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THE ANALYST.

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

THE EFFECT OF PRESSURE UPON THE POLENSKE AND REICHERT-MEISSL VALUES.

By VINCENT H. KIRKHAM, F.I.C.

Genuine butter fats analysed in the Government Chemical Laboratories, Nairobi, British East Africa, invariably give very low Polenske values, and the reason for this was made the subject of research.

When considering the explanation of the phenomenon, one of the first ideas to suggest itself was the possibility of the low atmospheric pressure affecting the composition of the distillate. Nairobi is situated at an altitude of about 5,500 feet above sea-level; the barometer generally read about 627 mm., and water boils at roughly 95° C.

In order to test this theory it was only necessary to devise a means of performing the Reichert-Meissl-Polenske distillation under different pressure conditions, and this was effected by attaching a Brühl jar to the receiver end of the condenser, and attaching to this jar a manometer, a bicycle valve and pump, and a Geryk vacuum pump.

All corks were carefully wired down and the lid of the Brühl jar secured, when pressures above that of the local atmosphere were required, by the use of clamps.

The only part of the standard apparatus which it was necessary or desirable to alter was the substitution of a 300 c.c. round-bottomed Jena flask, with neck cut down to the prescribed length, for the flat-bottomed flask normally used.

The butter fat used in these experiments was obtained from butter made in the laboratories.

Strict adherence to the prescribed conditions was observed in carrying out the observations, and it is unnecessary to describe here such a well-known process. The only points worth mentioning are that the times taken for distillation were a little over the twenty minutes—generally twenty-five minutes—that at very low pressures much difficulty was experienced in maintaining steady ebullition, and that one deviation from the usual procedure was made—*i.e.*, the 110 c.c. distillate was agitated and allowed to remain a few hours before filtration and titration. The reason for this

deviation is that a perfectly limpid filtrate is not obtained often by the usual rapid method, with the probable result that a trace of insoluble acid is passing into the filtrate.

The experimental results obtained were as follows:

Pressure. Mm.	Reichert-Meissl Value.	Polenske Value.
100	22·34	0·19
180	24·43	0·48
250	25·57	0·75
380	26·93	1·14
450	27·13	1·61
627	27·60	2·06
760	27·99	2·68
900	28·17	—
1,000	28·05	3·40

If these values are plotted against the pressures—and it will be seen at once that there is a considerable difference in the effect of pressure upon the Polenske and Reichert-Meissl values—the Polenske value increases steadily with the pressure, and the following empirical formula represents the relationship: $V = \frac{v(P-k)}{p-K}$, when P = pressure at which Polenske value is V; p = pressure at which Polenske value is v; K = constant, or pressure at which Polenske value is zero, in this case 45.

Therefore Polenske corrected to normal pressure $= \frac{\text{observed Polenske} \times (760-45)}{(\text{barometric pressure}-45)}$.

The variations in barometric pressure in any one locality may well lead to errors up to 10 per cent. of the value. In the case of laboratories situated at high altitudes the errors may exceed 25 per cent. Records made during seasonal depressions in the atmospheric pressure would, unless corrected, lead to the erroneous deduction that there was a seasonal depression in the Polenske value of the fat. In calculating adulteration the error might be very great and lead to serious consequences.

Pressure. Mm.	Reichert-Meissl.		Polenske.	
	Found.	Calculated.	Found.	Calculated.
100	22·34	22·58	0·19	0·19
180	24·43	24·19	0·48	0·48
250	25·57	25·10	0·75	0·73
380	26·93	26·23	1·14	1·19
450	27·13	26·69	1·61	1·44
627	27·60	27·60	2·06	2·07
760	27·99	28·12	2·68	2·55
900	28·17	28·60	—	—
1,000	28·05	28·87	3·40	3·40

In the case of the Reichert-Meissl curve the diminution of effect with increasing pressure suggested a logarithmic function, and trial was made of the following formula:

$$V = \frac{(v - K) \log P}{\log p} + K, \text{ when } K = 10,$$

and although the agreement is not very close it enables a correction to be applied which will reduce the error to a negligible amount.

The agreement between the formulæ and the experimental determinations is shown in the table.

Theoretical Considerations.

That such simple empirical formulæ can express the relationship between pressure and Polenske and Reichert-Meissl values might lead one to suppose that some equally simple laws were involved. It is disappointing to find that no such simple explanation is forthcoming, and that the simplicity of the result under the complexity of the various factors involved in the performance of a Reichert-Meissl-Polenske distillation appears to be fortuitous.

The fundamental difference between the Polenske and Reichert-Meissl variations with pressure may be attributed to the fact that, as Regnault showed, non-miscible liquids vaporise independently of each other, and the proportions of each in the vapour phase have no relationship to the proportions present in the liquid phase, but are entirely dependent upon the ratio of their partial pressures and vapour densities,

$$\frac{w}{W} = \frac{d.p.}{D.P.} \text{ (Nauman)},$$

whereas in the case of miscible liquids the proportions of each present in the vapour phase have a relationship with the proportions in the liquid phase, but that relationship is greatly affected by attractions between like and unlike molecules. In the simplest case, the relationship may be represented thus:

$$\frac{x_1}{x_2} = C\frac{W_1}{W_2} \text{ (Brown)},$$

where x_1 and x_2 are the fractions vaporised, W_1 and W_2 the masses in the liquid phase, and C a constant not differing much from the ratio of the vapour pressures of the substances at the temperature of distillation. But this simple relationship between the composition of the vapour and liquid phases is only true of miscible liquids of closely related constitution, or of other mixtures when

$$P = \frac{mP_a + (100 - m)P_b}{100} \text{ (Zawidski)},$$

and in the case of fatty acids and water the relationship does not hold good, particularly as butyric acid forms a maximum vapour pressure binary mixture.

To deduce the effect of pressure upon the proportions of soluble and non-soluble acids in the distillate from a knowledge of vapour pressures becomes hopelessly involved when it is remembered that in the R.M.P. mixture there exist—(1) water; (2) glycerol; (3) fatty acids of very low vapour pressures (non-volatile); (4) fatty acids of vapour pressures sufficient to yield a measurable mass in the distillate, (3) and (4)

being insoluble or only slightly soluble in water; (5) fatty acids of high vapour pressure, soluble in water.

The presence of the glycerol will reduce the partial pressure of the aqueous vapour, and its effect upon the partial pressures of the fatty acids will depend upon their solubility in glycerol. The fatty acids will constitute a series of miscible liquids, the relative proportions of which will affect the partial pressures of each constituent; while the non-miscibility, partial or complete miscibility, of the individuals of the series with water make the problem extremely complicated.

Molecules of all the fatty acids will occur in the distillate, and if the series form a mixture comparable with simple mixtures where

$$P = \frac{mP_a + (100 - m)\,P_b}{100},$$

then it is obvious that the proportions of the various fatty acids occurring in the liquid phase will affect the proportion occurring in the vapour phase (distillate), even though these various acids are not soluble in water. In other words, the Polenske acids must comprise oleic, stearic, palmitic, myristic, lauric, and probably capric (which has failed to dissolve in the R.M. acid and water) acids, in proportions depending to some extent upon their proportions in the liquid phase.

I am indebted to Prof. Sydney Young for pointing out that in the particular case of myristic acid and water the ratio of the partial pressures does actually increase in proportion to the total pressure when a simple mixture of these two substances is subject to experiment, but that with lauric acid the ratio of the partial pressures does not keep pace with the increase of total pressure. In my experiments it has been seen that the ratio of the partial pressures of the Polenske acid to that of water has increased in proportion to the increase in total pressure, precisely as would occur if water and myristic acid were distilled. The composition of the Polenske acids is not well known, but the composition of butter fat is as follows (Brown):

Glycerides of—	Per Cent.
Dihydroxystearic acid	1·04
Oleic acid	33·95
Stearic acid	1·91
Palmitic acid	40·51
Myristic acid	10·44
Lauric acid	2·73
Capric acid	0·34
Caprylic acid	0·53
Caproic acid	2·32
Butyric acid	6·23

The composition of the Polenske acids might be roughly deduced from a consideration of the vapour pressures of the above acids at the temperature of distillation and the molecular proportions in which they occur. The vapour pressure of lauric acid is something like two and a half times that of myristic acid, but there is present nearly four times as much myristic as lauric acid. The large proportion of palmitic acid must also contribute its quota to the Polenske acids, and in this case it is probable that the ratio of partial pressure of the acid to that of water would exceed

the ratio of total pressure, but, as was stated above, the behaviour of a mixture of a number of miscible substances cannot be predicted with accuracy, and it is remarkable that the experimental results should show that the mixture present in the R.M.P. process with a normal butter fat yields results at different pressures of such a simple character, and that these results should agree with what would occur if water and myristic acid alone were present.

As regards the Reichert-Meissl (soluble volatile acids), we may assume that they consist principally of butyric, caproic, caprylic, and possibly a portion of the capric acids.

It is difficult to predict anything from a knowledge of vapour pressures. Butyric acid forms a mixture of maximum vapour pressure of b.-pt. 99·2° (760 m.) containing 20 per cent. butyric acid (*vide* Young, " Fractional Distillation," p. 67). From this it might be expected that from 145 c.c. aqueous solution yielding 110 c.c. distillate the whole of the butyric acid would be obtained at most temperatures, and that the increase in R.M. figure at higher pressures and temperatures was to be attributed more to the increase in caproic and caprylic acids. It is unfortunate that the Kirschner figures were not obtained at the same time.

As was stated before, the relationship between the composition of vapour and liquid phases does in its simplest case approximate to

$$\frac{x_1}{x_2} = C\,\frac{W_1}{W_2},$$

when C is a constant not dissimilar to the ratio of the vapour pressures of the substances at the temperature of distillation. It is noteworthy that the ratio of the partial pressures of water and the lower fatty acids does not increase so rapidly as the temperature (and therefore total pressure) increases, as is the case with the higher fatty acids, and this fact alone explains why the R.M. figure cannot increase to the same extent as the Polenske when the distillation is performed at higher pressures (and temperatures), but no basis for a theoretical deduction of the empirical formula found by experiment exists.

Conclusions.

1. The Polenske value is a function of the pressure, and unless values are corrected to normal pressure serious errors are liable to be introduced.

With butter fat the relationship is as follows:

$$V = \frac{v\,(P - K)}{p - K}.$$

2. The Reichert-Meissl value is a logarithmic function of the pressure, and the errors introduced by ordinary variations in atmospheric pressure are quite small.

With butter fat the relationship is as follows:

$$V = \frac{(v - K)\log P}{\log p} + K.$$

Experiments are being conducted to ascertain the partial pressures of the several fatty acids with water, the partial pressures of various mixtures of acids and water, and the effect of glycerol upon these partial pressures.

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THE COMPOSITION OF MILK IN BRITISH EAST AFRICA.

By VINCENT H. KIRKHAM, F.I.C., and A. C. BARNES, A.I.C.

No figures have hitherto been published, except in official reports, concerning the variations in composition of milk in tropical British East Africa. Variations in composition are seasonal, and it is therefore of interest to compare the variations found to occur in the Southern with those occurring in the Northern Hemisphere.

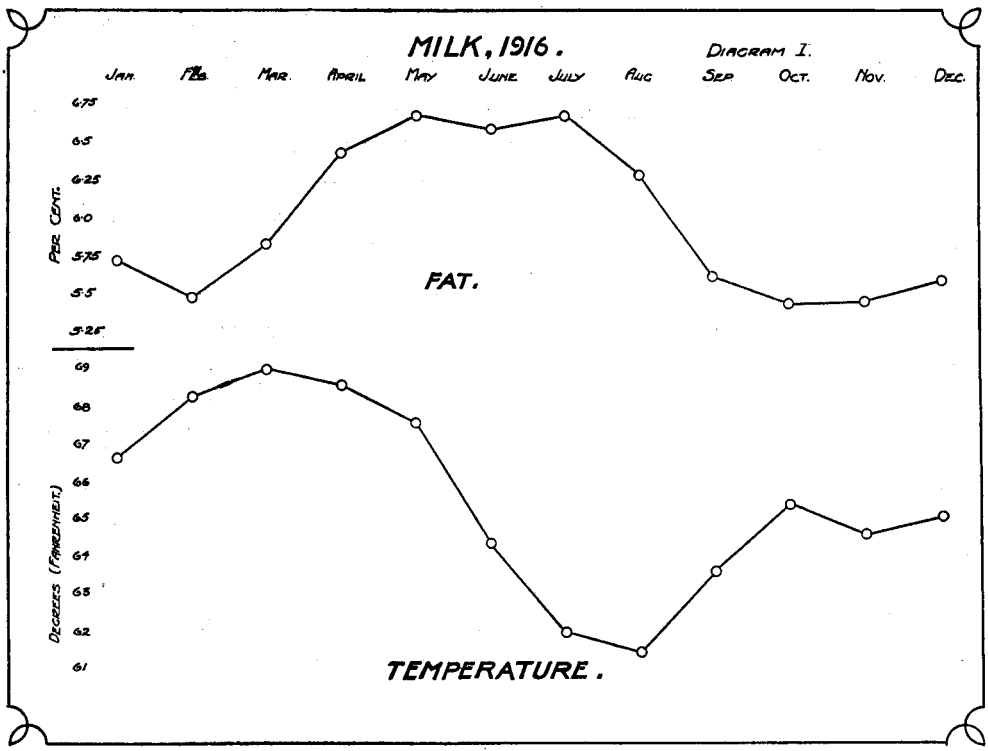

Diagram I.

In 1913 the variations of fat and solids-not-fat during the twelve months were found to show a marked relationship to the variations recorded by Droop Richmond for samples in England, the relationship being that every variation took place in the precisely opposite direction every month—*i.e.*, the graphical representations of the monthly variations of fat and solids-not-fat were in England the mirror images of the East African graphs (Nairobi Laboratory Report, 1913).

In 1916 a more detailed investigation into the composition of milk was carried out, and the results are shown in the accompanying diagrams.

1. Fat Content.

The variation in fat content follows closely the order discovered in 1913. The reason for the variations according to season appears somewhat obscure. Diagram I. gives a representation of the fat variations compared with the mean temperatures each month. No relationship is apparent. Diagram II. gives the same representation of the fat variations compared with the mean temperature variations three

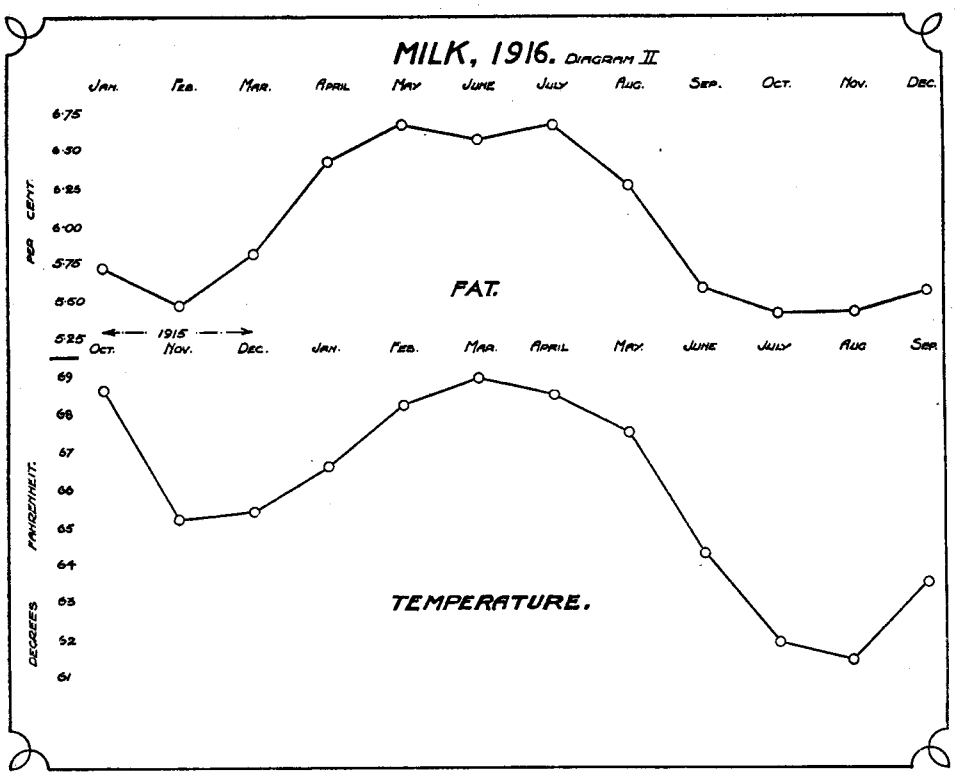

Diagram II.

months previously. A most striking relationship is apparent. If this curious relationship is really of the nature of cause and effect, we have to find an explanation for the time interval of about three months between cause and effect.

At first sight it would seem that the explanation was either (1) that the temperature affects the herbage first, and the altered composition of the grass subsequently alters the composition of the milk; or (2) that the temperature directly affects the cow, but that it takes at least three months for the altered metabolism of the animal to become apparent in the composition of the milk.

Further consideration has led us to correlate this temperature variation with the sexual function of the cow. The period of gestation is nine months, and should the temperature be responsible for the coming in season of the cows, then an explanation

is found for the three months' interval between the "cause" and "effect" upon the milk. We are not in possession of the data respecting calving in the herds from which these samples were taken, but usually there is a rush of calving in September, and consequently the cows are mostly in season during November and December—that is, three parts of the way up the temperature rise. In England cows come into season in early summer—*i.e.*, three parts of the way up the temperature rise—and this explanation therefore serves for both problems—the reversal in point of time in the two hemispheres, and the three months' interval between temperature and fat

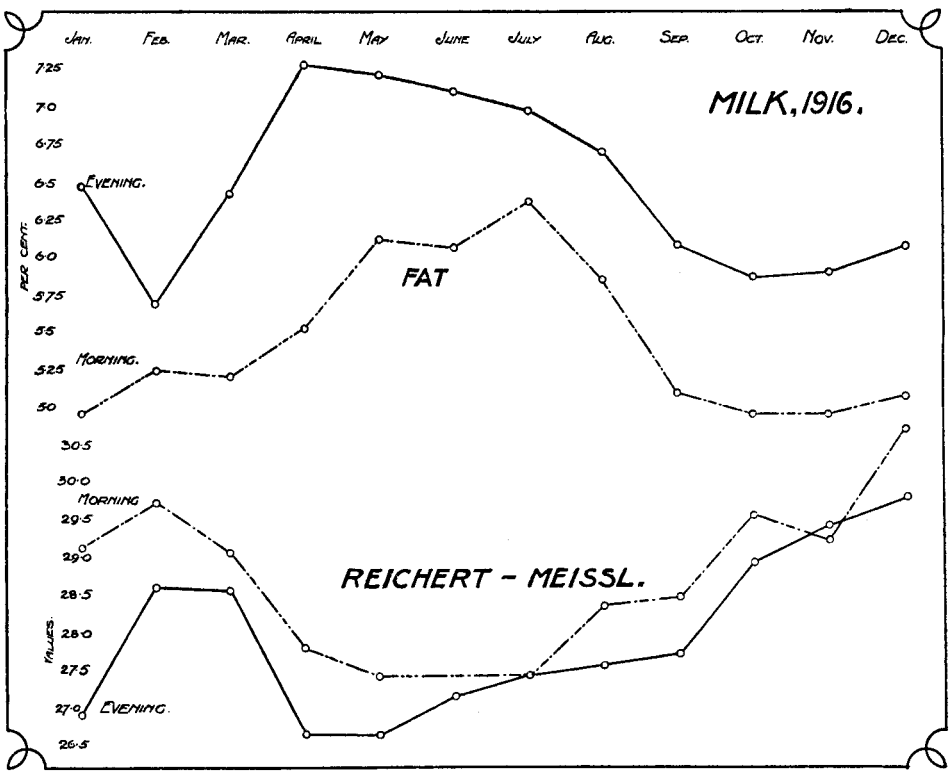

DIAGRAM III.

maxima—the variation in the composition of milk during the lactation period being too well known to require detailing here.

2. COMPOSITION OF THE FAT.

The daily samples of milk were set for cream, and butter was made weekly. From the butters so obtained the Reichert-Meissl figures in Diagram III. were found. It will be seen that there is a marked relationship between the percentage of fat in a milk and the composition of the fat. This, again, is correlated with lactation period.

3. Proteins.

This is a very constant figure, and therefore one which is of considerable importance when matters of adulteration are being considered. The comparatively small variations which occur are somewhat erratic, and are not easily correlated with any other observations.

4. Milk Sugar.

The variation in milk sugar content appears to be influenced by rainfall, though the relationship is not very exact and other influences are evidently at work.

5. Monthly Averages.

Month.	Percentages.		
	Fat.	Solids-not-Fat.	Total Solids.
January	5·71	9·12	14·83
February	5·46	9·25	14·71
March	6·42	8·99	15·41
April	6·66	9·24	15·90
May	6·57	9·21	15·78
June	6·66	9·45	16·11
July	6·27	9·68	15·95
August	5·58	9·63	15·21
September	5·41	9·43	14·84
October	5·42	9·24	14·66
November	5·56	9·19	14·75
December	5·96	9·32	15·28

The annual average for this herd of sixty odd cows is above the average for the country, which is:

Fat	5·25 per cent.
Solids-not-fat	9·25 „
Total solids	14·50 „

The cows are mostly native stock (the humped zebu), but grading is being carried out extensively in the country, and the effect of this upon the composition of the milk is not yet ascertained, though, as the quantity is undoubtedly increased, it is to be expected that the quality will deteriorate. Our analyses of milk from grade cows are not sufficient to enable us to state whether this is the case, but investigations into the merits of grade stock are proceeding.

In East Africa the cows are grazing all the year round, and have no cake or corn.

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NOTE ON THE REFRACTIVE INDICES OF MIXTURES OF ISOPROPYL ALCOHOL AND ACETONE.

By DOROTHY MURIEL PALMER.

During an investigation of the reduction of acetone to isopropyl alcohol it was found that none of the standard chemical methods was of use for the quantitative estimation of small quantities of alcohol in the presence of excess of acetone. An examination of the refractive indices of mixtures of the two substances showed, however, that the relationship between the percentage compositions and refractive indices of the mixtures could be represented by a very flat curve, and it was thought that this might serve as a rapid method for determining the composition.

The chief practical difficulty was due to the extreme volatility of acetone. Little adjustment of the refractometer could be made after placing the liquid in the observation cell, and the time allowed for its temperature to become constant had necessarily to be short.

The acetone was dried over calcium chloride, fractionated, purified by means of its compound with sodium iodide, according to the method of E. A. Werner and Shipsey (*J. Chem. Soc.*, 1913, **103**, 1255), and then refractionated under a Young dephlegmator stillhead. The final fraction boiled at 56·45° to 56·55° C. (barometer = 76·63 cm.).

The isopropyl alcohol was prepared from this acetone by reduction with hydrogen in the presence of heated nickel, according to the method of Sabatier. It was then dried over fused sodium sulphate and fractionated three times with an eight-pear column. The final fraction boiled at 80° to 81° C. (barometer, 75·02 cm.).

The readings were taken with a Pulfrich refractometer at a constant temperature of 22° C., values being observed for the hydrogen C and F lines.

Composition.	Refractive Indices.	
Per Cent. Alcohol.	Hydrogen C.	Hydrogen F.
0·0	1·35633	1·36296
1·38	1·35655	1·36324
1·95	1·35651	1·36316
2·41	1·35660	1·36324
3·5	1·35701	1·36358
5·07	1·35714	1·36378
8·24	1·35754	1·36425
9·71	1·35772	1·36436
13·49	1·35834	1·36492
15·1	1·35862	1·36526
16·2	1·35871	1·36534
29·3	1·36097	1·36768
53·8	1·36537	—
67·3	1·36779	1·37443
67·3	1·36763	1·37416
72·3	1·36940	1·37592
89·9	1·37225	1·37861
100·0	1·37470	1·38121

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NOTE.

The Editor desires 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.

ANALYSIS of drugs having powerful physiological effects is in many cases extremely difficult, particularly in the case of drugs extracted from natural sources, and which are mostly of extremely complex chemical constitution. Great success has recently attended the application of the spectrograph to such problems, the absorption spectra being in many cases in the highest degree characteristic of the substances. For instance, such a minute quantity of pyridine as 0·00001 grm. in 100 c.c. of aqueous ammonia can be readily detected. Much less than 0·5 mgrm. of strychnine, and as little as 3 mgrms. of cocaine have been verified. Very minute quantities of benzoic acid can also be identified by this method—a matter of particular interest, owing to the difficulty of detecting this acid. Again, 1 mgrm. of phenol is shown by its absorption spectrum. A physical method which does not destroy or alter the specimen should be of service to the analyst who has to deal with very small quantities.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Chemical Composition of Cotton-Seed Oil. G. S. Jamieson and W. F. Baughman. (*J. Amer. Chem. Soc.*, 1920, **42**, 1197-1204.)—A sample of oil expressed from Sea Island cotton-seed contained 23 per cent. of saturated fatty acids and 72·5 per cent. of unsaturated fatty acids when separated by the lead-ether method. The unsaturated acids were examined by converting them into bromine addition compounds, and the saturated acids by fractional distillation of their methyl esters, and fractional crystallisation of the fatty acids isolated from the fractions. From the combined results the conclusion was drawn that this cotton-seed oil consisted of glycerides of the following acids: Myristic, 0·3; palmitic, 20; stearic, 2; arachidic, 0·6; oleic, 35·2; and linolic, 41·7 per cent. C. A. M.

Estimation of Dry Solids-not-Fat in Separated Milk. R. Eichhoff. (*Milchwirtsch. Zentralbl.*, 1919, [17]; *Chem. Zeit. Uebersicht*, 1920, **44**, 169.)—The fat-free dry substance in milk, according to Fleischmann's formula, corresponds to $r = 2{\cdot}665.100\left(\frac{s-1}{s}\right)+0{\cdot}2\,f$. If in this formula the weight of unit volume is replaced by the volume of unit weight—*i.e.*, $s=\frac{1}{r}$—then $r = 2{\cdot}665.100\,(1-r)+0{\cdot}2f$. Now, $1-r$ is the reduction in volume with the increase in the amount of r. If V represents the per cent. by volume, $r = 2{\cdot}665-(100-\mathrm{V})+0{\cdot}2\,f$. In the

aræometer described the values for the diminution in volume are multiplied by 2·665, and the readings give the percentage of dry solids-not-fat in completely separated (fat-free) milk. The results agree closely with those obtained by the usual methods. C. A. M.

Analysis of Saccharin. O. Beyer. (*Chem. Zeit.*, 1920, **44**, 437-438.)—Saccharin, when submitted to acid hydrolysis (for this purpose the substance may be heated to 150° C. in a sealed capillary tube with a trace of sulphuric acid), yields ammonia and benzene sulphonic acid; the former may be identified by means of Nessler's reagent, and the latter by the test described by Klostermann and Scholta (ANALYST, 1916, **41**, 309). *p*-Sulphaminobenzoic acid does not yield these reactions. Saccharin may be estimated in commercial saccharin containing the para-acid (but no other impurity) by titrating 1 grm. of the sample with $\frac{N}{10}$ potassium hydroxide solution, using phenolphthaleïn as indicator; the percentage of saccharin (x) is calculated by the formula $x = \frac{2{\cdot}01329 \times c - 100}{0{\cdot}09845}$, where c is the number of c.c. of $\frac{N}{10}$ alkali solution used. W. P. S.

Analysis of Wines. W. Fresenius and L. Grünhut. (*Zeitsch. anal. Chem.*, 1920, **59**, 49-79.)—Directions are given in detail for the determination of the sp. gr. of wine by the pycnometer, and when the determination has been made at 17°/4° C., tables are given for correcting the results to 15°/4° C. To estimate the alcohol, the contents of the pycnometer are transferred to a flask and distilled; the sp. gr. of the distillate is determined, and reference to tables gives the corresponding alcoholic strength. Provided that the volatile acidity of the wine is not more than 1·2 grm. per litre (calculated as acetic acid), there is no need to apply a correction or to neutralise the distillate and redistil it. The sp. gr. of the distillation residue, after this has been diluted to its original volume, is also determined, and a table is given showing the weight of total solids per litre corresponding with different sp. grs. W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Blood Sugar Concentration and Blood Sugar Methods. H. F. Höst and R. Hatlehof. (*J. Biol. Chem.*, 1920, **42**, 347-358.)—This paper gives the results of sugar estimations made on normal and pathological blood and blood to which known amounts of dextrose had been added. On all samples four estimations were made by the following methods—viz: Bang's (*Biochem. Zeitsch.*, 1918, **87**, 264), Hagedorn's (*Ugesk. Læger*, 1918, **80**, 1217), Myers and Bailey's modification of Benedict's (*J. Biol. Chem.*, 1916, **24**, 147), and that of Folin and Wu (ANALYST, 1920, **45**, 227).

The results of these comparative estimations indicate that in the case of blood, substances other than dextrose affect the results obtained by each method and to a different extent, so that corresponding results are not in agreement. The highest results are given by the colorimetric methods of Benedict and Folin, while those of Bang and Hagedorn give approximately identical values.

All four methods yield satisfactory results for the dextrose added to the blood, whether normal or pathological.

Tables are provided giving the results obtained by the four methods, and a shorter one showing the average and greatest errors obtained by each method.

T. J. W.

Proximate Analysis of Coniferous Woods. W. H. Dore. (*J. Ind. and Eng. Chem.*, 1920, **12**, 476-478.)—*Water:* Two grms. of the fine sawdust are dried at 100° C. *Benzene Extract:* Two grms. dried as above are extracted for six hours, the solvent evaporated, and the residue dried for one hour at 100° C. and weighed. *Alcohol Extract:* The residue from the benzene extraction is extracted for six hours with 95 per cent. alcohol, the solvent evaporated, and the residue weighed. *Cellulose:* The residue from the alcoholic extraction is transferred to a Gooch crucible containing a cloth filtering disc and washed with water, and the cellulose is estimated by the method of Sieber and Walter (*Chem. Absts.*, 1914, **8**, 1202). *Lignin:* Two grms. of the material after extraction with benzene and alcohol are dried at about 60° C., and treated for three and a half hours with 20 c.c. of 72 per cent. sulphuric acid. This is treated first with 50 c.c. of cold water and then with 500 c.c. of hot water, and the residue collected in a tared Gooch crucible, washed thoroughly with hot water, dried, and weighed. *Hemicelluloses:* Except in the case of the soluble pentosans, the chlorination washings are unsuitable for the estimation of celluloses, and the presence of lignin derivatives interferes with the reducing sugar methods, or with separate estimations of mannan and galactan. *Soluble Pentosans:* The chlorination filtrates and washings from four cellulose estimations (=8 grms.) are evaporated to less than 500 c.c., and then made up to that volume, and aliquot portions of 125 c.c. are used for the distillation of furfural. This is precipitated as phloroglucide, dried, and weighed, and the results calculated into xylan by Krober's tables. *Mannan:* Schorger's method of estimation (ANALYST, 1917, **42**, 362) is used. *Galactan:* Five grms. of the material are mixed with 60 c.c. of nitric acid (sp. gr. 1·15) and the acid evaporated to about 20 c.c. at a temperature not exceeding 87° C. The liquid is diluted with hot water to about 75 c.c. and filtered, and the residual cellulose washed until the filtrate is colourless. The filtrate and washings are evaporated at 87° C. to about 10 c.c., and this residue is set aside for several days for the mucic acid to crystallise, the liquid being finally diluted with 20 c.c. of cold water. The crystals are washed with 20 c.c. of cold water (to dissolve other crystals, possibly of oxalic acid), allowed to stand for twenty-four hours, collected on a tared Gooch crucible containing asbestos, washed successively with 50 c.c. of water, 60 c.c. of alcohol, and finally with ether, dried at 100° C. for three hours, and weighed. The weight multiplied by 1·2 gives the amount of galactan.

C. A. M.

Properties of an Enzymic Extract (Polyzime) as compared with Malt Diastase. J. Takamine, jun., and K. Oshima. (*J. Amer. Chem. Soc.*, 1920, **42**, 1261-1265.)—An aqueous extract of diastatic enzymes, containing several other enzymes, has been prepared by cultivating *Aspergillus oryzæ* on media consisting mainly of wheat bran, and is termed "polyzime." The diastatic power of this preparation does not

decrease at temperatures below 40° C., and the enzymic activity remains unimpaired for more than six months when kept below that temperature. Starch is most readily liquefied by polyzime in neutral or slightly acid solution, the optimum temperature being 50° C. for a digestion of thirty minutes to two hours, and 40° C. for twenty-four hours' digestion. The preparation is three to five times stronger than ordinary malt extract in its amyloclastic power, as tested by Wohlgemuth's method, but has a weaker saccharifying power, as shown by Lintner's method. C. A. M.

Estimation of Hydrocyanic Acid from Beans. A. Czapski. (*Zeitsch. anal. Chem.*, 1920, **59**, 80.)—Paraffin wax is sometimes added to the contents of the distillation flask in the distillation of hydrocyanic acid from cyanogenetic beans in order to prevent excessive frothing. The author finds that the wax hinders the distillation of the acid, and less than one-half of the quantity actually present is found in the distillate. W. P. S.

Estimation of Manganese in Biological Material. C. K. Reiman and A. S. Minot. (*J. Biol. Chem.*, 1920, **42**, 329-345.)—The tissue or blood is placed in a quartz beaker and heated on a sand bath until thoroughly dry. The beaker is then placed over a burner in such a manner that the mouth is most strongly heated, until all tarry matter is destroyed, and is finally placed in an electric furnace at 600° to 700° C. until nearly all the carbon has disappeared.

To the residue about 3 grms. of a mixture of sodium and potassium nitrates is added, followed by 10 c.c. of sulphuric acid and 5 c.c. of hydrochloric acid, when the beaker is gradually raised in temperature to a cherry-red heat. If a large amount of carbon be left, a few c.c. of hydrochloric, nitric, and sulphuric acid should be added, and the fusion repeated. When cooling, the beaker should be rotated in order to prevent the fusion solidifying into a large cake. Fifty c.c. of water are added, and the beaker heated upon a sand bath until the contents have dissolved, when the solution is filtered. To the solution 1 c.c. of concentrated nitric acid is added, about 0·3 c.c. of 2·5 per cent. silver nitrate solution, and about 0·5 grm. of potassium persulphate; the mixture is then gently warmed for ten minutes.

A standard solution of potassium permanganate is prepared, completely reduced by the addition of sulphurous acid, and portions of known volume treated with nitric acid, silver nitrate, and potassium persulphate as above; finally, the pink colour is developed by gentle heating. In this manner a series of Nessler tubes containing from 0·002 to 0·025 mgrm. of manganese is prepared, and used for comparison with the solution to be estimated.

The method is a modification of the one devised by Bertrand (*Compt. rend.*, 1905, **141**, 1255, etc.), and yields more accurate results than the original method. The authors had much difficulty in obtaining apparatus free from manganese, and recommend that the beakers, etc., employed should be frequently submitted to blank tests during the course of the work. Tables are furnished comparing the results obtained by the present method and Bertrand's original method, the manganese content of normal and pathological human blood, and of various human viscera.

T. J. W.

Method for the Determination of Methæmoglobin and Hæmoglobin in Blood. W. S. McEllroy. (*J. Biol. Chem.*, 1920, **42**, 297-300.)—One c.c. of oxalated blood is transferred to a 50 c.c. flask containing 20 c.c. of distilled water. One c.c. of 4 per cent. potassium ferricyanide solution is added, and the flask is shaken to insure thorough mixing. After standing for five minutes the solution is diluted to 50 c.c., mixed, and the colour compared with a standard solution of methæmoglobin 10 or 15 mm. in length in a colorimeter. The result gives the total hæmoglobin (hæmoglobin + methæmoglobin) in grms. per 100 c.c. of blood. A further portion of the same blood is used to determine the oxygen capacity by the Van Slyke method (*J. Biol. Chem.*, 1918, **33**, 127), and from this the hæmoglobin content is calculated in grms. per 100 c.c.

The difference between the "total hæmoglobin" and the hæmoglobin gives the methæmoglobin content of the blood.

The standard solution of methæmoglobin is prepared from normal oxalated ox blood by the above method, using ten times the volumes given, and the hæmoglobin content is calculated from the oxygen capacity experimentally obtained. Should the standard be darker in colour than the solution under examination, it is diluted until the colours are approximately of the same intensity before comparison in the colorimeter. The method gives results rapidly and accurately.

T. J. W.

Detection of Urea. J. F. A. Pool. (*Pharm. Weekblad*, 1920, **20**, 178; *Chem. Zeit. Uebersicht.*, 1920, **44**, 165.)—When microscopic sections of soya beans are placed on a gelatin plate containing about 2 per cent. of urea and an aqueous extract of yeast, the urease in the beans decomposes the urea into ammonium carbonate, the calcium carbonate and calcium phosphate of the yeast are precipitated in amorphous condition, and colorations are produced on the surface of the plate (Beijerinck). In the absence of yeast, a plate containing 2 per cent. of agar-agar, 2 per cent. of urea, and a little phenolphthaleïn may be used for the detection of urease. Conversely, urea may be detected by this means in water, urine, etc. A small quantity of the liquid under examination is rendered neutral to phenolphthaleïn and boiled with 2 per cent. of agar-agar. The mass is poured on to a clock glass, a section of a soya bean applied to it after solidification, and the glass covered. In the presence of urea ammonia is liberated, and a red coloration spreads over the surface of the bean. In this way it is possible to detect 1 mgrm. of urea in 1 c.c. of liquid.

C. A. M.

Determination of Vitamine. R. J. Williams. (*J. Biol. Chem.*, 1920, **42**, 259-265.)—The author has previously shown that the anti-beri-beri vitamine is necessary for the nutrition of yeast (*J. Biol. Chem.*, 1919, **38**, 465), and this fact has been adapted to the estimation of the amount of vitamine present in solution. The rate of growth of yeast and the number of cells produced from one cell under standard conditions in eighteen hours is directly proportional to the amount of vitamine present.

This microscopical method, although yielding good results, is troublesome, and

the following gravimetric method, which yields more accurate results, has been adopted: The culture solution is of the usual type, containing cane sugar, asparagine, and various salts in water; 100 c.c. of this solution are placed in a 500 c.c. flask, the solution to be tested added, and the whole diluted with water to 110 c.c. The flask is plugged with cotton-wool, sterilised, and cooled to 30° C.

A suspension of fresh pressed yeast is made containing 0·3 grm. in 1 litre of sterile water, well shaken, and 1 c.c. is introduced into the culture medium with a sterile pipette. The flask is placed in an incubator at 30° C. for eighteen hours, and the growth is then stopped by the addition of a little formalin. The yeast is filtered off through a weighed Gooch crucible, washed with water and alcohol, dried at 103° C., and weighed. The increase in weight over that of a blank determination is directly proportional to the vitamine solution added. The " vitamine number " of a material is defined as the number of mgrms. of yeast produced by the addition of its extract computed to 1 grm. of the original material tested.

A discussion of the method is given, in which it is shown that the vitamine to be tested must be in solution, that foreign organisms present in the yeast offer no serious handicap to the working of the method, and that the usual substances present in vitamine solutions do not accelerate the growth of the yeast. T. J. W.

ORGANIC ANALYSIS.

New Method for the Estimation of Acetic Acid in Acetates. O. A. Pickett. (*J. Ind. and Eng. Chem.*, 1920, **12**, 370-371.)—The acetate is distilled with xylene in place of the water used in the usual method; 2·5 grms. of the acetate are mixed with 30 c.c. of water, 20 c.c. of 85 per cent. phosphoric acid, and 350 c.c. of xylene, and the mixture is distilled until only a thin film of xylene remains on the surface of the phosphoric acid solution in the distillation flask. The total distillate is then titrated. If the sample contains chlorides, allowance must be made for the hydrochloric acid in the distillate. W. P. S.

Modification of the Van Slyke Method for determining Arginine. A. E. Koehler. (*J. Biol. Chem.*, 1920, **42**, 267-268.)—Previous work by various experimentalists (*Am. J. Physiol.*, 1908-09, **23**, 194) has shown that arginine liberates one-half of its nitrogen as ammonia when boiled with concentrated alkali, and the apparatus described was devised to overcome the bumping produced when boiling such a solution. The apparatus consists of a flask for containing the boiling solution fitted with a long vertical reflux condenser and an inlet tube so arranged that a current of air may be drawn through the liquid after first passing through a wash bottle. To the top of the condenser is fitted an exit tube connected to a wash bottle containing the standard acid for absorbing the evolved ammonia, and the exit tube from this wash bottle is connected to a filter pump.

A slow current of air is passed through the apparatus during the heating and boiling of the solution, and this serves to prevent bumping and also to convey the

liberated ammonia into the standard acid. By using $\frac{N}{14}$ acid the value in c.c. neutralised is equal to the mgrms. of nitrogen in the ammonia absorbed.

T. J. W.

Comparative Method of determining the Heat of Carbonisation of Coal. G. Weyman. (*J. Soc. Chem. Ind.*, 1920, **39**, 168-169T.)—It is found in practice that the rate at which coal can be passed through continuous vertical retorts with efficient coking and with the same supply of heat to the heating flues varies up to 30 per cent. according to the type of coal used. To determine this variation experimentally, the author used a fireclay furnace, 8 inches in external diameter, enclosed in a metal vessel, from which it was separated at the sides and bottom by asbestos packing. A crucible containing 1 kgrm. of copper was placed in the furnace, and the metal melted by a blowpipe operating through an aperture in the vessels and lining; when the copper was molten the blowpipe was withdrawn, the hole packed with asbestos, and the asbestos lid placed in position. As soon as the first crystals of copper appeared, or when the temperature of the copper fell to some predetermined temperature (as read by a pyrometer), a thin steel tube containing a weighed quantity of the powdered coal was thrust into the middle of the copper. The tube communicated with a wash bottle and with a meter which was read every minute until the evolution of gas had practically ceased. The tube was then removed, and the pellet of coke examined. Experiments with different coals showed that the method yielded consistent results and gave a true indication of the comparative amounts of heat required to carbonise the coals.

W. P. S.

Analysis and Composition of Cresylic Acid. J. J. Fox and M. F. Barker. (*J. Soc. Chem. Ind.*, 1920, **39**, 169-172T.)—The phenol present may be estimated by a process described previously by the authors (ANALYST, 1917, **42**, 329), whilst Raschig's method (*ibid.*, 1900, **25**, 298) is trustworthy for the estimation of *m*-cresol. Another method for estimating *m*-cresol consists in treating about 1 grm. of the mixed cresols with a solution of bromine in carbon tetrachloride, removing the solvent at a temperature below 50° C. under reduced pressure, and determining the increase in weight due to bromination. *m*-Cresol yields a tribromo derivative, whilst phenol, *o*-cresol, and *p*-cresol yield dibromo derivatives. If W is the weight of bromo derivative obtained from 8 grms. of the mixed cresols, the precentage of *m*-cresol is $(100W - 246{\cdot}3)/0{\cdot}731$. A modification of Ditz and Cedivoda's method (*ibid.*, 1900, **25**, 74) may also be used for the purpose. About 1 grm. of the cresol is mixed with 5 c.c. of $2N$ sodium hydroxide solution and diluted to 200 c.c.; 10 c.c. of this solution are then treated with an excess (100 c.c.) of a mixture of equal parts of $\frac{N}{20}$ potassium bromide solution and $\frac{N}{100}$ potassium bromate solution, and 10 c.c. of hydrochloric acid. After the addition of 20 c.c. of 10 per cent. potassium iodide solution (this is added under conditions which prevent loss of bromine vapour) the mixture is placed aside for one hour and the excess of iodine then titrated. One grm. of *m*-cresol absorbs 4·444 grms. of bromine, whilst 1 grm. of *o*-cresol or *p*-cresol absorbs 3·080 grms. If Br is the actual weight of bromine absorbed, the percentage of *m*-cresol in a mixture is

$(100Br - 308)/1{\cdot}364$. The data obtained in the above three methods in conjunction with the sp. gr. afford the means for determining the *o*-cresol and *p*-cresol in a mixture of cresols. The sp. gr. at 15·5°/15·5° C. of phenol is 1·0774, of *o*-cresol 1·0516, and of *m*-cresol and *p*-cresol 1·0388. The formula connecting sp. gr. with composition is:

$$\text{Sp. gr.} = [1{\cdot}0774 \times P + 1{\cdot}0388 \times M + 1{\cdot}0516 \times O + 1{\cdot}0388\ (100 - P - M - O)]/100,$$

where P, M, O, and $(100 - P - M - O)$ are the percentages of phenol, *m*-cresol, *o*-cresol, and *p*-cresol respectively. This expression simplifies to $0{\cdot}0386P + 0{\cdot}0128O = 100$ (sp. gr. − 1·0388), in which O is the only unknown quantity. If phenol is not present, the equation is simply $0{\cdot}9128O = 100$ (sp. gr. − 1·0388). Approximate results for *o*-cresol and *p*-cresol may be calculated from the refractive index at 50° C. of a mixture of cresols; the refractive index of *o*-cresol is 1·5309, of *m*-cresol 1·5266, and of *p*-cresol 1·5260. The percentage of *o*-cresol (O) is given by the formula—

$$O = (100n_D - 0{\cdot}0006M - 152{\cdot}6)/0{\cdot}0059,$$

where M is the percentage of *m*-cresol and n_D the observed refractive index at 50° C. Analyses of cresylic acids are recorded showing that the proportions of the different constituents vary considerably in different makes. W. P. S.

Colour Changes of the Diphenylamine Reaction. E. M. Harvey. (*J. Amer. Chem. Soc.*, 1920, **42**, 1245-1247.)—Three distinct colorations may be produced in the diphenylamine reaction for nitric nitrogen, the nature and intensity of these colorations varying with the concentration of the sulphuric acid. In testing plant tissues for nitric nitrogen the best coloration is obtained when the concentration of the sulphuric acid is kept at about 72 per cent. It is also necessary to avoid variations of temperature in making a series of tests. For micro-chemical purposes the following modified reagent has the advantage that additional moisture will not affect the optimum conditions for the maximum coloration: Diphenylamine, 0·05 grm.; 95 to 96 per cent. sulphuric acid, 7·5 c.c.; and 10 per cent. potassium chloride solution, 2·5 c.c. C. A. M.

Analysis of Hydrogenated Oils. A. Grün. (*Chem. Umschau.*, 1920, **26**, 101; *Chem. Zeit. Uebersicht.*, 1920, **44**, 171.)—A trustworthy method of distinguishing between hydrogenated marine animal oils and hydrogenated rape oil has been based upon the determination of the molecular weights of the fatty acids of lower b.-pt. fractionated under reduced pressure. Only the hydrogenated marine animal oils contain acids with molecular weight lower than that of palmitic acid, whilst hydrogenated rape oil yields no acid fraction with molecular weight exceeding 201. In the presence of a fat of the coconut oil group, which may be recognised by the higher proportion of caprylic and lauric acid, the above method is untrustworthy. Hydrogenated marine animal and rape oils may be distinguished from other hydrogenated oils by containing a larger proportion of behenic acid or of other acids with higher molecular weight than stearic acid. In this case the least soluble fatty acids are separated by fractional crystallisation from various solvents, and their molecular equivalent determined. C. A. M.

Critical Study of Methods for the Detection of Methyl Alcohol. A. O. Gettler. (*J. Biol. Chem.*, 1920, **42**, 311-328.)—The author has examined fifty-eight tests described in the literature by employing them with the distillates from a number of liquors to which known amounts of methyl alcohol were added ranging from nil to 30 per cent., in addition to five typical confiscated methyl alcohol liquors—a total of eighteen. The various reactions are divided into two groups: (A) Those in which the methyl alcohol must be oxidised to formaldehyde before testing, and (B) those in which the methyl alcohol is tested for directly.

On the whole, the former class yields more reliable and sensitive reactions, and is subdivided according to the class of compound with which the formaldehyde reacts —*e.g.*, phenylhydrazines, phenols, alkaloids, proteins, amines, and miscellaneous substances.

The most satisfactory and sensitive reactions are: (*a*) Phenylhydrazine-ferric chloride-hydrochloric acid, (*b*) phenylhydrazine-sodium nitroprusside-sodium hydroxide, (*c*) apomorphine-sulphuric acid, (*d*) peptone-ferric chloride, (*e*) reduced fuchsine-sulphuric acid and two crystal-producing tests, (*f*) β-naphthol-hydrochloric acid, and (*g*) hexamethylenetetramine-mercuric chloride.

The five colour reactions are sensitive to 1 in 200,000, but the crystal-forming reactions are reliable down to 5 per cent. of methyl alcohol, and in solutions containing less than this amount the alcohol must be concentrated by fractional distillation.

Of the reactions classed under the heading of Group (B), only two out of twelve appear to be reliable and easily performed. These are—(*h*) boiling for seven hours with hydroxylamine and potassium hydroxide under a reflux condenser, when cyanide is produced and may be tested for in the usual way, and (*i*) determination of the sp. gr. and refractive index of the solution. The former test is very sensitive, while the latter is reliable for not less than 5 per cent. of methyl alcohol, and is liable to interference by the presence of substances other than ethyl and methyl alcohols and water.

Detection of methyl alcohol in liquors: 100 c.c. of the liquor are neutralised with sodium carbonate to phenolphthaleïn, and slowly distilled until 50 c.c. of distillate are collected. This is divided into two portions of 30 c.c. and 20 c.c., the latter being tested directly by the above reactions (*h*) and (*i*). To the 30 c.c. portion of distillate 100 c.c. of 10 per cent. sulphuric acid are added, followed by 6 grms. of potassium dichromate, and the whole allowed to stand ten minutes. The flask is connected to a condenser and distilled, so that about 30 c.c. of distillate are collected in one hour. This distillate contains most of the acetaldehyde and is rejected, and distillation then continued somewhat more rapidly until about 60 c.c. are obtained. This fraction, which contains nearly all the formaldehyde, is then tested by the above reactions in the following sequence: (*b*), (*c*), (*d*), (*e*), (*g*), (*f*). A definite reaction withone or two of these tests only may be due to foreign substances, but if methyl alcohol was originally present, all the results obtained will be positive.

Detection of methyl alcohol in tissues: 500 grms. of tissue are finely ground and placed in a large distillation flask with 500 c.c. of water. Sulphuric acid is added until a distinctly acid reaction is produced, and the mixture is then distilled in a current of steam. Three hundred c.c. are collected, neutralised, and again distilled

slowly, this distillate being oxidised as above, when subsequent distillation gives all the formaldehyde in the first 40 c.c. The final distillate is then tested by the same reagents as given above under examination of liquors, omitting the hexamethylenetetramine mercuric chloride test.

Full details are given for the preparation and employment of the various reagents, which are classed according to their reliability, sensitiveness, and ease of application.

T. J. W.

Estimation of Nitro Groups by Young and Swain's Method. L. Desvergnes. (*Ann. Chim. anal.*, 1920, **2**, 141-143.)—This method (ANALYST, 1897, **22**, 329), in which the nitro group is reduced with stannous chloride and excess of the latter titrated with iodine solution, yields trustworthy results with many organic nitro compounds; in the case of nitrophenols, nitrocresols, and nitronaphthalenes, however, the results obtained are too low. The author uses more alcohol (50 c.c.) than is prescribed by Young and Swain for dissolving the substance previous to the reduction.

W. P. S.

Diazometric Estimation of Phenol and of Certain of its Homologues. R. M. Chapin. (*J. Ind. and Eng. Chem.*, 1920, **12**, 568-570.)—The method depends on the quantitative coupling of phenols (phenol, cresols, xylenols) with diazonium salts to form insoluble hydroxyazo compounds. The reagent used is prepared by dissolving 14 grms. of *p*-nitraniline in 400 c.c. of water and 70 c.c. of concentrated nitric acid, heating the solution on a water-bath for two hours, allowing it to cool overnight, then filtering and diluting the filtrate to 1 litre; a portion of this solution is mixed with an equal volume of 1 per cent. sodium nitrate solution five minutes before it is required for a titration. This diazo solution may be standardised against β-naphthol. For the estimation, 20 c.c. of an approximately $\frac{N}{10}$ phenol solution are mixed with 50 c.c. of 10 per cent. sodium acetate solution, the mixture is neutralised with acetic acid, 10 c.c. of 30 per cent. basic lead acetate solution are added, and the diazo solution is run in from a burette with stirring. A further 10 c.c. of basic lead acetate solution is added as each 10 c.c. of the diazo solution is used. When the end of the reaction is near, as shown by spot test with drops of diazo solution and phenol solution respectively, the mixture is left at rest for two minutes, again stirred, and the point of a folded filter is immersed in the mixture. Two small quantities of the liquid passing inwards into the filter are transferred to a test-plate, and one is tested with phenol solution and the other with diazo solution. If no colour develops in either, a drop of 25 per cent. sodium hydroxide solution is added to each. If the end-point is at some distance on either side, the distinction is sharp, but if it is near, a strong coloration may appear in both tests. The titration may be continued until the end-point is clearly passed, and the limits thus coarsely defined are narrowed down by subsequent titrations.

W. P. S.

Durability of Exterior Varnishes compared with their Physical and Chemical Analyses. W. T. Pearce. (*J. Ind. and Eng. Chem.*, 1920, **12**, 552-555.)—The physical tests made were viscosity, sp. gr., and time of drying of the

varnish, and the elasticity, brilliancy, and resistance to moisture of the dry film; the working characters of the varnishes under the brush were also noticed, and varnished wooden surfaces were exposed in the open air, observations of their surface, etc., being made at the end of nine and twelve months respectively. The chemical analysis included estimations of the thinner, petroleum products in the thinner, non-volatile matter, and ash, resin, and oil. Comparison of the results and data obtained showed that there is a relationship between the viscosity, surface, elasticity, moisture test, etc., and the service (exposure) test. W. P. S.

INORGANIC ANALYSIS.

Titration of Ammonium Hydrogen Fluoride. W. S. Chase. (*J. Ind. and Eng. Chem.*, 1920, **12**, 567-568.)—Direct titration of ammonium hydrogen fluoride yields untrustworthy results owing to the fact that all the usual indicators are useless in the presence of free hydrofluoric acid. If, however, the hydrofluoric acid is precipitated by the addition of calcium chloride, the equivalent quantity of hydrochloric acid liberated may be titrated, using methyl orange as indicator. About 6 grms. of calcium chloride dissolved in 75 c.c. of water are added to 1·4 grms. of the fluoride dissolved in 125 c.c. of water, the mixture is stirred for one minute, and then titrated without filtration. W. P. S.

Rapid Method for the Estimation of Arsenic in Commercial Sulphuric Acid. A. A. Kohr. (*J. Ind. and Eng. Chem.*, 1920, **12**, 580-581.)—To estimate the arsenious acid present, 20 grms. of the sulphuric acid are diluted with a small quantity of water, methyl orange is added, and the mixture neutralised with saturated sodium carbonate solution, but the indicator must still exhibit a very faint pink coloration; 2 grms. of sodium hydrogen carbonate are then added, the solution diluted to 250 c.c., and titrated with $\frac{N}{10}$ iodine solution. For the estimation of arsenic acid, another portion of 20 grms. of the sulphuric acid is heated at 105° C. for one hour (this will remove nitrous and nitric acids), then diluted and treated with a slight excess of saturated sodium carbonate solution (red coloration with phenolphthaleïn); the mixture is boiled, filtered, and the filtrate treated with 3 grms. of sodium hydrogen carbonate, 150 c.c. of concentrated hydrochloric acid, and 1 grm. of potassium iodide. After five minutes the liberated iodine is titrated with $\frac{N}{10}$ thiosulphate solution; each c.c. of the latter is equivalent to 0·00495 grm. of As_2O_3 present in the arsenic form. The sum of the results of the two estimations gives the total quantity of arsenic as arsenious acid. Copper interferes with the estimation of the arsenic acid, and if an appreciable quantity of this metal is present it should be estimated and an allowance made for its amount; 1 molecule of copper liberates 1 molecule of iodine from potassium iodide. W. P. S.

Influence of Atmospheric Oxygen on the Iodimetric Estimation of Chromium. O. Meindl. (*Zeitsch. anal. Chem.*, 1919, **58**, 529-547.)—The statement of Wagner that potassium dichromate shows an increased iodimetric activity when subjected to the direct action of hydriodic acid has been confirmed, and has been

shown to be due to "activation" of the oxygen in the primary reaction between the chromic acid and hydriodic acid. The more slowly this reaction proceeds the greater is the induced activity, so that variable results are obtained under different conditions. Hence Zulkowsky's method (*J. prakt. Chem.*, 1868, **103**, 351) is unsuitable for the accurate standardisation of iodine solutions. C. A. M.

Estimation of Nitrates and Nitrites in Sulphuric Acid. L. B. Sefton. (*Chem. Trade J.*, 1920, **66**, 755-757.)—The diphenylamine test for nitrates is useless for the examination of battery acid, since the characteristic blue coloration is given by nitrites, iron, and arsenates, and by sulphuric acid itself. Denigès's strychnine reagent gives satisfactory results if applied as follows: Five c.c. of a 1 per cent. solution of strychnine sulphate are mixed immediately before use with 5 c.c. of concentrated hydrochloric acid, and reduced by treatment for ten minutes with 4 to 5 grms. of amalgamated zinc. Ten c.c of the battery acid (sp. gr. about 1·28) are mixed with 0·5 c.c. of the reagent, and then with 10 c.c. of concentrated sulphuric acid (sp. gr. 1·83). In the presence of nitrates or nitrites a pink coloration, which is permanent for several hours, will develop. The reaction is unaffected by 0·005 to 0·01 per cent. of ammonia, arsenic, copper, or chlorides. A solution containing 0·005 per cent. of iron gives an orange coloration which interferes with the test. The method will detect 1 part in 5,000,000 of nitrates or nitrites, and is more stable than the coloration given by brucine (0·2 grm. in 100 c.c. of pure strong sulphuric acid); the latter reaction is not affected by 0·005 to 0·025 per cent. of iron, arsenates, arsenites, chlorides, copper, or ammonia. In solutions of acid of sp. gr. below 1·7, nitrites react to the same extent as nitrates, but nitrites in solutions of sp. gr. 1·83 have no effect on the reagent. The most suitable sp. gr. of acid for applying the test is 1·65 to 1·7, and the speed of the reaction is increased by raising the temperature. The reagent should be freshly prepared for each test. In fresh electrolytes the method is sensitive to 1 part in 5,000,000, and in used electrolytes to 1 part in 400,000. A more sensitive reagent is prepared by dissolving 1 grm. of brucine in 2 c.c. of concentrated sulphuric acid, and mixing the solution with 50 c.c. of water immediately before use. Of the dilute solution, 5 c.c. are mixed with 10 drops of concentrated sulphuric acid, and reduced by treatment for five to ten minutes with 4 or 5 grms. of amalgamated zinc. Two c.c. of the resulting solution are used for each test. For the detection of nitrites the most satisfactory reagent is prepared by dissolving 2 grms. of dimethylaniline in 3 c.c. of strong hydrochloric acid and 25 c.c. of water; 3 drops of the reagent are added to 25 to 30 c.c. of the battery acid, and the mixture allowed to stand for ten to thirty minutes. The yellow coloration produced in the presence of nitrites is compared with standards under similar conditions. The test is capable of detecting 0·0001 per cent. of nitrites in fresh or 0·0004 per cent. in used, battery acid, and is not affected by the presence of 0·005 to 0·1 per cent. of any other impurities. C. A. M.

Short Commercial Analytical Methods for the Determination of Purity of Important Chemicals used in Pyrotechnics. H. B. Faber and W. B. Stoddard. (*J. Ind. and Eng. Chem.*, 1920, **12**, 576-578.)—Small amounts of sodium

nitrate in potassium nitrate may be estimated by precipitation as cæsium-sodium-bismuth nitrite (*cf.* Ball, ANALYST, 1910, **35**, 81). To estimate aluminium in aluminium flake or powder, 3 grms. of the sample are mixed in a fireclay crucible with 100 grms. of litharge and 30 grms. of borax, and the mixture is covered with a layer of 25 grms. of borax glass. The mixture is fused for twenty minutes at a bright red heat, cooled, the lead button separated from the slag, and weighed. The weight of the lead multiplied by 0·0872 gives the weight of the aluminium. The quantity of pure nitrate in a sample of commercial nitrate may be estimated by heating 1 grm. of the sample with 5 grms. of ignited tungstic anhydride; oxygen and nitrogen oxides corresponding empirically with N_2O_5 are liberated, and the amount of nitrate may be calculated from the loss in weight. W. P. S.

Sensitiveness of Qualitative Reactions. I. Potassium. O. Lutz. (*Zeitsch. anal. Chem.*, 1920, **59**, 145-165.)—With the object of obtaining a uniform view of the sensitiveness of various reagents for potassium, the author suggests that the tests should be made as far as possible under the same conditions. The following are the results found by treating 5 c.c. of potassium chloride solution with the various reagents, the temperature being 18° C. in each case, and the observation made after five minutes' contact; the figures represent the lowest concentration at which potassium can be detected: Perchloric acid, 1 : 435; phosphomolybdic acid, 1 : 561; platinum chloride, 1 : 587; sodium borofluoride, 1 : 970; aniline hydrosilicofluoride, 1 : 1,022; sodium tungstate, 1 : 2,170; phosphotungstic acid, 1 : 2,809; sodium cobalt nitrite, 1 : 25,000; sodium bismuth thiosulphate, 1 : 57,000; sodium picrate, 1 : 840; sodium-naphthol sulphonate, 1 : 1,022; sodium hydrogen tartrate, 1 : 1,050. It is also suggested that the results might be expressed in actual weights of potassium; for instance, perchloric acid will detect 1 part of potassium in 435 parts or 11×10^{-3} grm. of potassium. W. P. S.

Preparation of Sodium Amalgam in Flakes. A. D. Hirschfelder and M. C. Hart. (*J. Ind. and Eng. Chem.*, 1920, **12**, 499.)—A simple method of preparing flocculent sodium amalgam for organic work is to pour the melted amalgam slowly into xylene or kerosine, which is rapidly agitated by an electric stirrer. The flocculent deposit is dried on a porcelain plate in a current of air, and may then be readily pulverised. C. A. M.

Estimation of Minute Quantities of Oil in Sulphur. L. S. Bushnell and H. S. Clark. (*J. Ind. and Eng. Chem.*, 1920, **12**, 485.)—About 50 grms. of the powdered sulphur are shaken in a closed flask with about 50 c.c. of redistilled petroleum spirit at intervals of thirty minutes for several hours, and the extract then decanted through a filter. This treatment is repeated until the whole of the sulphur has been extracted, and the united extracts are then placed in a Wiley extraction apparatus in which has been suspended a roll of sheet copper foil (4 ins. × 15 ins.), in which no two points of the surface of the metal come in contact. This copper coil is cleaned with dilute nitric acid, washed with water and alcohol, and dried with ether before use. On boiling the petroleum spirit the whole of the dissolved sulphur will

be deposited on the copper, and the solvent is then filtered, the filtrate and washings evaporated, and the residue of oil weighed. C. A. M.

Application of the Rotating Zinc Reductor to the Estimation of Molybdenum. W. Scott. (*J. Ind. and Eng. Chem.*, 1920, **12**, 578-580.)—Molybdic acid in dilute sulphuric acid solution is reduced readily by means of a rotating zinc cylinder (*cf.* ANALYST, 1920, 60), and there is no need to use a current of electricity. The temperature of the solution should be between 20° and 30° C., and when the reduction is complete the mixture is titrated in the same vessel with standardised permanganate solution. If desired, the reduced molybdenum solution may be transferred to another vessel containing iron alum solution and phosphoric acid before titration; in this case the presence of the iron alum and phosphoric acid is essential. W. P. S.

Estimation of Zirconium in Steel. G. E. F. Lundell and H. B. Knowles. (*J. Ind. and Eng. Chem.*, 1920, **12**, 562-567.)—A method is given for the estimation of silicon, aluminium, titanium, and zirconium in steels which may possibly contain tungsten, chromium, vanadium, phosphorus, molybdenum, copper, nickel, cobalt, uranium, and cerium. Five grms. of the steel are dissolved in hydrochloric acid with the addition of a small quantity of nitric acid, the solution is evaporated to dryness, the residue baked, dissolved in dilute hydrochloric acid (1 : 1), the insoluble silica is collected, ignited, weighed, evaporated with hydrofluoric acid, and any remaining residue dissolved after fusion with potassium pyrosulphate. The hydrochloric acid solution is evaporated to a syrup, taken up with 40 c.c. of hydrochloric acid (1 : 1), and extracted with ether to remove most of the iron and molybdenum. The acid solution is heated to expel dissolved ether, the residue recovered from the silica is added, the solution oxidised with nitric acid, diluted, cooled, and treated with an excess of 20 per cent. sodium hydroxide solution. The precipitate is collected on a filter, dissolved in hydrochloric acid, again precipitated, and collected. (Filters from which precipitates have been dissolved should be ignited, the ash fused with sodium carbonate, washed with water, then dissolved in hydrochloric acid, and the solution added to the main bulk.) *Estimation of Aluminium:* If chromium and uranium are absent, the united filtrates from the sodium hydroxide precipitation are acidified with hydrochloric acid, boiled, and rendered just ammoniacal. Aluminium is precipitated as hydroxide contaminated with phosphate; the precipitate is collected, dissolved in hydrochloric acid, the solution diluted to 50 c.c., rendered ammoniacal, then acidified with nitric acid, heated to 50° C., and the phosphoric acid separated as ammonium phosphomolybdate. After filtration, the alumina is precipitated from the filtrate by ammonia, collected, ignited, and weighed. A trace of silica may be present, and is removed by treating the ignited aluminium oxide with hydrofluoric acid in the usual way. If chromium is present, the solution must be oxidised with bromine before the final precipitation of the aluminium, and, when uranium is present, this final precipitation must be made with ammonium carbonate in place of ammonia. In the case of steels containing vanadium, the aluminium hydroxide, after ignition, must be fused with pyrosulphate, the melt dissolved in dilute sulphuric

acid, the vanadium reduced and titrated with permanganate; the amount of vanadium oxide thus found is deducted from the weight of the aluminium oxide. *Estimation of Zirconium and Titanium:* The sodium hydroxide precipitate (see above) is dissolved in warm dilute hydrochloric acid, the solution diluted to 250 c.c., partially neutralised with ammonia (the solution should still contain 5 per cent. of hydrochloric acid), 2 grms. of tartaric acid are added, and the iron is reduced with hydrogen sulphide. Insoluble sulphides (if formed) are separated by filtration, the filtrate is rendered ammoniacal, and treated further with hydrogen sulphide. The precipitated iron, nickel, cobalt, and manganese sulphides are collected on a filter and washed with dilute ammonium chloride-ammonium sulphide solution. The filtrate is acidified with sulphuric acid, heated on a water-bath to coagulate sulphur, filtered, the filtrate cooled in ice-water, and treated with an excess of 6 per cent. "cupferron" solution. After ten minutes, the precipitate is collected, washed with cold 10 per cent. hydrochloric acid, ignited in a platinum crucible, and the combined zirconium and titanium oxides are weighed. The oxides are then fused with potassium pyrosulphate, the melt dissolved in 10 per cent. sulphuric acid, and the titanium estimated colorimetrically or volumetrically. W. P. S.

APPARATUS, ETC.

Colorimetric Determinations with Solutions containing two Coloured Substances. K. G. Falk and H. M. Noyes. (*J. Biol. Chem.*, 1920, **42**, 109-130.) —This paper gives details of an investigation into the principles underlying the quantitative estimation of dextrose by its action upon sodium picrate, resulting in the formation of sodium picramate. A Duboscq colorimeter was employed throughout, with a Mazda 75-watt electric lamp, and all the usual precautions necessary in colorimetric work were observed. The chief conclusions reached are as follows: The addition of sodium hydroxide to picrate solution deepens the colour, but sodium carbonate has no action unless the concentration is greater than three equivalents of carbonate to one of picric acid.

The colour values of free picramic acid are not proportional to the concentration and exposure to light deepens the colour. Sodium picramate is unaffected by excess of sodium hydroxide or carbonate, and by exposure to electric light for twenty-four hours.

Readings obtained with mixed solutions of sodium picrate and picramate give relative values ranging from 1-200 to 1-1,500, according to the proportion of each salt present, thus causing uncertainty in the results. Solutions of sodium picrate reduced by dextrose yield darker solutions with increased time of heating; the presence of other salts tends to reduce the rate of colour formation. The action of dextrose on sodium picrate solution gives rise to the formation of small amounts of substances other than sodium picramate, which adversely affect the accuracy of the readings.

Accurate results may be obtained by matching picramate solutions against a solution of potassium dichromate, providing that the latter is always of the same concentration and the same depth of solution is employed. The most accurate results are obtainable by matching the colour of a solution against a standard similar in composition and concentration. T. J. W.

Combination of Fractionation with Photospectrometry in Organic Analysis. W. E. Matthewson. (*J. Amer. Chem. Soc.*, 1920, **42**, 1277-1279.)—A method of estimating colourless substances in quantities of less than a few mgrms. consists in combining or condensing the substance to form a strongly coloured derivative, which is then separated by fractionation with an immiscible solvent from other coloured substances in the mixture, and subjected to spectrophotometric examination. Suitable reagents for the formation of coloured compounds are picryl chloride, dinitrophenyl-hydrazine, and diazobenzene-sulphonic acid. For example, in the case of acetone, 10 c.c. of the aqueous solution were treated with 5 c.c. of a reagent prepared by dissolving 0·1 grm. of 2·4-dinitrophenyl hydrazine in 1 c.c. of warm pyridine, and adding 10 c.c. of strong hydrochloric acid, the mixture being allowed to stand for fifteen minutes in a stoppered bottle, then acidified with about 7 c.c. of 2*N*-hydrochloric acid, shaken in a separating funnel with three portions of 19 to 20 c.c. of carbon tetrachloride, and these extracts shaken successively with 20 c.c. of 2*N*-hydrochloric acid. Finally, the combined carbon tetrachloride extract was diluted to 60 c.c., and its transmissive index at 435μ determined and compared with that obtained with a standard carbon tetrachloride solution of pure acetone-dinitrophenyl-hydrazone. C. A. M.

Photometric Turbidimeter. W. G. Bowers and J. Moyer. (*J. Biol. Chem.*, 1920, **42**, 191-198.)—An apparatus is described for comparing the light passing through a turbid suspension with a similar light reduced by a series of standard glasses. It consists of a closed box divided at right angles to its axis into five compartments. The two end compartments each contain an electric lamp, from which the light passes through a small hole into the next chamber. One of the chambers contains a parallel-sided glass cell 2 inches in thickness, in which the suspension is placed, the other being fitted with two revolving wooden wheels which support the standards of ground glass. The central compartment is provided with a grease spot illuminated on one side by light which has passed through the suspension, and on the other by light reduced in intensity by the standards. Two small mirrors are fitted close to the grease spot, and the images of this are viewed through a central tube fitted in the side of the box.

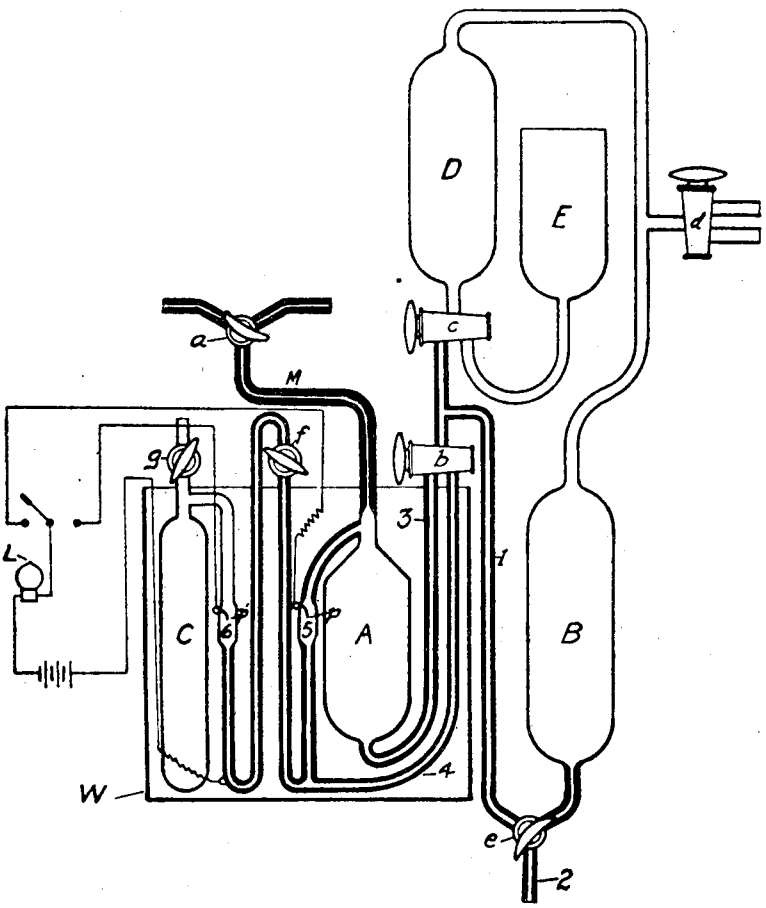
The apparatus is used by placing the suspension, prepared according to specified conditions, into the cell and revolving the standard wheels, one of which reads units and the other tenths, until both sides of the grease spot are equally illuminated.

The values of the standards in use are then read off from the upper portion of the wheels which project above the top of the box.

Tables giving series of measurements made with a barium sulphate suspension show that the greatest error between five different observers amounted to 0·075 per cent. Each substance estimated in suspension must have its own values worked out on the scales by preliminary experiments before measurements can be made. The authors find considerable practice necessary before coloured suspensions can be accurately compared with white light. T. J. W.

Weighing Burette for Gas Analysis. E. R. Weaver and P. G. Ledig. (*J. Amer. Chem. Soc.*, 1920, **42**, 1177-1185.)—The apparatus shown in the diagram

enables small amounts of gas to be accurately measured. When ready for use the measuring bulb A, and the tubes 1, 3, 4, and 5, are completely filled with mercury, and the tube 6 filled nearly to the contact point, p^1. Mercury can be drawn into or forced out of the bulbs B or D through the stopcocks *c* and *e* by means of a small motor-driven pump. When the gas is saturated with water vapour a drop of water is introduced into the compensating vessel C, and the walls of the burette are



moistened. In making a gas measurement, mercury is run into the tube 6 from D, so as exactly to close the contact p^1. The cocks *f* and *g* are then closed, confining a definite volume of gas in the compensator C, the bulb A is connected by means of *a* with the vessel containing the gas, and mercury withdrawn into D until the surface separating the gas from the confining liquid reaches M. The stopcock *c* is then closed, *e* turned to connect A and B, and the gas drawn into A, while the displaced mercury flows into B. The cock *a* is closed when the surface of separation between the gas and confining liquid reaches M. Mercury is now run from B into A until the pressure of gas in A is adjusted to equal that in C. Mercury is first drawn into B

through 4 until the contact point in 5 is uncovered, and then forced back again until the contact is just closed, as shown by the electric light L. The amount of mercury in the compensator between points 5 and 6 is thus adjusted. The stopcock *b* is next closed to tube 4 and opened to tube 3, and the cock *f* opened; and by running mercury between A and B through tubes 1 and 3, the pressure in A is adjusted until the contact in 5 is again just closed. Assuming the contact points *p* and p^1 to be on the same level, the pressure of the gas in A will be exactly equal to that in the compensator C, and its volume exactly equal to that of the mercury in B. By connecting B with tube 2 by turning *e*, the mercury is drawn off into a small flask in which it is weighed, and, from the weight, the volume of the gas in A is calculated. The parts of the apparatus which require to be maintained at constant temperature are immersed in a circular water-trough, W. C. A. M.

REVIEW.

THE IDENTIFICATION OF ORGANIC COMPOUNDS. By G. B. NEAVE and I. M. HEILBRON. Second Edition. Pp. 88. London: Constable and Co., 1920. Price 4s. 6d. net.

This small volume is intended as a practical handbook for the use of advanced students engaged in the identification of the simpler organic compounds.

The first chapter is devoted to preliminary tests, and this is followed by three pages giving the reactions for the elements. It will be noticed that no mention is made of the production of sodium thiocyanate (which may be tested for by means of ferric chloride) when a compound containing both nitrogen and sulphur is fused with sodium.

Chapter III. describes the tests employed for the detection of organic radical groups, and in this connection it may be pointed out that in the test for methoxy and ethoxy groups any compound will produce a precipitate in the alcoholic silver nitrate solution, since the hydriodic acid itself will volatilise under the conditions described.

The remainder of the book contains the reactions, melting-points, and boiling-points of a variety of substances arranged under the headings of hydrocarbons, ethers, halogen compounds, etc., and amounting to a total of between five and six hundred individual compounds. As the users of the volume are assumed to have had experience in organic preparations, very few practical details are given. A brief appendix gives a description of a convenient m.-pt. apparatus and methods for the preparation of certain special reagents.

An examination of the figures given for the melting-point and boiling-point, and also the numbers of pages furnished in the two indices, has failed to detect errors.

The authors have succeeded in producing a concise and reliable handbook which may be thoroughly recommended to students and others engaged in the identification of organic compounds. T. J. WARD.