* eosine) and then examined by the light of a Wood's quartz mercury vapour lamp, the bleached writing re-appears as dark characters on a luminous ground. The method has been successfully used to decipher bleached writing on cheques, on which nothing could be discerned by the ordinary chemical or photographic methods or by direct examination with a Wood's lamp. After staining the cheques with various fluorescent dyes and then examining them with Wood's light the writing became visible in violet black upon a luminous rose, yellow or orange ground.

Water Analysis.

Colorimetric P$_H$ Test of Water or Unbuffered Solutions. H. T. Stern. (*J. Biol. Chem.*, 1925, **65**, 677–681.)—In many cases of routine control of the hydrogen ion concentration within the neutral range, the only feasible test is the one by means of indicators, but variations occur with the different dye products which are difficult to explain. In unbuffered solutions there is a marked effect noticeable, due to the varying alkali content of the dye-product and possibly to variations in the dye constitution. Much influence has previously been ascribed to the carbon dioxide content of the air, but it is shown that carbon dioxide from the atmosphere does not seem to affect the colorimetric P$_H$ test. A bromthymol blue solution for testing unbuffered solutions may be satisfactorily prepared by adding alkali until a pure dark green colour is obtained. This solution is not stable. Bromthymol blue in solution undergoes changes which seem to be uncontrollable. Para-nitrophenol, covering approximately the same P$_H$ range, is recommended as a more reliable indicator for unbuffered solutions when it is used in a neutral solution.

P. H. P.

Agricultural Analysis.

Some Nitrogenous Constituents of the Juice of the Alfalfa Plant VI. Asparagine and Amino Acids in Alfalfa. H. B. Vickery. (*J. Biol Chem.*, 1925, **65**, 657–664.)—A fraction containing asparagine and the free amino

acids of the juice of the alfalfa plant has been obtained by the methods of Vickery (*J. Biol. Chem.*, 1924, **60**, 647) and examined by the methods of protein analysis. Asparagine, aspartic acid, tyrosine, phenylalanine, serine, leucine, valine and alanine were isolated. These substances make up at least 29·5 per cent. of the solids of the fraction and, together with the ammonia set free by hydrolysis, 54·8 per cent. of the nitrogen. The aspartic acid obtained after hydrolysis probably represents asparagine. At least 55 per cent. of the amide nitrogen of the amino acid fraction is accounted for as asparagine, and the aspartic acid found after hydrolysis indicates that more of this substance is present. Although no other amide has yet been found, other substances yielding ammonia on mild acid hydrolysis are probably present in the juice of the alfalfa plant. Serine and alanine, it is thought, have not previously been reported as occurring in plant juices, and both are difficult to isolate. The ester distillation method seems essential for their separation from complex mixtures. They were definitely identified as α-naphthylhydantoic acid derivatives. The presence in the alfalfa plant of the hydroxyamino acid serine is interesting, since this acid has long been known as a constituent of proteins and probably it is widely distributed in plants. P. H. P.

Determination of Nitrogen in Heavy Clay Soils. D. V. Bal. (*J. Agric. Sci.*, 1925, **15**, 454–459.)—In determining the nitrogen in heavy black-cotton soil, such as that of the Central Indian Provinces, low results are obtained by direct application of the Kjeldahl process to the air-dried soil. Materially higher results are obtained if to the air-dried soil are added 50 c.c. of water, and the mixture is allowed to stand for about half-an-hour before the addition of sulphuric acid, copper sulphate and potassium sulphate in the usual way. It appears that these soils contain a ferruginous cementing material which protects the organic substances in the interior of the particles from the action of the acid. This is borne out by the fact that if the residue after the dry treatment is moistened and re-treated, a further quantity of nitrogen is found which is equal to the difference between the amount indicated by the dry process and by the wet one. H. E. C.

Determination of Fluorine in Basic Slag. R. G. Warren, C. T. Gimingham and H. J. Page. (*J. Agric. Sci.*, 1925, **15**, 516–528.)—A modification of the Steiger-Merwin method for the determination of fluorine has been worked out for basic slags. It is based on the bleaching effect of fluorine on the yellow colour produced by hydrogen peroxide and titanium, but, as this colour is masked by vanadium, it is essential to eliminate this metal from the slag. The method is as follows:—One grm. of the slag is fused for an hour with 6 grms. of fusion mixture at a moderate temperature. The crucible is plunged, after partial cooling, into water, and the mass extracted. The solution is concentrated to 70 to 100 c.c., cooled, and 3–4 grms. of ammonium carbonate are added, and the whole allowed to stand over-night, then filtered, and the residue washed with ammonium carbonate solution. The residue is preserved for a second fusion and extraction, if necessary. The filtrate is evaporated to dryness, moistened and re-dried; then 50 c.c. of water saturated with phenolphthalein are added, and the solution titrated hot with

4 N sulphuric acid solution until the colour of the indicator almost, but not quite, disappears (it is necessary to boil after each addition of sulphuric acid to expel carbon dioxide). After the addition of 0·6 grm. of silver sulphate the mixture is set aside in the dark over-night, then filtered in the dark through a close double filter, and the residue washed with water, after which 10 c.c. of sulphuric acid (sp. gr. 1·55) and 3 c.c. of hydrogen peroxide are added. No brown colour should be produced. Ten c.c. of titanium sulphate solution are next added, and the whole made up to 100 c.c. The tint of this solution is compared with that of standard titanium solution containing the same amounts of titanium, acid, and peroxide. From the tint ratio the amount of fluorine is read off from a curve constructed by the addition of known amounts of fluoride to the titanium solution.

H. E. C.

Organic Analysis.

Nitrogen Tetroxide as a Reagent for Diazotisation. **B. Houston and T. B. Johnson.** (*J. Amer. Chem. Soc.*, 1925, **47**, 3011–3018.)—Experiments made with aniline and o-, m- and p-nitroanilines show that nitrogen tetroxide interacts with primary aromatic amines in benzene solution to form the corresponding diazonium nitrates and diazoaminobenzenes. This reaction is best explained by assigning to nitrogen tetroxide the structure of nitroxyl nitrate, $ON.O.NO_2$. ·   T. H. P.

Accurate General Iodimetric Method for the Determination of the Carbonyl Group in Organic Compounds. **E. G. R. Ardagh and J. G. Williams.** (*J. Amer. Chem. Soc.*, 1925, **47**, 2983–2988.)—This method is based on conversion of the carbonyl compound into its phenylhydrazone, and iodimetric determination of the residual excess of phenylhydrazine. Use is made of water, aqueous alcohol of suitable strength, or other solvent to dissolve the carbonyl compound, and of petroleum spirit or other solvent for extracting the phenylhydrazone. Distilled water boiled and then cooled under nitrogen is employed. If liquid, the carbonyl compound is sucked into a tared glass bulb and weighed, the bulb being afterwards broken under the water or other solvent, and the solution made up to a definite volume. Approximately 0·5 M phenylhydrazine hydrochloride solution is prepared from the recrystallised salt, which is carefully dried and kept in the dark. To maintain the hydrogen-ion concentration of the liquid between the limits for which the maximum formation of the phenylhydrazone takes place, use is made of 0·5 M or slightly weaker disodium phosphate solution.

For a determination, 20 c.c. of the phenylhydrazine solution, 20 c.c. of the 0·5 M phosphate solution (or more of a weaker solution), and sufficient of the carbonyl compound to react with about one-half of the phenylhydrazine taken, are mixed in a 100 c.c. flask which has been flushed out with nitrogen. The liquid is made up to the mark with saturated sodium chloride solution, and the stoppered flask left at room temperature, the reaction being usually complete in 30 minutes. If a solid precipitate forms, it should be filtered off as quickly as possible. Twenty-five c.c. of the aqueous solution are vigorously shaken for 2 minutes in a 75–100 c.c.

cylindrical separating funnel—previously flushed out with nitrogen—with 4 to 5 c.c. of petroleum spirit of b.pt. 40° to 60° C. After a settling time of 2 minutes, a portion of the aqueous layer is run into a calibrated 25 c.c. cylinder, and 10 c.c. pipetted from this into an Erlenmeyer flask (about 250 c.c.) fitted with ground stopper and containing nitrogen. Two drops of methyl orange solution are added, and then dilute sulphuric or hydrochloric acid, drop by drop, until the liquid turns pink. After introduction of sufficient 0·1 N iodine solution to give an excess of about 5 c.c., the stoppered flask is left for 5 minutes, after which fresh starch solution and excess (about 3 or 4 c.c.) of 0·1 N thiosulphate solution are added, the liquid being then shaken with about 5 c.c. of ether to dissolve the iodine from the drops of iodobenzene. The liquid is titrated with 0·1 N iodine solution in an atmosphere of nitrogen. The residues of the aqueous and ethereal solutions are run into the measuring cylinders and their volumes determined. A blank is carried out under similar conditions with the phenylhydrazine alone. The partition coefficient of the phenylhydrazine between water and petroleum spirit may be determined by shaking for 2 minutes with the solvent and testing the aqueous layer.

In an actual determination with acetaldehyde, 2·9743 grms. of the aldehyde in a glass bulb weighing 1·4773 grm. (volume of glass fragments, 0·5 c.c.) were made up to 99·5 c.c. The amounts of the various solutions taken were 25 c.c. of 0·5 M-phenylhydrazine hydrochloride solution, 20 c.c. of 0·5 M disodium phosphate solution, 10 c.c. of the acetaldehyde solution, and 45 c.c. of saturated sodium chloride solution. A dense white emulsion formed, a solid separating later. Of the filtrate, 25 c.c., on extraction with petroleum spirit, gave 24·9 c.c. of aqueous layer and 3·2 c.c. of petroleum layer. To 10 c.c. of the aqueous layer were added 30 c.c. of the iodine (0·0995 N) solution and afterwards 12 c.c. of thiosulphate (0·0995 N), 2·65 c.c. of the iodine solution being then required on titration ; 30 + 2·65 − 12 = 20·65 c.c. iodine solution. The blank on the phenylhydrazine alone was 47·55 c.c. of the iodine solution, and the partition coefficient for the phenylhydrazine in water and petroleum spirit was 0·055. The corrected volume for iodine required by the 10 c.c. aliquot portion extracted is 20·65 (24·9 + 3·2 × 0·055)/25·0 = 20·7 c.c. The weight of hydrazone formed and removed by filtration (calculated) = 1·04 grm. = say 1 grm., and correction of the iodine value for this gives 20·7 × 99/100 = 20·45 c.c. The iodine value for 1 c.c. of the acetaldehyde solution is thus 47·55 − 20·45 = 27·1 c.c. of 0·0955 N solution, and, since $CH_3.CHO \equiv C_6H_5.NH.NH_2 \equiv 2I_2$, 1 c.c. of 0·1 N iodine indicates 0·001101 grm. of acetaldehyde. Hence acetaldehyde found per c.c. = 27·1 × 0·995 × 0·001101 = 0·02969 grm., the amount taken being 2·9743/99·5 = 0·02989 grm. The corrections for partition coefficient and change in aqueous volume when petroleum spirit is used are small and may mostly be ignored.   T. H. P.

Gasometric Method for the Determination of Acetic Anhydride. E. L. Whitford. (*J. Amer. Chem. Soc.*, 1925, **47**, 2939–2940.)—In pyridine solution, oxalic acid is rapidly and quantitatively decomposed by acetic anhydride, with evolution of carbon monoxide and dioxide. This reaction serves for the

determination of acetic anhydride. The pyridine used is first dried by means of fused sodium hydroxide and barium oxide and is then treated with calcium carbide and distilled directly into the reaction flasks. The pyridine is next saturated with dry carbon monoxide and dioxide, and shaken with excess of anhydrous oxalic acid. The acetic anhydride, weighed in a glass capsule carefully protected from the air, is then dropped into the mixture. The gases, which are immediately liberated, are collected in a 100 c.c. burette over water saturated with the monoxide and dioxide, the reaction, $H_2C_2O_4 + (C_2H_3O)_2O = CO + CO_2 + 2C_2H_4O_2$, being complete in 15 minutes. A blank determination with the reagents alone should yield no gas. The results obtained are accurate to within 0·1 to 0·2 per cent.

T. H. P.

Determination of Lead Tetra-ethyl in Motor Fuels. G. Ferreri. (*Giorn. Chim. Ind. Appl.*, 1925, **7**, 625–626.)—The following method is found to yield accurate results when applied to ordinary petrols and petrol-benzol mixtures. Fifty c.c. of the motor spirit are heated over a small flame with 50 c.c. of concentrated hydrochloric acid in a 250 c.c. round-bottomed flask fitted with a reflux condenser and placed under a draught hood. The gaseous hydrogen chloride formed passes through the supernatant petrol and precipitates finely divided lead chloride, which dissolves later and leaves the petrol clear. The petrol and a large part of the aqueous liquid are then expelled by distillation, and the residue is transferred to a beaker, into which also the flask is rinsed with water. The lead may then be determined as chloride by concentrating the liquid somewhat, adding absolute alcohol, and, after an interval, collecting and weighing the chloride. More exact results are obtained by evaporating the liquid with concentrated sulphuric acid until it emits white fumes, the sulphate being filtered off through paper rather than through a Gooch crucible, and the precipitate and filter ash heated with a few drops of nitric acid and then with two drops of sulphuric acid ; any traces of carbonaceous matter are eliminated in this way. (*Cf.* ANALYST, 1925, **50**, 84).

T. H. P.

Vacuum Distillation Test (for Heavy Petroleum Oils). A. G. Peterkin and S. W. Ferris. (*Ind. Eng. Chem.*, 1925, **17**, 1248–1249.)—Fractional distillation of heavy petroleums affords reliable evidence as to whether any given oil is a " straight-run " product or a blend of light and heavy oils. An apparatus is described for the purpose, the essential feature being the pressure regulation device. This consists of a capillary, open to the air, and immersed to the proper depth in mercury. For example, if it is desired to work at 10 mm. absolute pressure with the barometric pressure at 763 mm., the tube is immersed 753 mm. When the pressure within the system reaches 10 mm. air will issue from the capillary into the system and maintain the pressure at that point. W. P. S.

Detection of Petroleum Vapour with the Burrell Methane Indicator. G. W. Jones and W. P. Yant. (*U.S. Bureau of Mines, Tech. Paper*, 352, 1924.)—The percentages and predominating hydrocarbons contained in petroleum vapour

ın tanks, etc., range from 0·01 to 80 per cent. of hydrocarbons from ethane to duodecane. Above heptane, however, the explosive limit would not be present at normal temperatures. The volumes of oxygen required and the lower limit of inflammability of the lower members were found to be :—

			Volume of oxygen required.	Lower limit of inflammability.
Methane	..	..	2·0	5·50
Ethane	..	..	3·5	3·10
Propane	..	..	5·0	2·15
Butane	..	..	6·5	1·65

The approximate average value of the product of these two figures for petrol vapour is 10·8. The safety limit has, however, been chosen as 0·3 per cent., because this proportion is found to be poisonous to some observers. By means of the Burrell indicator the petroleum vapour can be estimated in about 4 minutes, and with safety, even in closed or dangerous places. For a description of the instrument it is necessary to consult the original paper. H. E. C.

Relation between Boiling Point and some other Properties of Petroleum Products. J. B. Hill and S. W. Ferris. (*Ind. Eng. Chem.*, 1925, **17**, 1250–1252.)—The authors give a collection of data obtained by determining the physical properties, including distillation *in vacuo*, of a number of distillate fractions obtained from various crude oils. It is shown that, for fractions of the same boiling-point (as indicated by the 50 per cent. point on the vacuum-distillation) as the crude product varies from paraffinic to naphthenic character, the viscosity, the coefficient of viscosity change with temperature, the specific gravity and the refractive index all increase. The relation between the boiling point and the other physical properties is a good indication of the source of the oil. W. P. S.

Paraffin Wax. L. D. Wyant and L. G. Marsh. (*U.S.A. Technical Paper*, 1925, No. 368.)—The method of determining the paraffin wax content of oil and wax mixtures depends on the difference in solubility in acetone of the wax and oil. To a 5 grm. sample 35 c.c. of acetone are added, the mixture heated under a reflux condenser for a few minutes, and the hot solution transferred to a 12 inch test tube (120 c.c. capacity), which is at once stoppered to prevent evaporation, and 15 c.c. of acetone (used for washing out the flask) are added. The solution is shaken vigorously (to prevent formation of a lumpy mass difficult to wash) until the temperature has nearly reached 60° C., at which point it is then adjusted in a water bath. Test tubes (conveniently graduated into one 20 c.c. and two 15 c.c. portions), each containing 50 c.c. of fresh acetone are also placed in the bath. The liquid is filtered, the acetone solution drained off, and the filter washed with two successive portions of 15 c.c. of the acetone which has first been used to wash out the tube which contained the solution, and lastly any crystals remaining on the sides of the filter are washed down with 20 c.c. of acetone. As soon as this has drained, suction is applied for some 30 seconds. Nearly all the acetone is distilled off from the filtrate. the oil portion quantitatively transferred to a small flask and distilled,

and the residue dried *in vacuo* in a boiling water bath and weighed. The wax is recovered from the filter and its melting point determined. If this is low, the recovered wax is redissolved in fresh acetone (20 c.c. to 1 grm. of wax), the solution cooled to 60° C., filtered and washed, and the recovered oil treated as before. If, however, the melting point is abnormally high, the yield will probably be slightly low, and it may be necessary to recover an additional crop of crystals from the separated oil by redissolving it in acetone, cooling the solution to 60° C., and proceeding as before. This method may be successfully applied to slack waxes and such oil and wax mixtures as are obtained when slack wax is sweated to yellow scale or finished paraffins. D. G. H.

Inorganic Analysis.

The Gasometric Calcium Carbide Method for the Determination of Moisture. W. A. Jakowenko. (*Zeitsch. Unters. Nahr. Genussm.*, 1925, **49**, 360–370.)—The gasometric determination of water by measurement of the volume of acetylene generated from calcium carbide is found to give results varying according to the state of combination of the water. In the case of colloidal substances, such as cereals, the results agree well with those obtained by other methods, and it is characteristic that the gas is evolved rapidly at first and that then its rate of evolution diminishes to zero. In the case of crystalline substances containing water of hydration the results depend upon the temperature to which the mixture is heated, and the rate of the evolution of the gas is constant. The results are, of course, dependent on the vapour pressure of the salt hydrates. The method adopted is to connect the substance and powdered calcium carbide in two short tubes joined by a wide T-piece and connected with a mercury-filled nitrometer. After adjustment of the pressure the two powders are mixed by shaking, and the mixture heated to 100° C. for a few minutes. The volume of gas evolved is measured, and the percentage of water is given by $\dfrac{W}{10} - \dfrac{Vp}{S(1+\alpha t)\,760}$, where W is the weight of water which yields 1 c.c. of acetylene at N.T.P. S is the weight of substance, V = volume, p = pressure, t = temperature, and α is the coefficient of expansion of the gas. W varies with different samples of carbide and is found by heating the powdered carbide with a known weight of crystallised ammonium oxalate which contains 1 molecule of water and observing the volume of gas evolved. H. E. C.

Determination of Traces of Mercury. H. S. Booth and N. E. Schreiber. (*J. Amer. Chem. Soc.*, 1925, **47**, 2625–2629.)—The limit of sensitiveness of colorimetric, microscopical, or amalgamation tests for mercury is about 5 parts per million, but the electrolytic method applied as described below is sensitive to 1 part of mercury in a billion. A piece of 36 gauge copper wire is polished to a fine point with emery paper and cemented on to a glass slide with a central cavity (an ordinary culture slide) so that the free end just slopes into the cavity. A small platinum wire similarly mounted forms the anode. These electrodes are connected

with a source of current of 1·3 to 1·5 milliamps at 1·5 to 2 volts, and a drop of the liquid is placed in the cell. The tip of the copper cathode should only just touch the drop. After 2 or 3 minutes the circuit is broken, and the copper point is examined under the microscope for traces of a whitish amalgam of mercury. The limiting sensitiveness is about 1 drop of a solution containing 0·5 mgrm. of mercury per litre, and this limit may be increased 1000-fold by evaporating a large volume of the liquid in a vacuum desiccator. H. E. C.

Different States of Beryllium Oxide. H. Copaux and C. Matignon. (*Bull. Soc. Chim.*, 1925, **37**, 1359–1365.)—Beryllia prepared by calcining a beryllium salt decomposed at not too high a temperature shows properties differing materially with the degree of calcination. For example, the oxide prepared by calcining the basic carbonate at different temperatures showed the following densities at 15°/15° C. :—Calcined at 775° C., 2·876 ; at 875° C., 2·926 ; at 1100° C., 3·010. In order to obtain beryllia in a well-defined state it must be calcined at a sufficiently high temperature, which, when the basic carbonate is used as the initial compound, is of the order of 1000° C.

Analysis of Materials containing a Mixture of Metallic Iron and Iron Oxides. H. C. M. Ingeberg. (*Ind. Eng. Chem.*, 1925, **17**, 1261–1262.)—The reagents required are as follows :—560 grms. of crystallised cupric chloride and 245 grms. of potassium chloride dissolved in 1 litre of water ; 3 grms. of citric acid and 10 grms. of ferric chloride dissolved in separate 100 c.c. portions of the above solution ; and finely powdered manganese dioxide. The total percentage of iron (a) is determined in a portion of the sample, and the percentage of trivalent iron (b) is determined in another portion by placing 0·5 grm. of the sample in a stoppered flask filled with carbon dioxide ; 35 c.c. of potassium cupric chloride and citric acid solution are added while the flask is cooled below 16° C., and the closed flask is set aside for three hours. The mixture is then filtered, the insoluble portion washed with 2 per cent. citric acid solution until free from copper, and dissolved in hydrochloric acid in an atmosphere of carbon dioxide, and the trivalent iron is determined in this solution. The quantity of chlorine required to oxidise the metallic iron and the divalent iron is determined by placing 0·4 grm. of the sample in a small flask filled with carbon dioxide, adding 10 c.c. of the potassium cupric chloride and ferric chloride solution, and closing the flask with a rubber stopper. After three hours 20 c.c. of concentrated hydrochloric acid are added, the flask is fitted with a Bunsen valve, the contents are boiled for a few minutes, 1 grm. of manganese dioxide is added, and the chlorine evolved on boiling the mixture is passed into a receiver containing potassium iodide solution. The liberated iodine is titrated in the usual way. The quantity of chlorine yielded by a given amount of manganese dioxide is determined separately. If c be the grm. equivalent of chlorine required to oxidise the metallic and divalent iron, the weight of the sample m grms., and x and y the metallic iron and divalent iron, respectively, then $x + y + b = a$, and $3x + y = 55·84 \times 100 \times c/m$, from which equations the percentages of the three forms of iron may be calculated.

W. P. S.

Determination of Molybdenum in Ores. W. Hartmann. (*Zeitsch. anal. Chem.*, 1925, **67**, 152–155.)—The usual method consists in obtaining the metal in solution as molybdate by a sodium peroxide and hydroxide fusion. If tin is present, the solution is warmed, saturated with carbon dioxide, and filtered after some hours' standing. If tungsten is also present, the solution is evaporated to fumes with sulphuric acid, the cold mass diluted with water and hydrochloric acid, and the tungstic acid filtered off; it is dissolved in a little warm sodium hydroxide, and the small amount of molybdenum determined colorimetrically with potassium xanthate, after addition of phosphoric acid. If lime is present in the ore, an acid attack should be made and the molybdenum precipitated by hydrogen sulphide under pressure, as the leaching of an alkaline fusion mass results in the formation of insoluble calcium molybdate. Ores containing lead are decomposed by fusion with sulphur and sodium carbonate.—The alkaline molybdate solution is converted into a thiomolybdate one by addition of freshly-prepared ammonium or sodium polysulphide; molybdenum sulphide precipitated by acidification of such solutions filters easily after short boiling; the precipitate can be washed with hot water without running through the filter. Acidification is usually effected with sulphuric acid; it should here be borne in mind that the ore may contain zinc, the sulphide of which is less soluble in sulphuric than in hydrochloric acid. Zinc and copper sulphides do not separate readily from polysulphide solutions. Molybdenum sulphide is precipitated quantitatively by acidification of thiomolybdate solutions provided they are free from the lower oxyacids of sulphur: hence the use of freshly-prepared alkaline polysulphide. In presence of thiosulphate, etc., a partial reduction takes place, and a little molybdenum remains dissolved, forming a blue solution. In such a case the filtrate from the sulphide precipitate should be oxidised with hydrogen peroxide, and the treatment with ammonia, polysulphide, and acid repeated. The repetition of this treatment on a clear and colourless filtrate may often give a discoloured sulphur precipitate: this is almost invariably due to vanadium. The sulphide precipitate is converted into trioxide (in which form molybdenum is weighed) by roasting. It is not necessary to dry the paper and incinerate it separately; the moist filter and precipitate are dried, then heated more strongly, on an asbestos mat. When the excess of sulphur has been volatilised, roasting is continued until the oxide appears pale and begins to become crystalline.—The purity of the weighed oxide is ascertained by solution in warm dilute ammonia: silica, ferric oxide, alumina (and copper oxide, if substantial) remain undissolved, their combined weight being ascertained and subtracted. Any dissolved copper oxide is determined colorimetrically. The clear warm filtrate is next digested with excess of ammonium chloride, and with ammonium sulphide, giving zinc (and copper) sulphide. For a vanadium test the ammoniacal solution is evaporated with excess of sodium hydroxide until all the ammonia is expelled. The residue is transferred with water to a small distillation apparatus and distilled with a little potassium bromide and a large excess of strong hydrochloric acid in a current of carbon dioxide. The bromine liberated by the vanadic acid is received in potassium iodide solution and measured with thiosulphate.   W. R. S.

Examination of Plated Articles. A. Sauerland. (*Chem. Zeit.*, 1925, **49**, 1078–1080.)—The base metal is plated with the noble metal either by welding or electrolysis. If plated on one side only, the article is described as *doublé*; *triplé* is plated on both sides. Gold-plated alloys are attacked with a mixture of nitric (1 : 4 water) and tartaric acids previously warmed to 40° C. When the action is over, the acid is filtered, and the gold pellicles warmed gently with a few c.c. of fresh acid mixture, which also is filtered off. The residue is washed with distilled water, dried at 120° to 150° C., and weighed. The underside of the pellicles, if dark or black, proves the article to have been welded ; if the two sides of the pellicle are equally lustrous, it has been deposited electrolytically. The composition of the pellicle (gold, silver, copper) is ascertained by fire assay; the base metals are determined by the usual methods in the acid extracts. The examination of silver-plated articles is more complicated ; electrolytic solution, with the test-piece as anode (tension 3 to 3·5 volt) is most reliable. A platinum wire is used as cathode, sulphuric acid (1 : 5 water) as electrolyte ; the silver plating remains undissolved. If it is of appreciable thickness, digestion with *aqua regia* (3 volumes of hydrochloric and one of nitric acid, 10 of water) will leave a silver pellicle superficially converted into chloride. This can be reduced to metal by ignition in coal-gas. Generally speaking, the distribution of the silver in the article may not be ascertainable, in which case only the total silver content of the plated article can be given. Platinum-plated gold articles can be split up only by anodic solution in 5 per cent. cyanide solution ; platinum is not attacked. However, the plating is generally pure platinum; hence a determination of total platinum in the article suffices. If the plating consists of a platinum-palladium alloy, the two metals are determined separately by a wet method ; their combined weight is to be taken as that of the plating. A platinum plating is often applied to a white-gold base. As this alloy often contains platinum and palladium, the composition of the plating can only be ascertained by thorough scraping of a sufficient amount of material, and determination of the platinum (palladium) in the base. The total platinum content of the plated article is also determined ; the composition of the plating can be calculated.   W. R. S.

Benzoylmethylglyoxime as a Precipitant for Palladium. J. Hanus, A. Jilek, and J. Lukas. (*Chem. News*, 1925, **131**, 401–402 ; 1926, **132**, 1–4.)— The reagent is recommended instead of dimethylglyoxime, as it is claimed that gold and platinum are not precipitated. The slightly acid solution (6 c.c. of hydrochloric acid per 100 c.c.) is heated to boiling and precipitated with 40 per cent. excess of a 2 per cent. alcoholic solution of the dioxime. After a few minutes' boiling, the precipitate is left to settle for 12 to 24 hours, collected, washed with dilute hydrochloric acid, then with water, dried at 105° C., and weighed. Factor for $(CH_3.C_6H_5CO.C_2N_2O_2H)_2Pd$: 0·2064.   W. R. S.

Study of Ruthenium. IX. Solubility of Ruthenium in Hypochlorite Solutions and an Attempt to Utilise the Reaction for the Determination of the Metal. J. L. Howe and F. N. Mercer. (*J. Amer. Chem. Soc.*, 1925, **47**,

2926–2932.)—When finely divided, ruthenium and its compounds dissolve com-
pletely in alkali hypochlorite solution, giving only ruthenate if excess of alkali
is present, but otherwise a certain amount of ruthenium tetroxide.   By this means
ruthenium may be separated from all other platinum metals except osmium.
When a current of chlorine is passed through a solution of ruthenium in alkali
hypochlorite solution the tetroxide is formed and may be distilled off quantitatively
provided that the hypochlorite is present in considerable excess.   If osmium
also is present, it must be removed by distillation with nitric acid before the
ruthenium is separated.   No satisfactory method has been found of separating
the ruthenium quantitatively and in a weighable form from the tetroxide.

<div align="right">T. H. P.</div>

Physical Methods, Apparatus, etc.

Gallium-in-Quartz Thermometer Graduated to 1000° C.   S. Boyer.
(*Ind. Eng. Chem.*, 1925, **17**, 1252–1253.)—The thermometer tube is made of fused
quartz, and the filling liquid is pure gallium ; this metal has m.p. 29·7° C., and
b.p. 1700° C., and when sealed in quartz tubes under 2 or 3 microns' pressure may
be cooled to −20° C. before becoming solid.   In filling the thermometer a small
quantity of gallium is treated with dilute hydrochloric acid, solidified under the
acid, dried between filter paper and transferred to a small bulb at the top of the
thermometer tube.   The latter is then exhausted, and the metal heated to remove
traces of chloride on the surface and allowed to enter the thermometer tube.   After
removal of gas bubbles which form when the metal comes into contact with the
quartz, the tube is sealed-off below the pre-treatment bulb.   W. P. S.

**Determination of the Heating Value of Coals in Monel Metal Bombs.
J. C. Geniesse and E. J. Soop.** (*Ind. Eng. Chem.*, 1925, **17**, 1197–1199.)—
When a monel metal bomb is used for the determination of the calorific value of
a coal it is possible to apply a correction for the heat evolved by the solution of the
metal.   The correction involves a titration of the bomb washings and a deter-
mination of the total sulphur in the coal.   It is assumed that the amount of
nitrogen oxidised is small and approximately equal to 1·7 c.c. of 0·1 N solution,
that the total sulphur of the coal is oxidised to sulphur trioxide, that part of the
sulphur trioxide remains as sulphuric acid and the rest goes to form copper and
nickel sulphates, and that the amounts of nickel and copper dissolved are in the ratio
of 2 : 1.   The heats of formation and solution of SO_2–O–Aq, Cu–O_2–SO_2–Aq, and
Ni–O_2–SO_2–Aq are 2230, 3975 and 4944 calories per grm. of sulphur, respectively.
For example, a sample of coal showed 6498 calories, contained 2·90 per cent. of
sulphur, and the bomb washings required 0·2 of 0·1 N alkali solution for neutra-
lisation.   Since the nitrogen oxidised would require 1·7 c.c., 1·5 c.c. had reacted
with the monel metal; this 1·5 c.c. is equivalent to $1·5 \times 0·0016 = 0·0024$ grm.
of sulphur.   The total sulphur, 0·0290 grm., plus the 0·0024 grm. = 0·0314 grm.
of sulphur in the nickel and copper sulphates.   The correction is $1/3 \times 0·0314$
$\times 3975 + 2/3 \times 0·0314 \times 4944 = 145$ calories.   The corrected calorific value
$6498 - 145 = 6353$ calories.   The corrected values are within 0·4 per cent. of
those found when a gold lined bomb is used for the determination.   W. P. S.

Application of Capillarity Measurements to Fatty Acid Mixtures. R. Dubrisay. (*Compt. Rend.*, 1925, **181**, 160–162.)—A measurement of capillarity by the drop method, previously described by the author (*Compt. Rend.*, 1917, **177**, 589), affords a sensitive means of differentiating between fatty acids when chemical analysis or ordinary physical methods fail. Thus, when $N/1600$ sodium hydroxide solution is run into a 1 per cent. solution of stearic or myristic acid in benzene the volumes of 10 drops from the same jet are :—

Stearic.		Myristic.		c.c.
0	..	100	..	1·07
25	..	75	..	1·03
50	..	50	..	0·64
75	..	25	..	0·20
100	..	0	..	0·03

Application of this method to the problem of daturic acid shows that this compound differs materially from mixtures of stearic and palmitic acids in its superficial tension, which affords a further proof that it is a chemical entity and not a mixture of other fatty acids. H. E. C.

Photo-electric Determination of Coloured Gases. H. and A. Copaux. (*Compt. Rend.*, 1925, **181**, 1058–1060.)—The method consists in interposing between a photo-electric cell and a source of light a long column of the coloured gas-mixture and measuring the amount of transmitted light with the aid of a sensitive mirror galvanometer. An ordinary 50 c.p. lamp and a photo-electric pile made from the alkali metals is used. The intensity of light is then plotted against known gas mixtures in which the amount of the coloured constituent has been determined by chemical means. The method is applied to mixtures of nitrogen peroxide and air, and the intensity/concentration curve corresponds with the formula $K = \dfrac{1}{C} \log \dfrac{I_i}{I_t}$, where C is the concentration and I_i and I_t are the intensities of light incident and transmitted. The range of the experiment is from about 0·05 to 1·2 per cent. of nitrogen peroxide. H. E. C.

The Polarising Microscope as a Laboratory Instrument. A. V. Blom. (*Chem. Zeit.*, 1925, **49**, 1057.)—For the detection of crystalline substances in amorphous powders such as pigments, or, say, of lead oxalate in lead oxide, the micro-polariscope is far more sensitive than any process of chemical analysis. The difficulty to be overcome is that some anisotropic particles may be concealed in the mass and so not be visible ; to avoid this, a compensator is used which produces a sky-blue interference colour. In this light all such particles show up clearly as bright yellow specks in a blue field in all positions of the analyser, so that it is unnecessary even to rotate the field. Crypto-crystalline particles appear as a dull yellow and are easily distinguishable from true crystals. A special simple type of apparatus, available for particles down to 1μ diameter, is made by Messrs. Reichert. H. E. C.

Transparency of Natural Waters to Ultra-violet Rays.   J. Duclaux and P. Jeantet. (*Compt, Rend.*, 1925, **181**, 630–631.)—Investigation of the penetrating power of ultra-violet rays into water has shown that, whilst the ordinary mineral constituents of potable water do not diminish its transparency, organic impurities have a marked effect.   This fact may be utilised to indicate the purity of a supply by examining a column with ultra-violet rays from 1900–3000 Å.   Three mgrms. of ammonia per litre, or 4 mgrms. of albuminous matter are easily detectable.   Nitrates and nitrites, however, are not differentiated without recourse to chemical tests.   The method of examination, details of which will be given in a subsequent paper, consists in the observation of the ultra-violet absorption spectrum of a column of 50 cm. of the water.   H. E. C.

Reviews.

An Introduction to the Physics and Chemistry of Colloids.   By Emil
  Hatschek.   Fifth Edition.   Pp. xiii. +182.   London: J. & A. Churchill.
  1925.   Price 7s. 6d. net.

Laboratory Manual of Elementary Colloid Chemistry.   By Emil Hatschek.
  Second Edition.   Pp. ix. +153.   London: J. & A. Churchill. 1925.
  Price 7s. 6d. net.

These two books serve admirably as an introduction for the student taking up the subject of colloid chemistry.   The first appeared originally in 1913, and its present edition is substantially the same as that of the fourth edition, which was entirely re-written and enlarged.   It was reviewed in The Analyst (1922, **47**, 188).

For the fifth edition careful revision has been made and some important new matter added, including the work of Porter and Hedges on the vertical distribution of particles in suspension, recent investigations on non-aqueous colloid systems, and on the origin of the electric charge on colloid particles.   Recent work on the complications arising in investigations on adsorption from solution is dealt with in a brief but lucid manner.   The whole of the book is thoroughly up-to-date, concise and eminently readable.

The practical manual has been enlarged to include a wider choice of experiments including important recent work.   The main fields in practical colloid chemistry are introduced by well-selected exercises giving the student an excellent foundation for advanced work later.   William Clayton.

On the Chemistry of the Ancient Assyrians.   By R. Campbell Thompson,
  M.A., D.Litt.   158 folios, 12⅝ inches × 8 inches.   Six plates.   London:
  Luzac & Co.   1925.   Price 25s.

This book is printed in typescript for which the stencils have been cut by

Dr. Thompson himself, and it is illustrated with six plates of cuneiform tablets for which permission has been given by the Trustees of the British Museum. Dr. Thompson's work is so largely philological and depends so much upon the transliteration of the cuneiform characters into Assyrian and Sumerian equivalents, and their Arabic and Aramaic parallels, that it seems inevitable that he should make use of this method of publishing the results of his researches.

The texts which have been deciphered and of which the author gives an account in this work deal almost exclusively with the making of glass and pottery glazes in the seventh century, B.C. They are a notable contribution to the history of chemistry; quite as notable as those on Assyrian medicine which Dr. Thompson described in his "Assyrian Herbal." The recipes for a simple glaze for glazing bricks and for plain glass and varieties of coloured glass have been elucidated to an extent which makes it clear that the Assyrians of those days possessed a considerable knowledge of glass making in general, and of the materials which would produce transparent and coloured glasses. The alkali used seems to have been chiefly the ash of Salicornia and allied plants which consists largely of soda salts. This would probably be in such masses as are indicated in Pliny's well known story of the accidental discovery of glass. The use of ferric oxide, copper, tin and lead preparations, manganese oxide, arsenic as oxide and sulphides, as well as some preparation of gold, was known to these ancient artificers. Dr. Thompson's discussion of the use of gold in conjunction with tin in the preparation of a pink or coral glass leads us to think, with him, that it represents, in the particular formula he is referring to, " the prototype of the Purple of Cassius."

One would like to give other instances of the interest which this book possesses for chemists, but space will not permit. Its value for the students of philology and anthropology, however, must not be altogether overlooked. Dr. Thompson's contribution to the origin of the name "sapphire" is most suggestive, and the translations of the directions for treating the ingredients in the furnaces together with the means adopted for propitiating malignant influences by the use of "embryos," throw considerable light on rites observed by alchemists in later times.

The volume is enriched by two addenda, an excellent bibliography and five indexes. It is a very valuable contribution to science in the broadest acceptation of the word.

W. KIRKBY.

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY. Vol. VI. By J. W. MELLOR, D.Sc. Pp. vi. +1024. London: Longmans, Green & Co. 1925. Price 63s.

The first 134 pages of this volume deal with some of the compounds of carbon, but do not include cyanides and the combustion of hydrocarbons, which, the author states, may be considered in a supplementary volume. The remaining pages contain a very extensive account of silicon and its compounds, the treatment

accorded to silicates being undoubtedly the most exhaustive which has been published hitherto, and in this respect English-speaking chemists are extremely fortunate.

Dr. Mellor has regarded mineralogy as a subordinate branch of chemistry, inasmuch as it concerns the chemistry of minerals, and consequently considerable attention has been devoted to the great preponderance of naturally occurring silicates. The compilation of this matter must have been one of great difficulty in view of the amazing chaos which prevails, for, unlike the chemistry of carbon compounds, there appears to be no guiding principle ruling in their formation and constitution, in spite of such theories as the Werner Co-ordination Theory, the Hexite-Pentite Theory of W. and D. Asch, and the Complex Aluminium Silicate Theory of F. W. Clarke.

So far as the reviewer has been able to ascertain, the subject-matter includes work published up to 1925. Thousands of references are given, and in one case, that of Section 44 on the Alkaline Earth Aluminium Silicates, they take up no less than 33 complete pages. The value of the volume is greatly enhanced by the fact that many of the references scattered throughout the book are to memoirs, published in journals which are seldom within the reach of the chemist. Needless to say, ceramic chemistry, on which it will be remembered the author is a leading authority, finds a place in the volume, and is, moreover, covered by an excellent bibliography.

In conclusion, the heartiest congratulations of all chemists are again due to Dr. Mellor on producing yet another volume of his invaluable Treatise—one which will be of inestimable service to both the mineral chemist and the geologist.

HUBERT T. S. BRITTON.

THE CHEMISTRY OF WHEAT FLOUR. C. H. BAILEY, Ph.D. Pp. 323. Chemical Catalog Company, Inc. Washington. 1925. Price $4.

This book is one of the extensive American Chemical Society Monograph series, a series undertaken by the Society by arrangement with the Inter-allied Conference of Pure and Applied Chemistry of 1919.

Following a short historical chapter comes a chapter dealing with wheat in its relation to flour composition, in which the reader is introduced to the extremely numerous varieties of the wheats of the world, by name, and curious indeed are the names of wheats. Then comes a valuable, and rather unusual, chapter on the growth and development of the wheat plant and kernel. The influence of environment on the composition of wheat, the impurities in commercial wheat and the storage and handling of wheat are the subject matter of the next three chapters, succeeded by chapters on the chemistry of roller milling, ageing and colour and bleaching of flour. Flour strength in relation to enzyme phenomena and the colloidal properties of dough are dealt with in the two concluding chapters. Flour improvers are not considered, by intention, the author considering himself restricted by the definition of flour. Fortunately flour bleaching, in virtue of being related

to the colour of flour, is not excluded and references to the improving effect of chlorine gain access through a similar loophole. The bio-chemistry of baking is again, by intention, not discussed at any length, though the baking properties of flour are naturally the chief consideration of the last two chapters. Adequate Author and Subject indexes are included.

A striking feature of the book is the bibliography, containing about 650 references, and the book may be shortly described as an expansion of this bibliography, or an explanatory index of the work done on the chemistry of flour during the past twenty-five years with a bias rather towards American wheat— a reflection of the activities of the American State Agricultural Stations.

The result of this manner of presentation of the subject is that the book is an admirable and complete chronicle, but, so it seems to the reviewer, a rather dull chronicle. Of guidance there is but little, and the views of the author himself are hard to find. It is to be regretted that an author of the standing of Prof. Bailey does not indulge in more summing up of the present position and more pointing to the better of the roads that have to be trodden by cereal chemists in the immediate future. E. HINKS.

THE SCIENCE OF SOILS AND MANURES. By J. ALAN MURRAY, B.Sc. Pp. xiv.+298. London: Constable. 1925. Price 12s. 6d. net.

The third edition of this work has just been published, and in the preface it is stated that former editions found favour with Indian and Colonial planters and cultivators, as well as with farmers and gardeners in England, and that this edition should prove not less suitable for candidates for University degrees and College diplomas in agriculture and horticulture.

The work consists of 298 pages of printed matter divided into well defined chapters dealing with the physical, chemical and biological properties of soils, and then with their fertility, subsequent chapters being devoted to fertilisers; an appendix completes the book.

The work is written in clear and readable language, the author making his points, wherever possible, in a series of steps which are easily understood. However, detailed reasoning can be somewhat overdone, and passages such as "When a large stone is broken, two or more smaller ones are produced," do not seem altogether necessary. Again, the information that, if a particle of dust obtained from a stone be shattered into 100,000 pieces, that they would still be stones, is difficult to understand; but it may be presumed that this depends on one's idea of a stone.

The physical properties of soils are dealt with in practically 50 pages, and most phases of the subject are touched. The process given for the mechanical analysis of soils is stated to be the one now practised in this country, and consists in first sifting the soil through a 3 millimetre sieve with subsequent digestion of the fine earth with N/5 hydrochloric acid. Filtration and washing of the residue with water follow, when the residue is dried, ignited and weighed. The ignition of this

residue is a questionable procedure, and it would only seem reasonable to assume that the ignition would have an influence on the fineness of the fine earth. As extensive analyses have already been published, and made without this ignition, the process, for instance, published by Russell in *Soils and Manures*, might well have been adhered to, particularly as no material shortening of the process results from the modification.

A chapter on the chemistry of soils is not only well written, but it also contains a large amount of information in a very compact form. The author touches on both practical and theoretical aspects, and the student requiring more detailed information is repeatedly referred to papers or books dealing more fully with the question being dealt with. Empirical processes are outlined in several cases, and their practical utility commented on, but the author wisely abstains from more than casually mentioning reasons why results so obtained should fail to give satisfactory results when applied on a farm. A considerable amount of attention is paid to the fixing of nitrogen and to the nitrifying organisms found in soils; indeed, a large proportion of the matter dealing with the biology of soils is centred round these organisms.

The fertility of soils is dealt with in a dozen pages, and information that might have been included in this chapter is contained in other portions of the book. One ordinarily looks for information concerning the factors which limit the yield of various soils under this heading. Possibly for space economy, the manuring of farm and garden crops is only dealt with in a very cursory manner; but the title of the work suggests that only the science of manuring is dealt with, and not necessarily the commercial application of manures.

When dealing with phosphatic manures no fewer than four pages are devoted to a detailed description of the Bessemer process for the production of basic slag, which, we are finally informed, is now obsolete. In these circumstances, it is somewhat misleading to give a complete analysis of an old basic slag and to give very little information about the percentage composition of slags produced by the "Open Hearth" Process. Spent bone char is still used as a manure, and, though the statement is made that it contains no nitrogen, samples usually contain about 1 per cent.

Fish residues prepared for use as a fertiliser are referred to as "fish meals," formerly known as "fish guanos." To-day both terms are in common use, and a reference to merchants' price lists at once indicates that both the trader and the farmer understand a fish guano to mean a substance for use as a fertiliser, and fish meal to be a product suitable for use as a feeding stuff. It is a common practice, however, to distinguish the latter commodity by calling it "feeding fish meal." Whale guanos are included as fish meals without comment. Many, however, would take exception to this, particularly as, until recently, the whale product was worth considerably less than fish. The presence of large amounts of oil in fish is stated to retard the action of fish manures, and it is recommended that a 3 per cent. maximum oil limit should be demanded by purchasers. A maximum

standard of 5 per cent. of oil has been suggested in the case of feeding fish meals for certain reasons, but it is found in practice that this percentage is invariably exceeded. Generally, a fish guano contains somewhere about 8 to 13 per cent. of oil, and these guanos are accepted as quickly acting organic fertilisers, the demand exceeding the supply. It is doubtful whether an ordinary fish guano ever contains less than 5 per cent. of oil, though in the case of a small quantity of special fish waste this limit may not be exceeded. Under these conditions it is difficult to reason that an impossible practical standard should be demanded for the oil content of a fish guano.

Hoof and horn meals, when in a fine state of division, probably do not act as slowly as the author imagines, and, though they may be considered an adulterant if found in meat meals, their use for this purpose is unlikely, owing to the high value of hoof and horn meal.

An appendix of some two dozen pages completes the book. This appendix gives a wide variety of tables containing a large number of figures of great utility. Opinion varies respecting the position in a book which tables should occupy. Generally speaking, however, it may be stated that the appendix is the last portion of a book which is turned to when information is sought, and, therefore, it is possible that many tables given in this appendix could, with greater convenience to the student, have been given in the text.

The book is printed on paper of good quality, and the type is clear, and, as the author's style is lucid, the book should certainly appeal to anyone requiring information suggested by the title of the book. A feature of the book which particularly requires commendation is that of cross-indexing, and in almost every case when further information is obtainable in the book on a question being discussed, the page giving further information is clearly stated.

<div align="right">F. W. F. ARNAUD.</div>

PARRY'S CYCLOPAEDIA OF PERFUMERY. By E. J. PARRY, B.Sc., F.I.C. 2 Vols. Pp. 840. London: J. & A. Churchill. 1925. Price 36s. net.

This work fills a distinct gap, for it supplies a much-needed summary of scientific information on the source, composition and examination of the raw materials used in perfumery. Mr. Parry has been assisted in his task by several chemists* who are also recognised as scientific authorities on the subject of essential oils, and it is, therefore, hardly necessary to say that the book is clearly written, full of specialised information, and, so far as the reviewer has been able to test it, is a trustworthy guide.

Being arranged in the form of a dictionary, it can be consulted readily, and in most cases will give the chemist who is not a specialist in the subject the information he seeks, whilst, at the same time, much of it can be understood by those who deal commercially in these products but are not chemists.

* Messrs. C. T. Bennett, M. Dewhurst, T. H. Durrans, A. W. Garden, M. Salamon and W. H. Simmons.

The articles, grouped alphabetically, range in length from concise descriptions of the less important oils or constituents of oils, to fairly long treatises on the more important oils and groups of compounds. One of the most noteworthy is that on *Perfume in the Plant,* which discusses the genesis and functions of perfumes in plants; it fills thirty pages. Another important and very readable article is that on the *Perfume of the Rose* (32 pages), in which the subject is treated from the historical, scientific and practical points of view.

Analytical methods are found under the headings for various oils, etc. It would be an advantage if the more important of these were summarised and discussed (with cross references) under a special section on *Analysis,* which would then be complementary to the long section on *Distillation.*

A further improvement would be a fuller use of references to analytical methods. In some instances quantitative methods and tests of purity are described at some length, as, for example, under *Alcohol,* which even includes the tables used in the Government Laboratory, but in some other instances (*e.g. Glycerin*) the references to methods are not sufficient.

In this connection it would be advisable to point out that determination of the strength of commercial acetic acid from the specific gravity is only approximately correct for the lower strengths, and may be as much as 2 per cent. in error in the case of 80 per cent. acid.

These suggestions are put forward, not to detract from the value of a useful work, but with the idea of increasing its usefulness in the next edition, which will probably soon be required.

EDITOR.

Publications Received.

PRACTICAL PHYSIOLOGICAL CHEMISTRY. By S. W. COLE. 7th Edition. Cambridge: Heffer & Sons. Price 16s. net.

APPLIED CHEMISTRY: A PRACTICAL HANDBOOK FOR STUDENTS OF HOUSEHOLD SCIENCE AND PUBLIC HEALTH. Vol. II. FOODS. By C. K. TINKLER and HELEN MASTERS. London: Crosby Lockwood & Son. Price 15s. net.

THE SYNTHESIS OF BENZENE DERIVATIVES. By S. C. BATE. London: Ernest Benn, Ltd. Price 21s. net.

THE USE OF SOLVENTS IN SYNTHETIC ORGANIC CHEMISTRY. By D. W. MACARDLE. London: Chapman & Hall. Price 15s. net.

LA DETERMINATION COLORIMETRIQUE DE LA CONCENTRATION DES IONS HYDROGENE. Par I. M. KOLTHOFF. Paris: Gauthier-Villars et Cie. Price 50 fr.