THE ANALYST

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

The Estimation of Narcotine and Papaverine in Opium.

By H. E. ANNETT, D.Sc., F.I.C., and M. N. BOSE, M.A.

(*Read at the Meeting, November* 1, 1922.)

The published methods for the estimation of narcotine are those of Caspari (*Apoth. Zeit.*, 1904, **19**, 874), of Van der Wielen (*Pharm. Zeit.*, 1903, **48**, 267, and *Bull. Soc. Pharm.*, 1910, **17**, 59–63), and of the Imperial Institute (*Bull. Imp. Inst.*, 1915, **13**, 522).

We have already shown (Annett and Sen, Analyst, XLVI, 1920, 321) that Van der Wielen's method is unsatisfactory, whilst Caspari's method requires such large amounts of opium that it was useless for our work.

We made use of the method of the Imperial Institute in our preliminary work on opium. It is not convenient in manipulation, and can at best only give approximate results.

Plugge (*Arch. Pharm.*, [3], **25**, 793–811) showed that on the addition of sodium acetate to a solution containing opium alkaloids the only ones precipitated are papaverine, narcotine and narceine. He did not, however, meet with success in applying the reaction to the quantitative estimation of these alkaloids in opium.

After repeated attempts to obtain a reliable method for narcotine estimation we decided that a method based on the foregoing observation of Plugge gave the greatest promise of success.

We studied the reaction more in detail, and found that narcotine and papaverine can be completely precipitated by sodium acetate from a faintly acid solution of these alkaloids. Of the other opium alkaloids, narceine is the only one precipitated in any quantity. This is of no importance, however, since, on washing the precipitate produced by sodium acetate on a filter with water, narcotine and papaverine are quite insoluble, but the whole of the narceine goes into solution and so passes through the filter.

When, however, sodium acetate is added to an aqueous solution of opium, the precipitate produced contains large amounts of colouring and resinous matters, in addition to the three alkaloids named. These impurities can, however, be easily separated from the alkaloids, for they are readily soluble in dilute sodium hydroxide solution, whereas narcotine and papaverine are insoluble.

It is worth noting that narceine is soluble in dilute sodium hydroxide solution, and so would be removed by this treatment, even if it were not entirely removed in washing the precipitates produced by sodium acetate.

NEW METHOD.—The following are the details of the method as finally devised by us:—The opium (1·5 grms.) is rubbed up in a mortar to a pasty condition with 4 to 5 c.c. of 0·5 per cent. sulphuric acid, the acid being run in from a burette. More acid is then run in, with continual stirring, until 30 c.c. in all have been added. The liquid is stirred up with a pestle at intervals during half an hour and then filtered. Twenty c.c. of the filtrate (=1 grm. of opium) are taken for the estimation. They are placed in a small beaker, heated to boiling on a water bath, and an addition of 16 grms. of sodium acetate made.

The heating is continued until all the acetate has gone into solution. The beaker is well shaken and allowed to stand overnight. Its contents are filtered, and the precipitate completely transferred to the filter paper and well washed with water. The filter paper is then dried in the water oven. This renders much of the resinous and colouring matters insoluble on treatment with toluene, which is the next stage. To facilitate easy extraction with toluene, the dried precipitate is roughly powdered by rubbing one side of the paper against the other. Hot toluene is run through the filter into a separating funnel, 20 to 25 c.c. in all being used. Twenty c.c. of 10 per cent. sodium hydroxide solution are added to the toluene, and the funnel gently shaken in order to extract resinous and colouring matters from the toluene solution. The sodium hydroxide solution is then run off, and the toluene shaken twice successively with its own volume of water to remove sodium hydroxide.

The toluene is evaporated almost to dryness in a weighed glass dish, and 2 to 3 c.c. of alcohol added to facilitate crystallisation. Narcotine and papaverine rapidly separate in beautiful clusters of crystals. After drying in the oven at 100° C., they are weighed as narcotine and papaverine. The result we claim to be an accurate measure of the narcotine and papaverine content.

The narcotine in the product can then be estimated by a polarimetric process, depending on the fact that narcotine is strongly optically active, whilst papaverine is inactive.* The polarimetric estimation cannot, however, be carried out in acid solution, since in acid solution papaverine, though inactive itself, considerably depresses the optical activity of narcotine. Work on this point is being published elsewhere. We therefore dissolve the narcotine and papaverine in a known volume of toluene, filter the solution and examine it in a saccharimeter with

* If this polarimetric process be used, it is desirable to take a larger sample of opium, say 5 grms., for the analysis. The larger quantity of narcotine then available renders the polarimetric reading more trustworthy.

white light. Under these conditions papaverine has no influence on the optical activity of narcotine. Since we find that 2 grms. of pure narcotine dissolved in 100 c.c. toluene give a reading of −16·87 at 32° C. in the Hilger saccharimeter used, it is a simple matter to calculate the narcotine content of our product.

The following results illustrate the process:—Three samples of opium, A, B and C,* analysed, gave 7·65, 5·93 and 4·89 per cent. of narcotine plus papaverine respectively. Portions of 0·5, 0·4 and 0·4 grm. were weighed off from the product in the case of samples A, B and C respectively, and each was dissolved in 25 c.c. of toluene, filtered and its optical rotation read in a 200 mm. tube. The readings obtained were −15·35°, −12·61° and −12·21° respectively. If the product had been pure narcotine, the readings should have been −16·87, −13·50 and −13·50 respectively. Hence the samples contained the following percentages of narcotine and papaverine:—

	A.	B.	C.
Narcotine	6·97	5·54	4·42
Papaverine	0·69	0·39	0·47

TEST EXPERIMENTS WITH THE METHOD.—A. TESTS WITH PURE ALKALOIDS.—Experiments were made with pure narcotine, papaverine and narceine, singly and mixed in various proportions. The alkaloids were in each case dissolved in 20 c.c. of 0·5 per cent. sulphuric acid, the solution heated, and 20 grms. of solid sodium acetate added, the heating continued till all the salt had passed into solution, and the beaker allowed to stand overnight. The alkaloids were recovered exactly as we have described in the case of opium. The table sets out the results:

Expt. No.	Alkaloid taken	Grm.	Total alkaloids recovered Grm.
1	Narcotine	0·1250	0·1205
2	,,	0·1000	0·0973
3	,,	0·0750	0·0728
4	,,	0·0500	0·0483
5	Papaverine	0·0250	0·0250
6	,,	0·0125	0·0124
7	,,	0·0075	0·0073
8	Narceine	0·0250	0·0005
9	,,	0·0125	0·0010
10	Narcotine Papaverine	0·1000 0·0125	0·1078
11	Narcotine Papaverine	0·1000 0·0075	0·1034
12	Narcotine Papaverine Narceine	0·1000 0·0125 0·0125	0·1088

The recoveries of alkaloid both in the case of narcotine and papaverine must be considered satisfactory. In the case of the experiment with 0·1250 grm. of

* In the case of these samples 5 grms. were taken for the analysis.

narcotine there was a loss of 4·5 mgrms. of alkaloid. This is not very serious, and was the biggest loss we found. The results obtained with narceine show that this alkaloid cannot interfere with the method.

B. TESTS WITH OPIUM.—(*a*) *The quantity of sodium acetate required for precipitation of the alkaloid.*—Less sodium acetate is required to precipitate alkaloids from solutions of pure alkaloids than is required to precipitate the same amount of alkaloids from an opium solution. Thus, though we used 20 grms. of sodium acetate in the foregoing experiments with pure alkaloids, experiments have shown that less than half this quantity actually suffices. A series of experiments, however, showed that it was advisable to use 16 grms. of sodium acetate under the conditions we employ in opium analysis. These experiments will now be described.

An extract of opium was made with 0·5 per cent. sulphuric acid, and 4 portions each of 20 c.c. (=1 grm. opium) were taken. To each were added 8, 12, 16, and 20 grms. of sodium acetate respectively. The narcotine and papaverine were then recovered as described in the method, dried in the oven and weighed. The following results were obtained:

	1	2	3	4
Sodium acetate, grms.	8	12	16	20
Narcotine and papaverine obtained, grm. ..	0·0978	0·1067	0·1118	0·1119

It thus appears that, under the conditions we employ, 16 grms. of sodium acetate are required to precipitate all the narcotine and papaverine. We have made other experiments on this point and have obtained exactly similar results. It should be noted that the sample of opium used in the foregoing experiments was exceptionally rich in narcotine, and as 16 grms. of sodium acetate were sufficient in this case, they should be more than sufficient in the case of samples of opium with a lower narcotine content.

(*b*) *The necessity for acid in the extraction of the alkaloids from opium.*—It might be thought at first that water would dissolve all the narcotine and papaverine in an opium sample, owing to the acid reaction of the opium. We have found, however, that this is not the case under our conditions, and therefore we used weak acid (0·5 per cent.). In an experiment we estimated the narcotine and papaverine content in two portions each of 1·5 grms. drawn from the same sample of opium, by extraction in one case with 30 c.c. of water, and in the other with 30 c.c. of 0·5 per cent. sulphuric acid, as in our method. We obtained 0·0943 and 0·1119 grm. of alkaloids respectively in the two cases, thus showing the need for extraction with slightly acid water.

(*c*) *Quantity of opium required.*—In our method we take 1·5 grms. of opium and extract it with 30 c.c. of 0·5 per cent. sulphuric acid, and we take 20 c.c. of this (=1 grm. of opium) for precipitation of narcotine and papaverine with 16 grms. of sodium acetate. An advantage of our method is that it can be carried out on any quantity of opium from even 0·5 grm. up to large quantities of 10 grms. or more. In practice, however, we always use proportionate quantities of reagents. We give below figures obtained for the narcotine

and papaverine content of a series of opium samples analysed both in 1·5 grm. and in 5 grm. samples. In the case of the 5 grm. samples we extracted the opium with 100 c.c. of 0·5 per cent. sulphuric acid, and took 90 c.c. of the filtrate for precipitation with 90 grms. of sodium acetate. As a matter of fact, 72 grms. of the sodium acetate would have been sufficient, but at the time we analysed the 5 grm. samples we had been using 20 grms. per 1 grm. of opium. The following results were obtained:

Sample No.	1.5 grm. sample 20 c.c. = 1 grm. taken for precipitation. Narcotine + papaverine actually obtained	5 grm. sample 90 c.c. = 4·5 grms. taken for precipitation	
		Narcotine and papaverine actually obtained	Narcotine and papaverine calculated to 1 grm. opium
	Grm.	Grm.	Grm.
321	0·1118	0·5018	0·1115
322	0·0963	0·4545	0·1009
324	0·0823	0·3457	0·0768
386	0·0901	0·4026	0·0895
387	0·0676	0·3233	0·0718
388	0·0578	0·2567	0·0570

A comparison of columns 2 and 4 shows very satisfactory agreement, and so gives one confidence in the method. We have analysed the same sample of opium many times over by our method, and the results always agree very closely. To give one example, Sample 321 has given the following weights of narcotine plus papaverine on different occasions, the weight in each case corresponding to 1 grm. of opium:—0·1118, 0·1119, 0·1096, 0·1106, and 0·1116 grm.

(*d*) *Analyses of opium, with and without known added amounts of narcotine and papaverine.*—Five grms. of opium, Sample No. 321, were triturated with 100 c.c. of 0·5 per cent. sulphuric acid. From the filtrate three 20 c.c. portions, A, B and C, each equal to 1 grm. opium, were taken. To B and C were added 0·0100 and 0·0200 grm. of pure narcotine respectively. The narcotine and papaverine in A, B and C were then precipitated by the addition of 16 grms. of sodium acetate, and the estimation completed as usual.

The results were as follows:—A, 0·1116; B, 0·1207; and C, 0·1308 grm.

On the basis of the results obtained with A, the results for B and C should have given 0·1216 and 0·1316 grm. respectively, *i.e.* within 1 mgrm. of the actual result obtained.

A similar experiment was carried out with papaverine. Four portions, A, B, C, and D, each of 20 c.c., of solution were prepared as in the previous experiment, also from sample 321. To C and to D were added 0·0150 grm. with pure papaverine. On analysis, as before, we obtained 0·1096, 0·1106, 0·12[illegible] c.c. and 0·1218 grm. of narcotine plus papaverine respectively. The aver[illegible]one results from A and B, and C and D, were 0·1101 and 0·1210 grm. respectively[illegible]ps. Thus we recovered 0·0109 grm. of papaverine as against 0·0150 grm. add[illegible]cid

This is not such a close agreement as was obtained with narcotine, but the loss only amounted to 4·1 mgrms.

CONCLUSION.—A satisfactory and convenient method for the estimation of narcotine and papaverine together in opium has been devised. It is claimed that it gives accurate results, and it has the advantage that practically any weight of opium may be used for the analysis, no correction factors being required. The alkaloids are obtained in a pure condition. The method has been in use in the authors' laboratory for some time with excellent results.

Note on the Sulphuric Acid Test for Fish Liver Oils.

BY NORMAN EVERS, B.Sc., F.I.C., AND H. J. FOSTER.

(*Read at the Meeting, December* 6, 1922.)

THE sulphuric acid reaction for fish liver oils, depending on the production of a violet colour on the addition of a drop of sulphuric acid to a drop of the oil or a solution of the oil, has recently developed an increased importance from the observation of Drummond and Watson (ANALYST, 1922, **47**, 341) that the power of an oil to give this test runs parallel with the vitamin *A* content of the oil. Moreover, the test is not confined to fish liver oils, but is given by other oils rich in vitamin *A*, such as butter fat.

While making some experiments on the technique of the test we were led to add an oil which itself gave no colour with sulphuric acid, in order that the concentration of oil might be the same in each case. To our surprise, the sensitiveness of the test was very greatly increased, although we could not obtain the faintest trace of colour with the added oil in any amount. To take an example: A quantity of 0·04 c.c. of a cod-liver oil was the minimum amount which would give a violet colour, but, after the addition of 0·1 c.c. of olive oil, 0·01 c.c. of the cod-liver oil was the minimum amount giving a colour. This property was found to be possessed by all the natural oils or fats of animal or vegetable origin which were tried. Moreover, approximately the same amount of each oil was necessary in order to give the maximum sensitiveness to the test. Mono-palmitin, mono-olein, di-olein, oleic acid, stearic acid, and liquid paraffin did not possess this property. The property is completely destroyed by oxidation (heating to 120° C. for eight hours in a current of air), and by saponification, but is not destroyed by hydrogenation, since hardened oils had the same effect as the natural oils. Cholesterol prepared from sheep's brain had no auxiliary effect; further, the unsaponifiable matter of cod-liver oil, which consists chiefly of cholesterol, gave the colour in a much more pronounced degree after the addition of a natural oil. Cholesterol, therefore, cannot be the auxiliary factor, and since animal oils act in the same way as those of vegetable origin, it cannot be phytosterol.

It is known that old oils which have become oxidised, or those which have been oxidised in the laboratory, do not give the violet coloration, but, instead, give a brown coloration, the colouring matter of which dissolves in the petroleum spirit in exactly the same way as the oil in the same minimum amount as the violet colouring matter of the original oil. It is also increased by the addition of natural oils to the same extent. The brown compound therefore appears to be an oxidation product of the violet colouring matter, and, as it appears somewhat more stable than the violet compound, an investigation of it might lead to some interesting results.

Evidently, as a result of this observation, we cannot compare the results given by two oils with the colour test, unless we secure a maximum sensitiveness by the addition of another oil, because the increase in the colour is not in the same ratio with all oils. For instance, in the case of one cod-liver oil the minimum amount of that sample necessary to give a colour was reduced to one-fourth by the addition of olive oil, but in the case of a cod-liver "stearin" weaker in chromogenic substance the amount was only reduced by a half, and in the case of butter fat no difference was observed after the addition of the oil.

TECHNIQUE OF THE TEST.—Drummond and Watson (*loc. cit.*) in their work used a solution of the oil in petroleum spirit. Droop Richmond and England (ANALYST, 1922, **47**, 431) have suggested the use of liquid paraffin, adding one drop of the sulphuric acid to ten drops of the liquid paraffin solution and stirring the mixture. From an examination of the test it appears that the colouring matter is produced on the surface of the sulphuric acid and dissolves off into the solvent, but that too long contact with the sulphuric acid destroys the colour. The objects to be aimed at in carrying out the test are, therefore, (1) a large surface of sulphuric acid in contact with the solvent, and (2) minimum time of contact between the sulphuric acid and the oil. The second point is attained by the use of a light solvent such as petroleum spirit, and the first by shaking the sulphuric acid violently with a portion of the solvent, so that the acid is broken up into small drops, and adding the mixture to a solution of the oil in the remainder of the solvent. We find that the best solvent is petroleum spirit (b.pt. 40 to 60° C.) which has been thoroughly shaken with concentrated sulphuric acid and separated. Treatment with sulphuric acid is essential, because we have found certain samples of petroleum spirit which, although normal in other respects, contain some substance which seriously mars the sensitiveness of the test, and in some cases prevents the formation of any colour at all. Treatment with sulphuric acid appears to remove this impurity. We therefore carry out the test as follows:—The required amount of oil, or of a solution of the oil in petroleum spirit, purified as above, is measured into a test-tube; two drops of olive oil or some other natural oil, which itself gives no suspicion of colour with the test in any quantity, are added, and then petroleum spirit to 3 c.c. Seven c.c. of petroleum spirit are shaken violently in a small stoppered cylinder with one drop of sulphuric acid until the acid is completely broken up into small drops. The mixture is then quickly poured into the test tube. The drops of acid

rapidly sink to the bottom, the violet colour forming in the petroleum spirit as they sink. In this way the colour is uniformly distributed throughout the solution, and the results are more consistent. Care must be taken that only small drops of sulphuric acid do not fall into the test-tube.

Carrying out the test as above (with addition of olive oil), we obtained the following results with various samples of oil:

Oil	Minimum quantity giving colour c.c.	Colour
Cod-liver oil (cattle)	0·01	blue-violet
Cod-liver oil (Newfoundland) (unrefined)	0·015	,,
Cod-liver oil (North Sea A.)	0·015	,,
Cod-liver oil ,, ,, B.	0·015	,,
Cod-liver oil (refined), unknown origin	0·015	,,
Whale oil	0·015	red-violet
Ling-liver oil	0·02	blue-violet
Cod-liver oil (North Sea C.)	0·03	,,
Cod-liver oil (Norwegian) (unrefined)	0·035	,,
Cod-liver oil (Norwegian) (refined)	0·035	,,
Mixed liver oil (unknown origin)	0·07	,,
Cod-liver "stearin"	0·08	red-violet
Butter (three samples A, B & C)	0·2	,,
Butter D	0·2	brown

Though only four samples of butter have been tested, all gave the same minimum figure, but in one case the colour was brown, showing that oxidation had taken place. In a rough way, one may say that the less natural colouring matter the oils contained the lower down in the table do they appear; *e.g.* slightly coloured Norwegian oils are weaker than the more deeply coloured North Sea oils, but there are insufficient data for any generalisation on this point.

The above work was carried out in the Analytical and Research Department of Messrs. Allen & Hanburys Ltd., to whom our thanks are due.

Discussion.

Dr. J. C. Drummond said he thought we had not got very much further with the study of this colour reaction; the colour was not strictly proportional to the vitamin value of the oils examined, and variations might be due to differences in the petroleum spirit employed, while the presence of water or alcohol, in minute traces, weakened the test. It appeared that the colour reaction was mainly due to one substance, but the assumption that it was due to more than one substance might explain a rather disturbing factor, viz. the different shades of colour.

Mr. Evers, in replying, said that he thought the facts upon which Dr. Drummond based his contention might be explained by the presence of some unsaturated body—which might be removed by sulphuric acid. He considered the variations in the shades of colour were due to the amount of oxidation which the oil had undergone.

Sliding Scales for the Convenient Titration of Strong Liquids by Dilution and Use of Aliquot Parts.

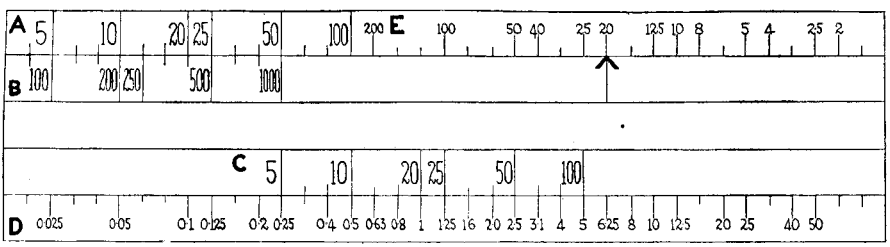
By C. H. D. CLARK, B.Sc., D.I.C., A.I.C.

(*Read at the Meeting, December* 6, 1922.)

Part I.

In the course of a certain investigation, it became necessary to compare the concentrations of a large number of solutions of widely varying strengths with that of a single standard solution. For this purpose, the ordinary method of dilution to a known volume and titration of aliquot parts was employed. The problem was to select quickly the most convenient dilution for the purpose, and the sliding scale, No. 1, here described, has greatly facilitated the work.

Scale I.



The calibrated pipettes employed delivered 5, 10, 20, 25, 50, and 100 c.c. respectively, and the measuring flasks contained 100, 200, 250, 500, and 1000 c.c. All the possible combinations involving the use of these measuring instruments have been considered, and the results are presented as concisely as is believed to be possible.

The scale may be quickly made out of a piece of folded ruled foolscap paper, which allows a second piece to slide inside it. A cursor can be arranged in addition, but this is by no means essential. The numbers must be copied exactly as shown, with spaces as indicated, the scale marks being at even distances.

There are 5 scales, A, B, C, D, and E; of these, A and C are identical, and B and C are on the slide. A shows the number of c.c. of strong liquid taken, B the volume to which this is made up, and C the amount of the diluted solution measured out. The arrow shows on scale E the ratio in which the volume has been increased, and only when this arrow is opposite a number on the scale do any suitable numbers on scales A and B coincide. The numbers on scale D give the required values.

Thus, for instance, supposing 5 c.c. of an approximately 12 *N* solution are diluted to 100 c.c., and 50 c.c. are taken, scale D shows the number 2·5, which means that $12 \times 2{\cdot}5 = 30$ c.c. of a *N* solution will be required for that aliquot part. Evidently the dilutions 5 to 100, 10 to 200, and so on, all correspond to an increase of volume of 20 times, and this is shown by the arrow on scale E. A very short investigation of the arrangement will show the principle upon which it is based.

The number on scale D is, therefore, the multiplier to convert the normal factor of the original solution into a value indicating the number of c.c. (if A, B and C are measured in c.c.) of a *N* solution required by the measured part.

The way in which the scale can be most conveniently employed is, however, by a reversal of the direct process explained above. Suppose we have an approximately 8 *N* solution, and desire to titrate it with a *N* solution, then, if a burette reading of 30 c.c. is considered convenient, the value of the multiplier is 30 divided by $8 = 3{\cdot}8$, and the nearest number to this on scale D is 4. If, therefore, different values on scale C be set opposite to this number on scale D, and the corresponding numbers which come opposite to each other on scales A and B are noted, it will be seen that with scale C at 5 and 25 no result is produced, but that the following will give the desired effect:

Dilute 100 c.c. to 250 c.c. and take 10 c.c.
,, 20.....100.....20....
,, 50.....250.....20....
,, 100.....500.....20....

and so on, taking out 50 c.c. or 100 c.c. on scale C. Which of these alternatives is selected will depend on which calibrated instruments are at hand, and on the amount of the original liquid available.

The case shown above is simple, and if only one dilution were required a rapid calculation would render the scale less necessary, but when a large number have to be made, I have convinced myself that there is a great saving of time and trouble when the scale is employed. A very little study of the scale will, I think, prove its usefulness and general applicability in volumetric work in the cases for which it is designed.

Joint Meeting of the Society of Public Analysts and Other Analytical Chemists and of the Nottingham Section of the Society of Chemical Industry.

(Held at Nottingham on January 17, 1923.)

Editorial.—For the first time in their history a joint meeting of our Society and of a Local Section of the Society of Chemical Industry has been held, more than 50 of our members going to Nottingham on January 17 to take part in a discussion on "The Estimation of Arsenic."

We were met at the station by Mr. Burford (Chairman), Mr. Wilkie (Hon. Secretary), Mr. H. D. Richmond and other members of the Local Section, and, after being shown over the works of Messrs. Boots Pure Drug Co., Ltd., we adjourned to dinner, as guests of the Section. A general invitation was also given to any of our members to accept hospitality for the night from individual members of the Section. The meeting was held in the evening in the lecture theatre of Nottingham University, where there was a crowded audience, who followed the discussion with keen interest.

Mr. H. D. Richmond may be congratulated on the success of the scheme, which he was the first to suggest, and the officers and members of the Nottingham Section upon the way in which the arrangements were carried out, while we who were made so welcome have incurred a debt of gratitude for the kindness shown to us both individually and as representatives of our Society.

THE DETECTION AND ESTIMATION OF SMALL AMOUNTS OF ARSENIC.

THE chair was taken by Mr. Burford, Chairman of the Nottingham Section of the Society of Chemical Industry, who, in welcoming the meeting of the two Societies, stated that it was largely due to the efforts of Mr. H. D. Richmond, Major Trotman and Mr. J. M. Wilkie.

Mr. A. CHASTON CHAPMAN, in opening the discussion, recalled that a similar discussion had been initiated in 1901 by Mr. Trotman in Nottingham, and that in 1902 the report of a Joint Committee of the two societies was issued. He mentioned that he had directed attention to the use of the Reisch method for detecting distinct contamination of brewing materials with arsenic (ANALYST, **1901, 26,** 8). Subsequently it became evident that a more delicate test was required, and the Joint Committee (1901) recommended a modification of the Marsh-Berzelius method, which was capable of detecting $\frac{1}{500}$ mgrm. of arsenic. In 1904 an "official" method was described by Dr. (now Sir E.) Thorpe (*J. Chem. Soc.*, **1904, 83,** 974), as the result of the investigations of a committee appointed by the Board of Inland Revenue.

Mr. Chapman stated that the Gutzeit test, as modified by the substitution of mercuric chloride for silver nitrate, gave a higher degree of certainty than the original method. It was useful as a sorting test, but the Marsh-Berzelius process, in one form or another, must be regarded as the standard method for the estimation of traces of arsenic.

After summarising his procedure, Mr. Chapman stated that if zinc of satisfactory quality were coated with cadmium sensitiveness of a high order was

obtained, with perfect blanks and correct mirrors of $\frac{1}{100}$ to $\frac{1}{250}$ mgrm. In his experience the intensity of the arsenical mirror obtained from materials containing phosphoric acid or phosphates was not in any way proportional to the amount of sample used, *i.e.* 4 grms. would not yield a mirror twice as heavy as 2 grms.

Mr. J. M. WILKIE stated that his experience was mostly with the electrolytic method. He called attention, however, to recent American work which seemed to point to the general substitution of rod zinc for granulated zinc in the zinc-acid method. His electrolytic apparatus (shown to the meeting) was essentially a combination of Sand and Hackford's apparatus with that of Thorpe, but with the use of a more opaque porous pot, and it also included Harvey and Hibbert's modification of the Gutzeit apparatus, in which the mercuric chloride paper was secured by means of a clip. His experience had led him to the conclusion that it was essential for the whole of the arsenic to be in the arsenious condition before the introduction of the material into the apparatus, and it was to be noted that the reaction appeared to be reversible. The results of experiments with potassium metabisulphite as a reducing agent, as first used by Thorpe, indicated that discrepancies observed might be due to the presence of small amounts of other sulphur derivatives. The objection to stannous chloride was that it was capable of reducing sulphuric acid and was liable to precipitate and coat the electrode. A small amount of potassium iodide was excellent as a reducer, but it required the use of an absorbent for the iodine liberated from it in acid solution. Terpin hydrate was suitable for the purpose. About 1 grm. of glycerin was added per 25 c.c., and also 5 drops of 10 per cent. potassium iodide solution, the liquid boiled to reduce the arsenic, and about 0·1 grm. of terpin hydrate added; this yielded terpineol which absorbed the iodine. It was subsequently found that glycerol which had been oxidised with permanganate acted similarly to terpin hydrate and had the advantage of being soluble in water. One c.c. of 80 per cent. glycerol is mixed with a tenth of its volume of 50 per cent. sulphuric acid and to the mixture two c.c. of 5 per cent. potassium permanganate are added. When colourless, the reagent is ready for use. With this reagent the hydrogen iodide is maintained at its original concentration. In analysing ferric salts he had found that, if only small quantities were used, the results agreed with those obtained in the absence of iron. In the case of *Ferri Ammon. Cit.*, for instance, 0·5 to 1 grm. was taken, and the iron reduced by using a small quantity of iodide in conjunction with sulphite in sufficient amount to give a nearly colourless solution at boiling temperature. Normal iodine solution was then added, drop by drop, until the solution was slightly tinted, the liquid then heated to boiling point, and, after the addition of the oxidised glycerol, again heated to boiling, and set aside for a few minutes. To preserve the porous pot of the apparatus in an active condition it was necessary to remove deposited iodine. This was readily done by placing the pots, when not in use, in a bath of 10 per cent. sulphuric acid containing an excess of sulphite. In the light of his experience he was of opinion that lead wool should only be used as an indicator in the Gutzeit test, and not as an absorbent, *i.e.* large amounts of reduced sulphur acids should never be put into the pot. He had found the best developer for the stains to be hydrobromic acid (of 10 to 15 per cent. strength). The sulphuric acid electrolyte was unsuitable in certain cases, notably in that of calcium salts; with lime, etc., a hydrochloric acid electrolyte was used, and different preliminary treatment was required. For the destruction of organic matter, satisfactory results could be obtained by the use of an arsenic-free solution of magnesium nitrate, with the addition of cotton wool to prevent frothing. Evaporation could then be effected directly over a hot flame.

Dr. G. MONIER-WILLIAMS pointed out that the greatest disadvantage of the zinc method was the influence of the personal equation, and he would always

advocate the electrolytic method unless constant practice were possible. He demonstrated the use of his form of electrolytic apparatus, which was a modification of that used in the Government Laboratory.* It was capable of detecting $\frac{1}{1000}$ mgrm., and could be used even by an inexperienced chemist.

Major TROTMAN was of opinion that the preliminary treatment of the material was the crucial point of the estimation. Errors in judgment had also a good deal to do with discrepancies in the results. He thought that it would be a suitable subject for a conference which could settle a standard process, as had been done, *e.g.* in the analysis of butter and the valuation of tanning materials.

Dr. L. T. THORNE stated that in the case of sugar and beer he could get $\frac{1}{500}$ mgrm. of arsenic with certainty, and $\frac{1}{1000}$ mgrm. fairly well. He had found the sodium method of purifying the zinc the most suitable, and an addition of cadmium then rendered the product sensitive, whilst if it became too active a trace of lead was added. Impurities in hydrochloric acid were removed by heating the acid with a copper-zinc couple, followed by decantation and re-distillation. The destruction of organic matter was suitably effected by heating a mixture of sulphuric and nitric acid in a second flask, and conducting the fumes into the sulphuric acid containing the organic material; the arsenic from the nitric acid then remained in the generating flask.

Mr. H. DROOP RICHMOND thought that the want of sensitiveness of the zinc was largely due to the presence of iron, which formed ferric salts, and that these caused oxidation, if non-reversibility were not ensured. This seemed the most important result of Mr. Wilkie's work.

Mr. J. WEBSTER said that, notwithstanding what had been said about the zinc method, he personally would keep to the electrolytic Marsh method. He never felt quite sure with zinc, for after running a control for half-an-hour and getting no trace of arsenic, a mirror would sometimes suddenly appear. He had had no experience with lead electrodes, but he put the limit of sensitiveness with platinum electrodes at $\frac{1}{500}$ mgrm. He had found potassium metabisulphite a satisfactory reducing agent. When working with a large organ like the liver there was necessarily a large multiplying factor; in one case he had made a gravimetric estimation of the amount on a large quantity as sulphide, and had found that it agreed well with the result of the Marsh test on a small portion.

Mr. JENSON stated that he had found the electrolytic process to be sensitive to about $\frac{1}{1000}$ mgrm. He combined it with the Gutzeit test, using a strip of mercuric chloride paper fitting tightly inside the tube.

Dr. B. DYER mentioned that by alloying the zinc with 0·1 to 0·2 per cent. of pure electrolytic copper it was attacked much more rapidly by acids, but was insensitive until the cadmium was added.

Mr. WEAVER advocated the use of a standard method of expressing the results. He agreed with previous speakers as to the necessity of using freshly-prepared mercuric chloride papers for the Gutzeit test, since, otherwise, owing to the action of moisture, no stain at all might be formed.

Mr. J. T. CONROY, in a letter read by Mr. Wilkie, suggested that manufacturers of food products might fix a limit for the arsenic content in any chemicals used in the preparation on the assumption that the whole of the arsenic in the chemical finds its way into the food.

Mr. P. A. ELLIS RICHARDS (President) and Mr. E. R. BOLTON (Hon. Secretary) expressed the thanks and appreciation of the Society of Public Analysts and other Analytical Chemists for the hospitality which had been shown to them by the Nottingham Section.

* A description of this apparatus will be published in a later issue.—EDITOR.

Note.

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.

AN ABNORMALITY FOUND IN WATER ANALYSIS.

As the writer is not aware of any previous mention of the point in chemical literature, it may be worth while to make brief record of an abnormality which has been encountered in water examination on two occasions and in samples of totally different origin.

In the first case the sample concerned was a peaty water from a small loch in the Orkney Islands, and in the second a water from a well, 11 feet deep, in Co. Kerry. The former sample was of satisfactory quality for drinking purposes; the latter gave some evidence of excretal pollution, was "dirty," and frothed on shaking.

The abnormality was most marked in the second case, and its cause was found in the estimation of albuminoid ammonia by Wanklyn's process. After the free ammonia had been estimated in the usual manner, it was found that, on addition of alkaline permanganate for the albuminoid ammonia estimation, the permanganate was almost completely reduced, and the distillate fractions gave such a marked yellowish-white precipitate on addition of Nessler's reagent that even approximate estimation of the albuminoid ammonia was impossible. In this connection it is interesting to note that Bougault and Gros (ANALYST, **1922, 47,** 405) have recently shown that such a precipitate is given by certain ketones.

ROBERT C. FREDERICK.

ROYAL NAVAL COLLEGE MEDICAL SCHOOL,
GREENWICH.

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.

FEDERATED MALAY STATES.

REPORT FOR 1921. CHEMICAL SECTION.

INSTITUTE FOR MEDICAL RESEARCH, KUALA LUMPUR.

THE total number of samples examined in the Government laboratories during the year was 5330. Of these, 55 were stained articles to be tested for blood, and 12 gave reactions characteristic of human blood in the precipitin test.

Toxicological.—Fifty-eight exhibits were examined for poison, 36 of which were human viscera. Arsenic was found in 5, morphine in 4, mercury in 2, opium in 1, alcohol in 1, and both arsenic and strychnine in 1 exhibit.

Chandu.—Fifty-three samples were examined and 6 found to contain illicit opium. Morphine estimations were also made in 118 samples of chandu dross, and the amount found to vary from 7·6 to 1·8 per cent.; average 5·58 per cent.

Milk.—The total number of samples examined, mainly under the provisions of the "Sale of Foods and Drugs Enactment, 1913," was 460. Of these, 16 per cent. were deficient in milk solids, and certificates were issued with respect to 78 samples which failed to comply with the standards.

Other samples examined included 48 for deleterious drugs, 647 alcoholic liquors, 345 of toddy, and 59 miscellaneous samples, including paint, alum, flour, urine, and fæces.

Coins and Coining Materials.—The total number of exhibits examined was 2995, of which 2948 were counterfeit, and 9 genuine coins. The remainder of the exhibits were moulds and pieces of metal.

R. W. BLAIR.

TRINIDAD.

ACCORDING to reports published in the Trinidad papers by Mr. H. Shrewsbury, the Government Analyst, the percentage of food and drugs of all kinds found to be adulterated in the Government laboratories has steadily fallen from 65·3 per cent. in 1891 to 6·6 per cent. in 1921.

Referring to the communication of Joseph and Martin on tropical milk (ANALYST, 1922, **47**, 426), the Government Analyst states that, while he is not prepared to make so strong a statement with regard to Trinidad, he has realised by experience that the Trinidad standards for milk (3·0 per cent. of fat; 8·5 per cent. of solids-not-fat) are lenient in the extreme, and that any effort to lower them affects the elementary rights of the public in that Colony. Even with the present standard, adulteration was very prevalent a few years ago, but there has been a continuous and marked decrease in the percentage of milks found to be adulterated, the figure having fallen from 59 per cent. in 1891 to 6·7 per cent. in 1921.

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.

ARSENIC IN COCOA.

TWO summonses issued by the Surrey County Council under the Sale of Food and Drugs Act, 1875, were heard at the Richmond Police Court on December 18th, 1922. The first summons was against the Home and Colonial Stores, Ltd., for selling cocoa "adulterated with arsenic (arsenious oxide) to the extent of one-fortieth grain per pound." The second summons was against Messrs. Rowntree and Co., of York, for aiding and abetting in the commission of the offence.

Mr. R. O. B. Lane, prosecuting, stated that a quarter of a pound of cocoa had been bought by an inspector of the Council. It was labelled "Home and Colonial pure cocoa essence, highest grade quality, guaranteed absolutely pure." A sample

sent to the public analyst was found to contain one-fortieth of a grain of arsenic per lb. Further enquiries were instituted, and it was found that the cocoa in question was a blend of seven different cocoas, one of which was manufactured by Messrs. Rowntree. Samples of the seven different cocoas were supplied, that of Messrs. Rowntree was found to contain one-tenth of a grain of arsenic per pound. The cocoa had been supplied as pure, and that the authorities' test showed that it had been so guaranteed without a sufficient test having been applied.

Mr. Travers Humphreys, for the defence, said that Messrs. Rowntree and Co. took absolute responsibility for the position in which the Home and Colonial Stores had been placed. The Stores bought from Messrs. Rowntree what they believed to be pure cocoa. Messrs. Rowntree wished to put before the public that in the opinion of competent scientific men there was not the smallest cause for anxiety as to illness or danger to the public from drinking this cocoa. What happened was that last July Messrs. Rowntree were informed by some chemist that some loose cocoa supplied contained faint traces of arsenic. Everything in the place was analysed, and finally it was found that the impurity was in the carbonate of potash, which had been used for years in small quantities to make the cocoa soluble and more digestible. They had instantly sacrificed the whole of the cocoa (350 tons), in order that nothing more might go out of their works. They had succeeded in getting supplies of alkali quite free from arsenic. Supplies of this cocoa had been sent out to the trade, but they had decided that it was absolutely useless to try to get it back. They had come to the conclusion that it was in the interests of the public not to create a quite unjustifiable scare.

Counsel asked the Bench to say that Messrs. Rowntree were not guilty of negligence, but were the victims of misfortune.

The Bench imposed a fine of 40s. upon the Home and Colonial Stores, on behalf of whom it was stated that they had at once withdrawn 65 tons of the cocoa from their shops and 20 tons from their warehouses, involving them in a loss of £12,000.

Messrs. Rowntree and Co. were fined £20, with 50 guineas costs.

ALLEGED DETERIORATION OF HYPOCHLORITE SOLUTION IN THE TROPICS.

F. A. Langley v. *"Milton" Manufacturing Co. Ltd.*

IN this case, which was heard in the King's Bench Division on December 18th, 1922, an action was brought to recover damages for breach of an agreement under which plaintiff was to sell the defendants' disinfectant "Milton" in S. America. Damages were also claimed for breach of warranty as to the quality of the disinfectant supplied.

Plaintiff's case was that he had been unable to sell any of the goods since they were not of the quality, strength or description represented, and were, he said, wholly worthless. "Milton" was usually put up in brown bottles, but that shipped to the plaintiff was in green bottles, and in hot countries, he submitted, the climate had a deteriorating and disintegrating effect on all such liquids. Defendants wrote regretting that the disinfectant had been put up in green bottles, as that might have had some deteriorative effect, and they offered to replace the shipments at their own cost; but plaintiff asked for reimbursement of his expenditure and indemnification against claims and his lost profit.

For the defence it was contended that there was no warranty of any kind. The disinfectant was perfectly good when it was shipped, and what happened to it afterwards was of no legal consequence.

Evidence was given by a consulting chemist that he had never known "Milton" lose its strength in this country, as plaintiff said it did abroad. Its basis, sodium hypochlorite, was the basis of a number of disinfectants, and all were unstable. In the case of "Milton" kept at 125° F. for 6 months he had found a reduction of hypochlorite by nine-tenths at least. In one case it went down from 1 per cent. to 0·13 per cent. in 5 months ending March, 1921.

Mr. Justice Branson, in giving judgment, said that plaintiff was suing defendants for breach of an agreement made verbally. It seemed unlikely that an agreement should be made by which plaintiff took all the risks of importing this fluid into hot countries. He found as a fact that plaintiff's account of the conversation which took place was true, and that a definite assurance was given that the fluid would be reliable in the country into which it was intended to import it.

Judgment for the plaintiff was given, with damages for £1630.

The Rowett Institute.

FIRST REPORT, 1922.

THE Rowett Institute was established in 1913 at Aberdeen as an Institute for Research in Animal Nutrition, and, under an arrangement between the Development Commission Scheme of Research and the Scottish Education Department, the research work is carried out in close co-operation with the North of Scotland College of Agriculture. This report includes an account of the development of the Institute, a description of the building and lands, and a report on the research work carried out in 1914, and in the years 1919 to 1922. The following particulars of some of the principal experimental work show the nature of the investigations undertaken by the Institute.

1. MINERAL REQUIREMENTS OF ANIMALS.—The feeding experiments with pigs were based on the assumption that sow's milk contains protein and different minerals in the proportions required for a growing pig (proteins, 7·25; lime (CaO), 0·41; and phosphoric anhydride (P_2O_5), 0·35 per cent.). Whilst sow's milk contains 1 part of lime to 16 parts of protein, maize has only 1 part of lime to 450 of protein, and oats, the best balanced of the feeding stuffs used for pigs, has 1 part to 75. The ratio of lime to phosphorus is also in the wrong direction. By adjusting the grain ration by the addition of mineral salts to give a total mineral content similar to that of sow's milk the young pigs grew at a normal rate in perfect health.

Pigs suffering from a form of malnutrition common in the district ultimately recovered when a mixture of salts rich in lime was added to their ration.

Analogous beneficial results were obtained in experiments with sheep, and afford a partial explanation, at least, of the effect of adding certain feeding stuffs, such as fish meal and milk residues, to a ration of grains and grain offal.

The effect of an excess of minerals in the case of a lactating goat was to cause a slight decrease in the volume of milk, but little, if any, alteration in the percentage composition of the ash of the milk. In the case of breeding ewes, however, a group receiving no addition of lime salt (calcium chloride) produced 21 healthy lambs, whereas the group receiving lime salt produced only 6 living lambs.

2. VITAMINS.—Feeding experiments with pigs extending over a period of 128 days gave no indications that boiling of the food had interfered with the health of the animals, or that the addition of vitamins had been accompanied by any marked beneficial effects. Young pigs fed on a diet deficient in anti-scorbutic vitamin showed no signs of ill effects after 110 days, whereas guinea pigs fed on the same diet succumbed in 3 weeks. The possibility of pigs suffering from deficiency of anti-scorbutic vitamin, under any conditions likely to occur in practical farming, seems remote. The pig is also much less susceptible to deficiency of the fat-soluble vitamin A than the rat. The influence of cod-liver oil on the pig was less marked than on other animals. It is probable that the rations commonly given to pigs contain a sufficiency of vitamin A to promote growth.

Experiments with sheep indicated that cod-liver oil has a much greater influence on the rate of growth of sheep than on that of pigs.

So far as present information goes, the payment of exorbitant prices for feeding stuffs stated to be rich in vitamins is not warranted. Any deficiency which may ultimately be indicated can be made good from cheap and easily available foodstuffs.

3. RICKETS.—Results of experiments have indicated that in pigs, at least, the chief factor in the production of rickets is the lack of proper amount and balance of the mineral matter in the food, and that the beneficial effect of fat-soluble vitamin A and sunlight on mineral metabolism is most marked in cases where the mineral balance of the food is defective.

4. LACTATION.—A correlation has been established between the daily output of nitrogen in the urine and the percentage of non-protein nitrogen in the milk. Both appeared to be determined by the amount of protein in the food.

The inter-relationship of daily volume and composition has suggested to Dr. W. Taylor the following theory of milk secretion:—The flow of milk is determined by a process of osmosis, and as the osmotic pressure depends mainly upon the amount of lactose present, the rate of the elaboration of lactose, therefore, is the factor that determines the secretion of milk. There is a state of osmotic equilibrium between blood and milk, and the lactose is kept at a more or less constant level by the flow of fluid from the blood to the milk. With a greater flow the other constituents of the milk suffer dilution, and, consequently, there tends to be an inverse proportion between the percentage of lactose and that of the other constituents. The percentage of lactose increases at the beginning of lactation, and decreases at the end, and the alteration in the daily volume at these periods is determined by the concentration of the lactose.

Samples of complete milkings have been obtained from 726 cows in all the counties of Scotland, and their physical and chemical constituents have been determined and the results statistically analysed by Dr. J. F. Tocher. Of the 726 samples, 40 had less than 3 per cent. of fat, 168 had less than 8·50 per cent. of solids-not-fat, and 55 less than 8·25 per cent. The average percentage of fat was 4·09, and that of the solids-not-fat 8·75.

A negative correlation of −0·56 was found between total protein and lactose. An increase of lactose is, therefore, accompanied, on an average, by a decrease in total protein. The correlation between casein and ash was positive (0·48).

The injection of adrenaline or ergamine had no influence on the rate of secretion of milk.

5. INDIRECT CALORIMETRY.—Expired air was collected by means of a mask with inlet and outlet valves, and was received in a rubber bag. It was analysed by the use of a modification of Haldane's gas apparatus, by which the percentages of carbon dioxide, oxygen and methane were estimated. Since, in the fermentation in the rumen, approximately 2·6 parts of carbon dioxide are

produced for one part of methane, it is possible to estimate how much of the total carbon dioxide has been produced in the tissues and how much in the fermentation process.

In a series of experiments on a goat with various common diets, the average heat output before the morning meal was 0·648 calories per minute, and about an hour later 0·855 calories. The difference represents the "work of digestion."

6. PROTEINS.—Experiments on pigs indicated that the rations usually given probably contain too small a proportion of proteins for very young animals, and too large a proportion for those in the later stage of growth.

In an investigation on the value of protein for the production of work it was found that from 2 to 10 per cent. more energy was expended by a man on a high protein diet, than by the same man on a high carbohydrate diet.

From experiments on the influence of water on protein metabolism the conclusion is drawn that animals, especially milk cows, which are offered water only once a day, utilise their rations less completely than those which can have water at more frequent intervals.

7. FEEDING TESTS WITH BY-PRODUCTS.—Experiments with fish meal have indicated that its beneficial effects are due to its yielding an ample supply of protein and of well-balanced mineral matter. Milk residues, such as "dried whey solids" and "dried lactalbumen," prepared by the Ministry of Agriculture at Crewe, are particularly valuable for growing animals. Samples of these products had the following percentage composition:

	Protein	Fat	Carbo-hydrate	Salts	Water
Solids of whey from which fat has been separated	12	1	69	8	10
Lactalbumen	76	2·5	7·5	3	14

Experiments with distillery residues gave satisfactory results, and a gallon of "pot ale" was apparently equivalent to about half a pound of meals.

8. ANALYSIS OF FOODS.—Analyses of about 900 human foods were made by Dr. Plimmer (*cf.* ANALYST, **1921**, **46**, 478).

9. HOUSING EXPERIMENTS.—The results indicated that the evil effects of an ill-balanced diet on pigs are accentuated by lack of light and poor ventilation. Even with a sufficient and well-balanced diet, however, light has evidently a pronounced influence on nutrition.

10. INFLUENCE OF NUTRITION ON THE INCIDENCE OF DISEASE.—Investigations have been carried out on the cause of certain diseases in sheep.

Distinctive Colouring for Poisons.

REPORT OF THE CODEX SUB-COMMITTEE TO THE COUNCIL OF THE PHARMACEUTICAL SOCIETY.*

A REPORT of experiments made for the Codex Sub-Committee with regard to the colouring of B.P. solution of strychnine hydrochloride was made on November 28, 1922, and is published with the permission of the Privy Council. After preliminary experiments with brilliant green, methyl violet, rosaniline hydrochloride, Bordeaux red, and orange OO, it was decided that methyl violet and brilliant green were the most suitable, and further tests were instituted to ascertain whether these dyes were inert, and not such as to interfere with delicate analytical tests, and so prevent the identification of strychnine.

* *Pharm. J.*, 1922, 109, 564–565.

Samples of the B.P. solution of strychnine hydrochloride were coloured with 0·004 per cent. of brilliant green and methyl violet respectively.

It was found that in each case the dye could be separated from the strychnine by shaking with chloroform in acid solution, and that neither dye, therefore, would be in the least likely to interfere with the detection or estimation of the alkaloid.

Both dyes are very unstable both in acid and alkaline solutions, especially in dilutions comparable with normal dispensed mixtures containing the B.P. solution of strychnine hydrochloride. As a result of these experiments it is recommended that, as a tentative and experimental regulation, the B.P. solution of strychnine may receive colour to the extent of 0·004 part by weight of brilliant green to 100 parts by volume of the solution. Brilliant green is recommended as being more distinctive than methyl violet. The action of reagents on the dye is not likely to prove inconvenient to dispensers or to the public.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Chemistry of the Strength of Wheat Flour. H. E. Woodman. (*J. Agric. Sci.*, 1922, **12**, 231–243.)—The strength of flour does not depend on the total quantity of its proteins, gliadin and glutenin, but appears to be connected with the identity of the glutenin. Ordinary chemical methods fail to reveal any differences between the gliadins and glutenins in strong and weak flours, but the application of the racemisation method (*cf.* Woodman, ANALYST, 1921, **46**, 504) shows that, though the gliadin in the two flours is identical, the glutenins are distinct chemical individuals. Gliadin and glutenin were separated from a strong (Manitoba) flour and from a weak (English) flour and their behaviour compared when racemised by dilute alkali at 37° C. under different conditions. The gliadin in the two flours had $\alpha_D^{37} = -93{\cdot}69°$ and a mean combining weight of 5077 (determined by titration in 80 per cent. alcohol solution with sodium hydroxide solution), from which figure it is inferred that there are three, or a multiple of three, free carboxyl groups in gliadin; the racemisation curves are the same. The glutenins show distinct differences in their optical behaviour; that from Manitoba flour had $\alpha_D^{37} = -99{\cdot}5°$ and that from English flour had $\alpha_D^{37} = -78{\cdot}8°$ in 0·5 per cent. solution in 0·04 N sodium hydroxide, and the racemisation curves were quite distinct. It appears, therefore, that the strong wheat synthesises one type of glutenin and the weak wheat a different type; intermediate strengths may be due to varying proportions of the two glutenins. Investigation of the action of alkali on solutions of glutenin at room temperatures has shown that the proteins can be extracted by means of 0·2 per cent. potassium hydroxide solution without suffering change.

H. E. C.

Estimation and Identification of Flours by Means of Standard "Crude Fibre" Types. A. Fornet. (*Chem. Zeit.*, 1922, **46**, 969–970.)—Pekar's method of valuing flours by comparing their colours with those of standard flours (König, *Chem. menschl. Nahr. Genussm.*, 1914, **3**, (ii), 536) is not applicable to baked products. In such cases a microscopical examination of the crude fibre isolated by the usual method of treatment with acid and alkali is made, and the colour and structure and size of particles of the residue compared with the characteristics of standard "crude fibres," analogous to Pekar's standard flours. It is shown by a series of illustrations that there is a remarkable agreement in the microscopical appearance of the "crude fibre" isolated from flours of different kinds and degrees of milling and from bread baked with the same flours. The method is also applicable to other substances such as spices, starch, chocolate powder, etc.

Analytical Elutriation Methods of Separating Cacao Husk from Cocoa Powder. R. Whymper. (*Trans. Faraday Soc.*, 1922, **18**, 49–52.)—The levigation processes for the estimation of shell in cocoa are reviewed, and the method of Baker and Hulton (ANALYST, 1918, **43**, 197) is considered most satisfactory when the husk and the cocoa have simply been ground together. Wind-sifting is, however, now general in the trade, and no method yet devised will separate well-washed finely-ground and wind-sifted husk which has been added to cocoa of the same degree of fineness. It is pointed out also that ash figures yield no information not only on account of de-fatting and treatment with alkali, but also because certain beans, *e.g.* Trinidad and Venezuelan, are commonly treated with clay to secure brightness and render them less liable to attack by moulds. H. E. C.

Estimation of Sugars by the Use of Iodine. F. A. Cajori. (*J. Biol. Chem.*, 1922, **54**, 617–627.)—The author has shown experimentally that dextrose is quantitatively oxidised to gluconic acid in a solution containing 1 or 2 per cent. of sodium carbonate and not less than three times the quantity of iodine theoretically required. At the ordinary temperature this reaction is completed in 25 minutes, and under these conditions neither lævulose nor sucrose is oxidised. By the use of this reaction, in conjunction with the reducing power on Benedict's or other copper solution and subsequent hydrolysis followed by estimation of the reducing power to either iodine or copper, data are obtained from which the amounts of dextrose, lævulose and sucrose in a mixture of these sugars may be readily calculated. During the progress of this work the most satisfactory conditions for the hydrolysis of sucrose were found to be heating the solution to 60° C. with 1 per cent. hydrochloric acid for 2 hours. Under these conditions the hydrolysis was completed without any destruction of the lævulose produced. Maltose is unaffected by similar treatment, and continuation of the heating for 24 hours causes only partial hydrolysis. This sugar is oxidised by iodine in a similar manner to dextrose, but requires a period of 35 minutes for complete oxidation. By employing maltase, in conjunction with the iodine and copper reducing powers, maltose may be estimated in a mixture containing any or all of the above sugars. The iodine method yields results accurate to within 3 per cent. when applied to

pure sugars, but the majority of sugar solutions contain other substances capable of reacting with iodine, and these must be removed before trustworthy results are obtainable. T. J. W.

Reaction Distinguishing between Acids derived from the different Sugar Groups. L. J. Simon and A. J. A. Guillaumin. (*Comptes rend.*, 1922, **175,** 1208–1211.)—Following on the work of Chavanne (*Ann. Chim. Phys.*, 1904, **3,** 507), the authors have prepared methyl-isopyromucic acid by distillation of the lactose of rhamnonic acid with sodium bisulphate, and describe the physical and chemical properties of this substance. Further investigation has led to the development of the following reaction: About 0·2 grm. of the acid or its salts, esters or lactone, is mixed with 0·5 grm. of finely powdered sodium bisulphate in a test tube of small diameter, the contents of which are strongly heated. A drop of ferric chloride solution is added to the liquid drops condensed on the cooler part of the tube, and the production of a transient green colour indicates the original presence of a dibasic hexose acid or a monobasic pentose or methylpentose acid. If no coloration is obtained, the presence of a monobasic hexose acid is indicated, and, on cautious oxidation of the original substance followed by a repetition of the above test, a positive reaction will confirm this. T. J. W.

Estimation of Gums in Sugar Products. H. T. Ruff and J. R. Withrow. (*J. Ind. Eng. Chem.*, 1922, **14,** 1131–1134.)—A method proposed for the estimation of gums in raw sugars, syrups, etc., is based on the precipitation of the gums by ethyl alcohol in a solution acidified with hydrochloric acid. Twenty c.c. of the sugar solution (which should contain about 50 per cent. of solids and be free from suspended matters) are weighed and acidified with 1 c.c. of concentrated hydrochloric acid, and 100 c.c. of 93 per cent. alcohol are added slowly while the mixture is stirred thoroughly. After fifteen minutes, the precipitate is collected on an asbestos filter, washed with alcohol, dried at 100° C. for one hour, and weighed. The filter and its contents are then ignited, cooled, and again weighed. The difference between the two weighings represents the weight of the gums present. W. P. S.

Guava Fruit. A. Azadian. (*Ann. Falsif.*, 1922, **169,** 405–408.)—The author has made a study of *Psidium guava piriferum* and *pomiferum*, the two varieties of guava most cultivated in Egypt. The proportion of seeds in the fruits varies from 6 per cent. in the larger fruits to 12 per cent. in the smaller. On boiling 200 grms. of fruit with successive portions of distilled water, filtering the liquid through muslin, and making the filtrate up to one litre, the solution gave on analysis:—Dry extract, 8·25; ash, 0·84; invert sugar, 3·65; and total sugar, 8·25 per cent. The separated seeds contained: Moisture, 10·30; proteins, 15·25; total ash, 0·84; alkalinity of ash as K_2O, 0·40; tannin, 1·30; fat, 14·3; cellulose, 42·40; and starch, 13·25 per cent. Average figures for the extracted oil were:—Specific gravity at 15/15, 0·9274; n_D^{40}, (Zeiss), 1·4632; saponification value, 197·1; iodine value, 131·1; acid value, 0·55; volatile acids, soluble, 0·26; insoluble, 0·25; essential oil, 0·27 per cent. The dried leaves contained 8·75 per cent. of tannin. D. G. H.

Oil of the Mexican Poppy. (*Bull. Imp. Inst.*, 1922, **3**, 292–294.)—The Mexican or prickly poppy (*Argemone mexicana*) is now common to most tropical and sub-tropical countries, where it grows wild. Seeds examined at the Imperial Institute were round and dark brown, with an average weight of 0·002 grm. They contained 7·7 per cent. of moisture, and yielded, on extraction with petroleum spirit, 36·5 per cent. of a brownish yellow limpid oil possessing a slightly acrid odour. The oil had the following characteristics:—Specific gravity at 15/15° C., 0·9220; n_D^{40}, 1·466; solidifying point of fatty acids, 22·8° C.; acid value, 21·6; saponification value, 192·7; iodine value, 123·7 per cent.; unsaponifiable matter, 1·14 per cent.; volatile acids, soluble, nil; insoluble, 1·16 per cent. The residual meal contained:—Moisture, 10·2; crude proteins, 24·6; and ash, 7·7 per cent. The oil was found to be unsuitable for paint or varnish or for edible purposes, and the meal could not be used for cattle feeding owing to the purgative action of any remaining oil, and the presence of an alkaloid. The oil would be suitable for soap making, and the meal as a valuable manure. D. G. H.

Detection of Diethylphthalate and Phthaleins in Spirits. R. L. Calvert. (*Amer. J. Pharm.*, 1922, **94**, 702–703.)—Diethylphthalate is employed in America as a denaturant for alcohol intended for use in perfumery, in the proportion of 2·5 per cent. In spite of the bitter and disagreeable taste of this compound, such denatured alcohol is frequently met with in whiskey, and may be detected by the following method:—The sample is rapidly distilled, and the distillate evaporated to a small volume (3 to 5 c.c.) on a water bath, after which 10 drops of phenol and 10 drops of concentrated sulphuric acid are added, and the mixture is heated slowly until the alcohol has evaporated and the liquid assumes a red colour. After cooling, 20 c.c. of water are carefully run in, followed by an excess of sodium or potassium hydroxide solution, and the development of a red colour indicates the presence of diethylphthalate or phthalein in the original sample. In some cases good results may be obtained by shaking out the sample with petroleum spirit and evaporating the solvent at a low temperature, instead of by distillation. The corresponding test described by Lyons, in which resorcinol is substituted for phenol, is shown to be unreliable, as a blank test yields a positive reaction.

T. J. W.

New Reagent for Alkaloids. R. Weinland and J. Heinzler. (*Süddeutsch. Apoth., Zeit.*, 1922, **61**, 46; *Chem. Abstr.*, 1922, **16**, 3730.)—"Pyrocatechol arsenic acid" (*o*-hydroxyphenyl arsenate), O:As $(O.C_6H_4OH)_3$, is prepared in crystalline form by mixing a solution of 27 grms. of arsenic acid in 70 c.c. of boiling water with 44 grms. of pyrocatechol, and allowing the filtrate to stand for some days. In concentrated aqueous solution it forms sparingly soluble salts with alkaloids and bases, but has the drawback that it also precipitates albumin and peptone. It gives a turbidity with solutions containing the following amounts of alkaloids:—Quinine sulphate, 0·03 mgrm. in 5 c.c.; hydrastine hydrochloride, 0·05 mgrm. in 5 c.c.; coniine hydrochloride, physostigmine sulphate, colchicine hydrochloride or apomorphine hydrochloride, 0·5 mgrm. in 5 c.c.

Extraction of Theobromine and Caffeine with Boiling Chloroform. O. P. A. H. Schaap. (*Pharm. Weekblad.*, 1922, **59**, 920–923.)—A modified form of Soxhlet extraction apparatus is described in which the lower portion, containing the cartridge of cocoa, tea or coffee, is immersed in a bath of water at 70° C. Experiments with mixtures of pure theobromine and of caffeine with powdered calcium sulphate yielded 100 per cent. of theobromine in 13 hours, and 99·7 per cent. of caffeine in 4 hours, whilst extraction of theobromine with cold chloroform yielded only 46·6 per cent. after 19 hours, and 52·1 per cent. after 27 hours.

Chemical Method of Assaying the Active Principles of Digitalis. A. Knudson and M. Dresbach. (*J. Pharm. Expt. Ther.*, 1922, **20**, 205–220; *J. Chem. Soc.*, 1922, **122**, A., ii., 882.)—Preparations of digitalis, when decolorised with lead acetate and treated with a solution of an alkali picrate, give a coloration the intensity of which has been found to stand in relationship to the pharmacological activity of the drug. A standard solution of ouabain is used as the basis for comparison, and the coloration which it gives under the same conditions is compared in a colorimeter with that given by the extract under examination.

Drugs in the Japanese Pharmacopœia. (*Pharm. J.*, 1922, **109**, 559–562.)—The exclusively Japanese drugs in the new edition of the Japanese Pharmacopœia include the following:

Amylum.—(*a*) Katakuri starch, prepared from the root of *Erythronium japonicum*. The granules are mostly oval, of diameter 0·007–0·092 mm. with indistinct striæ, and usually having the hilum near the narrow end. (*b*) Kudzu starch, prepared from the root of *Puerara hirsuta*. The granules are angular, and have a diameter of 0·002–0·018 mm.

Agar-Agar.—The bleached mucilaginous substance of the alga *Gelidium amansii* and other species prepared by freezing and drying. One grm., when boiled with 100 c.c. of water, should dissolve, leaving a small residue, and give on cooling a semi-transparent jelly. The mucilage should not redden blue litmus paper. On adding 1 drop of iodine solution to 3 c.c. of mucilage the yellow colour should remain, but a deep violet should be produced by adding 0·5 c.c. of iodine solution. On drying at 100° C. not more than 1·5 per cent. of the weight should be lost, and the ash should not exceed 4·5 per cent. of the solid residue.

Oleum Hydnocarpæ.—The oil expressed from the decorticated seeds of *Hydnocarpus*. It should have the following characteristics:—M.pt., 25–30°; iodine value, 80 to 90; saponification value, 195 to 215; degree of acidity under 7. Five grms. dissolved in chloroform and made up to 100 c.c. at ordinary temperature should have an optical rotation (α_D^{20}) of 2·4°. A green coloration should be produced after adding 1 drop of sulphuric acid to 5 c.c. of a chloroform solution (1:10) of the oil, and a deep blue colour when 5 drops of hydrochloric acid are added to 10 drops of the oil and slightly warmed. On warming the oil with 5 times its volume of absolute alcohol a clear solution should be formed, which deposits a white crystalline precipitate at the ordinary temperature.

Oleum tsubaki.—A yellow oil expressed from the husked seeds of *Camellia japonica* and having the following characteristics:—Specific gravity, 0·916; iodine value, 80 to 82; and saponification value, 189–192·6. A bluish green zone should be formed at the point of junction on adding 10 c.c. of a cold mixture of equal parts of fuming nitric acid, sulphuric acid and water, to 2 c.c. of oil. Ten drops of oil mixed with 1 drop of sulphuric acid should give a yellow colour turning brown. Halphen's cotton-seed oil reaction should give a negative result, and also Baudouin's test for sesamé oil, the latter even after boiling the mixture under a reflux condenser for 30 minutes. D. G. H.

The Active Principle of Chaparro. (*Prescriber*, 1922, **12**, 412; *Pharm. J.*, 1922, **109**, 562.)—The plant *Castela Nicholsoni*, known as *Chaparro armargosa* or bitter bush, and used in the treatment of amœbic dysentery, yields a glucoside, castelin, and a bitter principle, castelamarin. The glucoside, $C_{15}H_{22}O_8$, crystallises in long white needles, melting at 205° C. It dissolves in 85 parts of cold water and 25 of boiling water, is soluble in ethyl alcohol, and gives a deep violet coloration with concentrated sulphuric acid. It is dextro-rotatory, and is readily hydrolysed by dilute acids and alkalis, yielding castelaginin. D. G. H.

Examination of Hashish and Preparations containing it. A. Azadian. (*J. Pharm. Belg.*, 1922, **4**, 489–492; 505–507; *Chem. Abstr.*, 1922, **16**, 3729.) Hashish is prepared by macerating the flowering tops of *Cannabis indica* for 12 hours with cold water, then heating the mixture until half of the water has evaporated, after which fresh butter is added, and the boiling continued for 12 hours until the mixture becomes green. The liquid is then expressed and the fat strained off, when cold. It is the hashish of commerce, and is added in varying proportions to confectionery. To detect it in such products, from 5 to 10 grms. of the material are ground up with several portions of petroleum spirit, and the united extracts filtered and evaporated on the water bath. The residue is treated, while still warm, with 1 to 2 c.c. of a 5 per cent. solution of potassium hydroxide, which is added drop by drop. In the presence of hashish a violet coloration (Bearn's reaction) is obtained. The chromogenic substance is probably the active principle of the drug, and it may be found possible to base a colorimetric method of estimation upon the reaction. The following results were obtained in the examination of six authentic samples of hashish supplied by manufacturers in Greece:

Moisture Per Cent.	Ash Per Cent.	Ash sol. in HCl Per Cent.	Acidity mgrms. KOH per grm.	Sol. in petrol spirit Per Cent.	Sol. in ether after extraction with alcohol Per Cent.	Iodine value of ether extract	Iodine value of alcoholic extract	Iodine value of saponifiable residue
5·34	47·7	12·8	35·6	20·4	6·9	230	130	256
6·25	46·2	12·0	36·0	21·0	7·2	235	136	260
6·40	46·9	11·8	38·5	30·0	9·4	238	140	258
8·55	45·6	13·6	45·5	29·2	10·5	232	131	250
5·82	36·4	10·6	32·6	28·6	8·4	236	128	258
10·20	41·2	10·8	42·8	31·5	10·6	228	125	242

Estimation of Metallic Iron in Ferrum Redactum. C. E. Williams and A. E. Anderson. (*J. Ind. Eng. Chem.*, 1922, **14**, 1057–1060.)—Methods which have been proposed for the estimation of metallic iron in spongy iron and

ferrum redactum include the copper sulphate method, the mercuric chloride method and the ferric chloride method; in each of these the metallic iron is converted into a ferrous salt which is titrated subsequently. The hydrogen evolution method (measurement of the hydrogen evolved when the sample is treated with sulphuric acid) and the oxidation method (gain in weight on ignition in air) have also been used, but are not very satisfactory. The mercuric chloride method appears to be the most trustworthy, but it is rather tedious; the following modification of the copper sulphate method yields accurate results, and is therefore recommended for samples containing from 0·5 to 90 per cent. of metallic iron. A weighed quantity of about 0·5 grm. of the finely powdered sample is treated with 20 c.c. of 10 per cent. copper sulphate solution and 35 c.c. of hot water, the mixture boiled for fifteen minutes, then filtered immediately, and the insoluble portion washed with hot water. The filtrate is diluted to 100 c.c., 7 c.c. of concentrated sulphuric acid and a piece of sheet aluminium are added, and the solution is boiled until all the copper has been precipitated. The solution is cooled rapidly, filtered, the insoluble portion washed with cold water, and the filtrate titrated with standardised potassium permanganate solution. High results are caused by ferrous sulphide in all the methods mentioned above; the copper sulphate solution used must not contain iron. W. P. S.

Biochemical, Bacteriological, etc.

Characteristics of Vitamin *A*. K. Kashima. (*J. Ind. Eng. Chem.*, 1922, **14**, 1175.)—An outline is given of a communication made to the Chemical Society of Japan by Suzuki, who claims to have isolated 1 grm. of nearly pure vitamin *A* from 1 kilo. of cod-liver oil, and has shown that 0·0001 grm. of the preparation is capable of restoring the health of an animal dying from insufficient nutrition. Vitamin *A*, as isolated by Suzuki, is a light brown liquid which is soluble in nearly all organic solvents, forming a yellow to yellowish red solution. On treating the solution in chloroform with strong sulphuric acid a deep green colour develops, and a similar reaction is obtained in tests for cod-liver oil. The solution also gives a green coloration with Japanese acid clay. It has a reducing action on silver nitrate. Vitamin *A* is very easily destroyed by light and air, its oxidation product having a peculiar odour, but it is stable when dissolved in alcohol, ether or fatty acids. It contains no nitrogen and is probably an aldehydic compound.

Purification of Picric Acid for Creatinine Estimations. S. R. Benedict. (*J. Biol. Chem.*, 1922, **54**, 239–241.)—Many commercial samples of picric acid contain an impurity which yields an excess of colour upon the addition of alkali, and are therefore useless for the estimation of creatinine. According to Folin and Doisy (*J. Biol. Chem.*, 1916, **28**, 349) the colour produced by the addition of alkali to a picric acid solution should not exceed twice that of the solution before such addition. The following method was selected from a large number as the best and simplest for the purification of commercial picric acid:—Four hundred grms.

of moist picric acid, containing about 10 per cent. of water, are dissolved in 1 litre of boiling benzene and, after standing a few minutes, the solution is filtered through a hot funnel, leaving the residue of water, dirt, etc., in the flask. The filtrate is collected in a beaker and heated, if necessary, to dissolve any picric acid which has crystallised out, and is then allowed to cool slowly, without agitation, overnight. When cold, the liquid is poured off, and the crystals are washed with two 75 c.c. portions of benzene and allowed to drain for 30 minutes. The remaining benzene is removed by heating the crystals at 80° C. in an air-oven, with occasional stirring, for a few hours, and the dry product is powdered gently in a mortar and stored in a dark brown bottle. About 85 per cent. of the picric acid is recovered in the pure condition by this method. T. J. W.

Modification of Knoop's Reaction for Histidine. G. Hunter. (*Biochem. J.*, 1922, **16**, 637–639.)—This reaction is stated to be given by a 0·1 per cent. solution of the amino-acid, but the author has shown that the sensitiveness depends largely upon the variation in the excess of bromine added before heating. This difficulty may be overcome, especially with coloured solutions, by adding a definite excess of bromine, and shaking the liquid with small quantities of chloroform until no free bromine remains, after which the aqueous solution is heated in a boiling water bath. This procedure has the further advantage of removing much of the colour from highly coloured meat extracts, thus rendering the reddish-brown colour due to the histidine readily visible. Experimental investigation of the reaction indicates that chloroform does not remove any histidine from the solution, and that the maximum colour is developed when three atoms of bromine are added to one molecule of histidine. By the use of this modification a definite reaction may be obtained with a 0·01 per cent. solution of histidine. The coloured substance formed is not extracted from the aqueous solution by any of the usual solvents, and is unaffected by most reagents other than bromine. T. J. W.

Revised Method for the Estimation of Uric Acid in Blood. O. Folin. (*J. Biol. Chem.*, 1922, **54**, 153–170.)—Subsequent experience with the Folin-Macallum method for the estimation of uric acid (ANALYST, 1913, **38**, 154) has led the author to adopt various modifications. The standard now used is a modification of one described by Folin and Denis (*J. Biol. Chem.*, 1913, **14**, 96), and is prepared by dissolving 1 grm. of uric acid in 150 c.c. of water containing 0·5 grm. of lithium carbonate at 60° C. After cooling, the solution is diluted to 500 c.c., and 25 c.c. of 40 per cent. formaldehyde are added, followed by 3 c.c. of glacial acetic acid. The solution is then shaken and diluted to 1 litre, after which it is kept in the dark in small bottles filled to the neck. For use in blood analysis the standard solution is diluted 250 times. The actual colorimetric estimation of uric acid is modified as follows:—Five c.c. of the tungstic acid blood filtrate are transferred to a test tube containing 2 c.c. of water, and a similar volume of the diluted standard is added to another tube, together with 2 c.c. of water. Two or three drops of 20 per cent. lithium sulphate solution are introduced into each tube, followed by 2 c.c. of 15 per cent. sodium cyanide solution and 1 c.c.

of the Folin and Denis' uric acid reagent. After standing for two minutes, the tubes are immersed in a boiling water bath for 80 seconds, cooled, the contents are diluted to 25 c.c., and the colours produced compared in a colorimeter. The results obtained are somewhat higher than those given by the silver lactate precipitation method. Owing to the unreliability of this latter method, as originally described, the following modification has been adopted. The silver lactate solution contains 100 grms. of silver lactate in 700 c.c. of water to which has been added 100 c.c. of 85 per cent. lactic acid partly neutralised by the addition of 100 c.c. of 10 per cent. sodium hydroxide solution. Five c.c. of the tungstic acid blood filtrate contained in a centrifuge tube are treated with 7 c.c. of the silver lactate solution, without stirring, and the mixture is centrifuged. After decantation of the supernatant liquid 1 c.c. of 10 per cent. sodium chloride dissolved in 0·1 *N* hydrochloric acid is added to the residue, which is then thoroughly stirred and, after the addition of 4 c.c. of water, is again centrifuged. The liquid is transferred to a test tube, and to a similar tube 5 c.c. of the diluted uric acid standard are added. Two drops of lithium sulphate solution, 2 c.c. of sodium cyanide solution and 1 c.c. of the uric acid reagent are added to each tube, the subsequent procedure being as in the direct estimation above. Details are given of the difficulties encountered with different samples of sheep's blood, the instability of the sodium sulphite-uric acid standards, and the deterioration of sodium cyanide solution, and the various uric acid reagents proposed by other workers in recent years are discussed. T. J. W.

Estimation of Uric Acid. S. R. Benedict. (*J. Biol. Chem.*, 1922, **54,** 233–238.)—The author criticises a paper by Folin on this subject (see preceding abstract), pointing out that the varying behaviour shown by different samples of sheep's blood in regard to the recovery of uric acid indicates that the results given would be of little value when the method was applied to human blood. The implication that the Folin uric acid reagent was the first of its kind to be employed for this purpose is incorrect, since the use of phosphotungstic acid was described by Moreigne (*Ann. chim. anal.*, 1905, **10,** 15). The author claims that his arseno-phosphotungstic acid reagent (*J. Biol. Chem.*, 1922, **51,** 187) is of equal value to that devised by Folin and possesses the advantages of requiring 20 minutes' boiling for its preparation instead of several hours, and of being less liable to yield turbidities throughout the estimation. A description is given of a dilute uric acid standard (*loc. cit.*) which may be kept in a container connected with a carbon dioxide generator. This solution remains in good condition for at least 2 weeks after removal from the container. T. J. W.

Combined Uric Acid in Blood. A. R. Davis, E. B. Newton and S. R. Benedict. (*J. Biol. Chem.*, 1922, **54,** 595–605.)—Following an observation by Benedict (*J. Biol. Chem.*, 1915, **20,** 638) that the corpuscles of ox blood contain combined uric acid, the authors have isolated the compound by the following method : From fresh defibrinated blood the proteins were removed by heating with acetic acid, followed by treatment in the cold with colloidal iron. The filtrate

was evaporated to the original volume of the blood and treated with an equal volume of 0·5 per cent. mercuric acetate, to remove free uric acid. After filtration, the clear liquid was treated with an equal volume of 20 per cent. sodium acetate solution and allowed to stand 48 hours. The precipitate formed was well washed with cold water by centrifuging, after which it was suspended in hot water and decomposed by means of hydrogen sulphide, the precipitate of mercury sulphide being filtered off, and the filtrate evaporated under reduced pressure at 40 to 45° C. until crystals separated; these were washed with alcohol and ether and dried. From 15 litres of blood about 0·6 grm. of practically pure minute square crystals was obtained. This compound was soluble in boiling water and, on analysis, was found to have a composition corresponding with one molecule each of uric acid and *d*-ribose, minus one molecule of water. It appears to be a monobasic acid, and is practically insoluble in cold water, alcohol or ether, but dissolves readily in boiling water or in alkaline solutions. The sodium salt shows an α_D of $+20{\cdot}42°$, and the free acid is hydrolysed into uric acid and *d*-ribose on boiling with 0·1 *N* sulphuric acid. By estimation of the combined uric acid in the red corpuscles, leucocytes and serum of a sample of ox blood it was shown that this compound exists only in the former, the amount found being equivalent to that contained in the whole blood. The quantity of combined uric acid was found to be much higher in ox blood than in human blood, and traces only were found in the blood of the horse, sheep, pig, dog, and fowl. T. J. W.

Estimation of Formic Acid in Urine. E. M. Benedict and G. A. Harrop. (*J. Biol. Chem.*, 1922, **54**, 443–450.)—One hundred c.c. of urine are added to 500 c.c. of water, and 100 c.c. of 20 per cent. copper sulphate solution are run in, followed by a 10 per cent. suspension of calcium hydroxide until the reaction is alkaline. The mixture is diluted to 1 litre, mixed, allowed to stand about 30 minutes and filtered. Six hundred c.c. of the filtrate are transferred to a distillation flask, 2 or 3 drops of phenolphthalein and 1 or 2 c.c. of 85 per cent. phosphoric acid or an equivalent amount of tartaric acid added, and the flask is connected with a steam supply and with a condenser by means of a Kjeldahl head. From 15 to 20 c.c. of 0·1 *N* sodium hydroxide are run into the receiver and a few drops of phenolphthalein indicator added. The contents of the flask are rapidly boiled down to a volume of 50 or 75 c.c., after which the current of steam is increased, and this volume of liquid is maintained until 2 litres of distillate are collected in about 2 hours. The distillate is evaporated to dryness on a water-bath, and the residue is dissolved in water and diluted to 100 c.c. Of this solution 90 c.c. are slightly acidified with 0·1 *N* hydrochloric acid, and 10 c.c. of a solution containing 20 per cent. of mercuric chloride, 8 per cent. of sodium chloride and 30 per cent. of sodium acetate are added, and the mixture is heated for 1 hour at 100° C. in a flask fitted with an air condenser. On cooling, the precipitated mercurous chloride is filtered off into a weighed Gooch crucible, washed with 100 c.c. of cold 5 per cent. hydrochloric acid, then with water, alcohol and ether, and is finally dried at 105° C. for 1 hour. One grm. of mercurous chloride is equivalent to 0·0975 grm. of formic

acid, and the weight of mercurous chloride given by a blank estimation should be deducted from the amount obtained before calculation. Several estimations carried out with known amounts of formic acid added to normal and pathological urines showed a mean error of −2·4 per cent. and a maximum error of double that quantity. When 8 grms. of methyl alcohol were given to a dog weighing 7·2 kilos. there was a rapid increase in the formic acid content of the urine, which again declined to normal after a period of ten days. This increase is roughly proportional to the total organic acids present in the urine during the period of poisoning.

T. J. W.

Colorimetric Estimation of Cystine in Urine. J. M. Looney. (*J. Biol. Chem.*, 1922, **54**, 171–175.)—The following method is an application of one previously described (ANALYST, 1922, 360), and is based upon the development of a blue colour on the addition of phosphotungstic acid to a solution of cystine containing sodium sulphite. The same colour is formed by other urinary constituents in the presence or absence of sodium sulphite, and the cystine is estimated by the increase in colour produced on the addition of this salt to the mixture. One c.c. of a standard solution of 0·2 per cent. of pure cystine in 5 per cent. sulphuric acid is put into a graduated flask, together with 20 c.c. of saturated sodium carbonate solution, 10 c.c. of 20 per cent. sodium sulphite and 1 c.c. of 20 per cent. lithium sulphate solution. To a second flask from 1 to 10 c.c. of urine are added and similar additions are made, whilst a third flask contains the same volumes of urine and reagents with the sodium sulphite solution omitted. To each flask 3 c.c. of the Folin and Denis sodium tungstate reagent are added, and the contents mixed, allowed to stand 5 minutes and diluted to 100 c.c., after which the colours developed must be compared with the standard in a colorimeter within 8 minutes after addition of the tungstate reagent. Samples of urine from which a portion of the cystine has precipitated require to be separated from the solid by filtration or by centrifuging, and the cystine in the residue estimated after solution in 5 per cent. sulphuric acid. Should albumin be present, it must be removed before the estimation of cystine, by adding to 50 c.c. of the urine 5 c.c. of 20 per cent. trichloracetic acid solution, and diluting the mixture to 100 c.c., after which the liquid is shaken vigorously, and filtered. The maximum error obtained is about 6 per cent. of the total cystine present.

T. J. W.

Water Analysis.

Sulphated Waters of Essex. J. C. Thresh. (*Pharm. J.*, 1922, **109**, 557–558.)—In 1843 a spa was established at Hockley, but for many years, and until the comparatively recent demand for Vange water, this well had been almost entirely neglected. The amount of sulphates in the Hockley water exceeds those recorded for any Essex water prior to the discovery of the Vange well. This well, which is 16 feet in depth, was sunk about 20 years ago, and is known as Farmer Cash's well. The water is bottled and is also supplied on draught under the name of "Vange

Water." The following analyses, in parts per 100,000, of the true water in a bottle purchased at the well, and in a bottle obtained from a local druggist, show the difference between them:

	Calcium carbonate	Calcium sulphate	Magnesium sulphate	Potassium sulphate	Sodium sulphate	Sodium chloride	Water of hydration, silica, etc.	Total solids
Water from Farmer Cash's well	46·5	88·7	495·0	38·4	144·8	60·3	86·3	960
"Vange" water from Hockley	46·0	57·4	144·0	0·0	0·0	61·0	36·6	345

Agricultural Analysis.

New Method for the Mechanical Analysis of Soils and other Dispersions. G. W. Robinson. (*J. Agric. Sci.*, 1922, **12**, 306–321.)—The expression of the mechanical composition of soil by continuous curves instead of by the old fractional method is discussed. A new and rapid standard method requiring no elaborate apparatus is suggested, and the results may be expressed by showing the summation percentages as a function of the settling velocity. It is also shown that, on sedimentation, a reduction in velocity from the calculated value takes place in the case of clays by reason of the gel coating. The proposed method depends on the fact that when a soil suspension settles in a cylindrical vessel and samples are drawn from different depths (d) at suitable time intervals (t), at any given depth the concentration is equal to the sum of the partial concentrations of all fractions having velocities less than d/t. The procedure is to treat 20 grms. of the soil with 0·2 N hydrochloric acid, and to separate the sand and gravel, as usual, by sieving; the finer material which passes a No. 100 sieve is shaken with 600 to 700 c.c. of water containing 50 c.c. of 10 per cent. solution of ammonia for 2 to 4 hours, after which the suspension is made up to 1 litre (=2 per cent. concentration) and allowed to settle in a 1000 c.c. cylinder. Portions of 20 c.c. are carefully withdrawn at intervals by a pipette passing through a cork so adjusted that the point is at the desired depth (the pipette must be kept closed with the finger until that depth is reached), evaporated, and ignited, and the residue weighed. The following portions are so withdrawn:

	Depth cm.	Time hrs.	Time min.	Velocity cm/sec.	Giving percentage of
(a)	30	0	5	0·1	silt+fine silt+clay
(*b*)	12	0	20	0·01	fine silt+clay
(*c*)	6	16	40		
or	7·2	20	0	0·0001	clay
or	8·6	24	0		

To estimate the fine sand the suspension remaining after the last sampling is poured away to about 200 c.c., and the remainder (with the sediment) is washed into a beaker, and the fine sand estimated in the ordinary way, with the use of 10 cm. and 100 sec., or 7·5 cm. and 75 sec., sedimentation. The results may be expressed graphically by plotting the percentages against the log. velocity (cm./secs.), or may be tabulated in the usual way. It is shown that the method is more exact than the older process, but yields results quite in agreement therewith. H. E. C.

Mechanical Analysis of Humus Soils. G. W. Robinson. (*J. Agric. Sci.*, 1922, **12**, 287–291.)—The ordinary method for the mechanical analysis of soil yields low results for clay when the soil contains much organic matter; and even in soils with but little organic matter the cementing action of humus leads to slightly low clay figures. The acid or alkaline oxidising agents which have been suggested by various authors cause partial solution of the finely divided minerals, and so are objectionable; ammonium persulphate is also unsuitable. Hydrogen peroxide removes the organic matter without altering the mineral portion. The procedure is to treat 10 grms. of the soil with 50 c.c. of 20 vol. hydrogen peroxide on the water bath, adding a further 25 c.c. when the frothing has subsided; after action is over, water is added and the mixture boiled for about 15 minutes; the analysis is then continued in the usual way. A number of analyses of Welsh soils by the ordinary method and after treatment with hydrogen peroxide show about twice the percentage of clay when the organic matter is thus oxidised; in the ordinary method quantities of clay are wrongly grouped with the coarser fractions. H. E. C.

Toxic Constituent of Greasewood (*Sarcobatus vermiculatus*). J. F. Couch. (*Amer. J. Pharm.*, 1922, **94**, 631–641.)—This plant grows upon "alkali" soils, and is largely used as a fodder plant for sheep, although several cases of poisoning have been attributed to it. A detailed account is given of an investigation carried out to determine the toxic constituent. Owing to the large amounts of alkaline salts present the ignition of the material to ash was difficult, but the following method was successful:—The sample contained in a platinum dish was heated at a low temperature on asbestos board over a Bunsen flame until all volatile matter was driven off without fusing the ash. The dish was then heated rapidly to dull redness in about half a minute and removed from the flame as soon as fusion commenced, after which the trace of carbon remaining was unweighable. Analysis showed the presence of 11·54 per cent. of anhydrous oxalic acid in the dry plant combined as salts of calcium, potassium and sodium. The toxic nature of the plant is due to the large amounts of water-soluble oxalates present, which were shown by experiments made upon sheep to be more poisonous than an equivalent weight of free oxalic acid. Search was made for toxic alkaloids, glucosides, saponins, hydrocyanic acid and other volatile poisons, but with negative results. T. J. W.

Organic Analysis.

Alumina as an Absorbent for Water in Organic Analysis. H. L. Fisher, H. L. Faust and G. H. Walden. (*J. Ind. Eng. Chem.*, 1922, **14**, 1138–1139.)—Alumina is a suitable and convenient substance for use in the absorption of water; it is lighter than sulphuric acid, does not absorb carbon dioxide and remains a solid when fully hydrated. Theoretically, 10·7 grms. of alumina should absorb 1·92 grms. of water, so that this quantity may be used for several successive organic combustions. For use, the alumina is best prepared by dissolving 50 grms. of

crystallised aluminium chloride in water, adding 24 grms. of pumice stone (12-mesh), and evaporating the mixture to dryness, with constant stirring. The material is then transferred to a silica basin and heated in an electric furnace at 700° C. until all hydrogen chloride has been expelled. If a current of air is passed through the furnace during the heating, the time required is about forty-five minutes. If the heating period is too long, or the temperature too high, the alumina ceases to cling to the pumice, with consequent loss of "active surface." W. P. S.

Gasometric Method of Estimating Halogens in Organic Compounds. A. K. Macbeth. (*Chem. News*, 1922, **125**, 304–305.)—Following previous work on the nature of labile groups in certain organic compounds (ANALYST, 1920, **46**, 387) the authors use the reaction of hydrazine upon these compounds as the basis of a gasometric method for the estimation of halogens in them. One c.c. of hydrazine hydrate (50 per cent. solution) is run into the de-aminising vessel of a van Slyke nitrometer, the displaced air being allowed to escape by means of a three-way tap which is then turned into connection with the graduated column, and 5 c.c. of a solution of the halogen compound introduced into the vessel. The time taken for the steady stream of nitrogen to be completely evolved varies with the nature of the halogen compound and the strength of the solution. Thus, with chloro- and bromo- trinitromethane 1 minute is sufficient, whilst ethyl bromo-isosuccinate requires 6 or 7 minutes. Calculation of the weight of nitrogen evolved gives the amount of halogen or halogen compound employed. For example, acetobromamide reacts according to the equation, $2CH_3CONHBr + NH_2NH_2 = 2CH_3CONH_2 + N_2 + 2HBr$. In the higher substituted chloro- and bromo-malonic esters reduction is very slow, and is not complete above the propyl-compound; this is probably due to a steric hindrance effect. The authors give a list of compounds to which the reaction has been successfully applied, including various trinitromethane derivatives, malonic esters, and succinates, from which the halogen is completely removed; whereas with compounds of the type 4-chloro-4-bromo-1:1-dimethylcyclohexane-3:5-dione, 4:4-dibromo-compound cyclohexane-spiro-4-chloro-4-bromo-cyclo-hexane-3:5-dione and the 4:4 dibromo compound, one bromine atom is quantitatively removed, but the corresponding dichloro-compounds and the mono-halogen derivatives are unattacked by hydrazine hydrate in the cold. D. G. H.

New Reactions of Copper and Phenols. J. Aloy and A. Valdiguié. (*Bull. Soc. Chim.*, 1922, **31**, 1176–1179.)—Investigation of the cause of the blue colour produced on exposing a solution of hydroquinone in laboratory-made distilled water to the air showed this coloration to be due to the presence of traces of copper in the water. From this observation the following reaction was developed A solution of 0·2 grm. of hydroquinone in 100 c.c. of pure distilled water is treated with 20 drops of 0·01 *N* hydrochloric acid. About 10 c.c. of this solution are transferred to a test tube, and heated for about 30 seconds in a boiling water-bath, after which one or two drops of the solution under examination are added; in the presence of copper salts a blue coloration develops which rapidly increases

in intensity. The solution added should contain not more than 0·1 per cent. of metallic copper, and should not be alkaline or excessively acid in reaction. The test is sensitive to 0·001 mgrm., and may be used for the colorimetric estimation of copper, and is not given by any other common metal. Gold salts produce a similar colour, but this is not destroyed on the addition of acids. The above reaction may be employed for the detection of hydroquinone by adding 1 drop of 0·01 *N* hydrochloric acid to 10 c.c. of the solution under examination followed by 5 to 10 drops of 0·01 per cent. copper sulphate solution, after which the mixture is heated in a boiling water-bath for 1 minute. A distinct coloration is given by 0·1 mgrm. of hydroquinone, but the reaction is liable to be inhibited by the presence of large amounts of other organic substances, especially alcohol. Copper salts may be employed in a similar manner to distinguish between α-naphthol and β-naphthol, the former yielding a blue-violet colour, whilst with the latter no colour is produced. T. J. W.

Analysis of β-Naphthylamine. H. R. Lee and D. O. Jones. (*J. Ind. Eng. Chem.*, 1922, **14**, 961–963.)—Methods are given for the estimation of β-naphthylamine in the presence of its common impurities, namely, β-naphthol, β, β-dinaphthylamine and α-naphthylamine. If the amine content of a sample, as estimated by the sulphonation method (see below), is 96 per cent. or higher, and the melting point is 109° C. or higher, the absence of any appreciable amount of impurity is assured; otherwise, the β-naphthol content of the sample must be estimated by the benzene separation method and the β β-dinaphthylamine content by the solubility method. *Sulphonation method.* A quantity of 0·65 grm. of the sample is treated with 20 c.c. of sulphuric acid containing 25 per cent. excess of anhydride (oleum, cooled previously to 0° C.), the mixture is stirred and, if necessary to effect solution, allowed to rise to room temperature. The mixture is then poured on to clean ice, the solution boiled for fifteen minutes, cooled to 20° C., diluted to 200 c.c., treated with 15 c.c of concentrated hydrochloric acid and titrated with 0·1 *N* sodium nitrite solution, starch-iodide being used as external indicator. With the above quantities, each c.c. of 0·1 *N* nitrite solution is equivalent to 2·202 per cent. of β-naphthylamine. *Benzene Separation Method.* A portion of 3·5 grms. of the sample is placed in a flask, together with 300 c.c. of dry benzene, the flask is closed with a rubber stopper carrying a calcium chloride tube and a tube reaching to the bottom of the flask, and dry hydrochloric acid gas is passed into the mixture for two hours. The precipitated amine is collected on a filter (a double filter paper fitted in a glass funnel provided with a hot-water jacket), washed with 100 c.c. of dry benzene saturated with hydrochloric acid gas, and dried at 60° C. under reduced pressure. The precipitate is then dissolved in 200 c.c. of boiling water, the solution is treated with 25 c.c. of hydrochloric acid, cooled to 0° C., and titrated with 0·5 *N* sodium nitrite solution; each c.c. of the latter is equivalent to 2·043 per cent. of β-naphthylamine. *Estimation of β-Naphthol.* The benzene filtrate from the preceding estimation is evaporated to dryness, the residue is

dissolved in 10 c.c. of 20 per cent. sodium hydroxide solution, the solution diluted to 200 c.c., rendered slightly acid with hydrochloric acid, treated with an excess of sodium hydrogen carbonate and coupled with 0·05 *N* diazo-*p*-nitrobenzene solution. One c.c. of the latter solution is equivalent to 0·205 per cent. of β-naphthol. *Estimation of Acid-Insoluble Matter.* Five grms. of the sample are treated with 150 c.c. of boiling 1·5 per cent. hydrochloric acid, the mixture is filtered through a tared filter, the insoluble portion washed with hot water, dried at 100° C., and weighed. The insoluble portion consists chiefly of β β-dinaphthylamine, and this can be isolated by solvent extraction and weighed. *Estimation of Total Nitrogen.* One and a half grm. of the sample are sulphonated with 20 c.c. of 25 per cent. oleum, the mixture is kept at 20° C. for fifteeen hours, and then rinsed into a Kjeldahl flask with three 5 c.c. portions of hot concentrated sulphuric acid. One grm. of mercury is added, the neck of the flask is closed with a plug of glass wool moistened with sulphuric acid, and the mixture boiled for two hours. The neck of the flask and the glass wool are rinsed down with 5 c.c. of hot sulphuric acid, the digestion continued for ten minutes, the glass wool plug pushed into the flask, 10 grms. of sodium sulphate added, and the mixture is boiled for a further two hours, or until it becomes colourless. After cooling and diluting, the solution is distilled with the addition of 1 grm. of granulated zinc, 40 c.c. of 10 per cent. sodium sulphide solution and an excess of sodium hydroxide, and the ammonia is collected and titrated in the usual way. Each c.c. of 0·25 *N* hydrochloric acid used in titrating the ammonia is equivalent to 2·365 per cent. of β-naphthylamine. In the absence of appreciable amounts of β-naphthol or dinaphthylamine, the melting point of the sample gives an indication of the quantity of α-naphthylamine present. W. P. S.

Estimation of Abietic Acids and Colophony. F. Schulz and S. Landa. (*Bull. Soc. Chim.*, 1922, **31**, 1353–1360.)—The reduction of mercuric to mercurous acetate by the abietic acids extracted from colophony serves as the basis of a method for estimating those acids. About 0·5 grm. of the material is dissolved in 10 c.c. of a saturated solution of mercurous acetate in glacial acetic acid, and the liquid treated with a freshly-prepared solution of 3 grms. of mercuric oxide in 50 c.c. of acetic acid saturated with mercurous acetate, and heated for an hour in a water-bath at 50° C. The mixture is next left in the dark for an hour, and the scales of mercurous acetate which have formed then collected on asbestos in a Soxhlet tube and washed with a saturated solution of mercurous acetate in acetic acid. The precipitate is treated with 20 c.c. of hot 20 per cent. nitric acid and washed with boiling water until the wash water fails to react with stannous chloride. The solution thus obtained, which should occupy about 300 c.c., is boiled for 20 minutes with 20 c.c. of concentrated sulphuric acid and excess of potassium permanganate, the excess of which is then destroyed by addition of a small crystal of oxalic acid. The cold liquid is mixed with 50 c.c. of a solution containing 13 grms. of sodium chloride per litre and sufficient sodium nitroprusside to give it a faint yellow colour, the excess of sodium chloride being then titrated with

mercuric nitrate solution until a persistent turbidity appears; a solution of 24·2 grms. of mercuric oxide in dilute nitric acid, made up to 1 litre, corresponds almost exactly with the sodium chloride solution. Each c.c. of the chloride solution corresponds with 0·0241 grm. of mercuric oxide or with 0·0131 grm. of colophony, the last figure being the mean of those obtained from the qualities G to WW of American colophony. Owing to the readiness with which colophony oxidises in the air, small broken pieces, not powdered samples, should be used. The method gives results accurate to within about 10 per cent., and is applicable to the estimation of colophony in admixture with shellac. As regards its use for soap, it is found that palmitic and oleic acids and glycerol are not acted on by the reagent, which is however reduced by palm oil. Ceresin is inert, but is only slightly soluble in acetic acid. With the natural abietic acids of colophony, 1 grm. corresponds with an average of 1·974 (1·964–1·999) grm. of mercuric oxide, but the reducing power of the lævorotatory acid obtained by treating colophony with dilute mineral acid undergoes rapid diminution. T. H. P.

Effect of Hydrogen Ion Concentration on the Analysis of Vegetable Tanning Materials. J. A. Wilson and E. J. Kern. (*J. Ind. Eng. Chem.*, 1922, **14,** 1128–1129.)—The quantity of tannin in quebracho bark, as indicated by the official (American) method, increases with the P_H value to a maximum at 8, and then decreases rapidly towards zero. At the same time, the P_H value appears to have no effect on the estimation of tannin by the Wilson-Kern method when the value lies between 3·6 and 7·3, but the rate of tanning of hide powder decreases rapidly with increasing P_H value above 7. The rate of filtration of tanning liquors is considerably affected by change of P_H value, which fact is possibly due to changing degrees of dispersion of some of the solid matter. The addition of lime to tanning liquors causes a precipitation of tannin, but only at P_H values above 7·2.

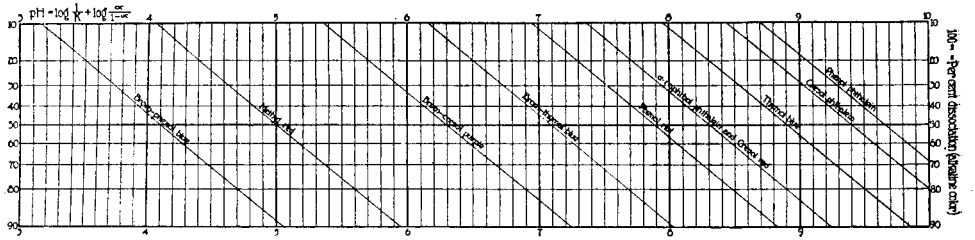
W. P. S.

Method for Distinguishing Flax from Hemp. C. R. Nodder. (*J. Text. Inst.*, 1922, **13,** 161–171.)—Fibres of the material under examination are isolated by immersion in warm water and the free end is viewed while drying in a warm room. Under these conditions fibres of flax and ramie always twist in a clockwise direction, whilst hemp and jute rotate in the opposite direction. A further confirmation is obtained by holding the fixed end of the dry twisted fibre in the right hand, with the free end pointing to the left, and rotating this free end in an anti-clockwise direction, when the alternate dark and light sections seen along the fibre will appear to travel towards the left in the case of flax, and conversely with hemp. These observations may be made the basis of the quantitative estimation of the two fibres in a fabric. The material is immersed in warm water and single fibres are removed from areas evenly distributed over the sample, the rotation of these being observed as they dry. In a warm dry room six or more fibres may be observed in a minute and, with careful sampling, a hundred observations is sufficient to obtain accurate results. The two films may also be distinguished by mounting in a strong calcium chloride solution tinted to a pale brownish colour

with iodine, and flattening the fibre by careful pressure on the cover glass without lateral movement. By examination of the compressed fibre under a moderate magnification the fibrillar structure in the outer wall will appear as a left-handed spiral in the case of flax, whilst hemp will show a spiral twisted in the reverse direction. By mounting in sodium hydroxide solution and examination between crossed Nicols with polarised light the structure is well shown. T. J. W.

Inorganic Analysis.

Chart for the Conversion of Colorimetric Indicator Readings into Hydrogen Ion Concentration. J. F. McClendon. (*J. Biol. Chem.*, 1922, **54**, 647–653.)—The chart described is based upon the curves given by Clark for different indicators showing the relation between hydrogen ion concentration and percentage dissociation of the indicator. The vertical divisions upon the chart



are arranged tentatively at such distances that the curves, when plotted, are represented by straight lines, the abscissæ representing the P_H values deduced from Clark's formula $P_H = \log 1/K + \log a/1 - a$, in which K is the dissociation constant and a is the degree of dissociation, whilst the ordinates give the percentage dissociation. When using indicators, such as phenolphthalein, which in the undissociated condition are colourless, equal volumes of the unknown solution and water to which alkali has been added are taken and the same quantity of indicator solution is added to each. The colours produced are then compared in a colorimeter, and, on the assumption that the dissociation of the indicator in the alkaline solution is 100 per cent., that of the unknown is deduced by dividing 100 by the ratio between the heights of the liquid columns. From the value obtained the P_H value of the unknown solution is readily determined by reference to the chart. With the sulphonic acid and other indicators in which the dissociated and undissociated molecules are of different colours, various modifications in procedure are necessary, and reference is given to the methods adopted by Barnett, Myers and Lyon (*Proc. Soc. Exp. Biol.*, 1920, **18**, 127; *J. Biol. Chem.*, 1922, **50**, 22; *J. Bact.*, 1921, **6**, 399.) T. J. W.

Modified Methyl Orange Indicator. K. C. D. Hickman and R. P. Linstead. (*J. Chem. Soc.*, 1922, **121**, 2502–2506.)—Experiments are described in which by the addition of an aniline dye to methyl orange the end-point of the indicator is considerably sharpened. A trial was made with several dyes, the

best result being obtained with xylene cyanole FF (Sandoz Chemical Co.) in the proportion of 1·4 parts by weight of the dye to 1 part of methyl orange. With the use of 0·1 *N* solution of acid and a total volume of liquid of approximately 55 c.c. the alkaline solution remained green to within 2 drops of the end-point, after which the addition of another drop produced a grey-green colour, and a further drop gave a colourless grey, corresponding to the end-point of methyl orange alone at a P_H value of 3·8. Further addition of acid changed the colour of the solution to magenta. Good end-points were obtained in the titration of ammonia with hydrochloric acid, and with phosphoric acid and sodium hydroxide, with the formation of the mono-sodium salt, but the indicator was useless with acetic acid. Xylene cyanole FF is stable in dilute solutions of acids and alkalis, but is decolorised by strong mineral acids, the original colour returning on dilution. Attempts were made to use methyl orange alone by artificial light filtered through screens coloured by dyes, but no improvement was obtained. The new mixed indicator gives results with a 100 watt blue glass "daylight" lamp equal to those obtained by daylight.

T. J. W.

Abstractor's Note.—This principle has been applied by Moerck (*Amer. J. Pharm.*, 1921, **93**, 675) with similar results, by the addition of indigo carmine to methyl orange indicator.

Purification of Sodium Hydrosulphite. W. G. Christiansen and A. J. Norton. (*J. Ind. Eng. Chem.*, 1922, **14**, 1126–1128.)—The method described is a modification of one developed by Jellinek (*Z. anorg. Chem.*, 1911, 93), which consists in saturating an aqueous solution of the hydrosulphite with sodium chloride; crystallised sodium hydrosulphite is thus precipitated and is subsequently dehydrated and dried. All the operations are made *in vacuo* or in an atmosphere of carbon dioxide. For the estimation of sodium hydrosulphite it is recommended that the solid hydrosulphite be added from a small weighing bottle, in small quantities at a time, to a known amount (about 1 grm.) of pure potassium ferro-cyanide dissolved in water containing a small quantity of non-acidified ferrous ammonium sulphate solution. The end-point is denoted by the disappearance of the blue colour. The reaction proceeds according to the equation:

$$2K_3Fe(CN)_6+Na_2S_2O_4+2H_2O=2K_3NaFe(CN)_6+2H_2SO_3.$$

W. P. S.

Detection of Gold. H. I. Cole. (*Phillipine J. Sci.*, 1922, **21**, 361–364.)—Fibres of viscose silk are heated for 10 minutes on a water-bath in a filtered 10 per cent. solution of stannous chloride containing 1·8 per cent. of actual hydrochloric acid and 10 per cent. of pyrogallol, and are then well washed with water and dried between filter paper. A drop of the neutralised solution under examination is placed on a glass micro slip and a prepared fibre is partly inserted in the drop. The fibre is then examined under the microscope, both before and after the spontaneous evaporation of the drop; a red colour with freshly-prepared fibres, or a dark blue colour with older ones, indicates the presence of gold. Fibres thus prepared retain their sensitiveness for at least 6 months and a positive reaction

is given by 0·000022 mgrm. of gold in one drop of solution. The reaction is interfered with by the presence of alkalis, mineral acids, oxidising and reducing agents generally, and potassium ferro- and ferri-cyanides. Chromates and silver nitrate change the colour of the fibre, but do not mask the gold reaction. Permanganates render the fibre brown in colour, and molybdenum compounds produce a light blue colour, which is readily distinguished from the dark blue given by gold. T. J. W.

Estimation of Aluminium as Phosphate. G. E. F. Lundell and H. B. Knowles. (*J. Ind. Eng. Chem.*, 1922, **14**, 1136–1137.)—Many modifications of the method of estimating aluminium as phosphate have been proposed, but, except in the case of very small quantities of the metal (less than 5 mgrms.), the method is untrustworthy. The results are usually too high under ordinary conditions; but much washing with water or the use of acidified water for the washing causes the results to be too low. The results are also too low when the precipitation is made in an alkaline solution, or when only a moderate excess of precipitant is employed. Iron behaves like aluminium in the precipitation, whilst titanium invariably yields low results. W. P. S.

Quantitative Analysis of Clays. O. Boudouard and J. Lefranc. (*Bull. Soc. Chim.*, 1922, **31**, 1145–1152.)—The following methods are based upon previous ones worked out by other investigators, and refer particularly to the pipe-clays found at Poivilliers (France). The full analysis of the clay is carried out in the usual manner, and a portion of the material is treated with boiling sulphuric acid, the insoluble residue being subjected to a similar analysis. The difference between the results obtained for each oxide present represents the amount of that oxide dissolved by the acid. By preliminary experiments it has been shown that orthoclase felspar and quartz are insoluble in boiling sulphuric acid, whilst clay, kaolin and mica are soluble. The composition of the clay is estimated by calculating the alkali and alumina in the soluble portion to mica and kaolinite respectively, and the alkali in the insoluble portion to felspar, whilst the proportion of quartz is deduced by deducting the felspar from the total insoluble matter. A further method of calculation is an application of one frequently employed in organic chemistry, in which the percentage of the base or acid is divided by its molecular weight. The potash present is calculated to its molecular equivalent of orthoclase felspar, the lime in a similar manner to anorthite, whilst the excess of alumina corresponds to the kaolinite. The free silica is found by deducting the combined silica from the total silica estimated. The figures obtained are multiplied by the molecular weights of the corresponding minerals to obtain the ratio present in the original clay, from which the percentage is readily calculated. Reference is made to the qualitative and quantitative analysis of mica by means of the petrological microscope, thus eliminating the estimation of alkalis in the above analyses. T. J. W.

Rapid Estimation of Magnesium in One Drop of Sea Water. G. Deniges. (*Compt. Rend.*, 1922, **175**, 1206–1208.)—The estimation is based upon an observation of Schlagdenhaufen (*J. Pharm. Chim.*, 1878, **27**, 378) that soluble salts of magnesium, on treatment with potassium hypoiodite, produce a reddish coloration and eventually a flocculent precipitate resembling ferric hydroxide in appearance. A 10 per cent. solution of crystallised magnesium sulphate is diluted with water until one drop diluted to 5 c.c. is equivalent to 0·01 grm. of anhydrous magnesium chloride per litre. To a series of test tubes similar in diameter from 0 to 12 drops of the standard magnesium sulphate solution are added, the contents of each tube are diluted to 5 c.c. with distilled water, and one drop of 3 per cent. sodium chloride solution is run in. One drop of the water under examination is added to a similar tube, together with 5 c.c. of distilled water, and to all the tubes 0·5 c.c. of 10 per cent. potassium iodide solution is added. After thorough mixture of the contents of each tube, 2 drops of sodium hypobromite solution are added, the tubes rapidly shaken, and allowed to stand not longer than 15 minutes, and the resulting colorations compared. The sodium hypobromite solution is prepared by adding 0·5 c.c. of bromine to a mixture of 5 c.c. of sodium hydroxide solution with 10 c.c. of water. The following results expressed as grms. of metallic magnesium per litre of sea water have been obtained: Pacific Ocean, 1·13; Atlantic Ocean, 1·18; Mediterranean Sea, 1·30; and the Red Sea, 1·70. T. J. W.

Note on the Colorimetric Method for the Estimation of Magnesium. F. S. Hammett and E. T. Adams. (*J. Biol. Chem.*, 1922, **54**, 565–566.)—The authors have compared their method (ANALYST, 1922, **47**, 368) with those of Briggs (ANALYST, 1922, **47**, 409) and Denis (*J. Biol. Chem.*, 1922, **52**, 411), and find that it gives slightly higher results. The discrepancy is due to the presence of phosphorus or other compounds in the asbestos or filter paper, used for filtration, capable of giving the Bell-Doisy colour reaction. The precipitation with ammonium phosphate has accordingly been carried out in centrifuge tubes, the walls of which are then well scratched, and the mixture is allowed to stand overnight. After centrifuging, the liquid is poured off, and the precipitate is washed twice with 10 per cent. ammonium hydroxide, and once with ammoniacal alcohol, and is then dried and dissolved in 10 c.c. of 0·1 *N* hydrochloric acid. The subsequent procedure is as previously described. The fading of the final colour produced in the Bell-Doisy method, as mentioned by various workers, was found to be due to the use of old carbonate-sulphite solutions in which oxidation had occurred. The authors therefore recommend the use of solutions which are not more than 2 weeks old and have been kept in tightly stoppered bottles. T. J. W.

Method of Analysis for Dolomite and Magnesian Limestone. S. D. Averitt. (*J. Ind. Eng. Chem.*, 1922, **14**, 1139–1140.)—An indirect method is described for the estimation of the calcium carbonate and magnesium carbonate in these minerals. A weighed quantity of 0·5 grm. of the powdered sample is boiled for ten minutes with 25 c.c. of 0·5 *N* hydrochloric acid and a small quantity

of water; the mixture is then cooled and the excess of acid is titrated with 0·25 *N* sodium hydroxide solution, methyl-orange being used as indicator. The total alkalinity of the sample is expressed as $CaCO_3$ per cent. (A). The neutralised solution is treated with 10 c.c. of 10 per cent. ammonium chloride solution and 2 drops of ammonia, boiled, the precipitate collected on a weighed filter, washed with hot water, dried at 100° C., and weighed. To the percentage amount of insoluble matter and ammonia precipitate (B) is added a small correction for moisture (M) in the sample. The percentage quantities of calcium carbonate and magnesium are then calculated by the formulæ

$$MgCO_3 = 5{\cdot}35[A - (100 - (B + M))] \text{ and}$$
$$CaCO_3 - MgCO_3 = 100 - (B + M).$$

W. P. S.

Electrometric Titration of Sulphurous Acid with Permanganate. W. S. Hendrixon and L. M. Verbeck. (*J. Ind. Eng. Chem.*, 1922, **14**, 1152–1153.)—Attempts were made to estimate sulphurous acid by oxidising it with an excess of permanganate, the excess of permanganate being titrated electrometrically with potassium iodide. The results obtained show that with a large or small excess of permanganate only about 90 per cent. of the sulphurous acid is oxidised to sulphuric acid, the remainder probably forming dithionic acid. The extent of the oxidation is somewhat variable, and appears to depend on small differences in conditions which cannot be controlled. W. P. S.

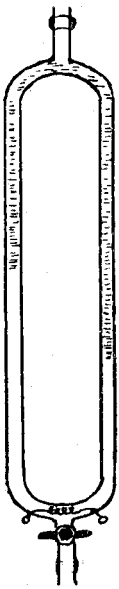
Sensitive Test for Phosphoric Acid. F. Feigl. (*Zeitsch. anal. Chem.*, 1922, **61**, 454–457.)—The precipitate obtained with ammonium molybdate is filtered off, washed a few times, and moistened with benzidine hydrochloride solution acidified with acetic acid, followed by a few drops of ammonia. In presence of phosphomolybdate the precipitate is coloured blue to black. The reaction can be used as a spot test for solutions which are too dilute for precipitation with molybdate solution. Two drops of solution, containing 0·0025 mgrm. of phosphoric anhydride, treated on filter paper with one drop each of molybdate and benzidine solutions and exposed to ammonia vapour, give a distinct blue coloration. A freshly-made molybdate solution should be used for the detection of traces of phosphoric acid. The blue colour is due to a lower oxide of molybdenum and to an oxidation product of benzidine. W. R. S.

Physical Methods, Apparatus, etc.

Quantitative Analysis by Measurement of Supersaturation-time of Reactions. H. Roder. (*Chem. Zeit.*, 1922, **46**, 1089.)—The general applicability of the measurement of supersaturation time to quantitative analysis as has been proposed by Hoppler (*cf.* ANALYST, 1922, **47**, 538) is criticised. The time which elapses before the product of a reaction becomes visible depends on many conditions besides those of temperature and concentration, both in colloidal and in disperse systems; in the former there may be present protective substances, and the gel may have differing water contents, and in the latter changes of phase may

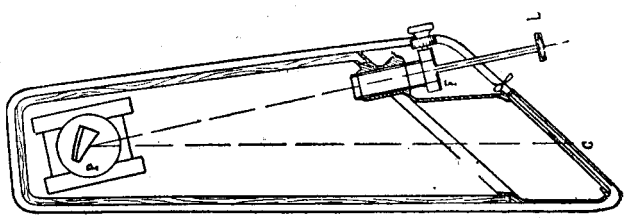
take place, as happens when magnesium is precipitated as magnesium ammonium phosphate. The method may be useful in the particular case of water analysis, because the extreme variations of conditions, such as the P_H value and the amount of salts present, are not large, but much further work is needed before the principle could be applied generally. H. E. C.

New Explosion Burette. A. Krieger. (*Chem. Zeit.*, 1922, **46**, 1060–1061.)—A modification of the explosion pipette of the Bunte apparatus is described for the estimation of hydrogen, methane or other combustible gas. It may be used in conjunction with the Hempel, Orsat or other apparatus, and has the advantage over the Bunte pipette that the combustion is always complete. In explosive mixtures the flame is propagated along a straight tube instead of in the usual conical or bulbous pipette, and the water in the limbs acts as a buffer, so that the explosion is so mild that no damage is occasioned; there is only a slight shock at the water surface of the levelling flask. The apparatus (see fig.) is 40 cm. in length from shoulder to shoulder, and is 8 cm. wide; it is connected in the usual way with the levelling flask, which is raised so that the level of water in the limbs is about 10 cm. high.



H. E. C.

Simplified Féry Spectrograph. (*Chem. Trade J.*, 1922, **71**, 734.)—This instrument is a smaller and less complicated model of the high-precision spectrograph devised by Féry about 10 years ago. Owing to this modification the cost of the apparatus is greatly reduced, and manipulation is much simplified, whilst the maximum length of the new model does not exceed 50 cm., and the spectra formed are approximately 80 mm. long. The construction of the instrument is shown in the diagram in which L is a quartz lens by which rays from the illuminant are focussed upon the slit F. The prism P is constructed of quartz, with a concave front surface and convex back face, the latter being silvered and thus acting as a concave mirror to focus the spectrum upon the photographic plate C. The angle at which the plate holder is set ensures a sharp image of all lines throughout the visible and ultra-violet spectrum. By means of this apparatus it is possible to detect the presence of one drop of aniseed oil dissolved in 20 litres of alcohol, and the instrument has been successfully applied to the study of fluorescence, phosphorescence, the grain of photographic plates, essential oils, etc. Reference is made to an apparatus invented by Beaudouin, a Parisian engineer, consisting of an electrical transformer for the production of rays rich in ultra-violet light and yielding spectra practically free from the usual lines due to the air and water vapour. T. J. W.



Molecular Polymerisation of Compounds in the Critical State. J. A. Müller. (*Comptes rend.*, 1922, **175**, 760–761.)—An expression for the mean degree of molecular polymerisation of substances in the critical state is derived, and is applied to a number of elements and inorganic and organic compounds. In all cases, with the exception of helium, polymerisation is shown in the critical condition, but is comparatively slight with compounds approximating to perfect gases under ordinary conditions of temperature and pressure. This degree of polymerisation lies between 1·39 and 1·45 for liquid hydrocarbons and monohalogenated derivatives of benzene, and between 1·45 and 1·48 for saturated esters of monobasic fatty acids, and still higher for alcohols; for water, acetic acid and nitrites it is about 2. Isomerism in compounds of similar chemical character has little influence on the polymerisation. T. H. P.

Reviews.

ATOMIC FORM. By EDWARD E. PRICE. Pp. 140. London: Longmans, Green and Co. 1922. Price 5s. net.

One cannot but be surprised that an author in 1922 should put forward a theory such as is propounded in this book. It is true that the author only asks for that impartial consideration of his theory to which it is entitled, but in view of the fact that it absolutely disregards not only current physical theories, but well-ascertained fact, and is at variance with most of the experimental research on atomic structure of the past decade, it is not likely to be favourably received or seriously considered by chemists generally.

The book is concerned almost exclusively with the carbon atom, but it is supposed that all atoms are formed on similar lines. The thesis is based upon the following conceptions: Atoms have definite geometric forms which distinguish each element from all others and upon which the properties of the element depend; those belonging to the same group may differ only in magnitude. Valency is conceived as the number of faces available for stable attachment. No experimental evidence is adduced in support of the hypothesis, which is built up on loose reasoning; it is urged that in nature all things are crystalline or angular, unless they have come under the influence of living agencies or rotational motion, and it is supposed that the elements are likewise crystalline and have no electrical properties. Ions, electrons, and a positive nucleus are denied, and no reference is

made to the observations of Thomson, Langmuir, Lewis, Bohr, or other masters of the subject. An irregular tetrahedron, called the carbonoid, in which all the sides are alike, is predicated for the carbon atom, and much ingenuity is displayed in building up from this the principal types of carbon compounds.

The book bristles with points which might be taken up and controverted, but, in view of the most serious fundamental objection that the author's conception is at variance with elementary facts, it is superfluous to deal with the proposals in detail. The subject of valency is always difficult to deal with in terms of atomic theory and, whether or not one accepts the electronic conception, the present theory fails absolutely upon this point, and puts forward no rational explanation, even for quite simple compounds.

The only aspect upon which the book can be commended is that of its presentation; the style and printing are good and the illustrations very good; one could wish that it contained more valuable matter. H. E. Cox.

THE MICROSCOPICAL EXAMINATION OF FOODS AND DRUGS. By HENRY G. GREENISH, F.I.C. Pp. xx.+386. London: J. and A. Churchill. 1923. Price 18s. net.

The volume under review is the third edition of this well-known text book, and since the previous edition was published (ANALYST, 1911, **36**, 384) the subject matter has been revised and brought up to date without increasing the size of the book to any extent.

The manual is intended as a complete introduction to the identification of foods and drugs by means of the microscope for students already possessing a general knowledge of botanical histology, and the author has wisely restricted his descriptions to a comparatively small number of typical plants and plant tissues, without reference to their natural orders.

The various sections of the book are devoted each to one particular portion of the plant, under the headings of starch, hairs and textile fibres, spores and glands, ergot, woods, stems, leaves, flowers, barks, seeds, fruits, rhizomes, and roots. In Section XIV descriptions are given of materials commonly employed for the adulteration of powdered foods and drugs, and in the next section a general scheme for microscopical examination of powders is given. Two appendices are provided in which various reagents of general utility and the physical and microchemical behaviour of various cell walls and cell contents are described.

This carefully written volume, which is admirably adapted to fulfil the purpose intended, contains little meriting adverse criticism, with the following exceptions. On page 5 we read, "The value of the subdivisions of the (eyepiece) micrometer will . . . vary with the eyepiece and objective used," but it would also be advisable to add, for the benefit of the student, that variation is also introduced by extension of the draw-tube and by the presence or absence of the nosepiece. The statement made on page 377 that inulin is insoluble in cold water is certainly questionable, since no uniformity of opinion appears to have been reached on this point.

The index provided shows a high degree of accuracy, but omits a few sub-sections which might be included with advantage. Among these are "Methods of separating Tissues into their Elements" on page 64, and "Cutting Transverse Sections" on page 45. A large number of excellent drawings of sections and typical structures of powdered drugs, as seen under the microscope, are provided throughout the book, but the student is at first liable to disappointment on seeing an actual slide in which so large a proportion of the material usually consists of unidentifiable débris, in comparison with these ideal representations.

The author has evidently a wide knowledge of the requirements of the student, and has omitted nothing essential to a thorough training in the principles of the microscopical examination of foods and drugs, whilst at the same time limiting the text entirely to the subject under consideration. The student who works conscientiously through this volume will have received an admirable training in microscopic methods and have gained a wealth of knowledge which should be of great value to him in the future. T. J. WARD.

THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES. By ERNEST J. PARRY, B.Sc., F.I.C. 4th Edition. Vol I, pp. 552; Vol II, pp. 366. London: Scott, Greenwood and Son. Vol I, 1921, price 30s.; and Vol II, 1922, price 21s.

The best and most reliable testimony to the value of this work consists in the fact that four editions have been called for, and that, although originally appearing in a single volume, the author has found it necessary, owing to the accumulation of material, to expand it into two.

Volume I may be best described as a series of monographs on the essential oils, and the very sensible method has been followed of classifying these according to the botanical relationships of the plants from which they are obtained. The number of new essential oils which are being constantly described in the various Journals devoted to this subject, is so considerable that it is highly convenient to have the available information collected within the covers of a single volume and submitted, as has evidently been the case, to a discriminating selection. To review a work of this character in detail is a practical impossibility, and the only plan which a reviewer can successfully adopt is to peruse critically those portions of the subject with which he himself is most familiar. Judged in this way, the subject matter of this volume possesses, so far as the writer can ascertain, the merit of being concise and accurate.

Volume II is divided into three parts: (1) the essential oil and its odour; (2) the constitutents of essential oils, synthetic perfumes, and isolated aromatics; and (3) the analysis of essential oils.

The first part of this volume includes a description of the manner in which the various oils occur in the plant, and an excellent chapter dealing with the fascinating question of the relationship between odour and chemical constitution. The author mentions among the problems which present themselves for solution, the origin of the essential oils in the plant, the alterations they undergo during the life history

of the plant, the mechanism involved in the translation of the constituents of the oil from one part of the plant to another, and the variation and possible control of the character of the essential oil as the result of variations in external and controllable conditions of culture. Much work will have to be done before these problems can be regarded as solved, but their solution is, as the author remarks, necessary if the essential oil industry is to be placed on a really scientific basis.

The second part of this volume, occupying 260 out of 365 pages, is concerned with a description of the various chemical substances entering into the composition of the essential oils. It may be said at once that in his selection of material, and in the necessary compression of the subject, the author has exercised wise discretion. Nearly all that the essential oil chemist needs to know will be found in these pages, and if any fuller information should be required reference can readily be made to larger treatises or to the original papers.

The third portion of the work deals with the analysis of essential oils. This occupies only some 50 pages, but it must be remembered that much matter of an analytical nature and the description of many special methods of analysis are to be found in Volume I under the various oils in question. The author has wisely refrained from describing at any considerable length apparatus and general methods, since these are, generally speaking, of a kind with which most chemists—and certainly those who would be likely to consult this book most frequently—are quite familiar.

The printing and illustrations are good, and the writer has noticed very few typographical errors. This work constitutes a valuable contribution to the literature of the essential oils, and is one without which no essential oil chemist's library could be considered as even approximately complete. If any fault is to be found it is with the binding, which is scarcely substantial enough for a standard work of this character intended for laboratory use.

A. CHASTON CHAPMAN.

MODERN GASWORKS CHEMISTRY. By GEOFFREY WEYMAN, D.Sc., F.I.C. Pp. x.+ 184. London: Benn Brothers, Ltd. 1922. Price 25s. net.

The present work on Modern Gasworks Chemistry deals not only with the problems intimately associated with the carbonisation of coal, but also contains chapters upon the analytical control of refractory materials, water supply, steam raising and lubrication.

The second chapter contains a description of the sampling, analysis and variation of coal and is reinforced by an adequate bibliography.

The third chapter is upon the carbonisation of coal, and it is unfortunate that Dr. Weyman has not treated this important branch in greater detail, especially in view of the researches he has carried out upon the subject. Dr. Weyman has assumed that the reader is familiar with the book by Vivian B. Lewes upon the "Carbonisation of Coal," but more should have been said upon this fundamental subject than is contained in one chapter of eleven pages.

The function of the chemist in a gasworks is not only to be able to control the working of the plant, but also to be prepared to suggest modifications in the process based upon the knowledge gained in the laboratory. This requires that he should possess an intimate knowledge of the various coals used in the works, and their behaviour when carbonised at high temperatures, and, equally important, when carbonised at low temperatures. A knowledge of the modification of the properties of coal by heat and other treatment is, therefore, of vital importance to the gasworks chemist.

Chapters V and VI are concerned with the maintenance of heats, and the refractory materials used in gas works. Both these chapters are suggestive contributions to the subject, and the emphasis laid upon the need for control of the refractory material is especially interesting.

Chapter VII contains the valuation of coal tar, but there is only a very brief reference to the important subject of pitch. The purification of gas by means of hydrated ferric oxide is critically examined in Chapter IX, and this chapter is one of the most valuable in the book.

The subject of the examination of towns' gas (Chapter X) is confined to the usual well-known methods of analysing and valuing coal gas.

The Appendix contains tables of the atomic weights, temperatures of saturated steam, strengths of ammonia liquor, the specific gravities and equivalent gallons per ton of tar, logarithms for the correction of the volumes of gas, the specific gravities and strengths of sulphuric acid and melting points of Seger cones.

At the end of each chapter is a bibliography containing the essential references when considered from the point of view of the English literature, but the work carried out in America, France and Germany is not given proportionate prominence.

The book will form a valuable addition to the library of every gasworks chemist, and if, as is suggested in the preface, it is read in conjunction with *The Carbonisation of Coal*, by V. B. Lewes, and *Modern Gas Works Practice*, by Alwyne Meade, it will provide all the necessary information required for the routine control of the chemical side of coal gas manufacture. H. S. SINNATT.

THE ANALYSIS OF RUBBER. By JOHN B. TUTTLE. Pp. 155. New York: The Chemical Catalog Company. 1922. Price $2.50.

The publication under review is one of a series of Scientific and Technological Monographs issued by the American Chemical Society, and, according to the author, it is addressed primarily to the chemists in the consumers' laboratories, and to those who, without any previous experience in the technology or analysis of rubber, may be called upon to deal with a problem in which the composition of rubber may play a more or less important part. Having regard to Mr. Tuttle's aim, it is not remarkable, therefore, that his volume contains a considerable amount of matter of interest to the non-expert, but which the specialist will regard as superfluous, and, *vice-versa*, much that the latter would have gladly seen collated in a handy form has been omitted. Since W. A. Caspari's *India Rubber Laboratory Practice* was issued in 1914 no specialised treatise on rubber analysis has—so

far as the writer is aware—been published in the English language, and, in view of the rapid development of the industry during the past decade, particularly in regard to the use of new compounding ingredients, the introduction of organic accelerators and novel methods of vulcanisation, a book of the nature indicated has long been over due.

Mr. Tuttle rather disarms criticism by his statement of programme, but, all the same, it is difficult to refrain from voicing the wish that, having gone so far, he had gone further. Within its somewhat limited scope the work is up-to-date, and regarded as an instructional volume for the non-expert, it broadly fulfils its purpose. Nevertheless, in view of the present void in specialised literature, it will also be distinctly welcome to the rubber chemist, and should find a place in his library.

Analysts will be interested to note that the author regards the estimation of "free" sulphur by simple oxidation with bromine as satisfactory, that he considers Tuttle and Yuron's nitrosite method as the only accurate direct method for the determination of rubber, and that he is opposed to the methods which involve an indirect determination of rubber and direct determination of fillers by means of a solution process—*i.e.* a separation, as Caspari puts it, of the "charge."

The monograph concludes with a bibliography which strikes one as rather indiscriminate, and appendices on the *Preparation of Materials for Rubber Manufacture* (which is in effect a sketch of rubber manufacturing processes), *Physical Tests* and a *Table of Specific Gravities.*

With regard to the physical tests, it is not likely that the author's curt dismissal of the ring-shaped test piece will meet with general approval. The statement that: "The ring-shaped test piece cannot be compared with the bar-shaped test piece. Its only advantage lies in the fact that an autographic chart may be made of the stress strain curve," suggests that the author's practical experience of the ring test piece is not of an extensive character. It is sufficient to add that the greater part of the fundamental work on the mechanics of vulcanisation carried out in Europe, and by British and Dutch chemists in Malaya and Java, was based on the use of the ring test piece, and that without the ring method the progress, both scientific and technical, made in this connection would, in comparison with actual achievements, have been greatly restricted.

PHILIP SCHIDROWITZ.