

THE ANALYST.

OBITUARY NOTICE.

JOHN RUFFLE, F.I.C.

MANY of the older members of this Society will mourn the death, on November 19, at the age of nearly seventy-eight, of John Ruffle, who joined the Society in its early days as a very welcome adherent to its ranks, when, unlike now, those who did not actually hold official appointments were in a decided minority.

Ruffle, who was born in Suffolk, went to Germany as a lad, and spent some years on an estate in the Rhineland. Having thus acquired a taste for agricultural pursuits, he returned to England in 1861 and became a student in the Royal Agricultural College at Cirencester, where he took his diploma and, being attracted especially by the chemical side of his studies, he became and remained for some years an assistant in the laboratory of the consulting chemist to the Royal Agricultural Society, viz., the late Dr. Augustus Voelcker, his old chemical professor. From there he went as chemist to the fertiliser factory of Messrs. Jas. Gibbs and Co. at Silver-town, where he remained until 1884. He then practised as a consulting chemist on his own account for two or three years in the City but relinquished his practice to take up the post of chemist to the "Cape Copper Company and Butenferry Chemical Works" at Neath in South Wales, where he remained until 1896. In 1897 he became a chemist in the works of Messrs. Allen and Hanburys, Ltd., at Ware, and this post he held until his death, which occurred almost suddenly.

Although his interest in both pure and applied chemistry was always keen and led him into a good deal of investigational work, his publications were not many. A paper on the "Examination of Copper Sulphate," read before a meeting of the Society of Public Analysts in 1893, was published in the ANALYST of that year. His most notable contribution to analytical literature, however, was his paper on the "Estimation of Nitrogen by Combustion, including Nitro-Compounds," published in the *Transactions of the Chemical Society* for 1881, in which he demonstrated that the admixture of sulphur with the material to be analysed and of sodium thio-sulphate with the soda-lime used resulted in the complete conversion of nitric nitrogen into ammonia, the process being especially designed for use in the analysis of complex fertilisers containing nitrates as well as organic and ammoniacal nitrogen. Although the soda-lime combustion process, whether in its original form or as modified by Ruffle, has now given way to the more easy and rapid Kjeldahl moist combustion method, with its modifications due to Jödelbauer, Gunning, and Arnold, the process of Ruffle has not been surpassed in its accuracy. In the *Journal of the Society of Chemical Industry* for 1887 two notable papers were printed embodying

the results of general work on the composition of superphosphate and compound manures derived therefrom, in which he showed that the then conventional methods of expressing the results of analyses of such materials were based upon erroneous conceptions. The titles of these papers were "Correct Analysis of Plain and Ammoniated Superphosphates" and "Moisture in Superphosphate." Various other contributions from his pen, some based on his own work and some in criticism of the work of others, also appeared from time to time in the same journal and in the *Chemical News*, but these do not now call for especial mention.

Ruffle's disposition was sensitive and retiring and very gentle, and he was much loved by his early colleagues and contemporaries. Living, however, in geographical retirement for many years past, and but rarely visiting his old scientific haunts, he would be personally unknown to most of those of the younger generations of our members.

He was married in 1871, and became a widower in 1906. He had two children, a daughter who died in 1898, and a son, Mr. Hugh W. E. Ruffle, who survives him.

BERNARD DYER.



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

THE ESTIMATION OF THEOBROMINE IN COCOA AND ITS PRODUCTS.

By RAYMOND V. WADSWORTH.

(*Read at the Meeting on December 1, 1920.*)

THE methods available at present for the estimation of theobromine are all, for various reasons, far from being satisfactory, yet they are so numerous that the introduction of another seems to necessitate an apology. As Whymper remarks (Allen, "Comm. Org. Anal.," vol. vi.), "The recorded values of theobromine are very variable and untrustworthy, arising from the lack of any very accurate and reliable method of estimation." It is this unreliability that has urged the author to search for some method which will be simple, efficient, and rapid, and at the same time give concordant results in the hands of different workers. At the present time, with most of the methods suggested, agreement between different workers is difficult to obtain. The process described below is given in the belief that it overcomes these difficulties.

PREVIOUS METHODS.—The methods suggested up to the present day may be roughly divided into four groups :

A. Those based on the precipitation of the alkaloid from the acid extract of cocoa by phospho-tungstic or phospho-molybdic acids, and the estimation of the

alkaloid in the precipitate, by the nitrogen content (Weigmann), by ignition (Wolfram and Legler), or by solution in a solvent (Kunze, Monthulé).

B. The cocoa, with or without a previous acid treatment, is extracted with water and an alkali; MgO in the method of Mulder, Bell, Savini, Trojanowski, Frommes, Beckurts, and Dekker; CaO in the method of Zipperer; Ba(HO)₂ in the method of Eminger; PbO in the method of Süß; and the alkaloid extracted by chloroform from the dried filtrate (Dekker, Frommes, Savini, Zipperer, Süß, Beckurts), or from the residue obtained by evaporation of the whole to dryness (Mulder, Bell, Eminger, Trojanowski). In the methods of Trojanowski and Bell the solvent used is alcohol.

C. The alkaloid is extracted directly with a solvent, such as chloroform (Diesing), or chloral alcoholate (Kreutz) from the dry material.

D. The alkaloid is extracted from the *wet* material by a solvent, phenol-chloroform (Maupy and Débourdeaux).

CRITICISM.—A criticism of most of these methods has been made by W. E. Kunze (ANALYST, 1894, 11, 194), but there are other criticisms which the author would like to offer—criticisms which the grouping of the methods facilitates.

A. The precipitation by phospho-tungstic or phospho-molybdic acids has been stated to be incomplete, and certainly in the hands of some operators it gives low results. The precipitate itself is one difficult to free from impurities owing to the nature of the materials precipitated together with the alkaloid, this operation taking a whole day to perform. The estimation of the theobromine by the nitrogen content of the precipitate obviously gives high results, as does the ignition of the aqueous or amylic-alcohol extract. The extraction of the alkaloid by chloroform has the drawbacks of low solubility, etc., mentioned below (under B.), though the actual alkaloid obtained is generally purer than that obtained by the methods of the second group.

B. The solution of the alkaloid in water, as before, but the precipitation of objectionable substances by alkalis, as magnesia, lime, baryta, or lead, has the disadvantage again of poor filtration, and also of incomplete precipitation. It has therefore been thought by some (Mulder, Bell, Eminger, Beckurts, Trojanowski) that filtration is unnecessary. In either case the result is much the same, other bodies besides the alkaloid being extracted by the solvents, as is apparent from the colour of the resulting alkaloid and the colour of its solution in water. The solubility of theobromine in chloroform, as has been previously pointed out by the author (ANALYST 1920, 45, 133), is very low; consequently a large quantity of solvent or long extraction is necessary, and so even slightly soluble bodies have every chance of being dissolved with the alkaloid. In addition to this, the extraction from a perfectly *dry* material is very slow, and in the author's opinion never complete. This seems to have been recognised by Savini and Frommes, who employed small quantities of ammonia in the solvent. Alcohol, as used by Bell and Trojanowski, which contains the small quantity of water found necessary for the extraction, is a better solvent for the alkaloid, but also has the great disadvantage of dissolving more foreign bodies than chloroform. Kunze obtained about four times more extract (theobromine?) by this than by any other method.

Many authors (Frommes, Kreutz, Eminger, etc.) have insisted on a treatment with acid being necessary as a preliminary to the estimation of theobromine,

suggesting that a compound is present from which the alkaloid cannot be obtained without this previous treatment. The compound is generally regarded as a glucoside. Kreutz (ANALYST, 1909, **34**, 20) remarks that "it is impossible to separate the free theobromine from that portion of the alkaloid existing as a glucoside." Fritsch ("Fabr. du Chocolat," p. 264) suggests a combination of theobromine with tannin. If Fritsch's assumption be correct, and this compound be formed or present, an acid treatment would be of no help, as this compound is not decomposed by acids. It is, however, readily soluble in boiling water, and easily decomposed by magnesia, baryta, lime, or lead by the precipitation of the tannin. The author has never been able to obtain an increase in the yield of theobromine by this acid treatment; in fact, combining this with Dekker's method, usually from 0.1 to 0.25 per cent. lower yield was obtained, but the alkaloid was obviously purer, being much whiter in colour. Any compound present—and a definite proof of its existence is still wanting—is decomposed by water and the compounds mentioned above. Even unfermented beans do not give a higher result after the acid treatment. The only way a higher result can be obtained is by a breaking down of the cellular tissue of the material by the acid, in cases where very fine powders are not used, or where no water is used, as with the methods of Kreutz and Diesing.

It has been stated (Diesing and Süß) that lime, and to a less extent magnesia, decomposes some of the theobromine on prolonged heating, and it is accepted that in the case of Zipperer's low results this was due to decomposition of the alkaloid by the lime. With magnesia the author finds a slight decomposition, reducing the percentage on prolonged heating at 100° C. by 0.1–0.2 per cent., but with short heating the result is not affected. Thus in the second group it is fairly certain that the small reduction in the percentage is brought about by the long treatment with alkalies. In the author's hands the acid treatments have never shown any decomposition of the alkaloid.

C. A direct and complete extraction of the alkaloid with a solvent from the dry cocoa is impossible. The quantity of material other than alkaloid extracted is very considerable, amounting, in the case of fermented cocoas, to 50 per cent. of the total extract, whilst the actual theobromine extracted is seldom more than half that really present in the material. The alkaloid is only slowly given up. After 80 hours' extraction the author found between 0.06 and 0.10 per cent. again extracted in 24 hours, though after 120 hours no more could be extracted. Again, the low solubility of the alkaloid in chloroform is a drawback, and, as Maupy has shown, water is absolutely necessary to the complete extraction. To extract the remainder of the theobromine, Kreutz, after a direct extraction with chloroform or chloral alcoholate and ether, gives an acid treatment, neutralises, dries, and extracts the alkaloid again with chloroform. This second extraction has the drawbacks mentioned above, and the method as a whole gives high results.

D. To overcome these difficulties, Maupy (ANALYST, 1897, **22**, 191) suggested and worked out a method, using phenol-chloroform as the solvent, and mixing the solvent to be extracted with water. Without water this method gives much the same results as Diesing's. Phenol-chloroform is a good solvent, but inconvenient to work with, and, unfortunately, dissolves out other bodies which precipitate with the

theobromine, thus giving high results. The amount of other matter depends upon the cocoa used, and varies between 0.2 and 0.5 per cent. With the object of purifying the product, Débourdeaux (*J. Soc. Chem. Ind.*, 1917, 612) added to the process a long and tedious method of purification. Dekker objected to the method on the ground that the alkaloid was not completely precipitated from solution. This only occurs on those rare occasions when a *very large* amount of foreign matter has come through, and in those cases precipitation is complete after standing overnight.

It is obvious from the above review that none of the methods as yet suggested gives satisfactory results. Even the methods most commonly in use (Dekker and Kunze) have very serious drawbacks. Coconos of different origin have been found to give very variable amounts of foreign matter in solution with the alkaloid, particularly in the case of fermented and unfermented coconos of the same origin. This, perhaps, accounts for the higher results obtained by some workers with fermented coconos, a result which led them to suggest the formation of theobromine during the process of fermentation. The method described below gives a pure extract in all cases, and is rapid and easy to work.

The solvent used is tetrachlorethane (acetylene tetrachloride), which, as has been previously pointed out (*ANALYST*, 1920, 45, 133), is one of the few good organic solvents for theobromine. Used on the damp cocoa, it has just the same drawbacks as phenol-chloroform, but with a previous treatment with magnesia this difficulty is overcome, and the complete extraction of the pure alkaloid is obtained.

NEW METHOD.—If the cocoa bean is to be extracted, it is necessary to remove the fat with petroleum spirit (of b.-pt. below 80° C.). If, however, cocoa or cocoa shell is being used, this preliminary extraction is not necessary.

Ten grms. of the material are placed in a small porcelain dish and well mixed with 2–3 grms. of freshly calcined magnesia. This mixture is very carefully triturated with 14 c.c. of water until every particle is wetted. The dish containing the damp mixture is then placed on the water-bath for half an hour to dry it partially. The mass should be mixed at intervals to prevent any part becoming perfectly dry. At the end of the half-hour the mixture is well triturated and transferred to a flask of about 250 c.c. capacity; 150 c.c. of tetrachlorethane are added, and the whole is boiled under a reflux air condenser for half an hour. It is then filtered, *while almost boiling*, into a second flask. The residue is transferred, together with the filter paper, to the first flask, 120 c.c. of tetrachlorethane added, and the mixture boiled for twenty to thirty minutes. The liquid is then filtered into the second flask, and the residue washed twice more as before. The united washings are distilled through an air condenser until reduced to 3 or 5 c.c. The residue is cooled, and 60–70 c.c. of ether (methylated, of sp. gr. 0.720) are added, the whole well mixed, and allowed to stand overnight. The precipitate is then collected on a tared filter paper, and washed with ether, dried at 100° C., and weighed. To this weight is added 0.004 grm., as representing the amount of theobromine dissolved in the 70 c.c. of ether used in the precipitation and in the washings.

Details and Precautions.—The material should only be extracted with petroleum spirit in those cases where it is impossible, owing to the fat present, to wet the material with water—*i.e.*, cocoa beans or mass. When extracted, even with petroleum

spirit, there is always a very slight loss of the alkaloid. The author has proved during his work that theobromine is slightly soluble in cacao butter, which accounts for the loss, also found by Süß, during extraction. Süß suggested that the loss was due to its being carried over mechanically, for he found theobromine absolutely insoluble in cacao butter. The author has found that the cacao butter of commerce is already saturated with both caffeine and theobromine at about 80° C. Süß's failure therefore to detect the solubility was possibly due to his using commercial fat. The amount of water necessary for the proper wetting of the material varies between 9 and 20 c.c. according to the substance used. Cocoa powder generally requires 14 c.c., but for cocoa shell 20 c.c. are required. The water should be added a few c.c. at a time, and the mixture well triturated after each addition. When the mixing, which should be very thorough, is finished, the whole mass should be easily compressible into a firm cake. The most convenient mixer for this process is a glass rod, with one end flattened. During the half-hour's drying on the water-bath the material should soon become easily broken up, and granular in appearance. When this happens the stirring should become a little more frequent. At the end of the half-hour the whole should be very thoroughly mixed again, so as to assure that every particle is damp, as this is very necessary for the extraction. When transferring the material to the flask a little of the powder will adhere to the basin owing to its dampness; this can be wiped off with a piece of moist filter paper, and the paper dropped into the flask. The filtered solvent from the extraction should, when hot, be perfectly clear and almost colourless, and, when a high percentage of alkaloid is expected, a fourth washing should be given. The final distillation of the solvent should be taken as low as possible, the alkaloid commencing to precipitate out some minutes before the end of the distillation. In practice it is found best to distil the majority of the solvent from each filtration whilst the next boiling is taking place. This enables a smaller flask to be used, and facilitates the final distillation, which should be carried as far as possible. After precipitating the alkaloids with ether, it will be found in most cases that one hour's standing is sufficient to ensure a complete precipitation of the theobromine. However, if the supernatant liquid be even slightly turbid, it should be allowed to stand overnight, and, where time is no object, this is the best method. The resulting alkaloid should be white and clean. It sometimes contains a small amount of insoluble matter and ash, amounting together to about 0.004 grm. on the average. For greater accuracy, therefore, it is advisable, after weighing, to wash the filter with boiling water to dissolve the theobromine, and to weigh the residue, care being taken that the washing is very thorough, as the alkaloid is not very easily dissolved. The filtrate is evaporated to dryness, ignited, and the ash weighed. Both are deducted from the first weighing.

The table on p. 37 shows a few results of the amounts of insoluble matter and ash obtained in experiments on different materials.

The magnesia treatment is too short to allow of any decomposition of the theobromine; it decomposes any compound of the alkaloid which may be present, and it precipitates or converts into an insoluble form all the bodies which would otherwise dissolve in the solvent. The presence of the water allows of a rapid and complete

solution of the alkaloid by swelling up the material, and thus allowing the egress of the theobromine from the otherwise almost impermeable cells through the medium of the water. The method thus combines the advantages of groups B and D described above, while overcoming their drawbacks. The time taken for a complete estimation on a cocoa powder may be as short as five or six hours, and two estimations can be performed as easily as one in the same time. The process estimates only the theobromine, which is the principal alkaloid of cocoa; the caffeine is left in solution when the theobromine is precipitated with the ether.

	Weight of Precipitate.	Weight of Insoluble Substances.	Weight of Ash.
	Grm.	Grm.	Grm.
A.	0·226	0·002	0·002
B.	0·238	0·002	0·001
C.	0·225	0·003	0·002
D.	0·199	Nil.	0·001
E.	0·220	Nil.	0·001

PURITY OF THE THEOBROMINE OBTAINED.—With concentrated sulphuric acid at 100° C. the product gives only a very light-brown coloration. The ash and the amount insoluble in water are practically nil. The nitrogen content estimated by the “absolute” method is 31·07 per cent., which is equivalent to 99·9 per cent. theobromine, the theoretical result being 31·11 per cent. The nitrogen in theobromine cannot be estimated accurately by the Kjeldahl method owing to the alkaloid volatilising without decomposition. By this method the nitrogen in pure theobromine varies between 27 per cent. and 29·5 per cent. according to the speed of heating and other details of manipulation. Thus the estimation of nitrogen in cocoa by the Kjeldahl method never includes the whole of that present in the theobromine. The percentage of silver in the salt obtained from the alkaloid is found to be 37·4, which is equal to 99·5 per cent. theobromine, the theoretical yield being 37·59 per cent. By the precipitation of the theobromine as the silver salt caffeine has been shown to be absent.

Thus the alkaloid obtained by the above method has a purity of 99·5 to 99·9 per cent.

The work was carried out in Messrs. Cadbury Bros'. Research Laboratory, and I wish to thank the firm for their permission to publish the results.



A NEW PROCESS FOR THE ESTIMATION OF SMALL QUANTITIES OF CHROMIUM IN STEELS.*

By B. S. EVANS, M.B.E., M.C., B.Sc., F.I.C.

THE following process was devised to meet a need that arose for the estimation of small percentages of chromium in steels. Existing processes cannot be relied upon for the estimation of amounts less than, say, 0·05 per cent., whilst the amounts requiring to be estimated were about 0·01 or 0·02 per cent.

The principle of the method is oxidation of the chromium to chromate in the presence of ammonium phosphate, pouring the boiling solution into excess of boiling sodium hydroxide solution, making up to a known volume, filtering, and determining the chromate colorimetrically.

The details of the process are as follows: 4 grms. of the sample are weighed out and brushed into a flask of capacity about 700 c.c.; 30 c.c. of 1 : 3 sulphuric acid and 20 c.c. of water are added, and the mixture heated till the steel is dissolved, more water being added if the ferrous sulphate begins to crystallise out; 5 to 10 c.c. of nitric acid are then run in to oxidise the ferrous sulphate and the carbon, and boiling continued till the red fumes are dispelled. About 25 grms. of ammonium phosphate are then added (the exact amount is immaterial, and the ordinary moist crystals are used) and 250 c.c. of water (and more nitric acid if ferric phosphate separates), and the whole heated to boiling again. When boiling, a saturated solution of potassium permanganate is added two or three drops at a time, till excess of permanganate is present, as shown by a permanent precipitate of manganese dioxide or by a permanent red colour, as the case may be, and then a further excess of about 12 drops, and the boiling is continued for fifteen minutes. While the oxidation of the chromium is progressing, 120 c.c. of 20 per cent. sodium hydroxide solution are placed in a large beaker, about 14 drops of saturated permanganate added, and the whole boiled for some minutes; if the purple of the permanganate are entirely changed to green during this time, more should be added, so that at the end there is still a purplish tinge. When the solution of the sample has boiled for fifteen minutes, the sodium hydroxide solution is taken off the plate, about 10 c.c. of 5 per cent. manganese sulphate solution added to destroy the permanganate, and the acid solution of the sample slowly poured into it, with constant shaking, the flask being gripped with rubber-covered tongs. The resulting liquid is then poured into a 500 c.c. measuring flask, a drop of it tested with litmus paper to ensure its being strongly alkaline, and it is cooled down; if, when tested, it is found to be acid, it should be made strongly alkaline with sodium hydroxide; this does not prejudice the result. When cool, 10 c.c. of strong acetic acid are added (the liquid should be again tested to make sure that it is acid) and it is made up to the mark, shaken well, and allowed to settle for a short while; it is then filtered through dry paper into a dry flask, the first few c.c. being rejected.

All colouring matter, other than chromate, has now been removed from solution, with the exception of a small amount of nickel or cobalt if those metals be present.

Communication from the Research Department, Woolwich.

If chromium be absent the solution is practically water-white. In the absence of nickel and cobalt the estimation of the chromium is proceeded with as follows: 100 c.c. of the filtrate are placed in one Nessler glass and a little less than that volume of distilled water in another; 20 c.c. of 1:3 sulphuric acid are added to each and $\frac{N}{100}$ potassium dichromate run into the blank glass till the colours match, the volume before the final matching being made up to the same volume as that of the test solution.

If nickel or cobalt be present they interfere somewhat with the colorimetric estimation, and the procedure must be modified as follows: The 100 c.c. of filtrate are measured into a flask, instead of a Nessler tube, and heated to boiling; the flask is then removed from the plate, and sodium hydroxide solution is added until a precipitate separates, a large excess being avoided. The liquid is then cooled, filtered through a small paper filter into a Nessler glass, 20 c.c. of 1:3 sulphuric acid added, and the colorimetric estimation finished as above.

There is usually a very small blank; this may be determined, for each separate estimation, as follows: After the tubes have been matched, a drop (or quantity just sufficient) of dilute ferrous sulphate solution is added to each, and they are compared again. The liquid in the standard tube is now practically water-white, whilst that in the sample tube may be very faintly coloured, and, if so, the depth of the colour must be determined in terms of $\frac{N}{100}$ potassium dichromate solution by filling a fresh Nessler tube with 100 c.c. of water and 20 c.c. 1:3 sulphuric acid and running in $\frac{N}{100}$ potassium dichromate solution till the colours match. This blank is then subtracted from the original burette reading; it is generally about 0.25 c.c., and is of a barely perceptible colour. Of course, this only applies to quantities of chromium so small as not appreciably to colour the solution in the reduced form; with larger amounts it is sufficiently accurate to ignore the blank, or to assume that it is 0.25 c.c.

If x be the number of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ used in the titration, and y be the number of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ used in the blank, then $(x - y) \times 0.0217 =$ percentage of chromium in sample.

The following results were obtained with electrolytic iron to which different quantities of chromium had been added. In all experiments throughout this work the chromium added was measured as $\frac{N}{100}$ potassium dichromate solution, and reduced before being added to the iron solution:

No. of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ added to 4 Grms. Fe.	No. of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ recovered per 4 Grms. Fe.	No. of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ required for Titration of 100 c.c.	Blank. c.c.	Per Cent. of Chromium added.	Per Cent. of Chromium recovered.
1.00	$0.17 \times 5 = 0.85$	0.42	0.25	0.0043	0.0037
2.00	$0.35 \times 5 = 1.75$	0.60	0.25	0.0087	0.0077
3.00	$0.55 \times 5 = 2.75$	0.80	0.25	0.0130	0.0120
4.00	$0.80 \times 5 = 4.00$	1.05	0.25	0.0174	0.0168
5.00	$1.00 \times 5 = 5.00$	1.35	0.35	0.022	0.022
10.00	$2.00 \times 5 = 10.00$	2.35	0.35	0.044	0.044
20.00	$4.00 \times 5 = 20.00$	4.35	0.35	0.087	0.087
40.00	$7.60 \times 5 = 38.00$	7.95	0.35	0.174	0.167

Some tests were made in a similar manner with electrolytic iron to which varying quantities of some other metals, and small proportions of chromium, had been added :

Metal added.		No. of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ added per 4 Grms.	No. of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ recovered per 4 Grms.	No. of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ required for Titration of 100 c.c.	Blank.	Per Cent. of Chromium added.	Per Cent. of Chromium recovered.
	Per Cent.				C.c.		
Nickel	... 5.8	2.00	$0.35 \times 5 = 1.75$	0.70	0.35	0.0086	0.0076
Nickel	... 6.2	3.00	$0.60 \times 5 = 3.00$	0.95	0.35	0.0130	0.0130
Nickel	... 6.2	4.00	$0.85 \times 5 = 4.25$	1.20	0.35	0.0174	0.0184
Vanadium	... 1.0	2.00	$0.40 \times 5 = 2.00$	0.65	0.25	0.0086	0.0086
Tungsten	... 5.0	2.00	$0.37 \times 5 = 1.85$	0.62	0.25	0.0086	0.0077
Molybdenum	... 1.0	2.00	$0.37 \times 5 = 1.85$	0.62	0.25	0.0086	0.0077
Cobalt	... 5.0	2.00	$0.45 \times 5 = 2.25$	0.70	0.25	0.0086	0.0097

In the nickel and cobalt experiments sodium hydroxide was added after filtration, as described above.

In order to test the process more stringently, the tungstic acid which separated in the initial stages was not filtered off. The final filtrates from the vanadium, molybdenum, and tungsten experiments were tested for these metals, but none was found.

From these results it is evident that vanadium, molybdenum, and tungsten are completely removed by the ordinary process, and nickel and cobalt by the further treatment with sodium hydroxide.

The percentage of chromium present in a number of steels of high chromium content and varying composition was estimated both by the method under discussion and by the Vignal process, to see how the results would compare. The figures obtained are as follows :

Approximate Composition of Steel.		Chromium by Colorimetric Process.	Chromium by Vignal Process.
	Per Cent.	Per Cent.	Per Cent.
(a) Ni 0.5; W 15.8; Co 5.0; V 0.8	...	3.11	3.07
(b) Ni 2.8; Mo 0.5	...	0.82	0.85
(c) Ni 2.2	...	11.77	12.35
(d) Ni 2.4	...	1.50	1.55
(e) Ni 2.9	...	0.82	0.84
(f) Ni 2.2	...	1.33	1.30

These two series show very fair agreement when it is borne in mind that the colorimetric process is not particularly adapted to the estimation of large amounts of chromium, and that the tendency of the Vignal process is to give high results ; the

figures, moreover, were obtained during the early stages of the process, and doubtless better agreement would be obtained now. To test the process to the utmost the full 4 grms. were taken in each case and the resulting deep-coloured solution diluted down. The last traces of nickel and cobalt were not removed with sodium hydroxide, the influence of the cobalt being evident in the high result of (a).

No correction has been made, throughout, for the volume occupied by the iron precipitate, the influence of which is well within the experimental error.

An attempt was made to get more delicate and concordant readings by adding potassium iodide to the acidified chromate filtrate and estimating the amount of iodine set free, but it was found that, at these dilutions, the decomposition of the hydriodic acid brought in a source of error considerably greater than that of the direct colorimetric process. Attempts were also made to complete the isolation of the chromium by precipitating it as lead or silver chromate; these, up to the present, have been unsuccessful, owing to the large amount of sulphate and phosphate present, whilst the mere presence of large amounts of alkali salts seem to prevent the precipitation of these small quantities of chromate.

The statement has been made that filter paper will reduce chromates either in acid or alkaline solution. In order to test whether the use of paper filters was having any influence, some of the results were repeated with the use of asbestos filters; the figures obtained were practically identical. It appears therefore that, under the conditions here set out, any error caused by reduction by the filter paper is negligible.

Another statement, which has been repeated in certain textbooks, *i.e.*, that traces of chromium are not completely oxidised by permanganate in strongly acid solutions, caused a good deal of trouble in the early stages of the process, as it could not be determined whether the low results first obtained were due to incomplete oxidation or to removal of chromium as basic ferric chromate; even after the introduction of ammonium phosphate had produced a thoroughly reliable method it seemed doubtful whether its action was not merely to reduce the acidity. This point, which appeared to be of some importance, was tested in the following way: Traces of chromium (in the reduced form) were added to two 4-grm. samples of electrolytic iron, and the process was carried through in the usual way, except that the ammonium phosphate was added immediately before the introduction into the sodium hydroxide solution instead of before the oxidation. The following results were obtained:

No. of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ added.	No. of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ recovered.	No. of c.c. $\frac{N}{100}$ $K_2Cr_2O_7$ required for Titration of 100 c.c.	Blank.	Chromium added.	Chromium recovered.
2.00	$0.40 \times 5 = 2.00$	0.65	C.c. 0.25	Per Cent. 0.0087	Per Cent. 0.0087
4.00	$0.75 \times 5 = 3.75$	1.00	0.25	0.0174	0.0163

From these results it appears that the chromium is completely oxidised in solutions of the acid strength here used. No reducing action caused by any manganese hydroxide, formed by the excess of manganese sulphate used, has been detected.

The action of the ammonium phosphate has not been fully explained. Some experiments were tried in which ammonium phosphate was replaced by sodium phosphate, but these gave very poor results; on the other hand, ammonium acetate was without any effect at all. It would seem that one function of the ammonium phosphate is to combine with the iron, preventing the formation of ferric hydroxide, which would drag down basic chromate.

In conclusion a few results may be cited, obtained by this process on samples of ordinary non-chromium steels:

Plain Carbon Steels. Chromium. Per Cent.	Nickel Steels. Chromium. Per Cent.
0·012	0·086
0·014	0·012
0·026	0·033
0·004	0·011
0·029	

* * * * *

NOTES ON THE REACTIONS OF FULMINATE OF MERCURY WITH SODIUM THIOSULPHATE.

BY F. H. DUPRÉ, M.B.E., AND P. V. DUPRÉ, M.B.E., A.C.G.I., F.I.C.

(Read at the Meeting on December 1, 1920.)

TITRATION.—During the war we had to examine large quantities of fulminate of mercury. The most rapid and accurate method seemed to be titration of the alkalinity in thiosulphate solution, but this involved the use of 3 grms. of potassium iodide for each titration—a rather expensive item with iodide at 18s. per lb. We therefore sought a substitute which, while being cheaper, would be equally effective in preventing the loss of alkalinity which occurs when the potassium iodide is omitted.

The problem was investigated from the point of view that if the alkalinity produced by the solution of the fulminate could be immediately neutralised, the secondary reaction causing the loss could not occur. A material, therefore, was looked for which could be mixed with the thiosulphate solution, and which, on the one hand, was capable of neutralising the alkali formed, and, on the other, would not act on the thiosulphate. Such materials as acetic acid, tartaric acid, oxalic acid, citric acid, salicylic acid, etc., all decompose thiosulphate. Boric acid was tried and found to be exactly what was wanted. It had the added advantage of having no action on methyl orange, and the titration could, therefore, be carried out exactly as when using iodide.

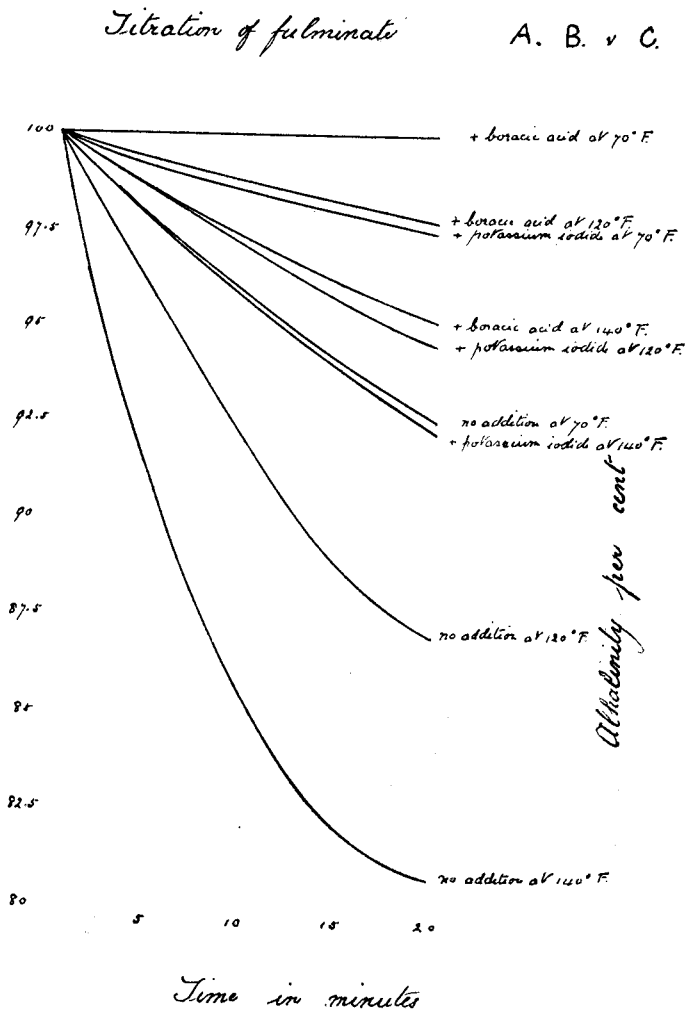
Comparative experiments were then made as follows:

- (1) 0·3 grms. fulminate, 25 c.c. 20 per cent. sodium thiosulphate solution.
- (2) 0·3 grms. fulminate, 25 c.c. 20 per cent. sodium thiosulphate, 3 grms. potassium iodide.

(3) 0.3 grms. fulminate, 25 c.c. 20 per cent. sodium thiosulphate solution, 1 gm. boric acid.

The results obtained at various temperatures are given in curves A, B, and C.

It will be seen that the boric acid is even more effective than potassium iodide, both at ordinary and raised temperatures. Since in the case of large crystal



fulminate its solution in thiosulphate takes some time, this effect of boric acid is very useful.

DESTRUCTION OF FULMINATE.—The next question which arose was connected with the destruction of waste fulminate. We had recommended the use of strong thiosulphate solution as being the quickest and safest method. It was suggested that the decomposition of the fulminate so caused was not permanent. In order to test this, a quantity of the solution of fulminate in thiosulphate solution was evaporated to

dryness and the residue examined. No trace of explosive property remained. In case this might be due to the heating, some of the solution was soaked up in filter paper and allowed to evaporate spontaneously at ordinary temperatures. Again it was found that not the faintest tendency to explosion remained. We therefore concluded that the decomposition was complete and permanent.* There are, however, two necessary precautions to be taken. Firstly, if the fulminate be simply put into the solution and allowed to settle to the bottom of the vessel, the complete destruction may take a very long time; efficient agitation of the liquid is therefore necessary; with such agitation the decomposition is rapidly completed. Secondly, an excess of thiosulphate is absolutely essential. If there be not sufficient thiosulphate present to destroy the fulminate completely, the cyanide produced in the reaction dissolves some unaltered fulminate, and this, on standing, crystallises out again. The danger involved in this is that, owing to the complete solution of the fulminate, it might be thought that the destruction was complete. The theoretical quantity of thiosulphate required is 1.746 grms. to each gm. of fulminate. We therefore recommended that a quantity of thiosulphate equal to three times the weight of fulminate to be destroyed should be used in the form of a 20 per. cent. solution.

A serious explosion which came to our notice occurred during the attempted destruction of detonators by boiling with thiosulphate solution. It is dangerous, in our opinion, to attempt to destroy detonators by treatment with thiosulphate, owing to the extreme slowness of the action, due partly to the compression of the fulminate, and partly to the protection from the solution by the shell, and, in some cases, covering metal discs or varnish, but it was thought desirable to try and discover the reason of the accident.

A considerable quantity of fulminate, about 25 grms., was put into the necessary amount of thiosulphate solution and vigorously stirred. The solution was completed in from a quarter to half a minute, and by taking the temperature before and after solution it was found that there was not the slightest rise in temperature, even when the solution was carried out at as high a temperature as 50° C. The solution which had been made at ordinary temperatures, however, showed on standing a slight rise in temperature.

Experiments were therefore made as follows: The solution was made as above, and the mixture immediately transferred to a thermos flask, the latter being closed by a cork through which a thermometer passed into the solution. The temperature was then taken at intervals extending over considerable periods, solution being made at various temperatures.

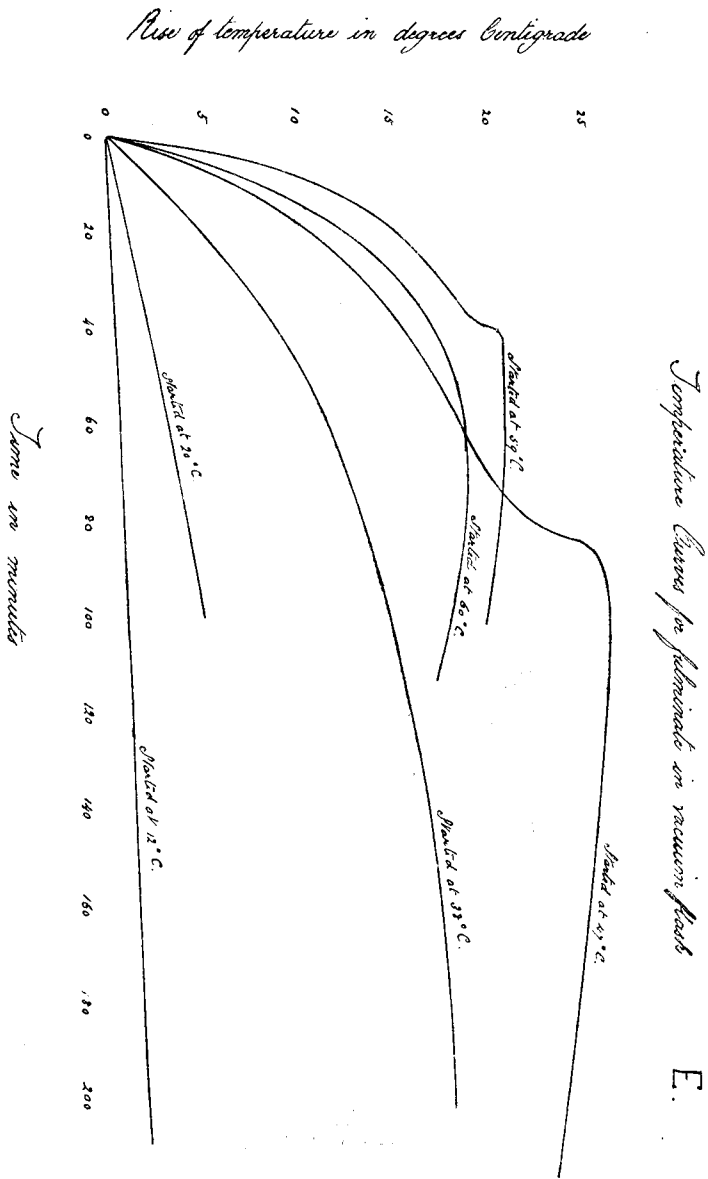
Curve E gives the results. It will be seen that in every case there is a marked rise in temperature, the more rapid the higher be the temperature at which the solution is made.

We therefore concluded that this might very possibly explain the accident. It seemed quite possible that sufficient heat might be generated by the decomposition of some of the fulminate to cause the ignition and explosion of the remaining unaltered fulminate.

In order to find the exact bearing the above effect had on our recommended

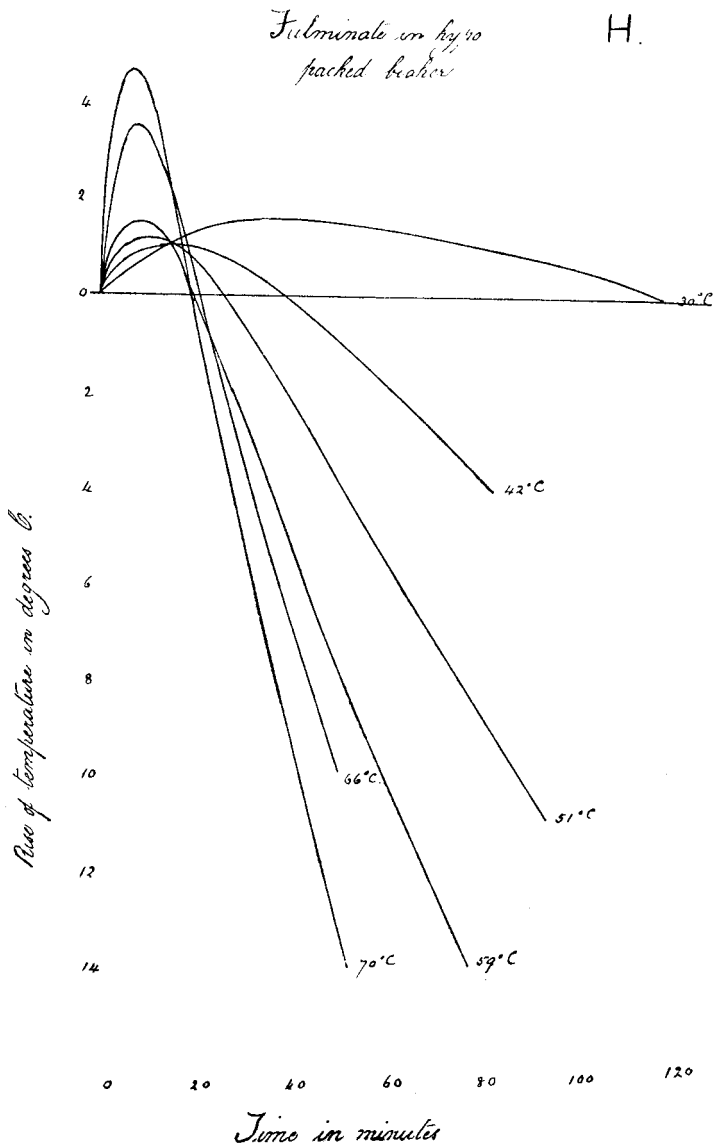
* The results of experiments described later confirm this.

method of destruction of loose fulminate, further experiments were made. Since the destruction was carried out in an open bucket the rate of loss of heat under such conditions from 100° C. downwards was determined. A beaker of a



convenient size for experiment was then packed in asbestos wool in such a way that the loss of heat occurred at as nearly as possible the rate found for the bucket, and the above experiment was repeated, replacing the thermos flask by the packed

beaker. It was then found that, even when solution was made at 70° C., after a slight rise during the first few minutes, the loss of heat by radiation, etc., was more than the gain of heat due to chemical action. We therefore considered that it was



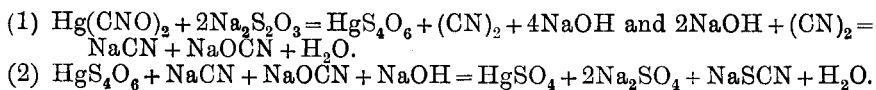
quite safe to continue the destruction of waste fulminate under the same conditions as before.*

Curve H gives the results of the experiments with fulminate.

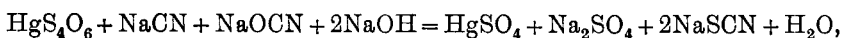
* Incidentally this, as mentioned above, confirms the supposition that the decomposition is non-reversible.

We then thought it would be of interest to try and follow the decompositions causing this rise of temperature.

There seems to be no entirely definite knowledge as to the reactions occurring during the solution of the fulminate or the ultimate product. Mr. Heaven, in a paper read before the Society of Chemical Industry (*J. Soc. Chem. Ind.*), gives Marshall's equation as follows:

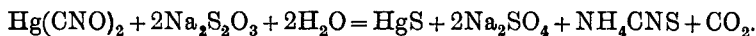


He points out that equation (2) is mathematically incorrect, and suggests that it can only be regarded as a statement in symbols. It is possible, however, that the mistake is one of printing, and that the equation should read:



which is, at any rate, mathematically correct.

As it was desired to ascertain the final products, the solution containing 2 equivalents of sodium thiosulphate to 1 of fulminate was boiled for a short time and then analysed. During the heating, a precipitate, sometimes red and sometimes black, was thrown down, and this proved to be sulphide of mercury; other radicles also present were sulphate and thiocyanate. Estimations were made of sulphide of mercury, sodium, SO_4 , and CNS , but these did not add up to the weight of fulminate and thiosulphate taken. A number of different experiments gave similar results. It had been noticed in the experiments with the thermos flask that when the temperature approached the maximum the solution appeared to boil. This proved to be due to the evolution of carbon dioxide, the amount of which was found to bring the sum of the products practically up to the weight of thiosulphate and fulminate taken; but still the equation could not be made to balance. It was then found that if the solution filtered from the mercury sulphide were evaporated to dryness, gently ignited, and weighed, it gave the same figure as when it was sulphated—*i.e.*, the whole of the sodium present was there as sulphate. This meant that the thiocyanate present was not the sodium salt.* Ammonia was therefore tested for, and found to be present. Applying this to the solution of the equation we get



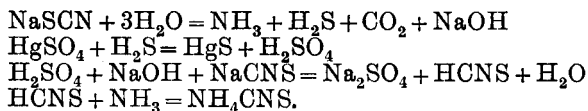
This is mathematically correct, and the analytical figures strongly support it. The following table gives the proportions of the different ingredients calculated from the equation and found by analysis, taking 100 grms. of fulminate and 174.6 grms. of sodium thiosulphate:

Substance.	Theory.	Found.
HgS	81.7	82.0
Na_2SO_4	100.0	100.0
NH_4CNS	26.8	26.6
CO_2	15.5	15.0

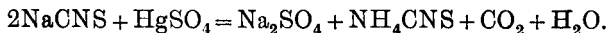
* This is not very conclusive, as the difference between the weight of sodium thiocyanate and its equivalent of sulphate is not very great.

This, therefore, is probably correct for the ultimate products, but it is very difficult to explain the presence of the ammonium thiocyanate if the second reaction given by Marshall is correct.

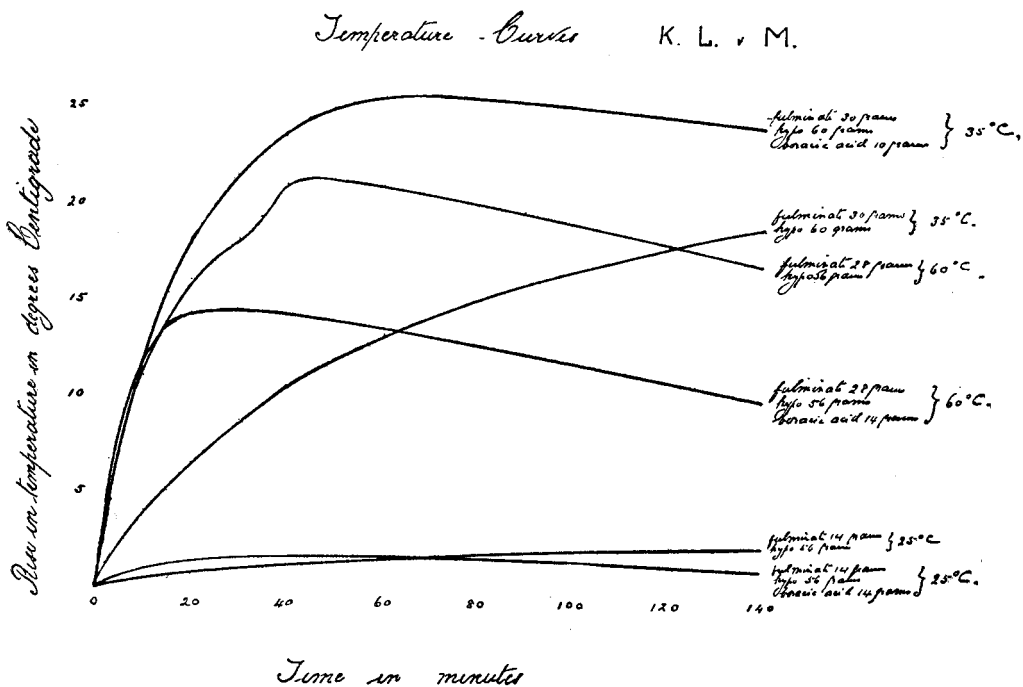
The following reactions are possible, and might explain the final result :



Collecting these we would get—



This would give the required result from Mr. Marshall's second equation, as amended.



EFFECT OF BORIC ACID.—Some experiments were then carried out to see whether the addition of boric acid to the solution in thiosulphate solution would prevent or delay the rise in temperature, since it did prevent the loss of alkalinity. The former experiments with the thermos flask were repeated with the addition of boric acid to the solution. The results are given in curves *K*, *L*, and *M*. It will be seen that the effect is somewhat unexpected, the addition of boric acid in the proportion of 1 part to 3 parts of fulminate considerably increases the rate of rise of temperature, the total rise being about the same as without addition. With 1 part boric acid to 2 parts fulminate the rate of rise is practically unaffected, but the total rise is

considerably diminished. With 1 part boric acid to 1 part fulminate the rate is increased for a short time, but the total rise is small. It must be remembered that in all the above curves the small loss of heat which occurs even with the thermos flask is ignored.

In the titration experiments the proportion of boric acid to fulminate was about 10 to 3; the above experiment was therefore repeated with the addition of a similar proportion of boric acid. It was then found that, allowing for the above-mentioned loss of heat, no change of temperature occurred for three hours. Parallel experiments to the above, in which small portions of the solution were titrated periodically, showed that whenever the temperature rose there was a corresponding loss of alkalinity, but in the last case no loss occurred in the three hours; in fact, after twenty-four hours the titration still gave the same figure. There was no sulphate nor thiocyanate present in this solution even after the twenty-four hours.

It thus appears that sufficient boric acid at least is required to form the usual sodium salt, the pyroborate or borax, $\text{Na}_2\text{B}_4\text{O}_7$. The proportions required, corresponding to the triborate, metaborate, and pyroborate, would be, 1 part fulminate, 0.29 parts boric acid; 1 part fulminate, 0.87 part boric acid, and 1 part fulminate, 1.75 parts boric acid respectively. Subsequent experiment has proved this to be the case.

* * * * *

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Comparison of Fat Tests in Milk as determined by a Milk-Testing Association and by a Creamery. H. C. Troy. (*Cornell Univ. Agric. Exper. Stat.*, Bull. 400, 1920, pp. 1-66.)—During recent years the practice of selling milk wholesale on a weight and fat-percentage basis has become general in New York State; the seller (farmer) is usually a member of an association which sends a tester once a month to examine the milk from each cow of the herd in the evening, and again the following morning. The mixed milk (not necessarily the whole supply of the herd) is delivered each morning at a receiving station, where a sample of the milk is placed in a composite sample bottle, and mercuric chloride is added as a preservative. Twice a month these composite samples are sent to the creamery and analysed. Results obtained during a year's working showed that when the fat was estimated once a month in two successive milkings the amount varied frequently by more than 0.5 per cent. from the preceding or following monthly test; the range of variation in the herd milk was less. The average fat content of the milk secreted at two successive milkings of a herd ranged from 0.2 to 0.3 per cent. above or below the fat percentage for the month, as found by the creamery, and differences of 0.5 per cent. for monthly periods were not unusual. During thirty-two complete

annual records, the differences between the two sets of tests were less than 0.1 per cent. in 59 per cent. of the records, and between 0.1 and 0.2 per cent. in 31 per cent. of the records. The daily fluctuations of the fat percentage in herd milk, and the association method of accepting the fat percentage in two successive milkings as the average for the month, did not ensure a close agreement between the results of the two tests for the monthly periods, but the association method permitted a fair estimate to be made of the fat content of the milk produced by a herd during a year.

W. P. S.

Comparison of Methods for the Estimation of the Fat Content of Skimmed Milk. T. J. McInerney and H. C. Troy. (*Cornell Univ. Agric. Exper. Stat.*, Bull. 401, 1920, pp. 1-85.)—Comparative tests with the Adams, Rose-Gottlieb, and Babcock methods for the estimation of fat in skimmed milk yielded results showing that the following modifications should be made in the Babcock method: At least 25 c.c. of sulphuric acid must be used, the temperature of the testing machine should be not less than 82°C., the centrifugal machine should have a disc at least 15 inches in diameter and be run at a minimum speed of 1,800 revolutions per minute, and the mixture should be centrifuged for ten, two, and one minute periods.

W. P. S.

Phosphorus in Butter. J. T. Cuisick. (*Cornell Univ. Agric. Exper. Stat.*, Memoir 30, 1920, pp. 159-186.)—In churning, about one-fourth of the total phosphorus of the cream is retained in the butter, the amount in the latter ranging from 0.025 to 0.041 per cent. of P_2O_5 . During storage, the soluble organic phosphorus compounds decompose, yielding inorganic phosphorus compounds, and the rate of this change depends upon the methods used in treating the milk and cream before churning. The presence of salt has a marked effect in causing decomposition of proteins in butter during storage, even at -10°C. The new alcohol-soluble protein discovered by Osborne and Wakemann (1918) in milk is also present in butter. Under certain conditions, bacteria are the controlling factors in the chemical changes of the phosphorus compounds of butter. The decomposition of lecithin and the formation of methylamine is the cause of fishy flavour in butter. When a fishy flavour develops in butter there is always an appreciable loss of soluble organic phosphorus.

W. P. S.

Lecithin Content of Butter and its possible Relationship to Fishy Flavour. G. C. Supplee. (*Cornell Univ. Agric. Exper. Stat.*, Memoir 29, 1920, pp. 101-150.)—Butter contains from 0.04 to 0.07 per cent. of lecithin, and there are indications that lecithin is the source of trimethylamine in butter, the amine giving a fishy flavour to the product. The presence of lactic acid and bacterial action are the controlling factors in the production of the trimethylamine. Certain butters, however, which possess a fishy flavour do not contain trimethylamine.

W. P. S.

Curua Palm Oil. (*Bull. Imperial Inst.*, 1920, 18, 172-174.)—Curua fruits (*Attalea spectabilis*), received from Brazil, were composed of pericarp, 15.5 per cent.,

shell, 71.3 per cent., and kernel, 13.2 per cent. The dry kernels yielded 65.3 per cent. of semi-solid greenish oil having the following characters :

Specific gravity at 100°/15° C.	0.8693
Refractive index at 40° C.	1.447
Melting-point	23.6° C.
Solidifying point of fatty acids	24.6° C.
Acid value	1.2
Saponification value	259.5
Iodine value	8.9
Unsaponifiable matter	0.36 per cent.
Reichert-Meissl value	equivalent to 6.26 c.c. of $\frac{N}{10}$ alkali per 5 grms. of fat
Polenske value	equivalent to 15.6 c.c. of $\frac{N}{10}$ alkali per 5 grms. of fat

W. P. S.

Cantaloup Seed Oil. W. F. Baughman, D. Brauns, and G. S. Jamieson. (*J. Amer. Chem. Soc.*, 1920, **42**, 2398-2401.)—Cantaloup (*Cucumis melo L.*) seeds yielded 30.4 per cent. of a pale yellow oil possessing a pleasant odour and taste, and having the following physical and chemical characters :

Specific gravity at 25°/25° C.	0.9210
Refractive index at 20° C.	1.4725
Iodine value (Hanus)	125.9
Saponification value	192.3
Reichert-Meissl value	0.33
Polenske value	0.26
Acetyl value	15.8
Acid value	0.43
Unsaponifiable matter	1.1 per cent.
Insoluble fatty acids	94.0 per cent.
Unsaturated fatty acids	80.2 per cent.
Saturated fatty acids	14.3 per cent.

The composition of the oil was: Myristin, 0.3; palmitin, 10.2; stearin, 4.5; olein, 27.2; linolin, 56.6; and unsaponifiable matter, 1.1 per cent.—Total, 99.9 per cent.

W. P. S.

The Otoba Nutmeg. (*Bull. Imperial Inst.*, 1920, **18**, 168-171.)—A forest tree (*Myristica otoba*), growing in the mountains of Columbia, produces spherical seeds 0.8 inch in diameter, consisting of shell 30 per cent. and kernel 70 per cent. On steam distillation the kernels yielded 7.2 per cent. of a colourless volatile oil, having the following characters :

Specific gravity at 15°/15° C.	0.894
Optical rotation	+79.550
Refractive index at 25° C.	1.502
Acid value	13.6
Ester value	Nil.
Ester value after acetylation	20.0
Solubility in 90 per cent. alcohol	Soluble in 16 vols. at 15° C.

The oil is deficient in certain odoriferous constituents present in ordinary nutmeg oil; it consists principally of terpenes, and cannot be used as a substitute for nutmeg oil. After the volatile oil had been removed, the dry kernels yielded 67.3 per cent. of fat somewhat resembling that obtained from nutmegs. The characters of this fat were:

Specific gravity at 100°/15° C.	0.892
Melting point	37.8° C.
Acid value	16.8
Saponification value	198.9
Iodine value	20.1
Titre test	37.2° C.

W. P. S.

Fractionation of Chaulmoogra Oil. A. L. Dean and R. Wrenshall. (*J. Amer. Chem. Soc.*, 1920, **42**, 2626-2645.)—It is not possible to effect a satisfactory separation of the chaulmoogric and hydnocarpic acids in the mixed fatty acids of chaulmoogra oil by direct fractional crystallisation or fractional precipitation with barium acetate. Fractional distillation of the ethyl esters is less satisfactory than direct fractional distillation of the fatty acids *in vacuo*. By this means three fractions are obtained, in the first of which hydnocarpic acid predominates, whilst the third contains the main portion of the chaulmoogric acid. The intermediate fraction consists of mixed fatty acids, probably a eutectic mixture, which cannot be separated by fractional crystallisation. By adding this mixed fraction to a further portion of fatty acids for distillation the yields of hydnocarpic and chaulmoogric acids are increased in their respective fractions. The chaulmoogric acid fraction is recrystallized from 80 per cent. alcohol, 20 c.c. being used for each 5 grms., whilst the hydnocarpic acid fraction is treated in the same way, except that material melting above 35°C. is recrystallised from petroleum spirit (30 c.c. per 5 grms.). Even in the case of low grade chaulmoogric oil, at least 100 grms. of pure chaulmoogric acid (m.-pt. 68°C.; iodine value, 90.1; specific rotation + 56°), and at least 50 grms. of pure hydnocarpic acid (m.-pt. 59°C.; iodine value, 100.2; specific rotation + 68.1°) should be obtained.

"Taifushi" Oil. S. Keimatsu. (*J. Pharm. Soc. Japan*, 1920, 283-286.)—"Taifushi" oil, which is the chaulmoogra oil of the Japanese Pharmacopœia, is apparently derived from the seeds of *Hydnocarpus anthelmintica*, and not from those of *Taraktogenos Kurzii*, the source of genuine chaulmoogra oil. A sample of the Japanese product had the following characters: M.-pt., 22-23° C.; sp. gr. 0.952 at 15° C.; $[\alpha]_D = +51.2^\circ$; acid value, 12.06; saponification value, 20.30; and iodine value, 85.05. It consisted mainly of the glycerides of chaulmoogric and hydnocarpic acids. The latter acid, when oxidised at a low temperature, yielded a dihydroxy-hydnocarpic acid, $C_{15}H_{27}(OH)_2.COOH$, melting at 83° C.

Estimation of Methyl Alcohol in Cacao-Beans and Husks. C. H. Koers. (*Chem. Weekblad*, 1920, **17**, 578-579.)—The total methyl alcohol was estimated in ten varieties of cacao-beans and five varieties of husks, with a view to the application

of this method as a means of determining the adulteration of cocoa with husks. The results were calculated free from fat and ash. In the beans the total methyl alcohol varied between 0.19 and 0.23 per cent., the results agreeing fairly closely with those obtained by von Fellenberg (*Mitt. Geb. Lebensmittelundersuch. und Hyg.*). With the husks, however, much lower values were obtained in some cases than those recorded by von Fellenberg; the amounts found were 0.43–0.89 per cent. No safe conclusion as to adulteration with husks can be drawn from an estimation of the total methyl alcohol content of cocoa. Further, seven varieties of manufactured cocoa contained only 0.10–0.26 per cent. of methyl alcohol. These low figures are possibly due to loss of alcohol brought about by the action of potassium carbonate used in the treatment of the beans.

W. J. W.

Detection of Methyl Alcohol in Liqueurs and Spirits. L. Hoton. (*Ann. Falsif.*, 1920, 13, 490-491.)—The test proposed depends on the determination of the initial boiling-point of the liquid. Two hundred and fifty c.c. of the sample are distilled, with the aid of an efficient fractionating column provided with a thermometer at the top, and the temperature of the vapours is observed. With a 20 per cent. (by vol.) ethyl alcohol solution, the temperature of the distilling vapours, after the first thirty seconds, reaches 78° C., and remains constant for some minutes. If a small quantity of methyl alcohol be present, this temperature is diminished by several degrees.

W. P. S.

Essential Oil from the Berries of *Juniperus phoenicea* from Sardinia. E. Puxeddu and F. Vodret. (*Gazz. Chim. Ital.*, 1920, 50, ii., 245-257.)—These berries, when macerated in water for at least two days and then distilled, yield about 2.5 per cent. of an essential oil which is colourless and transparent, but turns slightly yellow in the light. It has a pronounced aromatic odour and yields a smell of turpentine when a drop is rubbed between the hands. It tastes like camphor and burns with a smoky flame and an odour of resin. Its constants were: Specific gravity, 0.8658 at 15°; $[\alpha]_D^{26} + 16.84^\circ$; viscosity, $\eta = 1.7259$ at 18.5°; solubility at 27°, nil in 70 or 80 per cent. alcohol, 1.16 in 90 per cent. alcohol; refractive index for daylight at 20°, 1.4675; reaction, neutral; saponification value, 14-15; acid value, 2-49; acetyl value, 35; aldehydes and phenols, absent; Maumené figure, 136.80; iodine value (Hübl), 285.53, varying results being obtained if the proportion of iodine employed is varied; bromine value, 264.55. Various colour reactions are described. Distillation under diminished pressure yielded a principal fraction, boiling at 74° under 30 mm. pressure, and having specific gravity 0.8543 at 25°, refractive index 1.4644, $[\alpha]_D^{26} + 23.94^\circ$.

T. H. P.

Estimation of Morphine in Opium. A. Jermsted. (*Ann. Chim. anal.*, 1920, 2, 354-358.)—A modification of the Helfenberg method is recommended, the procedure being essentially that prescribed in the Swiss Codex. Six grms. of the opium are ground to a paste with 6 grms. of water; the paste is rinsed into a weighed flask, and water is added to make the weight up to 54 grms. The mixture is shaken occasionally during thirty minutes, and then filtered; 40 grms. of the filtrate are treated

with 2.9 grms. of *N* ammonia and filtered; and 36 grms. of this filtrate are shaken in a flask with 7 grms. of ether and 4 grms. of *N* ammonia. After ten minutes, a further quantity of 10 c.c. of ether is added, and the mixture is placed aside for thirty minutes, after which the ethereal solution is poured through a filter, and the crystalline magma is washed three times with 5 c.c. of water saturated with ether. The filter and precipitation flask are dried at 100° C.; the portion of the crystals on the filter is returned as far as possible to the flask, dissolved in 25 c.c. of $\frac{N}{10}$ hydrochloric acid, the solution poured through the filter, and the latter and the flask washed with about 75 c.c. of water. The filtrate and washings are then treated with 5 drops of methyl-red solution, and the excess of acid is titrated with $\frac{N}{10}$ sodium hydroxide solution. Each c.c. of $\frac{N}{10}$ hydrochloric acid is equivalent to 0.0285 gm. of anhydrous morphine.

W. P. S.

Quantity of Ammonium Salts in Various Opiums. L. J. Thomson.

(*Pharm. J.*, 1920, 105, 550.)—Opiums of different origin yielded the following percentage of quantities of ammonia (NH_3) when distilled with sodium carbonate solution:

	Highest.	Lowest.	Average.
Turkish (21 samples)	0.47	0.09	0.22
Indian (48 samples)	0.27	0.17	0.21
Persian (2 samples)	0.21	0.15	0.18

W. P. S.

New Reaction of Saccharin. L. Thevenon. (*J. Pharm. Chim.*, 1920, 22, 421-422.)—Diazotisation of saccharin and coupling of the resulting diazo-chloride with β -naphthol yields β -naphtholbenzoic acid, which is a red colouring matter. This reaction is carried out as follows: To 0.1 gm. of saccharin dissolved in 25 c.c. of water are added 10 c.c. of 0.1 per cent. sodium nitrite solution and 6 drops of dilute sulphuric acid (1:3), the liquid being shaken, allowed to stand for some minutes, and then treated with 0.1 gm. of β -naphthol. The red coloration thus developed is very intense and persistent, and is fixed by wool and silk. To detect saccharin in foodstuffs, the latter are extracted with water, alcohol, or other solvent, and the liquid extract mixed with a few drops of 1:3 sulphuric acid and treated as above.

T. H. P.

Yacca Gum. (*Chem. Trade J.*, 1920, 47, 803.)—The gum from *Xanthorrhœa hastilis* is soluble in alcohol and in aqueous solutions of the caustic alkalies, but is not dissolved by turpentine, benzene, linseed oil, or the usual hydrocarbon solvents. On addition of acid to the alkaline solutions the gum is more or less completely precipitated as a dull yellowish powder. Cold strong sulphuric acid partially dissolves the gum, forming a deep red solution, which, on the addition of water, gives a

brownish-red precipitate. When freed from sulphuric acid, this precipitate dissolves in water, and is reprecipitated on the addition of a little sulphuric acid to the solution.

T. J. W.

Adulteration of Gum Tragacanth with Gum Arabic. L. Thevenon. (*Ann. Falsif.*, 1920, **13**, 489.)—Powdered gum tragacanth is sometimes adulterated with the cheaper gum arabic. The presence of the latter may be detected by treating a portion of the sample mixed with water with an equal volume of 4 per cent. pyramidon (dimethylaminophenyldimethylpyrazolone) solution, and then adding 10 drops of hydrogen peroxide (12 vol.). A blue-violet coloration develops within five to thirty minutes, according to the quantity of gum arabic present. The test will detect as little as 1 part of gum arabic in 20 parts of gum tragacanth.

W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Estimation of Phosphatides. D. H. Brauns and J. A. MacLaughlin. (*J. Amer. Chem. Soc.*, 1920, **42**, 2238-2250.)—The method proposed involves the separation of the phosphatides from the other substances in the material to be analysed and the estimation of phosphorus, chlorine, and amino nitrogen in the mixed phosphatides. *Separation of Phosphatides.*—The material is extracted with hot alcohol, and the alcoholic extract is evaporated. Animal or vegetable tissues which cannot be reduced to a powder are dried previously with anhydrous sodium sulphate and calcium sulphate; liquids are treated similarly, whilst non-volatile liquid (*e.g.*, glycerol) preparations are boiled directly with alcohol. The dry alcoholic extract is mixed with anhydrous sodium and calcium sulphate and extracted with ether, and the ethereal extract is evaporated to a volume of about 40 c.c., and washed with 15 c.c. of saturated sodium chloride solution (this removes traces of inorganic phosphates). The sodium chloride solution is drawn off, washed with 10 c.c. of ether, the united ethereal solutions are evaporated, and the residue dried and weighed. If possible, such a quantity of original material should have been taken as would yield not less than 0.2 gm. of mixed phosphatides. *Estimation of Phosphorus.*—The mixed phosphatides are dissolved in 100 c.c. of alcohol, and 5 c.c. of this solution are evaporated to dryness in a large test-tube; the residue obtained is then heated with a mixture of nitric and sulphuric acids (2 c.c. of each), and the heating continued until fumes of sulphuric acid appear. The mixture is cooled slightly, a few drops of dilute cane-sugar solution are added, the mixture again heated to expel the last traces of nitric acid, then rinsed into a basin with 10 c.c. of water, 10 c.c. of 30 per cent. ammonium nitrate solution are added, the whole heated to boiling and treated with 4 c.c. of 10 per cent. ammonium molybdate solution. The yellow precipitate is collected on a small asbestos filter, washed with ammonium nitrate solution, then transferred to a beaker by the aid of a small quantity of dilute sulphuric acid, and treated with 0.5 gm. of stannous chloride. After thirty minutes the blue solution is filtered through asbestos, the filtrate diluted to 100 c.c. with dilute sulphuric acid, and the coloration compared with that given by a known quantity of phosphorus under similar conditions. *Estimation of*

Choline and Amino Nitrogen.—About 0.3 gm. of the ether-soluble phosphatides, or an aliquot portion of the alcoholic solution after evaporation, is boiled with 30 c.c. of $\frac{N}{5}$ sulphuric acid under a reflux condenser for forty-eight hours; the solution is then cooled, filtered, the fatty acids are washed with water, and the filtrate is neutralised with barium hydroxide solution. The precipitate is collected on a filter, washed with hot water, and the filtrate acidified and evaporated to dryness. The dry residue is extracted with alcohol, the alcoholic solution concentrated to a volume of about 10 c.c., and alcoholic platinum chloride solution is added. After some time the precipitate is collected, dried at 105° C., and weighed. It consists of choline platino-chloride containing some amino-ethyl alcohol platinum chloride. The filtrate from this precipitate is acidified with hydrochloric acid, evaporated to dryness, the residue rendered slightly alkaline with sodium hydroxide, acidified with acetic acid, diluted to 2.5 c.c., and the amino nitrogen estimated by means of Van Slyke's micro-amino nitrogen apparatus. The amino nitrogen is also estimated in a portion of the precipitate. The weight of amino-ethyl alcohol platinum chloride is obtained by multiplying the weight of nitrogen by 19. The weight of the precipitate minus the weight of amino-ethyl alcohol platinum chloride equals the weight of pure choline platino-chloride; the latter, multiplied by 2.608 gives the weight of lecithin. The sum of the amino nitrogen in the filtrate and in the precipitate is multiplied by 53.20 to obtain the amount of kephalin.

W. P. S.

Distribution of Enzymes and Proteins in the Endosperm of the Wheat Berry. F. J. Martin. (*J. Soc. Chem. Ind.*, 1920, 39, 327T.)—The enzymic activity of flour from various parts of the wheat berry was determined from the amount of carbon dioxide produced by a dough made from the flour, water, yeast, and a little salt, maintained at 29° C. for 24 hours. The results showed that the activity was highest in the portions close to the exterior of the endosperm, and gradually declined towards the centre. Portions of the same flours were used for the estimation of gluten, which varied from 13.8 per cent. in the centre to 21.6 per cent. in the outer portions. The consistency of the glutes obtained in the wet state was observed to vary considerably, and determinations made by measuring the volumes of the dough and the carbon dioxide evolved from doughs containing the same weight of gluten and consisting of flour, wheat starch, water, yeast, and salt, showed that the gluten from the centre of the berry possessed the highest gas-retaining capacity. The gas-retaining power is practically inversely proportional to the amount of gluten present, thus accounting for the uniform "strength" of flour from all parts of the berry. The above results were confirmed by baking tests, which showed that flour from all parts of the endosperm produced loaves obtaining the uniform value of 82 baker's marks.

T. J. W.

Presence of Hydrocyanic Acid in Linseed Cakes. Barishac. (*Ann. Falsif.*, 1920, 13, 487-489.)—From the fact that the whole of the hydrocyanic acid known to be present in linseed cakes is obtained only when the material is distilled in the presence of a relatively large excess of hydrochloric acid, it is possible that the cyanogenetic glucoside may pass unchanged through the alimentary tract of an

animal. If this be the case, there seems to be little risk of poisoning when the cake is consumed. Linseed cake has been used for a very long time and in large quantity without any injurious effect having been noticed.*

W. P. S.

Presence of Hydrocyanic Acid in Linseed Cakes. E. Kohn-Abrest (*Ann. Falsif.*, 1920, **13**, 482-487.)—The cyanogenetic glucoside occurring in linseed is concentrated in the pressed cake obtained when the oil is expressed, but the quantity in the cake appears to depend to some extent on the method of manufacture. Much of the hydrocyanic acid is lost during prolonged maceration of the seeds and by evaporation. Linseed grains of various origin (Indian, S. American, Russian, French, etc.) yielded about 0.02 per cent. of hydrocyanic acid; linseed cakes yielded up to 0.38 per cent. It is suggested that a maximum limit of 0.02 per cent. of hydrocyanic acid should be fixed for linseed cakes used for feeding animals.

W. P. S.

The Chemical Nature of Bacterial Anti-bodies. F. M. Huntoon, P. Masucci and E. Hannum. (*J. Amer. Chem. Soc.*, 1920, **42**, 2654.)—By a series of indirect chemical, physical, and biological methods the authors arrive at the following conclusions: Anti-bodies are of colloidal nature, and the molecule contains a large number of atoms. They are unaffected by trypsin, not precipitated by solutions free from electrolytes, are insoluble in ether, unaffected by short exposure to 30 per cent. sodium chloride solution, by certain dilute acids and alkalis, and by temperatures up to 60° C. Above this temperature they are destroyed or altered in nature. From these results it is deduced that anti-bodies are not serum proteins, nor globulins, but may belong to the peptide group having a carboxyl-amino linkage.

T. J. W.

ORGANIC ANALYSIS.

New Method for the Separation of Highly Unsaturated Fatty Acids in Fish Oils. M. Tsujimoto. (*J. Chem. Ind., Tokyo*, 1920, **23** [272], reprint.)—The method is based upon the fact that the lithium salts of highly unsaturated fatty acids are soluble in acetone containing a little water (about 5 per cent. by volume), whereas the lithium salts of saturated and less unsaturated fatty acids are insoluble. About 5 grms. of the fatty acids from the fish oil are freed from unsaponifiable matter and dissolved in 20 c.c. of anhydrous acetone, and the solution neutralised with 4*N*-aqueous lithium hydroxide solution (phenolphthalein as indicator), the number of c.c. required being termed *a*. Then (6 - *a*) c.c. of water and 75 c.c. of acetone are added, and the flask corked and chilled in ice for two hours, after which the solution is filtered through dry filter paper placed in a funnel surrounded by ice. The filtrate is allowed to stand until its temperature has risen to that of the room; 50 c.c. are then evaporated, and the residue of soluble lithium salts decomposed with dilute hydrochloric acid. The liberated acids are dissolved in ether, the solution

* According to some authorities this depends largely upon the age of the animal.—EDITOR.

dried with anhydrous sodium sulphate and evaporated, and the residual acids weighed. The following results are typical of those obtained by this method :

	Original Fatty Acids (Free from Unsaponifiable Matter).			Highly Unsaturated Fatty Acids.				Acids Free from Highly Unsaturated Acids.	
	Iodine Value.	Neutralisa- tion Value.	Poly- bromides.	Yield.	Iodine Value.	Neutralisa- tion Value.	Refractive Index, 20° C.	Iodine Value.	Neutralisa- tion Value.
			Per Cent.	Per Cent.					
Japanese sardine oil ...	171	187	49	29.9	357	—	1.4965	83	191
Herring oil ...	108	193	15	15.0	203	168	1.4890	73	197
Codliver oil ...	169	190	40	29.2	360	172	1.4927	91	196
Sunfish liver oil ...	164	192	43	30.8	338	174	1.4910	91	194
Whale oil ...	114	—	22	15.6	306	177	1.4887	69	196

Vegetable oils and terrestrial animal oils gave only relatively small yields of highly unsaturated fatty acids—*e.g.*, 1.2 per cent. in the case of sesamé oil and 9.3 per cent. in the case of linseed oil. The acids thus separated, however, still contain a certain proportion of solid and less unsaturated acids, but the separation may be completed by fractional distillation of the methyl esters of the fatty acids. Further investigation has shown that the clupanodonic acid, first isolated by the author from Japanese sardine oil, is not a definite chemical compound, and that its formula $C_{18}H_{28}O_2$ ($C_nH_{2n-8}O_2$ series) is also incorrect. The principal highly unsaturated fatty acids in this oil appear to be $C_{20}H_{30}O_2$ and $C_{22}H_{34}O_2$ ($C_nH_{2n-10}O_2$ series), and it is suggested that the formula for clupanodonic acid should be changed to $C_{22}H_{34}O_2$, which forms the bromide $C_{22}H_{34}O_2Br_{10}$, containing 70.76 per cent. of bromine.

Estimation of Dextrose and Starch. F. A. Quisumbing. (*Philippine J. Science*, 1920, **16**, 581-599.)—The estimation of starch in flours and other starch products is carried out as follows: Two to 3 grms. of the sample are well washed with 250 c.c. of cold water, and gelatinised by heating to boiling with about 150 c.c. of water, cooled to 40° C., and 25 c.c. of saliva, exactly neutralised with dilute hydrochloric acid, are run in, the temperature being maintained at 40° C. until the addition of iodine to a few drops yields no blue colour. The solution is filtered and diluted to 200 c.c., 15 c.c. of sulphuric acid run in, and the mixture boiled for three or four hours under a reflux condenser. On cooling, the solution is neutralised with sodium hydroxide solution and diluted to 500 c.c. Twenty-five c.c. of this solution, 50 c.c. of $\frac{N}{10}$ potassium permanganate solution, and 25 c.c. of 0.848 per cent. sodium carbonate solution, are mixed, and so heated that the temperature rises from 29° to 95° C. during a period of two minutes, and the latter temperature is kept constant for a further two minutes, after which 25 c.c. of 28 per cent. sulphuric acid and 25 c.c. of $\frac{N}{10}$ oxalic acid solution are run in, and the excess of oxalic acid titrated with $\frac{N}{10}$ potassium permanganate solution. The difference between the volumes of $\frac{N}{10}$ potassium permanganate solution used, and the $\frac{N}{10}$ oxalic acid added, represents the potassium permanganate used in oxidising the dextrose, and, by reference to a

table given in the original paper, the amount of starch present in the sample taken is found. When dealing with pure starches the preliminary gelatinisation and salivary digestion are omitted, whilst dextrose requires only the heating with alkaline permanganate and the subsequent titration. The method gives results showing excellent agreement with those obtained by Munson and Walker's modification of Fehling's method (*J. Assoc. Off. Agric. Chemists*, 1916, 1 and 2). Brief references are made to the work of earlier experimenters upon the action of alkalies and oxidising substances upon sugars, and preliminary experiments made during the evolution of the above method are described in detail. T. J. W.

The Individuality of Erythrodestrin. J. C. Blake. (*J. Amer. Chem. Soc.*, 1920, 42, 2673-2678.)—An erythrodestrin was isolated from five samples of dextrin (prepared by different methods from wheat and maizestarch), by the following series of operations. Fractional precipitation by alcohol of concentrations between 50 and 65 per cent., precipitation by ammonium sulphate, heating to 60° C. with slight excess of barium carbonate for two hours, precipitation by the addition of 42 per cent. alcohol and drying over calcium chloride to constant weight. The results of the operations were controlled by the determination on a 5 per cent. solution of the specific rotation at 25° C., the coloration produced by the addition of iodine, the time required for digestion to the achromic point (iodine) with saliva diluted 1 to 18, and the "glucose value" obtained with Benedict's reagent. The product obtained yielded the following values: Polarimetric reading +16.2; time required to reach achromic point, 2.25 minutes; and "glucose value," 1.6. The colour produced by iodine with erythrodestrin is at a maximum when the former is in slight excess, and a correction for the red colour due to this excess may be made by deducting from the red colour 40 per cent. of the total yellow colour observed. The presence of amylodestrin has no disturbing influence, since the blue colour produced neutralises the yellow colour of the iodine, until excess of the latter is present. The erythrodestrin obtained by the above method is of great use in the estimation of relative amylyolytic activity.

T. J. W.

Petrols containing Dissolved Gases. F. Bordas. (*Ann. Falsif.*, 1920, 13, 539-543.)—Certain motor spirits (petrol) sold recently in France have consisted of a "heavier" petroleum fraction containing an appreciable quantity (up to 10 per cent.) of dissolved gases, such as methane, ethane, propane, and butane. The quantity of gaseous constituents may be estimated by placing 200 c.c. of the sample in a flask attached to a reflux condenser, the top of the latter being connected with a tube which extends into a graduated cylinder containing 50 c.c. of ordinary kerosene; the cylinder is surrounded by a freezing mixture. The flask is heated to nearly the boiling-point of its contents for forty-five minutes, and the increase in volume of the kerosene then noted, after the latter has been brought to its original temperature. The difference in the specific gravity of a petrol before and after the removal of gaseous constituents is of the order of 0.010. W. P. S.

Melting-Point of Coal. G. Charpy and J. Durand (*Comptes rend.*, 1920, 171, 1358-1360.)—The finely-ground coal is moistened with water, moulded into small

cylinders about 35 mm. in length, dried at 105° C., and sealed in glass tubes from which the air has been displaced by a prolonged current of hydrogen. The tube is placed in a copper envelope and heated in a lead bath, the temperature being measured by a mercury thermometer up to 460° C., and by a thermo-electric couple beyond that. The temperature is gradually raised, the tube being removed at intervals for inspection. The coal at first contracts, then apparently expands, and afterwards undergoes a second contraction characteristic of true conversion into coke. It is at the temperature corresponding with the maximum of the first contraction that fusion occurs, this being characterised by softening of the coal, which fills the glass tube completely. Of eight coals examined, six melted between 395° C. and 550° C., and the other two did not melt below 600° C. The fusibility is independent of the content of volatile matter, but, like the tendency to form coke, is directly connected with the state of oxidation; coals oxidised by heating at 120° C. no longer melt.

T. H. P.

Estimation of Phenols in Sheep Dips. K. B. Edwards and G. A. Freak. (*J. Soc. Chem. Ind.*, 1920, 39, 326-327T.)—The method adopted by the U.S. Government consists in distilling the acidified dip with steam, dissolving the phenols in benzene, and shaking this solution with sodium hydroxide solution (1 : 3) in a graduated tube. After complete separation the increase in volume of the alkaline solution is measured, and each c.c. of the increase is assumed to represent 1 gm. of phenols. Investigation of this method by the authors has shown that in the case of pure phenols the results obtained vary within wide limits according to the nature of the phenol and its boiling-point. Thus phenol shows an apparent percentage of 92.5, whilst *p*-cresol yields a corresponding value of 102.5. Various fractions obtained by the distillation of commercial cresylic acid yielded similar results, that boiling below 195° C. showing an apparent percentage of 95; and the last fraction, boiling above 250° C., giving 117.5; whilst intermediate fractions showed a gradual rise in the percentage with the increase in the boiling-point. Since phenols, boiling above 250° C., are volatile with great difficulty when distilled with steam, the method is applicable only to those having a lower boiling-point, and any others present in the dips are omitted from the final estimation. Reference is made to a case where the specification required that 60 to 70 per cent. of the cresylic acid supplied should boil between 185° and 195° C. Tested by the method described, this sample showed 92 per cent. of phenols, whereas the actual amount present was 97 per cent.

T. J. W.

Oxidation of the Grignard Reagent. C. W. Porter and C. Steel. (*J. Amer. Chem. Soc.*, 1920, 42, 2650-2654.)—The authors have studied the reactions of phenyl magnesium bromide by bubbling pure oxygen through an ethereal solution of the compound, and hydrolysing the resulting mixture with ice and dilute hydrochloric acid, the final products being identified and estimated. The yield of phenyl bromide is practically constant, indicating that this compound is formed by the direct action of magnesium upon phenyl bromide during the preparation of the Grignard reagent. The optimum temperature for the production of phenol is 0° C.,

when a yield of 22.9 per cent. is obtained. The presence of certain compounds and the increase in the yield of phenol when hydrolysis takes place in the presence of a reducing agent suggest the presence of phenyl peroxide as an intermediate product.

T. J. W.

Detection of Nitroso Compounds and Estimation of Nitro Derivatives in Smokeless Powder. C. Lutri. (*Giorn. Chim. Ind. Appl.*, 1920, 2, 557-559.)

—Nitrous acid, nitrosamines, and nitroso-derivatives give an intense violet coloration with a 1 per cent. solution of α -naphthylamine in acetic acid. A similar coloration is also given by potassium chlorate, hydrogen peroxide, and lead peroxide, but not by ammonium persulphate or potassium nitrate. The presence of dinitrotoluene does not interfere with the application of the test to smokeless powders. *Estimation of Aromatic Nitro Compounds.*—Three grms. of the finely-divided explosive are extracted for about six hours with ether, the extract evaporated at a low temperature, and the residue heated on the water-bath beneath a reflux condenser for about six hours with 50 c.c. of 20 per cent. sulphuric acid, the flask being meanwhile frequently shaken. The liquid is then filtered, the filtrate extracted with benzene, the extract evaporated at about 50° C., and the residue weighed.

Estimation of Mineral Residue in Smokeless Powders. G. Lutri. (*Giorn. Chim. Ind. Appl.*, 1920, 2, 244.)

—A method of estimating mineral residues or graphite in smokeless powders is based upon the solution of the organic constituents in pyridine: Five grms. of the powder in a fine state of division are mixed with about 8 grms. of pyridine, and the beaker immersed at intervals in a hot-water bath, until, after forty-eight hours, the viscid mass has become liquid. The contents of the beaker are then diluted with 20 c.c. of alcohol and filtered through a weighed Gooch crucible, and the residue washed successively with alcohol, ether, hot benzene, dilute hydrochloric acid, and water. Finally it is ignited until it shows signs of incandescence, cooled, and weighed.

Inks: Their Composition, Manufacture, and Methods of Testing. (*Circular No. 95, Bureau of Standards, Department of Commerce, U.S.A.*, 1920, pp. 24.)—*U.S.A. Standard for Iron Writing Inks:* The U.S.A. Government has adopted the following specification for inks: The ink must be a gallotannate of iron ink, not inferior in any essential quality to one properly prepared according to the following formula: Tannic acid, 23.4 grms.; gallic acid, 7.7 grms.; ferrous sulphate, 30 grms.; dilute hydrochloric acid, U.S.P., 25 grms.; phenol, 1 gm.; and suitable blue dye, 2.2 grms., with water to make 1,000 c.c. at 15.6° C. *Duplicating inks* consist of a mixture of pigment (carbon, ferricyanides and ferrocyanides of iron, artificial ultramarine) and oil, such as castor-oil, sulphonated castor-oil, rosin oil, cotton-seed oil, sulphonated cotton-seed oil, and mineral oil. Some also contain rosin soap. **ANALYSIS OF WRITING INKS**—*Total Solids:* Ten grms. are evaporated to dryness, and the residue dried for one hour at 105° C. *Ash:* The residue is ignited at a low red heat. *Iron:* The ash is dissolved in 25 c.c. of hydrochloric acid, the solution diluted to 400 c.c., and the iron precipitated with ammonium

hydroxide and estimated gravimetrically. *Sulphuric Anhydride*: Ten grms. of the ink are evaporated in a silica dish, and the residue heated for an hour at 120° C., and then ignited and cooled, and the dish heated in water for an hour on the water-bath. The solution is filtered, heated for thirty minutes on the water-bath with 5 c.c. of bromine water, acidified with hydrochloric acid, and treated with 10 c.c. of 10 per cent. barium chloride solution. The barium sulphate is filtered off after twelve hours. *Tannin*: Ten grms. of ink are mixed with 10 c.c. of concentrated hydrochloric acid in Kempf's extraction apparatus, and water added to about 2 inches below the overflow tube. The bulb is then filled with ethyl acetate, and the apparatus shaken until all tannin has been extracted (about two hours). The ethyl acetate extract is washed three times with a semi-saturated solution of potassium chloride to remove any iron salts present, and then evaporated *in vacuo*, the residue taken up with a little water, the solution filtered if necessary, and evaporated in a weighed dish, and the residue dried at 105° C. and weighed. *Chromium*: Chromium, which is usually present in logwood inks, is estimated by fusing the ash with 10 grms. of sodium carbonate in an oxidising atmosphere; the fused mass is treated with water, and filtered, the filtrate acidified with acetic acid, heated to boiling, and treated with 10 per cent. barium chloride. In the presence of chromium a yellow precipitate will be obtained. It is collected in a Gooch crucible, ignited, cooled, and weighed as Cr₂O₃. *Specific Gravity*: This is determined at 15.6° C., and compared with water at the same temperature. *Streak Tests*: The ink is applied to pieces of all-rag writing-paper of good quality, 11 by 5½ inches, which are clamped on to a glass plate 8 inches wide, inclined at an angle of 45°, pipettes with a capacity of about 0.6 c.c. being used for the purpose. Regular streaks should be obtained, the head being oval, and the remainder of nearly uniform width. In the case of a very fluid ink the head is tapering, and the streak shows rapid contraction. *Resistance to Light and Reagents*: After the ink has become oxidised within the fibres of the paper (which will take from five to eight days) the streaks are cut laterally into four strips. One of these is immersed in water at the ordinary temperature, and a second exposed to ultraviolet light (or to direct sunlight), whilst the third and fourth are kept in the dark. Strip No. 4 is subsequently cut into small pieces and tested with various reagents, such as 95 per cent. alcohol; 90 parts by volume of water with 10 of ammonium hydroxide; 2 per cent. hydrochloric acid; 2 per cent. sodium hydroxide solution; and bleaching powder solution containing $\frac{N}{200}$ available chlorine. The tests are relative, and the results should be compared with those given by the standard ink. *ANALYSIS OF CANCELLING INKS—Substances Volatile at the Ordinary Temperature*: A weighed quantity (about 5 grms. of the ink) is exposed to the air, and weighed after eighteen hours, and then after each day. The percentage loss in weight ought not to exceed 15 per cent. during the first seven days. *Penetration Test*: Strips of white blotting-paper, about 12 mm. wide and 25 cm. long, are cut from the same sheet, and introduced into 5 c.c. of the ink contained in a homœopathic "shell vial" about 8 cm. long and 2 cm. in diameter. Portions of 5 c.c. of water are placed in two similar vials, and strips of blotting-paper also introduced into these. In each case the blotting-paper should be nearly vertical, and care should be taken that the liquid does not ascend by capillarity between the edges of

the strips and the sides of the vials. Exactly fifteen minutes from the time of insertion the height to which the liquid has ascended the strip of paper is measured by means of dividers and a millimetre rule, and a second set of readings is made after forty-five minutes. In each case the readings are expressed in terms of the penetrating power of water represented as 100, by dividing each result by the average of the results obtained with water, and multiplying the quotient by 100. The portions of the immersed strips may also be cut off, and extracted successively with petroleum spirit, alcohol, etc., to separate the constituents of the ink. The extent to which the dyes or lampblack have penetrated the paper affords an index of the quality of the ink. *Sedimentation Test*: The ink is introduced into a graduated 200 c.c. cylinder to the depth of 16 mm., and treated with a suitable solvent (alcohol, ether, benzene, petroleum spirit, etc.) so as to give 200 c.c. of solution. The cylinder is closed with a stopper and allowed to stand, and the layer of sediment measured, at intervals of fifteen minutes during the first hour, then each hour for several hours successively, and subsequently twice a day for a week to ten days. After settling is complete the height of the sedimentation should not equal or exceed 16 mm. The rate of sedimentation affords an index of the state of division of the carbon. In the case of some inks no appreciable layer is formed after ten days. *Lampblack*: Five grms. of the ink are diluted with a suitable solvent, and the deposited carbon collected in a Gooch crucible, washed with solvent, dried, and weighed, and the weight corrected for the amount of ash. *Glucose*: Three grms. of the ink are diluted with water, the dyestuffs precipitated with sodium hydroxide, the liquid filtered, and the sugars estimated in the filtrate by means of Fehling's solution.

Classification and Identification of Coal Tar Dyes. *Circulaire du Chef du Service des Finances et MM. les Chimistes en Chef des Laboratoires.* (*Ann. Falsif.*, 1920, 13, 193-456.)—Methods are described for separating the dyes into groups with a view to their subsequent identification, and suitable tests are described. An alphabetical list of the dyes is also given. The paper is unsuitable for abstraction, and the original should be consulted.

W. P. S.

INORGANIC ANALYSIS.

Conductimetric Titration. J. M. Kolthoff. (*Chem. Weekblad*, 1920, 17, 694-701.)—The conditions under which the conductimetric method is applicable to the titration of strong and weak acids and bases have been investigated. Phenol, boric acid, and hydrogen cyanide give good results, and the method is also suitable for the estimation of aniline and its derivatives and alkaloids. Formic, oxalic, and tartaric acid may be titrated with ammonia, but boric acid is too weak. With mixtures of acids it is sometimes advantageous to add alcohol in order to reduce the dissociation constant. With boric acid and acetic acid no definite break in the curve is obtained, but with oxalic and tartaric acid, boric acid may be satisfactorily titrated. Phenol behaves similarly. Hydrogen cyanide may be titrated in presence of acetic acid, but cannot be determined with oxalic acid. The author gives many more examples of the applicability of the method.

W. J. W.

Table of Highly Sensitive Rays of the Elements Applicable to Analytical Investigations. A. de Gramont. (*Comptes rend.*, 1920, 171, 1106-1109.)—The author gives for most of the elements the wave-lengths of the rays of great sensibility obtained in the condensed spark, either by direct observation on metals, alloys, and conducting minerals, or by fusion of non-conducting minerals or pulverulent precipitates with salts of the alkali metals. T. H. P.

Gas-Volumetric Estimation of Ammoniacal, Nitric, and Organic Nitrogen in Mixed Fertilisers. P. Baldi. (*Giorn. Chim. Ind. Appl.*, 1920, 2, 376-378.)—The fertiliser (10 grms.) is extracted with hot water, and the filtered extract and washings diluted to 200 c.c. Ten c.c. of the solution are used for the estimation of ammoniacal nitrogen by the hypobromite method, whilst nitric nitrogen is estimated by the same method in 50 c.c. of the solution, after reduction with Devarda's alloy, in presence of sodium hydroxide. Organic nitrogen in the solution and in the residue from the extraction is estimated by Kjeldahl's process, the ammonia being determined by the hypobromite method. The tabulated results show that the gas-volumetric method, applied as described, gives slightly lower proportions of nitrogen than those obtained by distillation of the ammonia.

Iodimetric Estimation of Amino Nitrogen. H. H. Willard and W. E. Cake. (*J. Amer. Chem. Soc.*, 1920, 42, 2646-2650.)—Material containing 10 or 15 mgrms. of nitrogen is weighed and heated with 15 c.c. of concentrated sulphuric acid for about ten minutes, or until the organic matter is completely charred and free evolution of sulphur dioxide has ceased. After cooling, solid potassium persulphate, weighing ten times the amount of the material taken, is added by means of a thistle tube, the mixture being gently warmed and then swirled until colourless, boiled for five minutes to decompose any excess of persulphate, diluted with 70 c.c. of water, and again boiled to remove any residual sulphur dioxide. After cooling, a few drops of methyl orange are added, and the solution is neutralised by the addition of 40 per cent. sodium hydroxide solution, the solution being frequently cooled in a stream of water to avoid loss of ammonia. Two drops of the sodium hydroxide solution are run in, followed by 10 c.c. of 0.6N sodium hypobromite, and the mixture allowed to stand for five minutes, after which 5 grms. of potassium iodide and 6 c.c. of hydrochloric acid are added, and the liberated iodine titrated with $\frac{N}{2}$ sodium thiosulphate solution. The sodium hypobromite solution is prepared by slowly adding 50 grms. of bromine to a well cooled solution of 30 grms. of sodium hydroxide in 800 c.c. of water. If kept in the dark at a temperature below 5° C. the solution retains its composition unaltered for a week, but at ordinary temperatures it should be standardised daily against pure ammonium sulphate or sodium thiosulphate. One c.c. of the 0.6N solution is equivalent to 2.8 mgrms. of nitrogen. Since nearly all samples of potassium phosphate contain ammonium salts, a blank determination should be made, and the result deducted from the results of any determinations. If iron salts be present, the addition of phosphoric acid will prevent the liberation of iodine due to these compounds. The method is more rapid than the usual Kjeldahl determination, and yields equally accurate results. T. J. W.

Estimation of Nitrite in Water. P. A. Meerburg. (*Chem. Weekblad*, 1920, 17, 577-578.)—The colorimetric reaction of nitrites in water with the Griess-Romijn reagent (naphthylamine, 1 part; sulphanilic acid, 10 parts; tartaric acid, 89 parts) is accelerated by the presence of sodium chloride, but retarded by bicarbonates. The latter salts should therefore first be neutralised with sulphuric acid, and 0.1 per cent. of sodium chloride should then be added both to the reagent and to the water under examination, after which the reaction will take place in thirty minutes.

W. J. W.

Rapid Method of Disintegrating Metal Alloys not attacked by Acids.

I. Compagno. (*Giorn. Chim. Ind. Appl.*, 1920, 2, 554-555.)—Metal alloys, such as ferrotungsten, ferrosilicon, etc., which are not attacked by mineral acids, may be rapidly disintegrated by fusing 0.25 to 0.5 gm. with a mixture of 52 per cent. of sodium carbonate, 20 per cent. of potassium nitrate, and 28 per cent. of coarse magnesium powder which has been dried for two hours at 100° C., and kept in a bottle with a tightly-fitting stopper. About 4 grms. of this mixture is placed in a nickel crucible, then the powdered alloy mixed with 2 grms. of the fusion reagent, and then 10 to 12 grms. of the latter, and finally 1 gm. of magnesium powder. After fusion the mass is cooled and treated with a mineral acid, and the solution boiled until gas is no longer evolved, and then analysed by the usual methods.

General Method for the Detection and Estimation of Arsenic. Kohn-Abrest. (*Comptes rend.*, 1920, 171, 1179-1182.)—Arsenic may be detected and estimated in any material, such as animal organs or liquids, foods, etc., in the following manner: One hundred grms. of the substance, chopped fine if necessary, are mixed in a flat-bottomed porcelain dish with 35 c.c. of a solution containing 200 grms. of crystalline magnesium nitrate per litre, and with 1 gm. of calcined magnesia. The basin is then heated to about 250° C. in an oven placed on a sand-bath. When the mass is dried and roasted, this usually requiring about three hours, the carbonaceous residue is ground in a mortar, returned to the basin, and introduced into a muffle furnace, the bottom of which is heated to dull redness (500° C.). After about two hours the ash, which is almost free from carbon, is mixed with 30 c.c. of dilute sulphuric acid (10 vols. per 100), which usually dissolves it completely. The liquid is diluted to 60 c.c., and the arsenic estimated by Marsh's method. When the percentage of arsenic in the organs to be examined lies between 0.04 and 0.00002, 70 to 80 per cent. of the total arsenic is obtained by this procedure. In the case of organic arsenic compounds, 0.15 to 0.2 gm. of the product is mixed in a 40 c.c. porcelain crucible with about 0.2 gm. of calcined magnesia and 6 c.c. of the 20 per cent. crystallised magnesium nitrate solution. The open crucible is kept in an oven at 110° C. until the mass is dry, and is then fitted with a flat-rimmed lid large enough to project about 5 mm. beyond the wall of the crucible, and placed in a muffle furnace heated to bright redness. After a few minutes the organic matter is burnt, the magnesium nitrate decomposed, and the arsenic converted into magnesium pyroarsenate. The ash remaining is dissolved in 30 c.c. of a hydrochloric acid solution containing 150 c.c. of acid of density 1.17 per litre, the solution being left

on a water-bath for five minutes, treated with 7.5 grms. of potassium iodide, and kept near the boiling-point for five minutes. The liquid is then cooled under the tap, and a rough indication of the arsenic obtained by titrating the free iodine with thiosulphate. The solution is afterwards rendered alkaline by the addition of sodium bicarbonate, and the arsenious compound titrated with iodine solution: 1 c.c. of $\frac{N}{10}$ iodine solution corresponds with 0.00375 gm. of arsenic. In most cases these two titrations give concordant results; but in one case in which the combustion proved difficult, this was not the case, the ash then consisting not entirely of arsenate, but partly of arsenite. This method gives good results. T. H. P.

Estimation of Arsenic and Phosphorus in Metallurgical Products.

I. Compagno. (*Giorn. Chim. Ind. Appl.*, 1920, 2, 493-497.)—The following simplified modification of the distillation method of Lundin and Blair (Carnot, *Méthodes d'Anal. des Fontes, des Fers et des Aciers*, 1895) is recommended for the estimation of arsenic and phosphorus in steel, etc.: The metal is finely divided, and 5 grms. dissolved in dilute nitric acid (1:1), with the subsequent addition of 10 c.c. of sulphuric acid. The solution is evaporated to dryness, and the residue calcined, ground up, and again calcined until fumes of sulphuric acid appear, and then dissolved in 200 c.c. of hydrochloric acid, and transferred to a distillation apparatus. After reduction of the liquid with 5 grms. of pure copper turnings, the arsenious chloride is distilled into 300 c.c. of water contained in a receiver chilled in ice-water. The arsenic in the distillate is precipitated in the cold by means of hydrogen sulphide, the excess of which is removed by means of carbon dioxide, and the arsenic sulphide collected in a Gooch crucible, washed successively with water, alcohol, and carbon bisulphide, dried and weighed. Phosphorus is estimated by one of the usual methods in an aliquot portion of the residue in the distillation flask, this being first filtered from silica and then oxidised by means of nitric acid and potassium permanganate. If only the phosphorus is to be estimated, the arsenic may be volatilised by treating the hydrochloric acid solution of the metal with hydrobromic acid, or after reduction with pure copper.

Estimation of Titanium and Iron in Rocks. F. Ferrari. (*Giorn. Chim. Ind. Appl.*, 1920, 2, 497-498.)—Titanium and iron are estimated in rocks by separating the silica in the usual manner, reducing the iron in a definite portion of the filtrate from the ferric into the ferrous condition by means of zinc, while a current of carbon dioxide is passed through the flask, and then titrating the titanium with methylene blue. The iron, which is in the ferric condition, is then estimated in another portion of the filtrate by titration with titanous chloride, potassium thiocyanate being used as indicator.

Detection and Estimation of Chromium in Steel. A. Ferni and P. Malaguti. (*Giorn. Chim. Ind. Appl.*, 1920, 2, 559-561.)—The method of detecting and estimating chromium by oxidising it to chromic acid by means of nitric acid and lead peroxide (*Gazz. Chim. Ital.*, 1919, 1, 251) has been adapted to its estimation in steel. One gm. of the sample is dissolved by boiling it with 30 c.c. of dilute (1:4)

nitric acid in a covered beaker, and after nitrous fumes have ceased to be evolved, the solution is treated with 20 c.c. of strong nitric acid (sp. gr. 1.4) and about 1 grm. of lead peroxide, and concentrated to about 4 to 5 c.c. This residue is diluted with 30×35 c.c. of cold water, and then heated nearly to boiling with 25 c.c. of 30 per cent. sodium hydroxide, cooled, diluted to 500 c.c., and filtered. An aliquot part (200 c.c.) of the filtrate is treated with 25 c.c. of 30 per cent. nitric acid (sp. gr. 1.2) which has been freed by prolonged boiling from nitrous acid, and then with 5 to 10 c.c. of 10 per cent. potassium iodide solution, and the liberated iodine is titrated with thiosulphate solution against which has been standardised $\frac{N}{10}$ potassium bichromate solution in the presence of 25 c.c. of 30 per cent. nitric acid.

Composition of Potassium Platinochloride. A. Vürtheim. (*Chem. Weekblad*, 1920, 17, 637-640.)—The double chloride of potassium and platinum retains a trace of moisture even after prolonged heating at 150° C. By precipitation of the salt from its aqueous solution with 96 per cent. alcohol as a very fine crystalline mass it may be obtained almost entirely free from water. The composition of the salt as found by analysis does not quite agree with the formula K_2PtCl_6 , the platinum being slightly higher, and the chlorine lower, than the theoretical amount. In the estimation of potassium as potassium platinochloride an empirical factor must be employed; the value found by the author was 0.1929-0.1930.

W. J. W.

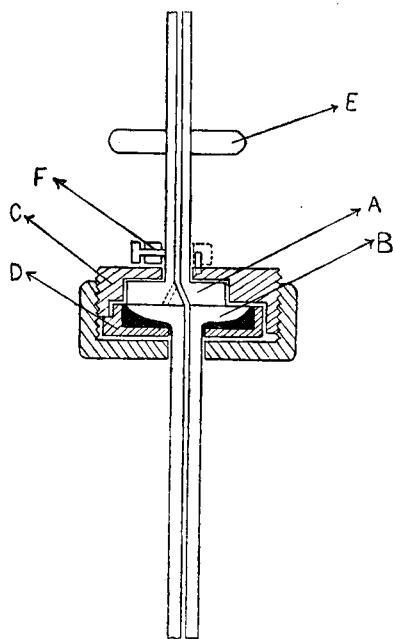
Perchloric Acid as a Dehydrating Agent in the Estimation of Silica. H. H. Willard and W. E. Cake. (*J. Amer. Chem. Soc.*, 1920, 42, 2208-2212.)—The silica in metals and silicates can be rendered insoluble by evaporating the acid solution of the sample with the addition of perchloric acid until dense fumes of the latter acid are evolved. Less silica remains in solution than is the case when the sample is evaporated to dryness with hydrochloric acid.

W. P. S.

Loss of Phosphoric Acid on Heating with Sulphuric Acid or Fusion with Pyrosulphate. W. F. Hillebrand and G. E. F. Lundell. (*J. Amer. Chem. Soc.*, 1920, 42, 2609-2615.)—Losses of phosphoric acid in estimations are due to faulty manipulation, conversion, or volatilisation. Those due to conversion of orthophosphoric acid by heating into the pyro- or metaphosphoric acids, which are incapable of estimation by any methods used for the former, may be rectified by reconversion, by boiling the solution for at least two hours with 10 per cent. sulphuric acid before precipitation. Losses by volatilisation are caused by the employment of excessive quantities of sulphuric acid or sodium pyrosulphate, prolonged heating to secure complete expulsion of sulphuric acid, and evaporation at temperatures above 150° C. In all cases evaporation should cease when fumes begin to appear. No losses occur in the case of evaporation involving only a few drops of sulphuric acid, as in the removal of silica by hydrofluoric acid. Fusion with sodium pyrosulphate should not extend over two hours, nor should the temperature be allowed to exceed that of dull redness.

T. J. W.

APPARATUS, ETC.



Metal-Glass Tap. W. E. Garner. (*J. Soc. Chem. Ind.*, 1920, **39**, 347T-348T.)—A metal-glass tap, for use with a mercury manometer for measuring pressures between 2 and 10 atmospheres, comprises a metal disc A attached to a steel capillary tube and a larger glass disc B fused to a glass capillary, the metal disc being perforated obliquely and the glass disc centrally, the perforations being continuous with the capillaries. The discs are placed in brass cells C and D, keyed together, the glass disc being fixed, but the metal one capable of revolution about an axis parallel to, but not in the same line as, the axis of the glass disc; a strip of metal E soldered to the steel capillary enables the metal disc to be turned. The surfaces of both discs are carefully ground, and an air-tight joint is made with grease. Communication between the discs is obtained in one position only, and the discs may be secured both in the open and closed positions by means of a collar and pin F. W. J. W.

Sulphuric Acid Concentrator and Vacuum Pump. O. Maass. (*J. Amer. Chem. Soc.*, 1920, **42**, 2571-2574.)—The apparatus described consists of an automatic vacuum pump working on the principle of the well-known Topley pump, but employing sulphuric acid as the motive liquid, this acting at the same time as a powerful absorbent of water vapour. In order to overcome the effect of heat due to the absorption of water, portions of the apparatus containing sulphuric acid are water-jacketed. The apparatus is partially exhausted by means of an auxiliary Geissler pump before use, and the movement of the sulphuric acid is regulated by a control previously described (*J. Amer. Chem. Soc.*, 1919, **41**, 53). The pump was designed to remove water, partially or completely, from large volumes of aqueous solutions, and has been found highly efficient in cases where corrosive and other gases are liberated in addition to water vapour. For details and diagram of the apparatus the original paper should be consulted. T. J. W.

Laboratory Apparatus for Measuring the Permeability and Heat-insulating Capacity of Textiles. G. Colombo. (*Giorn. Chim. Ind. Appl.*, 1920, **2**, 167-168.)—To determine the permeability of textile fabrics to water, the material is stretched across a framework of metal wire, which is fitted into a receiver so as to form a porous bottom, the edges of which are made watertight by means of mercury seals. A volume of water (*e.g.*, 40 mm.) is maintained at a constant level above the stretched fabric, and the quantity which passes through the material in a given

time at a definite temperature is calculated into the volume per sq. dcm. Or, in comparing the behaviour of two fabrics, the time in minutes required for the filtration of 500 c.c. of water per sq. dcm. under a constant pressure of 40 mm. may be determined. The apparatus for measuring the heat-insulating capacity consists of a cylinder filled with mineral oil and connected with an outside source of electric heat. This cylinder is suspended, by means of the thermometer passing through the cork, in an outer cylinder with perforated walls, so that there is an air space of 15 mm. between the cylinders. The material is stretched round the outer cylinder, the oil is heated to a given temperature, the apparatus placed under a bell jar, and the time required for the temperature to fall through a definite range is recorded.

Apparatus for Determining the Fluidity of Oils at Low Temperatures.

(*Giorn. Chim. Ind. Appl.*, 1920, 2, 388-390.)—The apparatus consists essentially of a U-tube with long arms, 6 m.m. in diameter, upon one of which is a scale graduated in mm. The oil is introduced into this tube up to the zero mark of the scale, and the tube is immersed in a bath, chilled to the desired temperature. A pressure of 50 mm. of water, regulated by a water manometer, is then applied to the other limb of the U-tube, and the degree to which the oil is displaced by the pressure is read upon the scale, and thus affords a measure of the fluidity. For the simultaneous examination of a number of oils, a series of such tubes is placed in a special chamber which contains an observation window, and is connected by means of a valved tube with a cylinder of liquid carbon dioxide, the expansion of which produces the low temperature.



REVIEWS.

PLANTATION RUBBER AND THE TESTING OF RUBBER. By G. STAFFORD WHITBY. Pp. xvi + 559, with 8 Plates and 48 Diagrams. London: Longmans, Green, and Co., 1920. Price 28s. net.

The first part of the work under review deals substantially with the preparation of plantation rubber in its widest aspect, with the character of the various grades produced, and with the chemical and physical nature of the non-rubber constituents (*i.e.*, the resin, and protein, and other serum constituents). Dr. Whitby has collated and handled the subject-matter exhaustively and in scholarly fashion, with the result that Part I. (consisting of 201 pages) may fairly be termed an up-to-date handbook of the Plantation Rubber Industry, with the qualification that the author does not treat of diseases or parasites or of matters other than those which may be claimed as coming within the purview of the rubber chemist and technologist. Part II.—*The Testing of Rubber*—deals essentially with the mechanical and physical character of crude rubber, of the vulcanisation process, and of the vulcanised product. Except and in so far as the determination of "combined sulphur" and the relation of the latter to mechanical and physical properties are concerned, chemistry plays a comparatively

small rôle in the author's scheme; but as he is dealing mainly with the fundamental principles relating to the characteristics of rubber and its behaviour towards vulcanisation with sulphur only, and not with rubber manufacture proper, no other course could well have been expected. As Dr. Whitby correctly points out, "Vulcanised rubber is in most connections technically valuable because of its mechanical properties. Hence, speaking broadly, the mechanical behaviour of the rubber after vulcanisation must be the final criterion for the purpose of evaluation. Chemical analysis, not only in the case of raw rubber, but also in the case of vulcanised rubber, will, finally, be of value only in so far as it can be correlated with the mechanical behaviour of the vulcanised rubber." The author has rendered a great service to those interested in rubber science and technology by collating and criticising the numerous researches on physical and mechanical characteristics and on vulcanisation published over the past century, researches frequently difficult of access and hitherto sadly in want of critical review. The merit of the work in this connection is enhanced by a most excellently compiled Bibliography. In conclusion, it should be stated that Dr. Whitby's book is one of the series of "Monographs on Industrial Chemistry," edited by Sir Edward Thorpe, C.B., F.R.S., and that the printing and illustrations are first-rate.

PHILIP SCHIDROWITZ.

THE DETERMINATION OF HYDROGEN IONS. By W. MANSFIELD CLARK, M.A., Ph.D.
Baltimore, U.S.A.: Williams and Wilkins Company, 1920. Price \$5.50.

A glance through the contents of this book shows that Dr. Clark could have chosen no portrait to face the frontispiece of his book more appropriate than that of S. P. L. Sørensen, the Director of the Carlsberg Laboratorium at Copenhagen. The lucid exposition of the relationships governing the dissociation of water in which electrolytes are dissolved, contained in the opening chapters, is developed *ab initio* from Sørensen's treatise published in the Carlsberg Laboratory Reports. For those who have not had the good fortune to work with the new Clark and Lubs series of indicators, it is instructive to note their nuances by the show of tints portrayed in excellent reproduction in colour. These pages are more ambitious than any previously published on this subject.

Passing through the book from chapter to chapter the pleasure increases in the thoroughness and practical insight of the author into this fascinating field of study. No phase is treated laboriously, yet all the essential matter is there and in detail—standard buffer solutions for colorimetric comparison (Chapter V.); the protein error and the salt error in colorimetric determinations; potential differences at liquid junctions (a difficult chapter this to write, but here excellently treated); the relation of hydrogen electrode potentials to reduction potentials; sources of error in electro measurement of P_H , etc., etc. These are all excellent, and not only the general theory and the details of its application to every-day laboratory practice, but the numerous details of equipment are dealt with in a manner that compels admiration and the desire that this book should be widely circulated to our more complete knowledge and advancement.

It is difficult to find any point of criticism. Chapter XIX., dealing with applica-

tions of the methods to the study of biochemical problems, is historical, condensed, to the point, and suggestive, and not less valuable is a bibliography of some 1,200 entries which for reference is of inestimable value.

G. S. WALPOLE.

MARGARINE. By WILLIAM CLAYTON, M.Sc., A.I.C. Monographs on Industrial Chemistry. Pp. 187. London: Longmans, Green and Co., 1920. Price 14s.

This monograph being undoubtedly, as the author states in the Preface, the first of its kind to be published in any language, it is natural to approach it with some considerable interest on account of the extraordinary secrecy and mysteriousness which have surrounded the manufacture of margarine, a manufacture which in itself is very simple. Its claim too, of course, only holds good in so far that the subject-matter is confined to margarine, as the section on Margarine in Hefter's "Technologie der Fette und Oele" contains a remarkably good history of the manufacture, etc., of margarine up to the date of its publication, and similar, if more condensed, articles are to be found elsewhere. It is, however, quite true that this present work is the only one extant which brings the history of margarine up to the present day, and for this reason must command considerable attention on account of the well-known experience of the writer.

The author has certainly succeeded in giving a concise account of the processes which are used in the best equipped margarine factories, though many undoubtedly will feel sorry that he has kept so carefully to the rules laid down in the Introduction—viz., that these monographs are not to be concerned with the technical minutiae of manufacture—as a rather more detailed account might have been hoped for.

In the chapter dealing with the oils and fats used in margarine manufacture, attention is drawn to nearly all the oils which have from time to time been used. The descriptions, etc., are clear, lucid, and correct, though, at the moment, the manufacture of margarine is confined to a comparatively few varieties of oils and fats.

It is doubtful if many manufacturers would agree that soya oil is admirably suited for margarine, and it is improbable that shea nut oil has found its way into the manufacture, except in very small quantities, as the refining of this oil is a somewhat difficult process. Some useful information, however, is given with regard to the use of hydrogenated oils, though the author appears to be somewhat over hopeful about the use of these fats in margarine manufacture, as, for many reasons, they have not proved as desirable as was at first hoped.

A chapter follows on the examination of the milk used in margarine manufacture. This is not as reliable in regard to detail as it might be, and, though useful to a trained chemist, might lead to unfortunate conclusions in the case of the less experienced works chemist. For instance, the test given for the presence of formaldehyde sometimes gives a coloration with pure milk. Also the use of vaseline in the test for *Bacillus enteritidis sporogenes* is to avoid anaerobic conditions of culture which are stated to be necessary. Again, among the tests for pasteurised milk, the cream-lime test is of doubtful utility, nor is it by any means possible to determine the method of pasteurisation by incubation of samples of the treated milk. It is necessary to draw attention also to the extraordinary differences in temperature

which are spoken of as being used in the preparation of milk for culture purposes. For instance, the temperature of "flash" pasteurisation is given in one place as 82° F., in another as 71° F., and for bulk pasteurisation as 70° C. for thirty to forty minutes, and in another place 60° to 65° C. for thirty minutes. The methods of pasteurisation are well dealt with, but few people will agree with the author that the "Tube" pasteuriser described on page 42 is the most satisfactory for "Holder" pasteurisation. When, however, one turns to the practical preparation of starters, one notes immediately that the temperatures given as being employed in sterilisation or pasteurising milk for such cultures are those of the practical man, and are very much more satisfactory in practice than those given in the theoretical discussion of the subject.

The section dealing with the inoculation and ripening of the milk for culture work is undoubtedly good, though, of course, ideas on this subject vary with different workers. The sections dealing with the actual manufacture of margarine are quite up to date, and well describe the modern methods of emulsifying, working, etc., though the statement that the older method of cooling by ice-spray washes out some of the milk is not true when emulsification has been correctly carried out. A chapter on the theory of emulsification will be of great interest to those engaged in the scientific control of margarine manufacture, and is distinctly helpful and suggestive of new lines of work.

The sections on the analysis of butter and margarine give a concise and adequate account of the methods usually employed for the analysis of margarine, and show careful discrimination. The section on deterioration in storage would perhaps have been somewhat more useful if it had dealt with the deterioration of margarine rather than that of butter, but, as little work has been published on this matter, it would be too much to expect any exhaustive treatment of the subject, though many will disagree with the author with regard to the inefficiency of boron compounds as a preservative, when properly applied. A useful epitome of work on the question of vitamins is added, and the work concludes with an exceedingly useful and full bibliography of papers, etc., published in connection with margarine and butter, the value of which cannot be over-estimated, and on the compilation of which the author is to be greatly congratulated.

As with all the other monographs of this series, the work is well printed, and this is exceedingly free from any serious errors.

CECIL REVIS.

BIOCHEMICAL CATALYSTS IN LIFE AND INDUSTRY: PROTEOLYTIC ENZYMES. By JEAN EFFRONT. London: Chapman and Hall, Ltd. 1917. Price 33s.

The sub-title of this treatise indicates its contents more clearly than the main title, for indeed it is only the proteolytic enzymes that are dealt with. The main subject-matter is divided into the coagulating enzymes (thrombin, myosinase, rennet); pepsin; trypsin; and erepsins, these being treated more or less from the standpoint of the physiologist and biological chemist. Although the treatment is modern, the translator has unfortunately not been able to bring the subject-matter up to date. For instance, in dealing with the coagulating enzymes, the work of Bordet, Morawitz,

and the earlier work of Mellanby, are collated and carefully discussed, but the later work of Dale (1916), which puts the whole theory of blood coagulation on a more secure footing, is not mentioned. The chapters dealing with trypsin and pepsin give the impression of systematic reading and collation, but of no particular intimacy with the subject from an experimental point of view. Similarly, that portion of the book (roughly about one-quarter) dealing with the erepsins is not particularly inspiring, although the subject is treated at greater length than is usually the case.

There are bibliographies at the end of each chapter, but the index is fragmentary and of little value.

G. S. WALPOLE.

THE ANALYST'S LABORATORY COMPANION. By ALFRED E. JOHNSON, B.Sc., F.I.C.
Pp. 176. London: J. and A. Churchill. 1920. Price 10s. 6d. net.

Practising chemists will welcome a new edition of this little handbook for the laboratory, for it gives in a form convenient for reference physical and chemical data constantly required in analytical work.

The tabular matter, details of the preparation of reagents, reports of Commissions on chemical subjects, statutory regulations, etc., have, in the main, been brought up to date, but there are still numerous important omissions. For instance, the strength and purity of glacial acetic acid can be most accurately estimated by the determination of the freezing-point, but Rüdorff's table is not given; nor is there even an abridged version of Oudemann's table, showing the relationship between the strength and specific gravity of acetic acid.

The notes on specialised branches of applied chemistry are less satisfactory, at all events in some cases, than the general matter. A chemist who has to deal with a problem outside his ordinary routine work would not consult this book for his information, but would go direct to a treatise on the subject. On the other hand, the specialist ought to be able to refer to this handbook as a *memoria technica*. If, for instance, we apply this criterion to the section on Oils and Fats, it will be found that some of the information is superfluous, whilst other data are lacking. For example, an oil chemist does not require a definition of the iodine value, but he does need to refresh his memory as to the proportion of the ingredients in Wijs' solution, or of the quantities of reagents to be used in Twitchell's rosin test, and such details as these are not given. Again, the analytical values quoted are not sufficiently extensive, and should have included all the oils and fats of commercial importance, whereas even an oil of such frequent occurrence as menhaden oil is omitted. Dalican's method or the "titre" test, for which the author, in common with many other chemists, adopts the ugly American translation "titer" test, is not sufficiently described to be of use to the chemist.

A similar criticism may be passed upon other sections, and it would greatly have increased the value of the book if these had been revised by specialists in each subject. It is with the object of improving the next edition that these suggestive criticisms are made.

EDITOR.

THE CENTENARY VOLUME OF CHARLES GRIFFIN AND COMPANY LTD., PUBLISHERS,
1820-1920.

Every chemist has upon his shelves one or more volumes published by Messrs. Charles Griffin and Co., and will therefore feel interested in a firm the history of which has run parallel with the development of chemistry as a practical science.

When the firm began its career in 1820 in Glasgow, it gave its chief attention to works of general literature, but it was not long before it began to specialise in technical and scientific subjects, its first chemical venture being *Chemical Recreations* by C. J. Griffin, which was published in 1826. This was followed in 1832 by Rose's *Manual of Analytical Chemistry*, and from that time onwards there has been a steady succession of technical works until, at the present time, there is practically no branch of applied science in connection with which thoroughly practical books have not been published by this house.

With regard to chemical literature it is interesting to note that Messrs. Charles Griffin and Co. were originally responsible for the publication of the first weekly journal devoted to chemistry—*The Chemical News*.

The book which has been issued to commemorate the centenary of the firm is an admirable specimen of the printer's and bookbinder's craft, and one lays it down with regret that it is not possible to have all one's books produced with the same distinction. The book opens with a general Introduction by Lord Moulton, who points out how indispensable to progress in any science is an efficient supply of trustworthy textbooks, and lays stress upon the services that the firm was able to render the country during the war, owing to its being in an exceptional position to supply such books.

After a brief account of the beginning of the business, the progress marked in the different branches of science by the publication of successive books is described in readable outline by authorities on their respective subjects. The metallurgical section is dealt with by Professor Gowland; mining, the production of petroleum, and geology by Professor Louis; and chemical technology by Dr. H. Hodgson, whose critical description of the development of the dyestuff industry is particularly interesting. The other sections on such subjects as textiles, and medicine and allied sciences, are also far from being mere catalogues of books.

Chemists will congratulate Messrs. Charles Griffin and Co. upon the celebration of their centenary, and acknowledge the assistance they have received from their publications, many of which they owe to the foresight of Mr. Francis J. Blight, who for over twenty-five years has controlled the destinies of the firm.

ORGANIC CHEMISTRY FOR MEDICAL, INTERMEDIATE SCIENCE AND PHARMACEUTICAL STUDENTS. By A. KILLEN MACBETH, M.A., D.Sc., F.I.C., etc. Longmans, Green and Co. Price, 6s. 6d. net.

This little book of 226 pages is interesting in view of the very large number of substances dealt with. When it is considered that the chief families of open chain bodies and cyclic substances, the sugars, glucosides, terpenes, alkaloids, stereo-isomerism, geometrical isomerism, oxime isomerism, proteins, etc., etc., are studied,

one begins to wonder how it can be done in such a very small compass. Our author's method is to concentrate and evaporate almost to dryness. In twenty-four pages he summarises on fats, carbohydrates, proteins, alkaloids, and terpenes. It is more of a notebook than a textbook, and to appreciate it properly a student should have a fair knowledge of organic chemistry. There are points that will require correcting in a future edition. On p. 98 CH_3NNOH should be placed in brackets to denote a probability, otherwise it is misleading. In dealing with acetoacetic ester, p. 108, some reference should be made to the two forms of this body, as in one equation it is written in the keto form, and in a more detailed view of its formation the enolic form is used. This is apt to be very confusing to a beginner.

There is a rather serious error where the formula for fructosazone is given on p. 159. It should be the same as glucosazone on the opposite page, and not as represented. On p. 192 it is stated that aniline treated with nitrous acid gives the diazonium hydrate. As a matter of fact, diazoamidobenzene is obtained. This error is repeated on p. 197. On p. 194, dealing with the detection of a primary aromatic amine the aniline should be dissolved in dilute HCl and well cooled before adding sodium nitrite and coupling with the phenol.

In the formation of diphenylamine from aniline and iodobenzene, on p. 195, the high temperature necessary for this reaction, somewhere about 400°C ., should have been mentioned. Again, in the preparation of methyl orange, p. 202, allusion might with advantage have been made to the use of sodium carbonate for dissolving the sulphanilic acid.

The book is very sketchy in character, but is probably sufficient for medical and pharmaceutical students who are supposed to have a profound knowledge of important and complicated organic compounds after about six months' study. Yet notwithstanding its limitations, it is very well arranged, concise, and to the point, and can be confidently recommended. Another good feature of the book is the schemes showing the relationship between the various organic substances. For example, starting with acetic acid, it is shown schematically how malonic, succinic, glycollic acids, etc., may be derived from it.

This is excellent, and it is only by constant practice in this way, backwards and forwards from one family of substances to another, that the student realises the connection between the various compounds, remembers general reactions, and obtains a true insight into the fascinating study of the chemistry of carbon compounds.

F. H. STREATFIELD.



THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

PASS LIST.

JANUARY (1921) EXAMINATIONS.

At the Examinations of the Institute of Chemistry held recently, Mr. Keith Alister Johnstone McClure, B.A. (Cantab.), passed in General Chemistry, and Mr. Cecil Chapman passed in Chemical Technology, with special reference to Coal Tar and Ammonia.

Both Candidates have been elected to the Associateship of the Institute.



**APPOINTMENT OF PUBLIC ANALYST FOR THE COUNTY
BOROUGH OF BRIGHTON.**

THE following correspondence and report have been received for publication from the Public Appointments Committee of the Institute of Chemistry :

THE TOWN CLERK,
TOWN HALL, BRIGHTON.

January 26, 1921.

SIR,

The attention of the Councils of the Institute of Chemistry and of the Society of Public Analysts has been directed to the conditions laid down by your authority for the appointment of Public Analyst for the County Borough of Brighton.

The Councils of the Institute and of the Society desire me to direct attention to the fact that the remuneration offered is far below that now generally obtained by Public Analysts in Great Britain. Assuming a reasonable proportion of milks and allowing for the salary of £50, it would appear that the average fee per sample is not more than 8s. 6d., while the average fee paid by all authorities throughout the country is approximately 15s.

The Councils would venture to remind your authority that apart from the advanced cost of living, the cost of assistance, apparatus, and materials has more than doubled. All of this must be borne by the Analyst, and would render it practically impossible, on the remuneration proposed, for him to carry out the duties of the office satisfactorily and with any margin of profit to himself. The Councils are aware, moreover, that several Public Analysts whose qualifications have already been approved by the Ministry of Health have declined to become candidates for the appointment. The number of candidates likely to apply for the appointment is therefore limited in a manner which is not in the best interests of the proper administration of the Sale of Food and Drugs Acts.

I am requested to ask you kindly to bring this letter to the notice of your Committee, and to express, on behalf of the Councils of the Institute and of the Society, the hope that your authority will consider the revision of the conditions before proceeding further with the appointment.

Yours faithfully,

(Signed) G. S. W. MARLOW

(Assistant Secretary, the Institute of Chemistry).

REMUNERATION OF PUBLIC ANALYSTS.

The Councils of the Institute of Chemistry and of the Society of Public Analysts have invited Public Analysts to provide data as to the remuneration and other conditions of their appointments in 1914 and in 1920 respectively.

Replies were received in respect of 140 appointments in England and Wales, and in respect of 102 appointments in Scotland ; of these, 9 and 1 respectively were whole-time officials.

PART-TIME OFFICIALS.

Public Analysts receive remuneration—

(Class A) by payment of an agreed fee per sample.

(Class B) by payment of an agreed salary, which is intended to cover the analysis of all samples of foods and drugs.

(Class C) by payment of a retaining fee, together with an agreed fee for each sample of foods and drugs.

(Class D) by payment of a retaining fee or salary in consideration of the analysis of an agreed number of samples, and by fee for the analysis of all samples in excess of that number.

The number of appointments held under each of the above classifications was :

	England and Wales.	Scotland.	United Kingdom.
Class A	56	26	82
Class B	7	2	9
Class C	63	59	122
Class D	5	14	19
	131	101	232

For the purposes of comparison, the total actual remuneration (including the proper proportion of the salary or retaining fee) for the analysis of each sample was calculated. The figures for the average remuneration are included in Table A (p. 78), which shows the remuneration received in 1914 and 1920 respectively. The table shows also the average remuneration per sample which applies to those appointments of which the conditions have remained unaltered since 1914, and the average remuneration of those in which the fee, retaining fee, or salary has been increased.

In a few cases in which the retaining fee or salary had not been altered since 1914, a reduction in the number of samples caused the remuneration per sample to increase, whilst the payment received by the Analyst had remained stationary or had decreased. Those appointments were treated in the tables as if their terms had remained unaltered.

Table B shows similar figures for the more important appointments (from which at least 100 samples were received during 1920).

Owing to the disturbed state of Ireland, no useful data can be given for that country.

WHOLE-TIME OFFICIALS.

Replies were received from 10 whole-time salaried Analysts. Of these 5 were required to perform analyses of samples other than foods and drugs, together with bacteriological examinations. The salaries of the other officials varied according to

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the number of samples submitted, but there was no possibility of assessing an average salary according to the number of samples.

The following table will, however, serve as a rough guide :

	Average Salary—		Average Increase per Cent.
	In 1914.	In 1920.	
	£	£	
Appointments with less than 100 samples (of all kinds) per annum	287	658	122
Appointments with more than 1,500 samples (of all kinds) per annum	620	1,036	67

TABLE A.—ALL APPOINTMENTS.

Total remuneration per sample of foods and drugs submitted to Public Analysts. (Average from 232 appointments: 131 in England and Wales, 101 in Scotland.)

	United Kingdom.	England and Wales.	Scotland.
	Average.	Average.	Average.
Fees in 1914	10s. 6d.	11s. 0d.	9s. 10d.
Fees in 1920	15s. 8d.	14s. 6d.	17s. 4d.
Fees which have not been increased since 1914	12s. 10d.	12s. 11d.	12s. 9d.
Fees which have been increased since 1914 (1920)	16s. 2d.	14s. 11d.	17s. 8d.

The fees have not been increased in the cases of 34 appointments in England and Wales and 12 appointments in Scotland.

TABLE B.—APPOINTMENTS FROM WHICH THE SAMPLES IN 1920 EXCEEDED 100.

Total remuneration per sample of foods and drugs submitted to Public Analysts. (Average from 98 appointments: 86 in England and Wales, 12 in Scotland.)

	United Kingdom.	England and Wales.	Scotland.
	Average.	Average.	Average.
Fees in 1914	10s. 7d.	10s. 8d.	10s. 3d.
Fees in 1920	14s. 8d.	14s. 3d.	17s. 2d.
Fees which have not been increased since 1914	12s. 1d.	12s. 1d.	—
Fees which have been increased since 1914 (1920)	15s. 1d.	14s. 9d.	17s. 2d.

The fees have not been increased in the cases of 17 appointments in England and Wales. They have all been increased in Scotland.