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THE ESTIMATION OF CODEINE.

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THE absence of methods capable of accurately estimating small amounts—*e.g.*, a few milligrams—of a particular alkaloid in the presence of large amounts of plant material is no doubt the reason why so little really satisfactory work has been carried out bearing on the manner in which alkaloids are produced in the actual plant.   In our work on the Indian opium poppy we have, therefore, paid considerable attention to methods of estimation of the three chief opium alkaloids— morphine, narcotine, codeine.   As a result we now claim to have devised methods which are capable of the accurate estimation of the small amounts of narcotine or codeine occurring in poppy capsules.   The methods will also accurately estimate the amount of either of these two alkaloids in opium.   We have not so far met with the same amount of success with morphine.   In addition to our need for methods for the actual estimation of the above-named alkaloids in the actual plant, it was an urgent matter for us to have methods which were rapid, since we are engaged in collaboration with Mr. H. M. Leake, Economic Botanist to the Government of the United Provinces in plant-to-plant selection work, having for its object the production of races of plants rich in a particular alkaloid.   The methods we have devised are far more rapid in their execution than any hitherto published.   They further possess the advantage that they can be used when only small amounts of material are available.

The published methods for codeine estimation are those of P. van der Wielen, (*Pharm. Zeit.*, 1903, **48**, 267, and *Bull. Soc. Pharmacol*, 1910, **17**, 59-63), Caspari (*Apoth. Zeit.*, 1904, **19**, 874), and Andrews (ANALYST, 1911, **36**, 489).   The last-mentioned, in his paper referring to the two former methods, states : " These are both unsatisfactory, for in Van der Wielen's method the separation of codeine and narcotine depends on the complete crystallisation of the latter from an alcoholic solution of the mixed crude alkaloids, and in Caspari's method there is loss of codeine owing to its being carried down with morphine when this alkaloid is precipitated by ammonia from an aqueous liquid containing the two alkaloids."   Andrews publishes

no experimental evidence to show that Van der Wielen's or Caspari's method gives unsatisfactory results. We in our turn have tested Van der Wielen's and Andrews's methods with pure alkaloids. As shown below, they gave such low results in our hands as to be useless for our purposes. A further objection to Andrews's method is the long time taken over the analysis. Caspari's process is also long, and 50 grms. of opium are required for a determination. We therefore did not examine it.

EXPERIMENTALS—*Test of Andrews's Method using Pure Codeine.*—The codeine used in this experiment had been twice recrystallised from alcohol and dried at 110° C. to constant weight. Three portions of 0·4, 0·2, and 0·1 grm. respectively were weighed out. Each portion was dissolved in 100 c.c. of water containing 1 c.c. of 10 per cent. of H_2SO_4. The first part of Andrews's method consists of extracting the opium with water to dissolve out the codeine. In the case of the pure alkaloid we had, of course, to use a small amount of acid to bring the alkaloid into solution, and since opium extracts are acid it was necessary that our extract should be acid for the sake of comparison. In each case to the 100 c.c. of codeine solution 20 c.c. of a 20 per cent. solution of lead acetate were added, and from this point onward the method was the same as described by Andrews. The results obtained are summarised in the table :

Weights of Codeine taken (Grm.).	0·400	0·200	0·100
Weight of codeine theoretically recoverable* ...	0·333	0·167	0·083
Weight actually recovered, gravity figure ...	0·1616	0·1040	0·0344
,, ,, ,, volume figure ...	0·1506	0·0793	0·0333
Percentage of codeine recovered on amount taken (volume figure)	45·2	47·6	39·9

Less than half the codeine has, therefore, been recovered in each experiment. The codeine is finally recovered by Andrews by extracting a solution made alkaline with caustic soda, four times with its own bulk of ether. The ether is then washed with water to remove caustic soda. In view of our low recovery, we again submitted the alkaline solution to four extractions with ether, with subsequent washings of the ether, and obtained 0·0412, 0·0316, and 0·0134 grm. respectively of a waxy residue. This residue was not codeine, however, since it was a neutral substance and gave no titration value when titrated with sulphuric acid. It seemed to us probable that when the ethereal solution of codeine is washed with water much loss of codeine might take place, because both codeine and ether are appreciably soluble in water. Thus Allen ("Commercial Organic Analysis," vol. vi., p. 463) states that one part of codeine is soluble in 120 parts of cold water. We have therefore tested this point and the results of our experiments show that it is obvious that the washing of the ethereal solution of codeine with water must result in appreciable loss of the alkaloid, even if only small quantities of water are used for washing purposes. We have made other determinations with Andrews's method both with pure codeine alone and in the presence of

* After addition of 20 c.c. of lead acetate solution to 100 c.c. of aqueous extract containing the codeine, Andrews filters and takes 100 c.c. of the filtrate only for subsequent recovery of codeine.

other alkaloids and also in opium. We have always obtained low results, and, more-over, our final product was not pure codeine.

Tests with Van der Wielen's Method using Pure Alkaloids.—In Van der Wielen's process (*loc. cit.*) both codeine and narcotine are estimated in the same sample. We have tested the process with pure codeine alone, pure narcotine alone, and with mixtures of pure codeine and narcotine. We followed the method as laid down in Van der Wielen's later paper. Four series of experiments were started.

Series I.—Crystalline codeine dried at air temperature (22° C.). *Series II.*—Anhydrous codeine dried at 110° C. *Series III.*—Codeine + narcotine. Codeine dried at 110° C. and narcotine dried at 100° C. *Series IV.*—Narcotine alone, dried at 100° C.

In each case the sample was boiled with 100 grms. of 70 per cent. alcohol in a tared Erlenmeyer flask under a reflux condenser for one hour. After cooling, any loss in weight was made good by addition of 70 per cent. alcohol. Van der Wielen takes 10 grms. of opium with 100 grms. of 70 per cent. alcohol. After restoring any lost weight after the hour's boiling with 70 per cent. alcohol, he filters and determines the dry extract in 5 grms. of the filtrate. He then proceeds with the method by taking such a quantity of this filtrate as is equivalent to 3 grms. opium. In the case of these pure alkaloids it was sufficient for us to take $\frac{3}{10}$ of the total weight of the alcoholic solution, since the alkaloids went into solution. The quantities taken were evaporated to 3 c.c. in a small dish. In series I. and II. we obtained a yellow liquid with fine yellow suspended particles. In series III. and IV. (containing narcotine) the solutions set to a solid mass. The contents of the dish were then washed out into a flask with 7·5 c.c. of water ; 90 c.c. of ether were next added, and after shaking, 5 c.c. of 10 per cent. of NaOH solution. The flask was then allowed to stand, with frequent shakings, for three hours ; 3 grms. of gum tragacanth were next added to aid separation of the ether, and exactly 75 c.c. of the ethereal solution (which equals 2·5 grms. of opium in the actual method) were decanted off and evaporated to dryness. The residue was dissolved in 4 grms. of 90 per cent. alcohol and set aside for twenty-four hours. The crystals of narcotine, if any, which separated were collected on a filter, washed with 5 c.c. alcohol, dried at 100 C., and weighed. As narcotine is not entirely soluble in alcohol, a correction of 0·016 must be applied. (Note.—We found that this correction factor under our conditions of temperature, etc., was about 0·021.) The filtrate from the narcotine was diluted with 10 c.c. water and then evaporated to 10 c.c. ; series I. and II. (pure codeines) give no precipitate, but with series III. and IV. (containing narcotine) instantaneous precipitation took place on addition of water, and a copious precipitate came down on concentration to 10 c.c. Van der Wielen filters off at this stage in the case of an opium analysis and discards the precipitate as a resinous one. Unfortunately we did not examine the precipitate, but we dried and weighed it. These weights were as follows : Series III.—(*a*) 0·0234, (*b*) 0·0256, (*c*) 0·0270 grm. Series IV.—(*a*) 0·0218, (*b*) 0·0210, (*c*) 0·0072 grm.

If we included this weight with that of the narcotine obtained instead of the solubility correction (0·016 grm.) laid down, the figures for narcotine recovery would in all cases but the last be fairly near the theoretical. Since we get no such precipi-

tate in the case of the pure codeine series, the presumption is that this precipitate is narcotine. The precipitate is filtered off, and the filter well washed with water. Excess of $\frac{N}{10}$ HCl was added to this filtrate and a few drops of methyl orange. After standing for fifteen minutes the excess of $\frac{N}{10}$ HCl was titrated with $\frac{N}{10}$ NaOH. It was determined by actual titration that 1 c.c. $\frac{N}{10}$ HCl = 0·0307 grm. crystallised codeine, or 0·0299 grm. amorphous codeine.

The results obtained are set out below :

Series.	Weights of Alkaloids taken.	Weight of Narcotine found (excluding Correction 0·016).	Actually present.	Per Cent. Recovery.	Weight of Codeine found.	Actually present.	Per Cent. Recovery.
		Grm.	Grm.		Grm.	Grm.	
I. Pure crystallised codeine	(a) 0·400 grm.	0·0162	0·0000	—	0·0698	0·1000	69·8
	(b) 0·200 ,,	0·0096	0·0000	—	0·0339	0·5000	67·8
	(c) 0·100 ,,	0·0048	0·0000	—	0.0165	0·0250	66·0
II. Pure amorphous codeine dried at 110° C.	(a) 0·400 grm.	0·0180	0·0000	—	0·0646	0·1000	64·6
	(b) 0·200 ,,	0·0092	0·0000	—	0·0345	0·6500	69·0
	(c) 0·100 ,,	0·0036	0·0000	—	0·0152	0 0250	60·8
		(including correction 0·016).					
III. Pure amorphous codeine + pure narcotine	(a) 0·400 grm. codeine, 0·400 grm. narcotine	0·0904	0·1000	90·4	0·0723	0·1000	72·3
	(b) 0·200 grm. codeine, 0·200 grm. narcotine	0·0384	0·0500	76·8	0·0291	0·0500	58·2
	(c) 0·100 grm. codeine, 0·100 grm. narcotine	0·0198	0·0250	79·2	0·0191	0·0250	76·4
IV. Pure narcotine dried at 100° C.	(a) 0·400 grm. narcotine	0·0884	0·1000	88·4	0·0000	0·0000	—
	(b) 0·200 grm. narcotine	0·0412	0·0500	82·4	0·0000	0·0000	—
	(c) 0·100 grm. narcotine	0·0208	0·0250	83·2	0·0000	0·0000	—

In our hands, therefore, Van der Wielen's method has proved unsatisfactory, and has only recovered about $\frac{2}{3}$ of the codeine present. Of the codeine as much as 15 to 20 per cent. is seen to have been precipitated from 90 per cent. alcohol at the

stage where narcotine should have been obtained. As regards narcotine, the method has given results rather nearer the theoretical, but it must be remembered that a big correction factor for solubility in alcohol has been largely responsible for this.

We agree with Andrews that it is unsatisfactory to use a method for estimation of codeine and narcotine in which the separation of the two alkaloids depends on complete separation of narcotine from codeine by crystallisation.

We have found, in short, that Van der Wielen's method gives such unsatisfactory results with pure alkaloids that it can hardly be of much use in opium analysis.

The following are the details of the method we have devised. The method can be used for opium, pure alkaloids, or for plant material with appropriate modifications as to amounts of material taken.

When working with opium it is preferable to dry the substance first, otherwise allowance has to be made in the subsequent calculations for water present in it. In the analysis of opium we usually take 10 grms. of the dry substance and rub it down very thoroughly in a mortar with 4 grms. of freshly slaked lime and sufficient water to make a paste. More water is then used until 100 c.c. have been added in all. The whole is well stirred at intervals during half an hour and then filtered on a Buchner funnel. To 50 c.c. of the filtrate (=5 grms. of opium) are added 40 c.c. of 2 per cent. acetic acid and 10 c.c. of basic lead acetate solution of sp. gr. 1·25. The whole is vigorously shaken and filtered. To 75 c.c. of the filtrate (=3·75 grms. opium) are added 2 grms. of freshly slaked lime, and the flask is then shaken at intervals during half an hour and the contents filtered; 50 c.c. of the filtrate, representing 2·5 grms. of opium, are then shaken with three successive portions each of 50 c.c. of toluene. The combined toluene extract is filtered and 120 c.c. (2 grms. of opium) are placed in a distilling flask, and dry hydrochloric acid gas is cautiously bubbled through it. Codeine hydrochloride separates instantly as a white flocculent precipitate. Care must be taken to avoid great excess of hydrochloric acid; we usually pass a steady stream of gas for one minute. A stream of air is next passed through the flask for ten minutes to remove excess of acid. The toluene is then filtered into a fresh distilling flask, and hydrochloric acid gas is again passed through it in order to see if the precipitation of codeine hydrochloride is complete. If a further precipitate is obtained, the toluene is again aërated, and then filtered through the same filter-paper. After experience in the method we find that all the codeine can be separated by the first treatment with hydrogen chloride. The flasks and filter-paper are then washed with small quantities of water through the filter into a small weighed glass dish, 10 to 15 c.c. of water being usually sufficient. This is then evaporated on the water-bath, fine clusters of crystals being obtained. The dish is finally dried in the water-oven and weighed. The gravimetric figure may also be checked by a chlorine estimation, but in view of the low chlorine content of the hydrochloride we place greater reliance on the gravimetric figure.

The final product is usually somewhat coloured, but experience shows that the amount of colouring matter is of no significance, and it can be entirely separated if

desired by adding ammonia to the aqueous solution, and allowing the latter to stand over-night. On filtration the codeine can be separated by extracting with toluene. The hydrochloride is precipitated as before by gaseous hydrogen chloride.

For rapid estimations quite good results can be obtained by dispensing with the basic lead acetate treatment. The final product is then strongly coloured, but it seems that the colouring matter does not introduce an error greater than about 5 to 10 per cent. It can be removed fairly completely with animal charcoal with only slight loss of alkaloid.

The method depends on the fact that when opium is treated with slaked lime and water all the morphine and codeine pass into solution. The codeine can then be completely separated from this lime solution by agitation with toluene ; the morphine, by virtue of its phenolic hydroxyl group, is held in solution in combination with the lime, whereas the codeine forms no such compound. A study of the literature and our own experience shows that no appreciable quantity of any other alkaloid passes into our final product. Narcotine we have shown (ANALYST, 1918, 43, 205) to be completely insoluble in lime and water. Narceine is stated to be soluble in alkalis (Henry, "Plant Alkaloids," p. 242), but it is insoluble in toluene. Papaverine is insoluble in alkalis (Pictet, "Vegetable Alkaloids," p. 286), and so does not influence the method. Thebaine is also insoluble in alkalis (*ibid.* p. 283). The remaining alkaloids are present in such small amounts in opium that they cannot affect the method in any case. We have shown (*loc. cit.*) that 50 c.c. of water in the presence of 1·25 grms. of slaked lime are capable of dissolving 0·38 grm. of codeine. In the B.P. (1914) method for the estimation of morphine in opium the quantities used are 8 grms. opium, 2 grms. slaked lime, and 80 c.c. water. These amounts of lime and water would dissolve about 0·61 grm. of pure codeine. In 8 grms. of opium this represents a percentage of 7·6. We have, so far, not had an opium containing as much codeine as this, but if one should be found the method could still be used by taking only half the quantity of opium laid down by us.

It will be noticed that after making the lime solution we acidify with acetic acid and add basic lead acetate. We find that this procedure removes a number of substances, notably colouring matters, which, in the case of Indian opium at least, are apt to contaminate the codeine hydrochloride precipitate. Basic lead acetate removes no codeine or morphine. The filtrate from the lead precipitate was, of course, treated with lime, in order to set the codeine free again for extraction with the toluene. The toluene extract, as far as we have been able to investigate, contains only very small amounts of substances other than codeine. We tried to estimate the codeine in the toluene extract polarimetrically, but the results were not satisfactory.

After various attempts to separate the codeine in a pure form, we found that the most satisfactory results could be obtained by isolating it as hydrochloride. Beal and Brady (ANALYST, 1916, 41, 132), working with coniine, state that they obtained an oil as well as the crystals, and assumed the oil to be a higher hydrochloride. We also, in the case of codeine, frequently obtained an oil by passing in too great an excess of hydrochloric acid gas. The codeine hydrochloride we recover is in a

crystalline form, occasionally contaminated with some slight amount of colouring matter.

The method has been tested with pure codeine in varying amounts. Samples of opium with and without known added amounts of codeine have been examined by it. We have also carried out Andrews's method and our method on the same sample of opium. Andrews's method has given in our hands only 40 to 50 per cent. of the codeine which our method gave in the same samples. Our experiments with Andrews's method in pure codeine recovered only 40 to 46 per cent. of the codeine taken. This is a further indication of the correctness of our method.

EXPERIMENTS WITH PURE CODEINE.—Six portions of 0·05, 0·10, 0·20, 0·30, 0·40, and 0·50 grm. of pure crystalline codeine were each triturated in a mortar with 2 grms. of lime and 80 c.c. of water. They were stirred at intervals during half an hour, and the contents filtered. In each case 50 c.c. ($= \frac{5}{8}$ of the total quantity taken) were placed in a 100 c.c. flask, together with 40 c.c. of 2 per cent. acetic acid, and 0·5 grm. dry basic lead acetate, and the contents made up to 100 c.c. After shaking and filtration, 80 c.c. of each filtrate was then shaken up with 2 grms. freshly slaked lime and filtered. Fifty c.c. ($= \frac{5}{16}$ of the original quantity taken) were then extracted with three successive portions of 50 c.c. of toluene, and 120 c.c. of the filtered toluene extract were then taken for separation of the codeine as hydro-chloride. The following results were obtained :

Weight of Crystalline Codeine taken.	Weight of Codeine Hydrochloride corresponding with Five-Sixteenths of the Codeine taken.	
	Actual Yield.	Theoretical Yield.
0·050 grm.	0·0148 grm.	0·0143 grm.
0·100 ,,	0·0302 ,,	0·0286 ,,
0·200 ,,	0·0588 ,,	0·0572 ,,
0·300 ,,	0·0934 ,,	0·0858 ,,
0·400 ,,	0·1110 ,,	0·1114 ,,
0·500 ,,	0·1472 ,,	0·1430 ,,

Allen ("Commercial Organic Analysis," vol. ii., p. 391) states that the composition of codeine hydrochloride after drying at 100° C. is $C_{18}H_{21}NO_3HCl,1\frac{1}{2}H_2O$. This corresponds with our experience, and we have used this formula in our calculations.

EXPERIMENTS WITH OPIUM WITH AND WITHOUT KNOWN ADDED AMOUNTS OF CODEINE.—Four portions, each of 8 grms., of finely powdered air-dried opium were weighed, and to the second, third, and fourth portions respectively were added 0·04, 0·08, and 0·16 grm. of pure codeine. Each portion was then triturated with 4 grms. of lime, and a little water as described, and more water was added, until 80 c.c. had been added in all. After filtration, 50 c.c. were taken for addition of 40 c.c. of 2 per cent. acetic acid and 10 c.c. of basic lead acetate solution. Seventy-five c.c. of the filtrate from this treatment were shaken with lime, and 50 c.c. of the resulting filtrate were extracted with three successive portions of 50 c.c. of toluene. Of the

combined filtered toluene extract, 120 c.c. were in each case taken for separation of the codeine hydrochloride. The following results were obtained :

| | | Codeine Hydrochloride. | |
Opium taken.	Codeine added.	Actual Yield.	Theoretical Yield* on Basis of Expt. No. 1.
8 grms.	Nil grm.	0·0984 grm.	— grm.
8 ,,	0·04 ,,	0·1148 ,,	0·1105 ,,
8 ,,	0·08 ,,	0·1275 ,,	0·1226 ,,
8 ,,	0·16 ,,	0·1407 ,,	0·1468 ,,

CONCLUSION.—The method we have devised for codeine estimation gives accurate results. It has the advantage that the codeine can be isolated in a pure crystalline form as hydrochloride. The method is, moreover, rapid and easy of execution.

We have made use of a modification of the method for the estimation of codeine in plant material such as poppy capsules with eminently satisfactory results. It is hoped later to make a further communication on this work.

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THE INFLUENCE OF THE FREE FATTY-ACID CONTENT IN THE VALUATION OF CHINESE WOOD-OIL BY THE BROWNE POLYMERISATION TEST.

By PHILIP E. JAMESON.

IN testing Chinese wood-oil ("tung-oil") for varnish-making purposes, advantage is taken of the remarkable property of the oil to solidify at elevated temperatures. This phenomenon is due to polymerisation, and, as far as is known at present, is not characteristic of any other glyceride.

The Browne method (ANALYST, 1912, **37**, 410) is the one commonly used by varnish chemists in this country, and is officially adopted by the American Society for Testing Materials (Standard Specification for Raw Tung-oil, D. 12-16). Briefly, it consists in heating 5 c.c. wood-oil in a test-tube immersed in an oil-bath kept at a constant temperature of 540° F. By means of a glass rod placed in the sample the operator judges when the oil has solidified completely. This should not take more than twelve minutes for a pure oil. Browne (*loc. cit.*) showed that on mixing pure wood-oil with soya-bean, cotton-seed, and other oils, so that the mixture contained 10 per cent. foreign oil, the time required for polymerisation was increased from

* 0·100 grm. codeine = 0·121 grm. $C_{18}H_{21}NO_3HCl$ $1\frac{1}{2}$ H_2O.

two and a half to three minutes. This has led to the idea that when an oil fails to pass the twelve-minute limit it is necessarily adulterated with one of these foreign oils.

In reviewing the literature of chinawood-oil testing, the writer noticed that none of the investigators has taken into consideration the influence of the free fatty-acid content on the time of polymerisation. In fact, very few chemists have even stated the percentage of free acid present in the oils under examination.

In the course of testing several hundred samples of wood-oil in this laboratory, it was found that the free acid content has a direct influence on the time required for polymerisation—in other words, since the fatty acids do not themselves possess the property of solidifying with heat, it follows that the time of polymerisation is increased in proportion to the amount of free fatty acid present in the oil.

The time of polymerisation of the majority of wood-oils available in the present market exceeds the twelve-minute limit. In order to eliminate the influence of the free acid, the time of polymerisation of oils from which the acid had been entirely removed was determined. Several methods were tried for removing the acid without otherwise changing the oil. The following was found to give the best results: 5 grms. dry calcium hydroxide of at least 75 per cent. strength are added to 100 c.c. wood-oil, stirred well at intervals for fifteen minutes, and then filtered through a 25 cm. "quantitative" filter-paper on a 12 cm. "ribbed" funnel. The oil so obtained will be clear and lighter in colour than the original, and should be entirely free from fatty acid. The time of polymerisation is now determined and compared with that of the original.

The results of the examination of a number of samples from different importers are shown in the table:

Sp. Gr. at 60° F.	Percentage Free Fatty Acid.	Time required for Polymerisation at 540° F.	
		(a) Original Oil.	(b) Acidless Oil.
0·940	1·9	13 mins.	12 mins.
0·940	2·8	$13\frac{1}{2}$,,	12 ,,
0·939	4·6	$14\frac{1}{2}$,,	12 ,,
0·939	4·5	$14\frac{1}{2}$,,	12 ,,
0·940	2·8	13 ,,	$11\frac{3}{4}$,,
0·939	3·7	$13\frac{1}{2}$,,	12 ,,
0·939	3·8	$13\frac{1}{2}$,,	12 ,,
0·940	2·4	13 ,,	$11\frac{3}{4}$,,
0·940	2·7	13 ,,	$11\frac{1}{2}$,,
0·940	3·2	$13\frac{1}{2}$,,	$11\frac{3}{4}$,,
0·940	3·3	13 ,,	$11\frac{1}{2}$,,
0·939	3·4	$13\frac{1}{2}$,,	12 ,,

SPECIFIC GRAVITY.—Determined at 60° F. by means of a Westphal balance.

PERCENTAGE FREE FATTY ACID.—Twenty-five grms. oil are weighed into a 500 c.c. flask and shaken with a mixture of 100 c.c. redistilled alcohol and 100 c.c. redistilled neutralised benzol. The mixture is then titrated with $\frac{N}{5}$ potassium hydroxide solution, with phenolphthaleïn as indicator, until

the red colour remains after stoppering the flask and shaking. The results are calculated to percentage of eleostearic acid, 1 c.c. $\frac{N}{5}$ KOH being equivalent to 0·056 grm. eleostearic acid, M.W. 280.

HEATING TEST.—The Browne method (*loc. cit.*) is used as originally published with the exception of the following modification : Instead of the 6 cm. by 12 cm. oil-bath a larger one, 12 cm. by 12 cm., was used. This enables the operator to maintain a more uniform temperature, and at the same time permits the use of three tubes instead of one, the first being used for the sample "as received," the second for the acidless oil, and the third for the "standard." The latter is a wood-oil of known purity which serves as a check on the results. (The standard used by the writer contained 0·5 per cent. free acid and polymerised in eleven minutes at 540° F.)

The figures in the table show the variation in amount of the free fatty acid. After testing several hundred samples of wood-oils by this method, few samples were found which failed to polymerise in twelve minutes or less following the removal of the free fatty acids.

The fact that most oils which fail to pass the twelve-minute requirement "as received" will do so when rendered neutral supports the conclusion that such oils are not necessarily adulterated but contain too much free acid for varnish-making purposes, since the free acid is more deleterious than foreign oil. This matter of excessive free acid should receive more consideration from exporters in the future. The high acid content, as well as the dark colour of most of the oils in the market to-day, is no doubt due to the practice the Chinese producers make of heating the kernels before pressing. A prime wood-oil for varnish-making purposes should not contain over 1 per cent. free acid.*

The author hopes that the use of this modification of the Browne heating test will enable chemists to judge more accurately the quality of wood-oils in the future and revise specifications accordingly. The proportion of tri-eleostearin, to which the phenomenon of polymerisation is due, undoubtedly varies in oils from different localities according to soil conditions, botanical variation, etc.

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APPARATUS FOR EVOLUTION METHODS OF ANALYSIS.

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THE apparatus shown in Fig. 1 was found to be exceedingly convenient for the examination of pyrolusite, and has been since used for various evolution methods, such as the estimation of sulphur in steel by the ammoniacal cadmium sulphate process.

The diagram is self-explanatory: the bulk of the absorbing liquid is placed in the large test-tube C, a smaller quantity in the U-tube E. It is easy to charge, and

* The American Society for Testing Materials Specification for Raw Tung-oil, mentioned above, allows a maximum of 3 per cent. free fatty-acid. The writer has seen very few wood-oils of this high acidity which would pass the twelve-minute limit with the heating test.

is proof against sucking back, as on the slightest diminution of pressure in the flask A air bubbles in through the tube B. It is found in practice that in most cases complete absorption takes place in the tube C, which at the end of the distillation is very easily detached and washed out.

The apparatus shown in Fig. 2 was primarily designed for the estimation of carbon in steel by the wet combustion method, absorbing the CO_2 in barium hydroxide solution, and afterwards titrating the barium carbonate. It, however, has been used for other evolution methods where it is desirable to have a condenser above the boiling flask. It consists of a boiling flask, A, fitted with a short Liebig
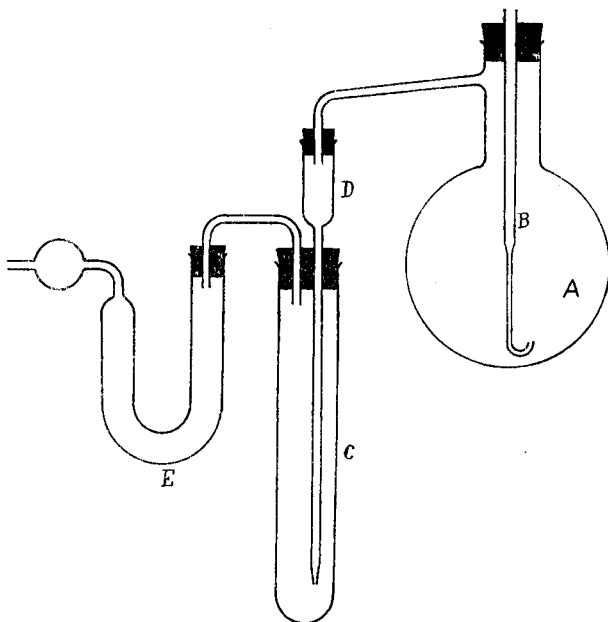

FIG. 1.

condenser, B, through which passes the long stem of a tap funnel, C. The whole is connected, as shown, with a 100 c.c. burette containing a Young's rod and disc, which fits loosely, and extends about two-thirds of the length of the burette. The top of the latter is attached by a three-way tap to an aspirator. For the carbon estimations, after the apparatus has been washed out with a stream of CO_2-free air, 30 c.c. of barium hydroxide solution are sucked up into the burette, the flask A charged, and the estimation proceeded with, controlling the flow of gas by means of the burette' stopcock, sufficient head of water being maintained in the aspirator all the time to prevent any escape of the barium hydroxide through the lower tap. When the absorption is complete, the tip of the burette is passed through a rubber stopper fitted into a wide filter-tube, the liquid run straight from the burette through the filter, the burette and precipitate being washed by allowing the filter-pump to draw

portions of the aspirator water through the apparatus. In this way the barium carbonate can be filtered off and washed without any contact with the atmosphere.
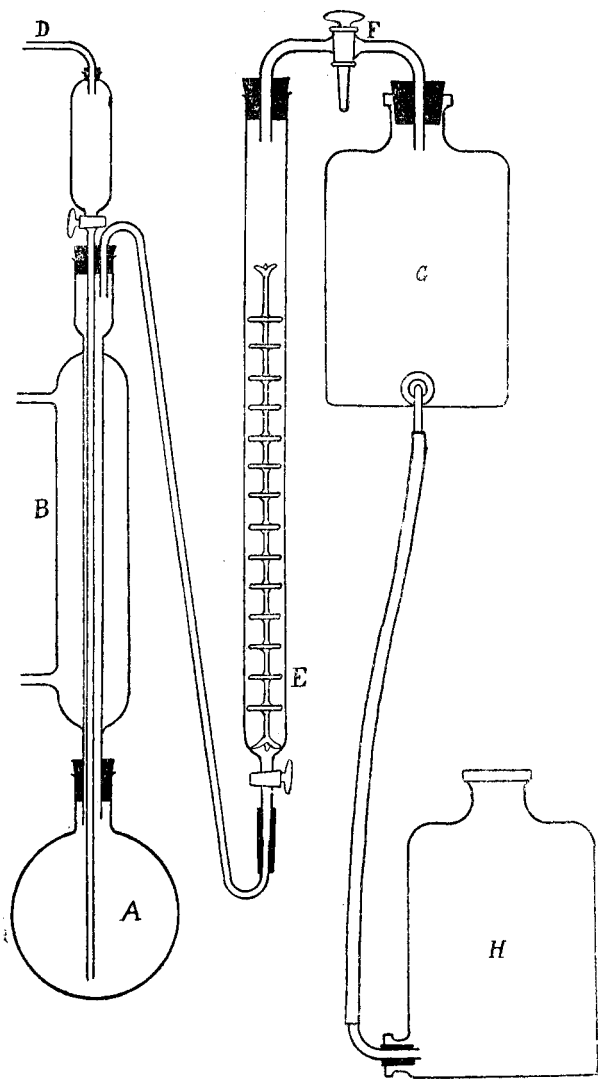

FIG. 2.

The burette fitted with the rod and discs forms a very efficient absorption apparatus, and may be used for many purposes.
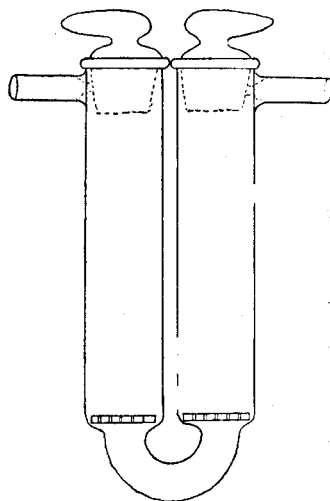
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AN IMPROVED FORM OF U-TUBE.

By E. R. DOVEY.

THE form of U-tube shown in the sketch has been found to be more easily cleaned and charged, and also much less fragile than the ordinary form. The two limbs are brought together so that the rims at the top are in contact. A slight squeeze when holding the tube during charging or connecting is much less likely to result in fracture than in the ordinary form. Two perforated Gooch discs rest at the bottom of each limb, keeping the bent portion free from absorbent material.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Estimation of Caffeine in Coffee Mixtures and so-called Caffeineless Coffees. E. Vautier. (*Ann. Chim. anal. Appl.*, 1920, **2**, 168-172.)—The method of estimating caffeine previously described (ANALYST, 1918, **43**, 410) gives sufficiently accurate results in the analysis of ordinary coffees, but in the case of coffees or mixtures poor in caffeine it is necessary to eliminate the sources of error in the sublimation process, either by estimating the nitrogen in the crude product or by purifying the residue of alkaloid. In the first method the crude caffeine is heated in a Kjeldahl flask with 10 c.c. of sulphuric acid, 5 grms. of potassium sulphate, and 0·5 grm. of crystallised copper sulphate, and the ammonia distilled, Congo red being used as indicator. A blank estimation should be made under the same conditions. Each 1 c.c. of $\frac{N}{10}$ acid corresponds with 0·00485 grm. of anhydrous or 0·00530 grm. of hydrated caffeine. In the second method the solution of crude caffeine is evaporated to dryness on the water-bath with 0·1 to 0·2 grm. of sodium carbonate, and the residue repeatedly treated with small portions of chloroform, which does not dissolve the sodium salts of the humic acid-like impurities. The united filtrates from the insoluble residue are evaporated to dryness and the purified caffeine dried at 100° C. A caffeineless coffee yielded 0·13 per cent. of caffeine by the sublimation method, 0·05 per cent. calculated from the nitrogen, and 0·05 to 0·06 per cent. after purification with chloroform.   C. A. M.

Oxalic Acid in Rhubarb and the Removal of Oxalic Acid from Rhubarb Products. J. Angerhausen. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1920, **39**, 81-87.)—Rhubarb stalks contain 0·25 per cent. and rhubarb leaves 0·50 per cent. of oxalic acid. The latter is not present in the free state, but as alkali and calcium salts, the alkali salts predominating. The whole of the latter pass into solution when rhubarb stalks are boiled with water. When the leaves are cooked for consumption, the water in which they are boiled should be rejected, and it is advisable to add calcium carbonate (about 1 per cent. of the weight of the leaves) during the cooking operation. W. P. S.

Pentosans as a Basis in Determining the Milling Grade of Flour. J. Gerum. (*Zeitsch. Untersuch. Nahr. Genussm*, 1920, **39**, 65-69.)—Estimation of pentosans in flour is of little use in determining its grade; " 82 per cent." flour yields 7·47 per cent. of phloroglucide and " 94 per cent." flour 8·77 per cent. The starch and ash contents of the flour afford more trustworthy evidence for the purpose. W. P. S.

Identification of Sulphonal and Trional. W. Zimmermann. (*Apoth. Zeit.*, 1920, **35**, 27 ; through *Chem. Zeit. Rep.*, 1920, **44**, 176.)—An odour of mercaptan is observed when 0·1 grm. of sulphonal or trional is fused with 0·1 grm. of sodium salicylate and the mass then boiled with water; if 5 drops of alcohol and 5 drops of concentrated sulphuric acid are added, followed by a further 5 drops of the acid after one minute, and the mixture then warmed, a turbid red-coloured solution is obtained having an odour of methyl salicylate. A violet-coloured residue is produced when 0·2 grm. of either substance is ignited in a porcelain basin ; the residue dissolves in a drop of water giving a violet-coloured solution, the colour changing rapidly to brown. The addition of a drop of hydrochloric acid produces a yellow colour, the separation of a brown precipitate and liberation of sulphur dioxide. Santonin yields a red coloration when heated with sodium salicylate. W. P. S.

Paraguay Tea. C. R. Hennings. (*Ber. Deut. Pharm. Ges.*, 1920, **30**, 22-26 ; through *Chem. Zeit. Rep.*, 1920, **44**, 179.)—Analysis of Paraguay tea (maté) yielded the following results : Water, 9·00 ; water extract, 33·10 ; ash in water extract, 3·8 ; alkaloids, 2·1 ; tannin, 9·79 ; total ash, 6·62 ; soluble ash, 2·26 ; silica, etc., 1·44 ; alkalinity of ash (as K_2O), 0·69 ; crude fibre, 15·45 ; ether extract, 9·8 ; volatile extract, 2·05 ; total nitrogen, 2·17 ; resins, 9·1 per cent. W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Reaction of Benzoic Acid and its Application to the Toxicological Detection of Atropine, Cocaine, and Stovaine. M. Guerbet. (*Comptes rend.*, 1920, **170**, 40-41.)—On treating benzoic acid with fuming nitric acid (sp. gr. 1·49), it gives a mixture of o-, m-, and p-nitrobenzoic acids, and these when heated with stannous chloride are reduced to o-, m-, and p-aminobenzoic acids, which when treated with nitrous acid in hydrochloric acid solution are converted into the corresponding

diazoic chlorides. Lastly, these chlorides combine in ammoniacal solution with β-naphthol to form the isomeric o-, m-, and p-β-naphtholazobenzoic acids, in the form of an orange-red precipitate. The reaction is also given by benzoates, and compounds, such as cocaine and stovaine, which contain the benzoyl radicle, or which, like atropine, yield benzoic acid on oxidation. In applying the test a minute quantity of the substance (e.g., the extract obtained in Stas' method) is treated with 3 or 4 drops of fuming nitric acid on a clock-glass and the liquid evaporated to dryness on the water-bath. The residue is treated with 1 drop of a 10 per cent. solution of stannous chloride, heated for two or three minutes, cooled and treated with 2 drops of sodium nitrite solution (1 : 100). Finally 3 or 4 drops of a 1 per cent. solution of β-naphthol in 10 per cent. ammonia solution are added, and the formation of a reddish-orange precipitate will indicate the presence of benzoic acid. The reaction is obtained very distinctly with 0.1 mgrm. of the above-mentioned alkaloids.

C. A. M.

Biochemical Study of Copra Meal. F. O. Santos y Alvarez. (*Philippine J. Sci.*, 1920, **16**, 181-189.)—Investigation of the nitrogen distribution in that portion of copra meal insoluble in hot water showed that the meal is rich in the amino-acids necessary for the maintenance of growth; arginine, histidine, and crystine are present in considerable quantity, but the amount of lysine is small. Only 47·55 per cent. of the total protein nitrogen is soluble in 0·2 per cent. potassium hydroxide solution ; in the case of lupine seeds, 96 per cent. of the protein nitrogen is soluble in alkali solution. Feeding experiments with copra meal indicated that when fed alone the meal cannot promote growth in pigs, but that when mixed with green leaves it furnished a fairly perfect fodder. W. P. S.

Volumetric Method for the Determination of the Diastatic Capacity. J. T. Flohill. (*J. Ind. and Eng. Chem.*, 1920, **12**, 677.)—One c.c. of a 5 per cent. malt extract prepared by Lintner's method is introduced into 100 c.c. of a 2 per cent. solution of soluble starch in a 200 c.c. flask, and the mixture allowed to stand for one hour at 20° C. The liquid is then treated with 10 c.c. of $\frac{N}{10}$ sodium hydroxide solution and made up to 200 c.c. Twenty-five c.c. are transferred to an Erlenmeyer flask, treated with 10 c.c. of each of the Fehling solutions, and the volume made up to 50 c.c. The mixture is boiled slowly for two minutes, and immediately cooled in running water, but not much below 25° C. Ten c.c. of 30 per cent. potassium iodide solution, or 3 grms. of potassium iodide and 10 c.c. of 25 per cent. sulphuric acid, are added, and the liberated iodine titrated with $\frac{N}{10}$ thiosulphate solution. A blank test is made simultaneously, and the difference between the amounts of thiosulphate used in the two titrations is equivalent to the copper sulphate reduced by the maltose. If 25 c.c. of the above-mentioned solution reduce Fehling's solution equivalent to m c.c. of thiosulphate solution, its strength is

$$\frac{\dfrac{m}{62 \cdot 5n} \times 100}{20} = 320\frac{m}{n}$$

degrees Lintner, where n represents the thiosulphate equivalent of the amount of iodide liberated by the copper sulphate in a blank test. C. A. M.

Serum obtained by the Spontaneous Curdling of Milk. Its use in detecting Adulteration. J. Grossfeld. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1920, **39**, 140-145.)—The serum obtained by allowing milk to curdle spontaneously may be used for the usual investigations applied to sera; it possesses the advantage that no foreign substance is introduced, and the only correction necessary is that for the effect of the acidity on the specific gravity. For each c.c. $\frac{N}{10}$ alkali solution used in neutralising 10 c.c. of the milk, 0·00011 is added to the specific gravity found.

W. P. S.

Estimation of Tyrosin and Dibasic Amino Acids in Yeast Proteins. P. Thomas and A. Chabas. (*Comptes rend.*, 1920, **170**, 1622-1625.)—The colorimetric methods of estimating tyrosin are not absolutely specific for that substance, but also indicate phenolic constituents of proteins free from tyrosin. By the method of Folin and Denis (*J. Biol. Chem.*, 1912, **12**, 245) the yeast protein, cerevisine, was found to contain 6·77 per cent., and the protein, zymocaseine, 7·54 per cent. of tyrosin. The results obtained with Millon's reagent, after eliminating sulphates, were 7·33 and 4·23 per cent. respectively. Direct gravimetric estimation of the tyrosin extracted from the products of the hydrolysis gave 4·13 per cent. for the cerevisine and 2·85 per cent. for the zymocaseine. The amounts of glutamic acid, isolated as hydrochloride and purified by fractional crystallisation from alcohol, were 6·26 per cent. for cerevisine and 0·94 per cent. for zymocaseine, whilst in each case the amount of aspartic acid was less than 1 per cent. C. A. M.

ORGANIC ANALYSIS

Estimation of Acetaldehyde in Paraldehyde. W. Stuve. (*Apoth. Zeit.*, 1920, **35**, 145; through *Chem. Zeit. Rep.*, 1920, **44**, 178.)—Ten c.c. of $\frac{N}{10}$ mercuric chloride solution, 2 grms. of potassium iodide, 20 grms. of 15 per cent. sodium hydroxide solution, 50 grms. of water, and 5 c.c. of the paraldehyde are mixed, shaken occasionally during fifteen minutes, then diluted to 100 c.c. and filtered. Fifty c.c. of the filtrate are treated with 0·5 grm. of gum arabic, 5 c.c. of sodium hydroxide solution, and 3 c.c. of formaldehyde; after fifteen minutes, the mixture is acidified with 15 c.c. of dilute acetic acid, cooled, the reduced mercury is dissolved by the addition of 10 c.c. of $\frac{N}{10}$ iodine solution, and the excess of iodine is titrated with $\frac{N}{10}$ thiosulphate solution. The number of c.c. of iodine solution used by the mercury is multiplied by 2 and subtracted from the number of c.c. equivalent to 10 c.c. of the mercuric chloride solution; each c.c. of $\frac{N}{10}$ iodine solution is equivalent to 0·0022 grm. of acetaldehyde. W. P. S.

Adsorption by Charcoal. Relation of Service Time to Adsorption and Absorption. H. H. Lowry and G. A. Hulett. (*J. Amer. Chem. Soc.*, 1920, **42**, 1393-1408.)—Measurements of the adsorption of nitrogen and carbon dioxide by charcoals showed that the adsorptive capacity per grm. of charcoal at 25° C. and 760 mm. may vary as much as 100 per cent., and there appears to be no relation between service time and adsorption of a gas by various charcoals. (Service time

denotes the period elapsing before a toxic gas can be detected in the effluent air when air containing a known quantity of the gas is passed at a definite rate through a sample of charcoal of standard dimensions.) Adsorption of nitrogen and carbon dioxide by charcoal may be considered to be in a condensed layer 1 molecule deep. Measurements of the isothermal adsorption of water-vapour by charcoal at 25° C. showed that water is not adsorbed by charcoal, but is held by capillary action— i.e., is absorbed. Using Anderson's formula connecting radius of a capillary with vapour pressure, the mean diameters of the capillaries of the four charcoals used in the experiments were calculated, and found to vary between $2 \cdot 8 \times 10^{-7}$ cm. and $1 \cdot 2 \times 10^{-7}$ cm. By means of this same formula and the isothermals for water the surfaces of the charcoal were found to vary from 160 square metres to 436 square metres per grm. of charcoal. This variation in surface was not always accompanied by a corresponding variation in adsorptive capacity. No relation was found to exist between the service time of the charcoals and the volume of the capillaries; the same was true for the saturation points and retentivities, indicating that factors other than adsorption and capillary action influence the minute service of a charcoal.   W. P. S.

Estimation of Cyanamide and Dicyano-diamide in Calcium Cyanamide. Marqueyrol, P. Loriette, and L. Desvergues. (*Ann. Chim. anal. Appl.*, 1920, **2**, 164-167.)—The total nitrogen is estimated by Kjeldahl's method. The estimation of the cyanamide is based upon the fact that an aqueous solution of calcium cyanamide treated with nitrate or acetate of silver in presence of ammonia yields a precipitate of silver cyanamide containing the whole of the cyanamide nitrogen. The amount of cyanide is then calculated from the proportion of nitrogen estimated by Kjeldahl's method. Estimation of the silver in the precipitate, as proposed by Kappen, gives inaccurate results, owing to the composition of the precipitate varying considerably. The error is reduced by using very dilute solutions of cyanamide, silver nitrate and ammonium thiocyanate, dissolving the calcium cyanamide in the minimum amount of nitric acid, and rendering the solution slightly ammoniacal before precipitating the silver cyanamide. The estimation of the dicyano-diamide depends upon the fact that its aqueous solution treated with nitrate or acetate of silver, in the presence of potassium or sodium hydroxide, yields a precipitate containing the whole of the dicyano-diamide nitrogen. After precipitation of the cyanamide, the liquid is filtered, the filtrate boiled with a little 10 per cent. potassium hydroxide solution until all ammonia is expelled, the resulting precipitate separated and washed, and its nitrogen estimated by Kjeldahl's method. It has been shown by Caro (ANALYST, 1911, **36**, 76) that the composition of the precipitate varies with the quantities of dicyano-diamide and silver salt used, and for this reason volumetric methods based on the estimation of the silver are inaccurate. There are also present in calcium cyanamide other nitrogenous compounds—viz., urea, up to about 0·5 per cent. of nitrogen calculated on the cyanamide; compounds insoluble in water and in nitric acid (0·5 to 1·5 per cent. of N on the calcium cyanamide); and a small quantity of soluble nitrogen not precipitated by silver.   C. A. M.

Estimation of Glycol. B. Müller. (*Chem. Zeit.*, 1920, **44**, 513-515.)—For the estimation of ethylene glycol (made and sold in Germany as a substitute for glycerol) the dichromate and acetin methods used in glycerol analysis may be used, but the acetin method is unsuitable in the case of dilute aqueous solutions of the glycol. In the dichromate method, heating for four hours is necessary for complete oxidation. The glycol may also be estimated by oxidation with chromic acid and sulphuric acid and weighing the amount of carbon dioxide produced. Since the glycol is not oxidised completely to oxalic acid by alkaline permanganate solution, Benedikt and Zsigmondy's method for glycerol cannot be applied to glycol.

W. P. S.

Comparison of Different Methods for Estimating the Iodine Value of Fats. T. Sundberg and M. Lundborg. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1920, **39**, 87-95.)—The Hanŭs method yields results which agree most closely with those found by the Hubl method; Wijs's method gives higher results, whilst those obtained by Winkler's method are lower than the Hubl values. In the case of linolic acid, the Hubl value lies nearer to the theoretical iodine value than does the Wijs' value. The Hanŭs method is preferable to the Winkler method on account of the shorter reaction period required.   W. P. S.

Detection of Oxalic Acid and Lactic Acid, especially their Differentiation from Tartaric Acid. K. Brauer. (*Chem. Zeit.*, 1920, **44**, 494.)—When heated with concentrated sulphuric acid and resorcinol, oxalic acid yields a brilliant violet coloration, whilst lactic acid and tartaric acid both give a red coloration. If dilute sulphuric acid (1 : 1, or even lower concentration) is used in the test the coloration obtained with the different acids is : Tartaric acid, yellow ; oxalic acid, green ; lactic acid, red. Solutions of the acids should be evaporated to dryness and the tests applied to the residues.   W. P. S.

Rectified Petroleum Spirit from the Toluene-Petrol Fraction of Borneo Petroleum. W. A. Silvester. (*J. Soc. Chem. Ind.*, 1920, **39**, 187-188T.)—The experiments cited do not support the conclusion of Evans (*J. Soc. Chem. Ind.*, 1919, **38**, 401T) that a further fractionation of the two main fractions of this petrol is impossible. It is shown that repeated cumulative fractionation is capable of separating the paraffinic and naphthenic constituents of the two principal fractions, notwithstanding the small differences in the boiling-points. Methylcyclohexane (hexahydrotoluene) was, in fact, separated from the fraction of b.pt. 102°-103° C., and the want of homogeneity, even in the best fraction (103°-104° C.), was obvious. The distillation apparatus used in the laboratory, with the exception of the Hempel and Lindemann columns and their modifications (*cf.* Washburn, ANALYST, 1920, 112), rely mainly on fractional condensation to effect the separation, and are therefore much less efficient than the column still-heads, in which there is also a pronounced interchange of heat between the rising vapour and the returning condensate, causing the " heavy " constituents of the vapour to condense out, whilst the " lighter " portions of the condensate are re-volatilised.   C. A. M.

Direct Estimation of Rubber Hydrocarbon in Raw and Vulcanised Rubber. **W. K. Lewis and W. H. McAdams.** (*J. Ind. and Eng. Chem.*, 1920, **12**, 673-676.)—McIlhiney's method of determining the bromine value of unsaturated oils (ANALYST, 1895, **19**, 14) has been adapted to the estimation of rubber hydrocarbon $(C_{10}H_{16})_n$, which forms an additional compound $(C_{10}H_{16}Br_4)_n$. The amount of substitution which takes place under specified conditions is determined, and twice the amount substituted is deducted from the total bromine absorbed, to obtain a measure of the true bromine addition. In the case of raw rubber, the sample is extracted with acetone to remove the resins, dried and dissolved in pure carbon tetrachloride, and the solution filtered from proteins and other insoluble substances, and evaporated, and the residue weighed. A known volume of carbon tetrachloride solution, containing about 0·2 grm, of the rubber hydrocarbon, is treated with a measured volume of a solution of bromine in pure carbon tetrachloride, so that an excess of about 150 per cent. of bromine is present, and the mixture allowed to stand for three hours in a dark room in a stoppered bottle. Ten c.c. of 3 per cent. potassium iodide solution (10 c.c. for vulcanised rubber) are then added, and the liberated iodine titrated. To determine the substitution 10 c.c. of 5 per cent.. potassium iodate solution are next added, and the iodine corresponding to the hydrobromic acid titrated. A blank determination is made under the same conditions to eliminate errors due to impurities in the reagents. In applying the method to vulcanised rubber, the finely divided sample is extracted with acetone to remove resins, free sulphur, etc. The residue is dissolved by heating it for several hours with purified tetrachloroethane beneath a reflux condenser, the solution diluted with carbon tetrachloride to a definite volume, and an aliquot portion taken for the bromination. Substitution of bromine may be reduced to a minimum by titrating the brominated liquid in dim light. An estimation of combined sulphur in the rubber is made by the method of Davies (CHEMIST-ANALYST, 1915, **15**, 4), the residue from an aliquot portion of the tetrachloroethane solution being treated with 10 c.c. of saturated arsenic acid solution, 10 c.c. of fuming nitric acid, and 3 c.c. of bromine water, the mixture evaporated to a syrup, and the sulphuric acid estimated gravimetrically. The percentage of sulphur multiplied by 2·13 gives the amount of rubber hydrocarbon combined with sulphur, whilst the amount of uncombined hydrocarbon is calculated from the bromine result. C. A. M.

Volumetric Method for the Estimation of Reducing Sugars. **A. Jonescu and V. Vargolici.** (*Bul. Soc. Chim. Románia*, 1920, **11**, 38-45.)—The method depends on the reduction of potassium ferricyanide ; 1 molecule of dextrose reduces 5 molecules of ferricyanide in alkaline solution and under the conditions given. The reagent solution contains 46 grms. of potassium ferricyanide and 56 grms. of potassium hydroxide per litre and is standardised against pure dextrose. Ten c.c. of the reagent and 20 c.c. of water are boiled and titrated with a 0·5 per cent. dextrose solution, until the yellow ferricyanide is reduced completely to colourless ferrocyanide. Exactly 10 c.c. of the dextrose solution should be required. With coloured sugar solutions a few drops of picric acid may be added as an indicator ; as soon as all the ferricyanide has been reduced, further addition of dextrose or other reducing sugar

reduces the picric acid and produces a red coloration. The method may be used for the estimation of sugar in urine (after clarification with lead acetate and sodium carbonate) and of lactose in milk. In the latter case, the lactose solution is prepared by treating 10 c.c. of the milk with 10 c.c. of a mixture containing 20 grms. of acetic acid and 10 grms. of picric acid per litre and filtering the mixture; 10 c.c. of the filtrate are neutralised with sodium hydroxide solution, diluted to 40 c.c., and this solution is used for the titration.   W. P. S.

Titration of Sugars.   N. Schoorl. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1920, **39**, 180-182.)—In using a method described previously by the author (*Zeitsch. angew. Chem.*, 1898, **11**, 633) for the volumetric estimation of sugars based on the iodiometric titration of the excess of cupric salt, the proportions of Fehling solution, sugar solution, etc., prescribed must be used, otherwise the tables for calculating the amount of sugar present are useless.   A reprint of these tables is given.

                                                                W. P. S.

Estimation of Thiocyanates in Ammoniacal Liquors.   J. A. Shaw. (*J. Ind. and Eng. Chem.*, 1920, **12**, 676-677.)—The ammoniacal liquor (500 c.c.) is treated with an aqueous solution of 3 to 5 grms. of ferrous sulphate and about 100 c.c. of 10 per cent. sodium hydroxide solution, allowed to stand overnight, and filtered, with the aid of suction, through an asbestos filter.   This removes organic and inorganic substances insoluble in alkali solution and sulphides, and converts cyanides into ferro-cyanides.   The precipitate is washed with water containing about 30 grms. of sodium hydroxide per litre, and the filtrate and washings are heated to 60° C., slightly acidified with dilute sulphuric acid, and the ferrocyanides precipitated with 10 per cent. ferric chloride solution.   The sludge is filtered off on an asbestos filter, washed with 5 per cent. sulphuric acid containing 5 per cent. of sodium sulphate, and used for the estimation of the cyanogen.   The filtrate is made up to definite volume, and aliquot portions of $\frac{1}{10}$ taken.   These are heated to 70° C., and treated with about 15 c.c. of 1 per cent. sulphuric acid (1 : 4), followed by a decided excess of sodium hydrogen sulphite solution, and the thiocyanate precipitated with hot 10 per cent. copper sulphate solution.   The copper thiocyanate is separated after ten minutes in a Gooch crucible containing paper pulp, and washed with water at about the same temperature as the original liquid before filtration.   The residue and paper pulp is then treated with 25 c.c. of $\frac{N}{1}$-sodium hydroxide solution, the copper oxidised with bromine water, the liquid filtered, the filtrate treated with more bromine water and digested at 100° C. for an hour, after which it is acidified with hydrochloric acid, boiled to remove bromine and evaporated to dryness.   The residue is treated with hot water containing a little hydrochloric acid, and the solution filtered from silica.   Finally, the sulphate is precipitated with barium chloride, and the sulphur in the barium sulphate calculated into thiocyanate.   The method, which is applicable to the waste liquors from ammonia stills in the coking industry, gives the true amount of thiocyanate within 0·01 grm. per litre.   C. A. M.

INORGANIC ANALYSIS.

Detection of Natural Barytes in Lithopone, etc. S. Stewart. (*J. Soc. Chem. Ind.*, 1920, **39**, 188T.)—Inferior qualities of lithopone and other pigments composed essentially of zinc sulphide and barium sulphate sometimes contain natural barytes. This reduces the opacity and covering power of the pigment, and causes it to give a yellowish white when used in linoleum. The natural mineral may be detected by mixing a trace of the sample with a drop of water, drying the mixture, and examining it under the microscope with a $\frac{1}{4}$ to $\frac{1}{6}$ inch objective, the diaphragm being closed so as to form a dark background. Precipitated barium sulphate will then appear as a fine powder composed of minute crystals of uniform size, whilst in the case of natural barytes transparent irregular fragments of larger size will be seen. The test is rendered more certain by first removing the zinc sulphide by treatment with dilute hydrochloric acid and potassium chlorate, and examining the insoluble residue. C. A. M.

Titration of Chlorides with Silver Nitrate. H. W. Bolam. (*Chem. News*, 1920, **20**, 292.)—In the case of a chromate, such as barium chromate, less soluble than silver chromate, the titration of the chloride with silver nitrate becomes difficult as regards the end-point of the reaction. This may be overcome by adding potassium chromate in quantity slightly larger than is sufficient to precipitate the barium radicle; the titration can then be carried out with silver nitrate as usual. The formation of a faint brown tinge, which is not discharged on shaking the flask, shows that the reaction is complete. H. F. E. H.

Electrometric Titrations with a Hydrogen Electrode. W. D. Treadwell and L. Weiss. (*Helv. Chim. Acta*, 1920, **3**, 433-446.)—An apparatus is described with a hydrogen electrode, the change in the potential of which in acidimetric titrations can be measured with sufficient accuracy with a millivoltmeter. The electrode consists of a tube of unglazed porcelain, 6 mm. in diameter, the exterior of which is electrolytically coated with a thin film of gold, and then at its lower end for a length of about 7 cm. with a thin film of palladium black. For acidimetric titrations two such electrodes of equal size are combined to form an element. One is introduced into a suitable liquid ($\frac{N}{10}$ sodium bicarbonate solution, or a citrate solution with hydrogen exponent $p=5$) as a comparison electrode, whilst the other is immersed to the depth of about 2 cm. in the liquid to be titrated. The upper ends of the two electrodes are passed through a small glass bell-jar, which will form a water seal over the vessel containing the liquid. Ordinary hydrogen moistened with water is passed through the comparison electrode at the rate of 2 to 3 bubbles per second, thence through the titration electrode, and finally into the air through a capillary tube bent upwards. A short capillary tube filled with potassium sulphate connects the two electrodes. The liquid is titrated through a small opening in the bell-jar, of such size that it is completely filled by the capillary tube of the burette tap. The titration may also be effected in an open vessel, only the electrode (contained in a tube through which hydrogen is passed) being allowed to dip into the

liquid, or a tube coated inside with palladium may be used; but the results thus obtained are less accurate. In the case of weak acids the equilibrium constant may be readily calculated from the fall in potential in the course of the titration. The method is also applicable to the estimation of strong acids in the presence of weak acids. C. A. M.

Estimation of Zirconium and Titanium in Zirconium Ores. G. E. F. Lundell and H. B. Knowles. (*J. Amer. Chem. Soc.*, 1920, **42**, 1439-1448.)—The zirconium and titanium are precipitated by means of "cupferron," and the procedure recommended provides for the presence of all the elements which have been found in zirconium ores. The ore is fused with borax, the melt dissolved in hydrochloric acid, and the solution evaporated with the addition of sulphuric acid until fumes of the latter acid are evolved; after cooling the solution is diluted and filtered to separate silica and a small quantity of zirconium phosphate. This insoluble matter is ignited, treated with sulphuric and hydrofluoric acids to remove silicon, fused with sodium carbonate, the melt extracted with water to remove phosphate, and the insoluble residue fused with potassium sulphate, dissolved in sulphuric acid, and the solution added to the main solution. Interfering quantities of such elements as calcium, magnesium, potassium, sodium, lithium, copper, cobalt, manganese, zinc, and boron are removed by an ammonia precipitation followed by filtration. The ammonia precipitate is dissolved in dilute sulphuric acid, the solution treated with hydrogen sulphide to remove tin, lead, bismuth, and any remaining copper; after filtration, the filtrate is treated with tartaric acid, ammonia, and hydrogen sulphide, and filtered. The filtrate is acidified with sulphuric acid, boiled to expel hydrogen sulphide, cooled to 0° C., and treated with an aqueous solution of "cupferron," whereby zirconium and titanium are precipitated together with varying amounts of thorium, cerium, and other rare earths. The ignited and weighed "cupferron" precipitate is fused with potassium pyrosulphate, dissolved in sulphuric acid, and the solution divided into two parts for the estimation of titanium and the rare earths. Small amounts of titanium may be estimated colorimetrically, whilst large amounts are estimated by titration with permanganate solution after reduction to TiO. The rare earth oxides are estimated by a preliminary hydrofluoric acid treatment followed by an oxalate separation.
W. P. S.

APPARATUS, ETC.

Calorimetric Method for Standardising Thermometers by Electrical Energy. T. W. Richards and S. Tamaru. (*J. Amer. Chem. Soc.*, 1920, **42**, 1374-1377.)—The method consists simply in supplying heat in successive small equal quantities to a calorimeter and noting the readings of the thermometers produced by each step. From the known heat capacity of the system the rise of temperature which ought to occur is readily calculated. The heat is derived from electrical energy supplied at known voltage through a definite constant resistance, and the procedure is essentially like that suitable for the determination of heat capacity where temperature changes are known. W. P. S.

Fluoremetry. Quantitative Analysis by Comparative Fluorescence. L. J. Desha. (*J. Amer. Chem. Soc.*, 1920, **42**, 1350-1363.)—A method of micro-analysis is described, of the same order of sensitiveness as colorimetry and nephelometry, which should prove to be generally applicable to the estimation of very small quantities of substances which are either fluorescent themselves or may be rendered so by the addition of a suitable reagent. Ultra-violet rays from a quartz-enclosed mercury arc, filtered from most of the visible radiation, are used to excite fluorescence in solutions of the substances contained in the comparison cylinders of the Kober nephelometer. The intensity of the fluorescent light thus produced, as observed in the eyepiece of the instrument, is equalised in the usual way by altering the heights of the exposed columns. Experiments with solutions of quinine sulphate in $\frac{N}{1}$ sulphuric acid (0·5 to 2 mgrms. per litre) and aniline iodeosine in $\frac{N}{10}$ alkali solution (2 to 4 mgrms. per litre) showed that the curves obtained by plotting the scale readings against concentrations are quite regular in the case of dilute solutions.

W. P. S.

Glass to Metal Joints. E. C. McKelvy and C. S. Taylor. (*J. Amer. Chem. Soc.*, 1920, **42**, 1364-1374.)—Methods are given for the construction of two types of glass to metal joints. To solder a glass tube into a steel, iron, copper, brass, or nickel tube, the inside of the metal tube is tinned and the end of the glass tube is platinised. For the latter purpose, the end of the tube is roughened with sand or emery, painted with a colloidal solution of platinum in lavender oil mixed with Burgundy pitch, and then heated to redness to burn off the organic matter and fuse the platinum into the glass. This end of the glass tube is inserted in the tinned end of the metal tube, a small quantity of zinc chloride solution is added as a flux, and the joint heated until the tin melts; it is then allowed to cool slowly. Soft glass tubing may be fused to iron or steel tubing by using a flux prepared by melting together equal weights of zinc oxide, borax, and powdered soda glass. The joints withstand sudden changes in temperature and are vacuum-tight. W. P. S.

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ANALYTICAL STANDARDS.

THE Council of the Society of Public Analysts have transmitted to the Council of the Institute a Report, abstracted below, of a Committee, consisting of Messrs. L. Archbutt, W. J. A. Butterfield, G. Nevill Huntly, and G. Rudd Thompson, appointed to consider the desirability of making provision for supplies of standard chemical substances.

The Committee is satisfied that there is a demand for analytical control standards, which is now being chiefly met by private enterprise and by the importation of the U.S.A. Bureau of Standards Samples, and that the demand appears reasonable for checking and educational rather than commercial purposes. The Committee think that every effort should be made to secure control of the supply of such standards by a responsible body representative primarily of analytical chemists, which might with advantage seek the co-operation of the manufacturing interests, the Engineering Standards Association, the U.S.A. Bureau of Standards, as well as perhaps the existing private organisation.

The Committee recommend that the Society of Public Analysts should take the initiative in forming a representative Analytical Standards Committee, the objects of which shall be :

1. To decide for which chemicals, commercial metals and alloys, and perhaps ores and certain other products, it is desirable to supply standard samples.

2. To settle how samples shall be provided and issued.

3. To take steps for securing comparative analyses of the proposed standard samples by groups of chemists engaged in the analysis of the particular class of materials to which the sample belongs.

The Analytical Standards Committee should consist of five to seven members of the Society of Public Analysts, actively engaged in analyses of pure chemicals, alloys, metals, etc.; and as the Society numbers among its members representatives of other bodies, such as the Institute of Chemistry, the Association of British Chemical Manufacturers, the Society of Chemical Industry, the Iron and Steel Institute, the Institute of Metals, etc., the Committee suggest that it would be easy to select members for the Standards Committee, who, subject to the approval of the above bodies, would act as their representatives.

The Analytical Standards Committee should at the outset arrange :

1. For the provision of certain chemicals, such as benzoic acid, sodium oxalate, and sugar.

2. To report, after making full inquiries of manufacturers, users, and teachers, whether there is any legitimate scope for the extension of the scheme on the lines of the U.S.A. Bureau of Standards.

Further, the Standards Committee should ascertain to what extent and by what procedure the Department of Scientific and Industrial Research would support the Committee by a grant until the Committee's work becomes self-supporting.

The Council of the Institute have concurred with the proposals contained in the Report, and have nominated Mr. F. H. Carr, Dr. J. T. Dunn, Mr. Lewis Eynon, and Mr. F. W. Harbord, any of whom would be willing to act as representatives of the Institute in this connection.

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REVIEWS.

APPLIED CHEMISTRY.   By C. KENNETH TINKLER and HELEN MASTERS.   Vol. i.,
    283 pp. and Index.   Crosby, Lockwood, and Son.   Price 12s. 6d.

Under this somewhat misleading though literally correct title Dr. Tinkler and
Miss Masters have written the first volume of a work which is, we believe, unique
alike in its intention and its scope.

It is an outcome of the establishment by the London University of a diploma in
Household and Social Science. In view of the previous absence of any complete and
definite scheme of instruction in the scientific aspects of domestic matters the
importance of this new departure is obvious.

Until towards the end of the eighteenth century almost all the great country
houses and many of the smaller ones were to a large extent self-supporting. Behind
the scenes they were hives of industry; and kitchen and laundry, brewhouse and
bakehouse, stillroom and spicery, loom and spinning - wheel, exacted from the
housewives of the time wide and practical if not a scientific knowledge of what
were then domestic arts and have now become matters of wholesale trade and
manufacture.

The development of machinery, the applications of science to industry, and
changed manners and customs now render us almost entirely dependent on
commercial sources for the necessaries as well as the luxuries of life. For the full
understanding of domestic matters under the new conditions, knowledge of an
entirely different kind is required, the acquirement of which has hitherto been by no
means an easy matter.

The book before us deals with almost everything which could be reasonably
included under the head of household science, food alone excepted, on which a
further volume is to follow.

It is mainly intended as a guide to the *practical* work for the degree, matters of
theory being left to the lectures except where necessary for the proper understanding
of the experimental work.

As its title suggests, the major portion of the book is concerned with chemistry,
treated chiefly but by no means exclusively from an analytical standpoint. Although
they have already been dealt with in numerous textbooks, such subjects as the
analysis of water, water softeners, soaps, dry-cleaning preparations, bleaching agents,
disinfectants, air, coal gas, and liquid and solid fuels, together with the chemical and
microscopical characters of the chief textile fibres, could hardly have been omitted
from a work of this kind, but the authors have gone farther afield than this and
have included in their syllabus the examination of paints, oils, and varnishes; of
polishes for metal, wood, and leather; and of enamels and glazes for pottery and
ironware.

The outstanding feature of the work, however, really lies in the attention devoted to subjects in which chemistry plays a minor part. Among these may be mentioned experiments in emulsification; in the measurement of surface tension (as an aid to the better understanding of the action of detergents); methods for determining the efficiency of gas stoves and geysers, also of the efficiency of the ventilation of rooms.

In fact, foods and building materials excepted, there is hardly a substance, process, or apparatus used in, on, or about a house which the authors have not taken within their purview; even the reading of gas meters and the explanation of the basis of the fuel equivalents in the now happily defunct Fuel Rationing Order receive due meed of attention.

The student who conscientiously does all the work described in this volume will have received a most valuable training in analytical and investigatory work. It is perhaps open to doubt whether such a mass of diverse subjects can be profitably dealt with in so brief a period as a single academic year; but apparently it is not intended that all the experiments, etc., described should be carried out by each student individually, some being included in the lectures and a few in the earlier years of their training.

This may to some extent justify what must otherwise be regarded as a defect in the book—namely, the inequality of the treatment of the various topics dealt with. Except for the purpose of teaching it to others, it is difficult to see exactly what use those who take the course for this degree will make of the knowledge they have acquired; but, whatever the answer to this problem, it can hardly justify the allocation of some thirty-two pages to a detailed description of the method employed for the analysis of water, while only half that space is given to the examination of paints, varnishes, distempers, metal, furniture, and boot polishes, glazes and enamels, the analysis of which is often a matter of the utmost difficulty, and the published information about which is scanty and far to seek.

Taking the book as a whole it is most clearly and concisely written, and is remarkably free from errors, typographical or otherwise. It is very well printed, and most of the illustrations are excellent, except those of some of the ordinary pieces of apparatus (Figs. 1, 2, 3, and 4), which are very crude and in some instances quite out of proportion.

The authors may be congratulated on having written a most interesting work, which from its wide and novel range should appeal to many others besides those for whom it is specially intended.

CECIL H. CRIBB.

COURS DE CHIMIE. 2 vols. By R. DE FORCRAND. 1918-19. Paris: Gauthier-Villars et Cie. Second Edition. Price: Vol. I., 14 francs; Vol. II., 18 francs.

Professor Forcrand's book is written primarily for the guidance of French students preparing for the Certificat d'etudes supérieures de physique, chimie et sciences naturelles. The syllabus for this certificate comprises "the whole of chemistry," and the necessary instruction is to be conveyed, in eighty to ninety hours, to students who may begin with little or no chemical knowledge. While we must

admire the skill with which Professor Forcrand covers this comprehensive syllabus in a thousand pages, we must doubt whether his book can be of great service to those more fortunate students whose first year of study does not include "the whole of chemistry."

The book is divided into five sections dealing successively with General and Physical Chemistry, Inorganic Chemistry, Organic Chemistry, Analytical Chemistry, and Chemical Arithmetic. The section on Analytical Chemistry is necessarily restricted by the nature of the book. It suffers badly from the comprehensive programme; within one hundred pages the author deals with qualitative and quantitative inorganic and organic analysis, water analysis, and gas analysis. The section contains a good exposition of the general principles of analysis, but a few only of the detailed methods are given under each heading, and mention of these is often too brief to have much teaching value, either from the practical or theoretical standpoint. As it was not the intention of the author to write a guide to laboratory work, he might have made this section far more valuable by using his earlier chapters on theoretical chemistry to develop a more detailed system of one branch of analysis. Insufficient use has been made of the knowledge imparted in the first three sections. The statement (on page 332 of the second volume) that a test-tube is a thin, cylindrical glass tube, closed and rounded at one end, appears, for example, out of place; a student who has already been introduced to such subjects as the quinine and morphine alkaloids will know this.

The first section is the most valuable for the general reader. It contains an exceedingly clear and logically developed account of the fundamental chemical and physico-chemical principles. The section on inorganic chemistry is in need of further revision. The structural representation of the chlorine oxyacids with chains of oxygen atoms, and of hyposulphurous acid with two directly connected sulphur atoms, does not give the best graphical summary of the chemical properties of these compounds. In the same way, the statement that tannic acid is a digallic acid should have disappeared by now, even from the elementary textbook.

D. CLIBBENS.