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THE ANALYST.

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

ORDINARY MEETING, JUNE 2, 1920.

HELD at the Chemical Society's Rooms, Burlington House, Mr. Alfred Smetham, President, in the chair.

A certificate was read for the first time in favour of Mr. T. K. Ghose, B.A.

A certificate was read for the second time in favour of Mr. Udolphus Aylmer Coates.

The following were elected Members of the Society: Misses Dorothy Gertrude Hewer, B.Sc. (London), Rita Catherine Hawkins Johnson, Messrs. Harold Hall, F.I.C., Geoffrey Trelawney Bray, A.I.C., Frank William George King, and John Herbert Stubbs, M.Sc. (Victoria), F.I.C.

The following papers were read: "The Estimation of Nitroglycerine," by H. Droop Richmond, F.I.C.; "The Perchlorate Method for Potash," by R. Leitch Morris, F.I.C.; "Apparatus for Evolution Methods of Analysis: An Improved Form of U-Tube," by E. R. Dovey, A.R.C.S., A.I.C.

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ESTIMATION OF THE AGE OF INK IN WRITING.

BY C. AINSWORTH MITCHELL, M.A., F.I.C.

(*Read at the Meeting*, *May* 5, 1920.)

QUESTIONS as to the age of ink in writing are frequently raised in connection with the examination of documents. Sometimes, for instance, there may be reason for doubting whether an entire document is as old as it purports to be, or information may be wanted as to whether the whole of the writing was written at the same time, or, if not, which portion was written first. In many cases the problem is insoluble, but in others the facts enable a definite opinion to be expressed, and may even afford convincing evidence.

Anachronisms in the composition of the ink in the writing are among the most conclusive of such facts, and it is, therefore, a matter of considerable importance to know the approximate dates at which such changes have occurred.

EVOLUTION OF WRITING INKS.

The writing ink of the Greeks and Romans, like some of the modern inks still used in the East at the present day, was a mixture of fine lamp-black or other form of carbon with a dilute solution of gum or glue. It is not possible to state the exact period when carbon inks of this type were replaced by iron-gall inks. The earliest reference made to the latter by the monk Theophilus is in an encyclopædia of Christian art of the eleventh century, and it is probable that by the end of the thirteenth century the modern type of ink had practically replaced the ancient inks.

Originally the modern inks were simply prepared by mixing an infusion of galls with iron sulphate and gum, and were allowed to undergo considerable oxidation before being used.

Logwood was used in the eighteenth century to a limited extent to intensify the colour of iron-gall inks (Ribeaucourt, *Ann. de Chim.*, 1792, **15**, 113), whilst the use of indigo for the same purpose is mentioned by Eisler (Dintefass, 1770), and was adopted in this country in 1836 (*Mechanics' Magazine*, 1836, **25**, 229). The use of aniline dyestuffs was first claimed in England by Croc (Eng. Pat., 2,972, 1861). I have the authority of Mr. W. Baker, of Messrs. Mabie, Todd and Co., for stating that aniline blue dyes of different kinds were commonly employed in the manufacture of blue-black ink upwards of forty years ago. In my own experience I have been able to trace a blue pigment in writing in old ledgers for about thirty-five years, the writing prior to that date in the same ledgers being in iron-gall inks which did not show any indication of blue pigment.

This point has been found of great importance on several occasions in connection with fraudulent claims for old age pensions. For example, in support of the claim family Bibles have been produced in which entries supposed to be seventy years old have been found to be written in ink containing an aniline dye.

In the case of Rex *v.* Menzies, tried in 1916, the defendant was accused of having uttered fabricated documents dating from 1719 to 1772 in support of his claim to a baronetcy. Certain alterations in these documents were alleged to have been written subsequently to 1914, a mixture of blue-black ink and an aniline red ink having, it was stated, been used for this purpose. Evidence was given that the ink in this writing did not contain aniline dyes, and that old ink had, therefore, not been imitated in the manner stated. As there was no evidence that the alterations in the documents had been made subsequently to 1914, when the defendant had acquired them, he was acquitted.

An earlier case of a similar kind is cited by Wills in his "Circumstantial Evidence," p. 142, in which Alexander Humphreys was tried at Edinburgh in 1839 for forging several documents in support of his claim to the Earldom of Stirling. On the margin of one of these documents, dated 1639, lines were drawn in red ink, but it was officially proved that such lines were not introduced into the Chancery Office until 1780. Evidence was also given that the ink in some of the attestations was a modern ink made to imitate ink which had become old. It would be instructive to know the grounds on which this last conclusion was based.

ARTIFICIAL AGEING OF INK.

In a case in which I was consulted a few years ago there was no doubt as to the artificial ageing of the writing. A cashier confessed that he had falsified certain entries in a ledger, and to make them appear older had written them in a mixture of blue-black ink and Indian ink. I was asked to examine these entries, and found that the writing in question contained carbon particles, which were distinctly visible under the microscope, and that it could not be bleached either by hydrochloric acid or by hypochlorous acid. My results, therefore, confirmed the statement that Indian ink had been used. Incidentally I might mention that the colour of the mixture of Indian and blue-black does not agree very well with that of a naturally aged iron-gall ink.

MICROSCOPICAL DIFFERENCES IN OLD AND RECENT INKS.

For many years after it has been put upon the paper, an ordinary iron-gall ink of the blue-black type will usually have the appearance of a crystalline structure, which appears to be due to pigment attaching itself to the fibres of the paper. Eventually, as the organic matter of the ink decomposes, there is more or less formation of iron oxide or of basic tannates, and the ink not only becomes yellow, but also appears much more amorphous, and in some cases shows isolated patches of darker pigment. Good examples of this are frequently to be seen in writing of the eighteenth century.

As steel pens were not invented until 1808 (Eng. Pat., 3,118), the presence of heavy margins to the lines in writing prior to that date would be a suspicious circumstance. In the case of Rex *v.* Menzies, mentioned before, evidence was given that the additions to a document of 1719 had been made with a steel pen, whereas the rest of the document had the appearance of having been written with a quill pen.

COLOUR OF OLD AND NEW INKS IN WRITING.

When freshly applied to the paper, a mixed solution of iron sulphate and a tannin is pale grey, but it gradually absorbs oxygen from the air, and rapidly darkens as the insoluble tannate forms. In the modern type of blue-black inks containing both the latent blackish pigment and an added dyestuff to give colour pending the formation of the iron tannate, the colour is first bright blue, and rapidly becomes violet as the other pigment is formed.

The completion of this change—*i.e.*, the production of the maximum intensity of colour—will vary greatly with the conditions. The statement which I published some years ago (ANALYST, 1908, **33**, 80) was correct for the conditions of my experiments, in which thin washes of the inks were applied to paper with a brush and then exposed to a strong light. Under such conditions the maximum colour is reached in about a week, and pure iron tannate then begins to fade, turning yellow at the edge. Thus, thin washes of inks when exposed to the air underwent the following colour changes on Lovibond's colour scale :

Days.	1.			2.			3.			4.			5.			7.		
	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.
Iron tannate	0·9	0·3	—	1·0	0·5	—	1·3	0·6	—	2·0	0·8	0·2	1·8	0·9	0·3	1·6	0·9	0·3
Blue-black ink	3·0	—	—	3·75	0·5	0·3	4·0	0·7	0·5	4·0	0·7	0·5	3·2	0·7	0·3	3·2	0·6	0·3
Blue-black ink (old) ...	2·1	—	—	2·8	—	—	3·0	0·5	0·5	3·0	0·5	0·5	3·0	0·5	0·5	3·0	0·6	0·5

Days.	10.			17.			23.			28.			35.			43.		
	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.
Iron tannate	1·6	0·9	0·3	1·4	1·0	0·3	1·2	0·9	0·3	1·2	0·9	0·3	1·1	0·9	0·4	1·1	0·9	0·4
Blue-black ink	3·2	0·6	0·3	3·2	0·6	0·3	3·0	0·6	0·2	3·0	0·6	0·2	3·0	0·6	0·2	3·0	0·6	0·2
Blue-black ink (old) ...	3·0	0·7	0·4	2·85	0·7	0·3	2·85	0·7	0·3	2·85	0·7	0·3	2·85	0·7	0·3	2·85	0·7	0·3

If, however, the ink is applied in an ordinary way with a pen, it is left in a deeper layer, and if then kept in a closed book the final intensity of colour may not be reached for upwards of a year.

For example, I found that specimens of writings of the same blue-black ink applied with a pen to the paper at intervals of over a year attained their maximum intensity after a period of eight to ten months. They then had the following colour on Lovibond's colour scale : Blue, 3·6 ; red, 0·4 ; yellow, 0·4.

METHODS OF RECORDING THE COLOUR.

It is obvious that if a record be taken of the initial colour of an ink, and the writing is subsequently found to darken rapidly in colour, it is probably comparatively recent, and at any rate will not be more than eighteen months old.

In one case in which I was consulted an ink alleged to be upwards of two years old darkened very materially in a few days, and was thus clearly a forgery.

In the paper which I read before this Society in 1908 I called attention to the use of Lovibond's tintometer for comparing the colour of inks, but did not describe the methods I used. As viewed with the naked eye, the ink in writing on paper is too minute to be satisfactorily examined with the tintometer alone, and so I prepared a series of broad colour stripes with aniline dyes, matched these with the ink in the writing under the microscope, and then took the record with the tintometer from the coloured stripe. This is a cumbersome method, but I have found it useful for demonstrating the colours in court. For most purposes, however, it is much more simple to make a direct comparison between the ink and the tintometer glasses by means of Osborn's comparison microscope, a description of which I gave in a former paper (ANALYST, 1917, **42**, 3). This instrument has slots in both tubes in which the tintometer glasses can be placed, and the coloured surfaces then appear as two halves of a sphere.

In recording the colour of inks it is sometimes necessary to take into consideration the colour of the paper. For example, a faded brown ink of 1868 gave the following readings: Blue, 0·55; red, 0·7; and yellow, 0·1. This was written on blue paper, which gave a reading of blue 0·50, and evidently contributed to the reading shown by the ink.

Other specimens of old faded inks have given the following readings:

	Blue.	Red.	Yellow.
Ink of 1718	1·9	1·0	1·9
,, 1792	—	1·2	0·9
,, 1823	—	1·1	1·2
,, about 1850	—	0·6	0·6

I am indebted to Mr. A. W. Johnson, of Messrs. Brown, Johnson and Co., for specimens of writing done with freshly-made ink in the year 1906, before and after the addition of aniline blue, and with and without blotting. The other readings were those given by the specimen of blue-black ink of 1895 (shown on the screen).

	Blue.	Red.	Yellow.
1. Iron-gall ink without aniline blue	2·5	1·4	1·0
2. ,, ,, ,, blotted ...	1·1	0·4	0·5
3. ,, with aniline blue	4·0	1·2	0·9
4. ,, ,, ,, blotted	2·0	0·4	0·4
5. Ink in writing of 1895	2·4	1·4	1·1

The ink of No. 5 was originally a well-known bright blue-black ink. It now shows no trace of the original blue dye, and has faded to the colour of No. 1, an ink which contained no aniline blue.

Influence of Blotting on the Colour of Ink.

As ordinary blue-black ink contains two pigments, one of which is latent, the effect of blotting is to remove variable quantities of these pigments, and the colour of the ink left on the paper will vary with the length of time before blotting.

In the case of Rex *v.* Cohen, a doctor was accused of "doping" a man to keep him out of the army. He asserted that the man was a regular patient, and as proof thereof produced his books. There were some seven or eight entries of this man's name on various dates, and by a curious coincidence the ink in these were all paler than adjacent entries. Mainly from this circumstance a handwriting expert gave evidence that these entries were open to grave suspicion of forgery, and Dr. Cohen was sentenced to a fine of £100 and six months' imprisonment. He appealed against this sentence, and when I subsequently examined the books I found that there was absolutely nothing to justify any charge of these entries being made subsequently to adjacent entries. Apart from the many possibilities affecting writing done at different times, the fact that the entries were blotted at different periods, some at the end of a series and sometimes after a single entry, was in itself sufficient to account for variations in the colours and intensity of the inks of adjacent entries.

This is clearly shown in the following series of readings of the colours of ink washes which were applied to the paper for measured periods and then blotted. This colour chart which was shown in court on the hearing of the appeal, proves conclusively that the paleness of the ink in writing is no criterion of the age of the ink, but depends upon the relative proportions of the pigments left upon the paper prior to oxidation.

	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.
	5 secs.			10 secs.			15 secs.			30 secs.			90 secs.		
Blue-black ink, faded in bottle	0·3	0·1	—	0·4	0·1	—	0·9	0·1	—	1·0	0·2	0·1	1·5	0·2	0·1
	5 secs.			15 secs.			40 secs.			90 secs.			2 mins.		
Blue-black ink, same manufacture	1·95	—	0·1	3·2	0·3	0·4	3·0	0·3	0·6	3·5	0·6	0·6	3·5	0·9	0·4
	10 secs.			40 secs.			1 min.			2 mins.			3 mins.		
Black ink, German ...	1·1	1·5	—	1·6	2·0	0·1	1·7	2·1	0·3	1·9	2·6	0·2	2·6	3·0	0·8
	20 secs.			1 min.			90 secs.			2 mins.			3 mins.		
Black ink, English ...	0·8	1·2	0·2	3·0	2·0	2·0	4·0	3·2	2·7	4·2	3·2	2·7	4·5	3·2	2·7

SEQUENCE OF STROKES AS PROOF OF PRIOR WRITING.

If two pen-strokes in ink cross each other while wet, the point of intersection is indicated by a heavier deposit of pigment, but it is rarely possible to ascertain which stroke is uppermost. If, however, the first stroke is dry before the second is applied, the lines are generally quite distinct, and it is usually possible, with the aid of the microscope, to decide which stroke is uppermost, or in other words more recent.

Osborn has cited some striking instances of the kind in his book, " Questioned Documents," pp. 375-393, showing that the method may give conclusive evidence of later additions to a document.

In this case of Rex *v.* Cohen, one of the alleged recent entries touched the entry immediately below it at two points, and in each case the line came below and not above the intersecting line of the following entry. Hence, there could be no doubt but that this suspected entry was written prior to those which immediately succeeded it. A conviction could not be upheld in the face of such facts as these, and the sentence on the defendant was quashed.

COPYING METHODS.

The use of the ordinary copying process for determining whether the whole of the ink upon a document is contemporaneous was suggested by Sittl (*Chem. Zeit.*, 1891, **15**, 1833), who found that a good copying ink would yield a fair copy on " flimsy " paper for about eight days after writing, whilst even after four weeks a faint copy might be expected.

This method was studied by Habermann and Oesterreicher (*Zeitsch. anal. Chem.*, 1901, **40**, 725), who found that under certain conditions distinct copies could be obtained by the use of a press from the moistened writing in ordinary iron-gall ink for about five months, and in exceptional cases up to nineteen months.

Carré (*Comptes rend.*, **78**, 1213) had previously suggested the use of dilute hydrochloric acid (1 : 11) in place of water as a copying medium. He found that writing of eight to ten years of age would yield a good copy, whereas writing thirty years old have a faint unreadable copy, and ink of 1787 only yielded traces of pigment to the copying paper.

My experiments with these methods show that the results should only be accepted with great caution. If, however, there is a very pronounced difference between the copying capacity of two parts of the same document, and chemical tests indicate that the inks are of the same type and the writing is of equal intensity, it is extremely probable that the writing was not done at the same time. More definite conclusions, however, may be drawn if the ink is supposed to be an ancient one and yet gives a sharp copy.

Chemical Tests for Age.

Iron-gall ink, when recently applied to the paper, reacts rapidly with various reagents, but after the lapse of a year or so will only react slowly ; and, finally, after a period of six to ten years will remain unaffected for a long time. This difference was first noted by Sonnenschein (Lehrbuch der gerichtlichen Chemie, 1881, p. 364), and has also been recommended by Irvine (Workshop Receipts, Spon, fifth series, 1892, p. 88).

Various reagents have been suggested for the purpose, such as dilute hydrochloric acid, bromine water, hypochlorous acid, hydrogen peroxide, etc.

In my experience a 5 per cent. solution of oxalic acid is the most useful reagent, a drop being applied to the place on the writing by means of a capillary pipette. The effect is then followed by means of a lens, and the amount of the diffusion, if any, of blue pigment noted. It is remarkable that in old blue-black ink in writing the aniline blue, if still present, is prevented from diffusing by the insoluble tannate which has been formed. For example, in the case of the iron-gall inks of 1906, mentioned above, the specimens to which blue dye had been added did not react any more readily than the same inks without the dyestuff.

In forming any estimate of the age of ink in writing from the speed of the reaction and amount of diffusion it is essential that the dates of the inks should not be too close to each other, that the inks should be of the same type, and that the differences should be very pronounced.

All these conditions were present in the case of Rex *v.* Pilcher, which was tried in 1910. Colonel Pilcher was accused of forging his cousin's will, the alleged date of which was 1898. All the inks on the will, including the signatures of the supposed witnesses, reacted immediately with various reagents, and showed pronounced diffusion of blue pigment, the ink running all over the paper. On the other hand, a series of parallel tests applied to cheques which had been written by the alleged testatrix gave the following results :

(1) 1907. Rapid diffusion.
(2) 1906. Diffusion after a time, action less rapid.
(3) 1905. July. Heavy writing. Diffusion more rapid than (2), less rapid than (1).
(4) 1905. January. Diffusion less rapid than (3).
(5) 1904. July. Slight diffusion, less rapid than (4).
(6) 1904. January. Heavy writing. Diffusion fairly rapid. More pronounced than (5).
(7) 1903. June. Very slight diffusion.
(8) 1903. January. Very heavy writing. Diffusion very slight.
(9) 1903. March. Medium writing. No diffusion.
(10) 1902. June. Heavy writing. No diffusion.
(11) 1902. February. Very heavy writing. Slight indication of diffusion.
(12) 1902. January. Heavy writing. Very slight diffusion.
(13) 1901. June. Heavy writing. No sign of diffusion.
(14) 1901. February. Very heavy writing. No sign of diffusion.

Other tests proved that these were all written in the same kind of blue-black ink and of the same type as the inks on the will.

Similar results were also obtained in tests applied to a recipe book and various letters of the testatrix. I therefore concluded that the alleged will was probably not more than four or five years old at most. Eventually Colonel Pilcher confessed that he had altered the will, knowing it to be a forgery, but that he had no knowledge as to how it had been forged.

In another criminal case (Rex *v.* Seddon) a will written in ink showed no indications of having been written at a date later than was stated upon it.

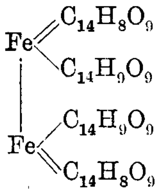
CHEMICAL CHANGES IN THE DRYING OF INK.

Hitherto the greater resistance offered to reagents by older inks on paper has been accepted as an empirical fact, and no attempt seems to have been made to give a chemical explanation of it. For several years I have made systematic experiments on this subject, and have obtained results which appear to account for the phenomena.

When solutions of ferrous sulphate and gallotannic acid are mixed, a pale ferrous tannate appears to be formed. This is indicated by the fact that any ferric salt present is immediately reduced to the ferrous condition, as is easily demonstrated by mixing ethereal solutions of ferric chloride and gallotannic acid, when an insoluble tannate is precipitated and the ether becomes bright green. But the gallotannic acid is not oxidised to gallic acid, at all events in an aqueous solution, for it can still be completely absorbed by hide powder. When the ferrous tannate solution is exposed to the air it is slowly oxidised, and forms incrustations and insoluble deposits of iron tannates. I have repeatedly separated these tannates as they formed, dried them at 100° C., and estimated the amount of iron. The results in the following table are typical of those obtained:

Iron Salts.	Gallotannic Acid, etc.	Iron in Precipitates (per Cent.).			
		1.	2.	3.	4.
Grms.	Grms.				
Ferrous sulphate :					
3	2	5·75	5·94	—	—
3	3	5·49	6·04	7·17	—
3	1	5·38	7·74	7·72	—
—	+ pine oil	8·15	—	—	—
—	+ small amount H_2O_2	14·18	—	—	—
3	2 + excess H_2O_2	24·29	21·05	22·4	21·46
3	2 + pine oil	8·15	—	—	—
—	+ saliva	7·98	—	—	—
Ferrous ammonium sulphate :					
2	2	5·08	6·90	—	—
3	2	5·36	6·16	—	—
Ferric sulphate :					
2	2	6·16	17·1	—	—
4	3	15·70 (from filtrate diluted)	7·7	—	—
Ferric chloride	—	8·56	—	—	—
Ferrous sulphate :	Galls, 2·5 per cent. extracts :				
1	Japanese galls	7·91	7·71	8·12	—
1	Aleppo galls	6·03	7·72	7·68	—
3	Chinese galls	6·86	7·56	7·57	—
3	Valonia	8·07	8·80	—	—
3	Myrobalans	5·74	—	—	---
3	Divi-divi	6·77	7·77	—	—
3	Chestnut extract	7·37	—	—	—

It will be seen that the earliest precipitates contain Fe approximating in composition to Wittstein's iron tannate, $Fe_2(C_{14}H_9O_9)_6$, containing 5·53 per cent. of iron (*Jahresber. der Chem.*, 1848, **28**, 221). As the oxidation proceeds the successive precipitates contain more iron, and eventually approximate in composition to the precipitate which Pelouze obtained by exposing a solution of ferric sulphate and gallotannic acid to air for a month (*Ann. de Chim.*, 1833, **54**, 337).



This compound, however, is not formed at first from ferric sulphate, but the presence of ferric salts promotes the oxidation to the more highly oxidised compounds.

I attempted to accelerate the oxidising process by adding hydrogen peroxide to the ferrous tannate. The addition of a small amount gave a precipitate containing 14·18 per cent. of Fe, approximating in composition to Wittstein's tannate with 14·21 per cent. of iron, whilst if large amounts of hydrogen peroxide were added, a heavy precipitate containing 21 to 24 per cent. of iron was immediately thrown down. This approximates in composition to Ruoss's basic tannate $(C_{14}H_7O_9)\ (FeO)_2$

with 24·42 per cent. of iron (*Zeitsch. anal. Chem.*, 1902, **41**, 732). Neither of these compounds, however, appears to be formed in the normal oxidation of ferrous tannate, although if ferric sulphate is used instead of ferrous sulphate precipitates containing upwards of 16 per cent. of Fe are eventually obtained.

I then tried the effect of a catalytic agent, and added a few drops of pine oil to a solution of ferrous tannate. Immediately a dense precipitate containing 8·15 per cent. of iron was obtained. In a duplicate experiment the amount of iron present was 8·10 per cent. Hence, under these conditions, Pelouze's tannate is formed at once. In like manner, the addition of 5 c.c. of saliva accelerated the oxidation, and after two days a heavy precipitate containing 7·98 per cent. of Fe was formed. The oxidation to the more insoluble form of precipitate was thus accelerated, and it would seem that the precipitates containing amounts of iron between 5·53 and 8·0 per cent. are probably mixtures of these two tannates. Incidentally these experiments suggest a chemical explanation of the use of ink as a reagent for the development of secret writing in saliva or scent. The presence of certain substances in different kinds of galls appears to have a similar accelerating influence on the oxidation. These two tannates, when dried at 100° C., differ in properties. The first feels like soft chalk, is somewhat soluble in water, and readily soluble in dilute hydrochloric acid. The other is more granular and has a resinous appearance, and is very difficult to dissolve completely, even in strong boiling hydrochloric acid. The intermediate precipitates show increasing insolubility as the oxidation proceeds.

Here, then, we have the probable explanation of the behaviour of inks in writing on paper. The tannate first formed is sufficiently soluble to allow copies to be taken for a short time, and is readily soluble in dilute acids, but as the oxidation proceeds the resinous tannate is slowly formed, until eventually the ink becomes not only difficult to dissolve in weak acids, but also protects the soluble aniline dyestuff from the action of the reagent. When the oxidation has reached this stage, the addition of acid will slowly cause the ink to turn blue if the blue dye has not yet faded, but there will be little, if any, sign of diffusion or smudging.

DISCUSSION.

Mr. G. R. THOMPSON said he was not quite clear about one slide which showed an ink of 1906 and one of 1895. He said that from tintometric analysis of these two inks he found that they were practically identical.

	1895.	1906.
Blue	2·4	2·5
Red	1·4	1·4
Yellow	1·1	1·0

This is a difference of eleven years, and yet the results are similar. He asked if any light could be thrown on the age of inks by the use of panchromatic plates through screens of varying intensities. He thought it might be stronger proof if demonstration of the actual difference in colour were shown rather than a string of figures of tintometric results.

With regard to the estimation of iron, was this done on the actual inks or from the writing on the documents?

Mr. BUTTERFIELD inquired to what extent concentration and ageing or oxidation of ink which had been left standing in the inkpot would affect the judgment as to the age of the writing. He said he sometimes used a fountain pen filled with copying ink, but if the pen ran out he dipped it into an inkpot which was rarely used, and might have ink filled from the same stock bottle as the fountain pen, but which had been exposed for three or four months in the loosely-covered inkpot. He noticed that the writing with the fountain pen was totally different from that written with the stale ink from the inkpot. He wondered to what extent judgment as to the age of two consecutive lines of writing of the same letter would be vitiated by such a change from fresh to stale ink of the same original supply, which would occur merely from the accident of a fountain pen running dry between the two lines.

Mr. CHASTON CHAPMAN said that most of the ink supplied to-day, even by the best makers, appeared to throw a considerable deposit in the inkpot after a few weeks, and inquired whether the age of the ink at the time of writing might not seriously affect the conclusions drawn from an examination of the writing at some subsequent date.

He (Mr. Chapman) had also been wondering what would be the effect of writing with a pen which had just been moistened with saliva. If, for example, a person were to wet a new nib with saliva before writing his signature, and another person were a little later to dip the pen into the same ink and append his signature to the same document, would there be any difference between the two writings such as might lead to the conclusion that the same ink had not been used in both cases?

He would also like to ask Mr. Mitchell whether, in the case of writing with inks containing mixed dyes on common and slightly absorbent paper, he had ever observed any tendency in the direction of the separation of the dyes, owing to the capillary action of the fibres. If so, such separation might materially affect the mixed colour value as determined by the tintometer.

In reply to Mr. Thompson's questions, Mr. MITCHELL said that the determination of the iron was made on the inks themselves specially prepared. There was no doubt that old ink in writing resisted reagents much more than new inks, and it was a reasonable hypothesis to draw conclusions from the behaviour of the deposits thrown down by inks. In some cases attempts had been made to follow the action with a stop-watch, but conclusions from such data were dangerous. When a crust formed on the ink, it was in all probability very similar to what was formed when the ink was placed on the paper.

With regard to the effect of oxidation of the ink in the bottle, Mr. Mitchell said that in the case of insufficiently matured ink there was generally a deposit, but the deposit thrown out was, as a rule, not iron tannate, but some form of tannin. Even if the ink had become oxidised in the pot, the oxidation would continue on the paper. In the case of copying inks the problem was much more complicated. There would be a very decided difference in the behaviour of two inks known to be copying inks, for it was dangerous to compare copying ink with ordinary ink. The change by oxidation was very much slower in the case of copying ink than with ink without the extra amount of gum and pigment which copying inks contained.

In reply to Mr. Chapman's question, Mr. Mitchell said that the only distinction would be a chronological one. The ink of 1895 would not react so readily as one of 1906, but it would not be possible to state that one ink belonged to one period or the second to the other. As a test of the age of writing the tintometer was only useful for comparing fairly recent inks on paper.

With reference to Mr. Thompson's suggestion of the use of colour screens, Mr. Mitchell remarked that he had tried the use of screens and colour sensitive plates some years ago, and found that the main difference in the results was due to differences in intensity rather than in the colour of the inks.

In reply to Mr. Chapman's suggestion with regard to the effect of absorbent paper in separating dyes, Mr. Mitchell said that this method had already been used for separating the pigments in inks, but it would not be practicable in the case of dried ink on paper.

The action of saliva on the inks in writing required further investigation, but presumably wetting a new pen would only affect one or two letters and would be more likely to cause a deposit on the inkpot.

With regard to carbon ink, as a rule it could easily be washed off the paper, since carbon ink did not penetrate into the fibres. The nearest approach to a result of that sort was obtained with a fine suspension of colloidal graphite, which was not at all a bad carbon ink when mixed with a certain amount of water, as the particles did not separate out easily.

With regard to the question of dye in the ink in writing and the blue colour being reproduced on the addition of an acid, Mr. Mitchell said that it was quite possible in cases where the dye did not run that the fixation of the dyestuff might be due not merely to its being mechanically retained by an enveloping resinous tannate, but also to chemical combination.

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A RAPID VOLUMETRIC METHOD FOR THE ESTIMATION OF IRON, APPLICABLE IN THE PRESENCE OF HYDROCHLORIC ACID, PHOSPHORUS, OXY-ACIDS, AND ORGANIC MATTER.

By H. DROOP RICHMOND, F.I.C., and EDITH M. ISON, B.Sc., A.I.C.

(*Read at the Meeting, May* 5, 1920.)

Owing to the presence of sugar, phosphorus compounds, and other compounds in syrups, the conventional methods of iron determination are not applicable, and as much of the therapeutic effect of the syrups is due to the iron present, it is highly desirable to be able to estimate its amount rapidly and with accuracy.

The method we describe, which is both rapid and accurate, depends on the following facts:

1. In $5N$ hydrochloric acid solution iron is completely ionised, even if phosphates and organic matter be present.

2. Permanganates oxidise ferrous ions to ferric ions in the presence of sugars, and also destroy the colouring matters used in the syrups. In oxidising ferrous to ferric ions by standard permanganate, the amount used before the colour is discharged shows that oxidation of the ferrous ion takes preference over that of the dye, while the sugar is attacked in a still less degree.

3. A small excess of permanganate is reduced completely by the sugars, and practically no chlorine is liberated.

4. Ferricyanides are sensitive indicators for the production of ferrous ions, and thiocyanates for their removal.

5. Stannous chloride reduces ferric to ferrous ions, and in an atmosphere of carbon dioxide the reduction is a measure of the iron present.

We operate thus: 5 or 10 c.c. of the syrup is measured (or weighed) into a 100 c.c. flask, a few drops of strong hydrochloric acid added, and $\frac{N}{10}$ permanganate solution run in till a transitory purple is produced throughout the solution, the colour of such syrups as *Syrupus ferri phosphatis compositus* or *Syrupus ferri glycerophosphatis compositus* being destroyed during the addition of the permanganate. The purple colour vanishes rapidly, and usually the solution contains no free chlorine, and the iron present is entirely in the ferric state. An equal bulk of strong hydrochloric acid is added, and a little sodium bicarbonate dropped in to give an atmosphere of carbon dioxide in the flask; 1 drop of $\frac{N}{10}$ stannous chloride solution is added, and a drop of the mixture added to a drop of a freshly prepared ferricyanide solution on a white tile; a blue coloration generally results, except in cases where a great excess of permanganate was added, and in these cases stannous chloride must be added till a reaction for ferrous iron is given. The solution, which has the usual bright yellow colour of ferric salts in strong hydrochloric acid, is now titrated till the colour becomes faint, and the titration continued till a drop no longer colours a drop of a solution of a thiocyanate on a white tile. The number of c.c. used multiplied by 0·0056 will give the weight of iron present.

With careful oxidation the use of the ferricyanide indicator may be dispensed with, and with non-coloured solutions the disappearance of the yellow marks the end point.

The results below show the accuracy of the method:

Iron solution containing by gravimetric analysis 0·837 grm. Fe per 100 c.c.; aqueous solution, 0·833; after re-oxidising, 0·832; sugar solution, 0·835.

Syrupus ferri phosphatis, B.P. theory, 0·87 per cent. (three samples): 0·835 and 0·825, 0·86, 0·868.

Syrupus ferri phosphatis compositus theory, 0·437 per cent.: 0·437 and 0·422.

Another sample + 5 per cent. extra iron, theory 0·46 per cent.: 0·46.

Syrupus ferri phosphatis compositus, another sample strong in iron: 0·482 and 0·485.

Syrupus ferri glycerophosphatis compositus, B.P.C. theory: 0·087 per cent. (two samples): 0·088 and 0·087, 0·084.

Syrupus ferri hypophosphatis, made to contain 0·48 per cent.: 0·46, 0·49, and 0·48.

Easton's syrup theory, 0·87 (three samples): 0·835, 0·88, 0·85.

Ferri phosphas saccharatus (one of strength below B.P. requirements, one of B.P. strength) : 51·8, 64·1 ; Romijn's method, 51·4, 64·6.

Syrupus glycerophosphatis cum formatibus, B.P.C. theory, 0·087 per cent. (known to be low) : 0·069, 0·067 ; after oxidation, 0·066.

Glycerinum glycerophosphatum compositum, B.P.C. theory : 0·081, 0·087.

We find that if the stannous chloride solution be kept in an atmosphere of hydrogen, it loses strength at so slow a rate that occasional checking of its titre only is required. In the absence of organic matter this method may be combined with a permanganate titration in hydrochloric acid solution thus : the iron having been brought to the ferrous state by any of the usual methods, the solution is titrated with $\frac{N}{10}$ permanganate ; half the volume of strong hydrochloric acid is added, and the solution titrated back with $\frac{N}{10}$ stannous chloride, using ferricyanide as indicator, and the amount used subtracted from the permanganate titration, and the remainder gives an estimation of the iron. The titration with stannous chloride may be continued to the thiocyanate end point, and gives another iron estimation which agrees closely with the corrected permanganate figure.

This work was carried out in the analytical laboratory of Boots' Pure Drug Company, Ltd., to whom our thanks are due.

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THE ESTIMATION OF NITROGLYCERINE.

By H. DROOP RICHMOND, F.I.C.

(*Read at the Meeting, June* 2, 1920.)

Nitroglycerine is used in medicine, a 1 per cent. solution being official in the B.P. under the name of *Liquor trinitrini*, and in the U.S.P. as *Spiritus glycerylis nitratis*. The test given in the B.P. is a dilution test with water, and useless as a quantitative indication; the U.S.P. prescribes the weighing of the residue after spontaneous evaporation and drying over sulphuric acid.

In the hope of finding a simple routine method for estimating nitroglycerine, not only in the official preparations, but in the stronger solutions marketed under the name of *Liquor glonoini*, I have examined many of the methods proposed.

Hay (*Trans. Royal Society of Edinburgh*, **32**, 67 ; also *Chem. Centralb.*, 1884, 108) concluded that the action of alkali is—

$$C_3H_5(NO_3)_3 + 5KOH = KNO_3 + 2KNO_2 + HCOOK + CH_3COOK,$$

and suggests the estimation of the nitrite. Allen ("Commercial Organic Analysis, third edition, vol. ii., part i., 335) states that he has attempted to measure the potash required for saponification, and though finding fairly concordant results, mentions that the dark colour of the solution prevents the end point being distinct ; as he gives no figures, it is to be presumed that he did not consider this a practicable method. Hempel

(*Zeitsch. anal. Chem.*, 1881, 82) dissolves the nitroglycerine in sulphuric acid, and measures the nitrous oxide given off in a nitrometer; but states that 5 c.c. only of sulphuric acid must be used, otherwise the results are low. He does not find saponification to give good results.

Champion and Pellet (*Ann. Chim. anal. Appl.*, 1900, **5**, 365) have devised methods depending on the reduction of the nitro groups to nitrous oxide by ferrous sulphate. The Kjeldahl-Jodlbauer method for estimating nitrogen and reduction by stannous and titanous chlorides are used for the estimation of nitro-nitrogen.

Siberrad, Ablett, and Merryman (*J. Soc. Chem. Ind.*, 1906, **25**, 628) heat for six hours with sodium ethylate, and reduce the nitrate and nitrite formed to ammonia with a suitable alloy (*cf.* Lowry, Browning and Farmery, *J. Chem. Soc.*, 1920, **117**, 552).

My first experiments were the evaporation of the alcoholic solution at a low temperature, solution of the residue in sulphuric acid (5 c.c.), and estimation of the nitrous oxide given off by shaking with mercury in a nitrometer; but as I obtained 89·0 and 65·1 per cent. of the theoretical quantity in two experiments, I did not pursue the method further.

Next I attempted to evaporate the solution after adding sodium hydroxide, dissolving in small amounts of water, in which the residue was very soluble, and making a nitrometer estimation. The results were:

	Per Cent. of Theory.
Approx. 8 molecules NaOH, rapid evaporation ...	105
„ „ „ slow „ ...	132, 107
Approx. 4 „ „ rapid „ ...	97·5, 96·0, 96·0, 99·5
„ „ „ slow „ ...	101

Although fairly concordant results were obtained by rapid evaporation in the presence of limited amounts of alkali, the method was considered to be dependent too much on conditions difficult of attainment.

Attempts were made to estimate the nitrous oxide given off by treating the residue after evaporation with alkali with potassium iodide and sulphuric acid in a nitrometer. The results were:

	Per Cent. of Theory for per Cent. $-NO_2$.
Approx. 8 molecules NaOH, rapid evaporation ...	102·6, 90·4, 104·4, 119·6
„ 4 „ „ „ „ ...	95·7, 87·9, 89·7

In two cases the residue after evaporation was made slightly acid, and air passed over the solution till all smell of nitrous fumes was removed, and the nitrate estimated in the nitrometer; 94·8 and 114·6 per cent. of theory for $1-NO_3$ were given in two experiments. An experiment was made by adding eight molecules NaOH to the alcoholic solution, and allowing the mixture to stand for twenty hours, decanting the alcoholic portion, and washing the brown syrupy residue with alcohol. The alcoholic solution was evaporated, and gave total nitrogen, 103·8 per cent. of theory; nitrous nitrogen, 98·2 per cent.; nitric nitrogen, 94·2 per cent.; while the syrupy residue gave no nitrous oxide in the nitrometer, but an appreciable amount of CO_2.

An attempt was made to estimate the nitrous nitrogen in the residues after evaporation with 8NaOH by the urea method.

The figures were :

	Total Gas at N.T.P. from 0·05 Grm.	Of which N_2.
Short evaporation ...	31·4 c.c.	Not estimated.
Medium evaporation ...	35·7 c.c.	17·5 = 89·3 per cent.
Long evaporation ...	40·7 c.c.	17·85 = 91·1 per cent.

Some experiments were tried by adding 8NaOH, allowing the solution to stand in the cold, pouring the alcoholic solution direct into the nitrometer, adding potassium iodide solution and dilute sulphuric acid, as in the B.P. method for examining *Spiritus ætheris nitrosi*, and measuring the gas. The results were :

Time of Standing.	Per Cent. of Theory.	Per Cent. of 95·7.
5 minutes...	91·5	—
30 „	96·3	100·6
30 „	94·6	98·9
1 hour	95·4	99·7
3 hours	96·8	101·1
4 „	95·4	99.7

Or a mean of 95·7, excluding the five-minute results.

This appeared to be a rough empirical method, giving results of sufficient accuracy for control purposes.

The details are : to 5 c.c. of *Liquor trinitrini* in a corked test-tube add 0·2 c.c. 7·5N NaOH solution; after one-half to two hours pour into the cup of a nitrometer filled with saturated brine, rinse the tube with small amounts of alcohol, and add 5 c.c. of a with 10 per cent. solution of potassium iodide and then 5 c.c. 3N sulphuric acid. Shake till evolution ceases, measure the gas, and correct to N.T.P. number of c.c. at N.T.P. × 0·1062 = per cent. nitroglycerine w/v.

Estimations made by treating the alcoholic solution with 8NaOH for five minutes, one hour, and eighteen hours, and estimating the nitrogen by Devarda's method, gave 90·0, 92·3, and 88·6 per cent. of theory, but if a small quantity of hydrogen peroxide were added before the alkali, practically theoretical results were obtained. It is evident from the above results that Hay's equation does not represent the change that takes place; CO_2 was detected in the gas in the nitrometer on several occasions; though it was proved that during the evaporation of alcohol with the amount of caustic soda used not enough CO_2 was absorbed from the atmosphere to give any in the nitrometer. It was noticed on adding the alkali that the alcoholic solutions almost immediately became turbid, that heat was evolved as noted by Hay, and that a dark syrupy layer was deposited on the bottom of the vessel in a short time; the alcoholic solutions were not very dark.

Notwithstanding Hempel's criticism, estimations were made of the alkali required for hydrolysis; in the first series 25 c.c. $\frac{N}{2}$ alcoholic soda solution were added to 10 c.c. of a 5 per cent. solution in 90 per cent. alcohol, allowed to stand for various times, and the excess titrated with $\frac{N}{2}$ acid without disturbing the syrupy layer, with results as follows :

Time of Standing.	c.c. $\frac{N}{2}$ Alkali used per Grm.
22 hours ...	19·50
22 „ ...	19·42
1 hour ...	18·77
15 minutes ...	18·18
5 „ ...	17·79
2 „ ...	17·72

It was seen that if the results were plotted out as a curve, the point for zero time would be very close to 17·62, the theoretical amount for 4NaOH ; it was thought that the higher results were probably due to the retention of some alkali in the syrupy phase as well as possibly to the gradual formation of carbonates. It was found that the one-hour titration, when violently shaken, became alkaline again, and required 0·6 c.c. $\frac{N}{1}$ acid per grm. to become neutral, although all the syrup could not be removed from the bottom by shaking.

The deposit in one of the twenty-two-hour titrations on solution in water required 1·45 c.c. per grm.

It appeared probable that no further alkali was being absorbed in any change that was taking place, but was simply being removed from solution. Another series was started in which the alkali was allowed to act for a limited period, and the solution shaken violently during titration. A solution of soda in methylated spirit, one of soda in pure alcohol, and one of potash in pure alcohol, all nearly $\frac{N}{2}$, were used but the only difference observed was that the potash caused a slightly greater darkening than the soda in all cases; when a few c.c. of alkali had been added, the solution became turbid and slightly warm, and evidently the action was very rapid.

Ten c.c. of 5 per cent. solution and 25 c.c. of approximately $\frac{N}{2}$ alkali were used, and titrated back with $\frac{N}{2}$ acid. The results were:

		c.c. N per Grm.
1.	KOH, 2 minutes	17·28, 17·18, 17·17
	KOH, 5 „	17·22, 17·28, 17·21
	NaOH, 2 „	17·28
	NaOH, 5 „	17·28, 17·19, 17·23

Or a mean of 17·23, which is equivalent to 3·909 molecules. This is equal to 97·8±0·3 of the theoretical quantity, assuming that four molecules are required.

The concordant results were found, however, to be due to the same conditions being observed, for in the next series the conditions were the same, except that $\frac{N}{1}$ acid was substituted for $\frac{N}{2}$, thereby introducing less water, with results as follows:

2. All five minutes: 17·64, 17·58, 17·78, 17·80, 17·80, or a mean of 17·72 c.c. per grm.

3. Two c.c. of a 5 per cent. solution + 8 c.c. alcohol with 10 c.c. $\frac{N}{2}$ alcoholic soda gave, titrated with $\frac{N}{2}$ acid, 16·25, 15·70, 15·95, a mean of 15·95 c.c. per grm.

4. Four 4 c.c. of a 5 per cent. solution + 16 c.c. alcohol with 10 c.c. $\frac{N}{2}$ alcoholic soda gave, titrated with $\frac{N}{2}$ acid, 17·90, 17·88, 17·42, 17·80, a mean of 17·75 per grm.

5. Two c.c. of a 5 per cent. solution + 8 c.c. alcohol with 10 c.c. $\frac{N}{2}$ alcoholic soda gave, titrated with $\frac{N}{1}$ acid, 17·12 c.c. per grm.

6. Ten c.c. of 5 per cent. solution with 25 c.c. $\frac{N}{2}$ alcoholic solution, titrated back with $\frac{N}{1}$ acid in 80 per cent. alcohol, gave 17·64, 17·64, 17·54 c.c. per grm.

It is evident that the final alcoholic strength influences the result; tabulating alcoholic strength and c.c. per grm. we get:

	Final Alcoholic Strength by Volume.	c.c. per Grm.
3	66	15·95
1	75	17·23
5	77	17·12
2	81	17·72
4	81	17·75
6	90	17·60

The experiments show that four molecules of alkali are necessary, and—

1. Potash and soda give the same results.
2. Variation of the concentration of nitroglycerine from 0·5 grm. in 35 c.c. to 0·2 grm. in 30 c.c. produced no appreciable variation.
3. Excess of alkali varying from 43 per cent. to 200 per cent. did not make differences outside the limits of experimental error; it was found, however, that when the excess was dropped to 27 per cent. the results were low (16·70 c.c. per grm.).
4. A final alcoholic strength of 81 per cent. was necessary.

The acidity of an alcoholic solution of nitroglycerine could be titrated by adding to 10 c.c. 50 c.c. of water and titrating with baryta, taking as the end point the appearance of a pink colour throughout the whole solution, permanent for a second or two; this end point, though fugitive, was sufficiently definite. Results are:

Acid added as c.c. $\frac{N}{10}$. X	c.c. $\frac{N}{10}$ used. Y	Acidity calculated.
0·0	0·1	0·0
1·75	1·95	1·8
2·0	2·25	2·1
2·5	2·65	2·5
5·1	5·3	5·1
12·5	12·65	12·3

There was evidently a slight hydrolysis, and the results were calculated by the formula $X = \frac{Y - 0{\cdot}1}{1{\cdot}02}$

The agreement is satisfactory, and shows that acidity can be estimated with sufficient accuracy.

The method for the analysis of the commercial nitroglycerine solution is: to 5 c.c. of a 10 per cent. solution + 5 c.c. 90 per cent. alcohol, or 10 c.c. of a 5 per cent. solution, add 25 c.c. $\frac{N}{2}$ alcoholic sodium hydroxide, or to 20 c.c. of a 1 per cent. solution add 10 c.c.; allow the mixed solutions to stand for about five minutes, add phenolphthaleïn, and titrate back with ^{N} acid, shaking violently when near the end point, which is quite sharp. To avoid adding too much water, alcoholic $\frac{N}{1}$ acid may be used for titration of the excess of alkali.

If more than 3 to 4 c.c. of acid are required, the determination must be repeated, increasing the alcoholic strength, as the amount of water introduced must not exceed 10 per cent. of the total volume. Correct the volume of alkali absorbed, expressed as c.c. $\frac{N}{1}$ for the acidity, estimated as above, and the weight of nitroglycerine will be the c.c. of $\frac{N}{1} \times 0{\cdot}05675$. The results above in eleven experiments gave from 98·9 to 101·5, mean 100·4.

By adding 2 c.c. of 100 vol. hydrogen peroxide before the addition of alkali no discoloration takes place, and a white precipitate settles; the results correspond closely to the absorption of 4 molecules, and the final alcoholic strength has much less influence on the titration. I recommend this modification.

The sp. gr. of nitroglycerine is 1·600, and that of 90 per cent. (by vol.) alcohol is 0·8337, and if made up strictly according to the B.P. directions the sp. gr. of *Liquor* *trinitrini* should be 0·8385, and not 0·840, as stated in the B.P.; there is no appreciable alteration in volume on dissolving nitroglycerine in alcohol; and the sp. gr. of a solution of 50 grms. in 1 litre being found to be 0·8576, the figure calculated assuming no contraction.

It is evident that the equation given by Hay does not express the reaction which takes place; the deposition of the syrupy precipitate, the formation of carbonates in quite large amounts, the presence of aldehyde and ammonia (both of which were detected), as well as the fact that only four molecules of alkali are required, all show that an action of a different nature occurs. By the action of two molecules or less of alkali I have found that the amount of nitrite formed is practically equivalent to the alkali added, and I suggest that the first action is the formation of two molecules of alkali nitrite and a molecule of mono-nitroglycerine peroxide; from this, one molecule of alkali nitrate and one of an alkali glycerate is produced by the further action of alkali. The alkali glycerate partly splits up into aldehyde and alkali carbonate, and the aldehyde reduces some of the nitrite to ammonia and possibly other nitrogen compounds; some of the nitrogen would be lost as nitrogen gas, owing to the formation of ammonium nitrite. In the presence of hydrogen peroxide the peroxide is catalytically decomposed with the formation of a hydroxypyruvate. Acetic acid found by Hay would result from the oxidation of the aldehyde.

This work was carried out in the analytical laboratories of Boots' Pure Drug Company, Ltd., to whom my thanks are due.

DISCUSSION.

Mr. DUPRÉ remarked that there are few explosives which can be treated with alkali in which nitroglycerine would be the only body present which reacts with it even after extraction. He said it was a most difficult question; there are many reactions like this one, where small subsidiary reactions prevent one getting a theoretical result. For instance, oxidation by permanganate and estimation of oxalic acid found will sometimes give good results, but unless the estimations are carried out under exactly the same conditions of temperature and concentration, consistent results cannot be obtained. He said that a point which required elucidation was the estimation of nitroglycerine in the presence of partially nitrated bodies, such as mono-nitro- and tri-nitro-toluol. This could not be done satisfactorily by means of the nitrometer, because the nitro-bodies become further nitrated, and the resulting compounds not being acted upon by the acid and mercury, a loss of nitric oxide occurs.

One method which is fairly satisfactory is to make up a mixture of nitroglycerine and nitro-compounds containing the proportions of nitro-compounds probably present in the explosive under examination, make the estimation in the nitrometer, and from the results obtain a correction to be applied to the figure given by the explosive itself.

Much the same trouble would occur if alkali were used; all these nitro-bodies inter-react with alkali, and again incorrect results are obtained. A method is needed in which a definite reaction with nitroglycerine is obtained and which is not affected by nitro-bodies.

Mr. G. Nevill Huntly asked if Mr. Richmond had tried a reduction method, and suggested the use of titanous salts for this purpose.

Mr. Browning said that in one stage of the reaction (cordite, lime, and pyridine water) nitric oxide is liberated, even when a rapid current of air is passing through it. The quantity is, however, much reduced when air is present.

Mr. Richmond, in reply, said that with regard to the question of titanous chloride and stannous chloride they were both suitable, but gave results which were rather low, the explanation of which was shown in a paper in a recent number of the *Journal of the Society of Chemical Industry* by Callan, Henderson, and Strafford, in which it was proved that chloramines are apt to be formed, and titanous sulphate was recommended, which gave practically theoretical results. He had not observed the evolution of nitric oxide, but the quantities used did not exceed 0·5 grm., and it might easily have been missed in small amount. With reference to Mr. Dupré's remarks, his criticism was quite just, and he (Mr. Richmond) had seen such difficulties, and for that reason confined his paper to the pharmaceutical estimation, but possibly the extreme rapidity of the hydrolysis of nitroglycerine might serve as a basis for its estimation in the presence of other substances.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Estimation of Nitroform by Potassium Permanganate. P. V. McKie. (*J. Chem. Soc.*, 1920, **117**, 646-648.)—Nitroform may be accurately estimated in the presence of nitric, nitrous, and sulphuric acid by oxidation with potassium permanganate solution—

$$CH(NO_2)_3 + 2O_2 + H_2O = CO_2 + 3HNO_3.$$

Twenty-five c.c. of the nitroform solution are added to a measured excess of $\frac{N}{10}$ permanganate solution acidified with 10 c.c. of 10 per cent. sulphuric acid, and the mixture heated for one minute (not more) at 30° C. (not higher); then treated with 20 c.c. of 2·5 per cent. potassium iodide solution, and the liberated iodine titrated with $\frac{N}{10}$ thiosulphate solution. Or any nitrous acid may be destroyed by boiling the liquid for about a minute with ammonium nitrate (3 grms. per 0·2 to 0·3 grm. of nitrous acid) prior to the oxidation at 30° C. Or the nitroform may be distilled in a current of steam (100 c.c. acidified with 15 c.c. of phosphoric acid, sp. gr. 1·7) after treatment with ammonium nitrate, and the distillate titrated. C. A. M.

Separation of Saccharin and Benzoic Acid. E. Schowalter. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1919, **38**, 185; through *Chem. Zeit. Ubersicht*, 1920, **44**, 138.)—Benzoic acid and saccharin are extracted together in the usual methods for the estimation of benzoic acid, and the two substances cannot be separated from each other by sublimation, since they both begin to sublime at about 120° C. Saccharin and its sodium salt are insoluble in carbon tetrachloride, and this solvent may be used for the separation of the benzoic acid. The ethereal solution of the two substances obtained as described in Von der Heide and Jacob's method for the detection of benzoic acid (ANALYST, 1910, **35**, 166) is evaporated at a low temperature, the residue is dried under reduced pressure if it contains acetic acid, and is then extracted with carbon tetrachloride. The dissolved benzoic acid may be titrated, whilst the residue insoluble in carbon tetrachloride may be tested for the identification of the saccharin. Saccharin and benzoic acid are absorbed to a considerable extent by animal charcoal, and this should not be used for the preliminary decolourisation of coloured solutions. W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Volumetric Estimation of Uric Acid by a Modification of Blarez and Tourrou's Method. G. Pegurier. (*Ann. Chim. anal.*, 1920, **2**, 109-110.)—Fifty c.c. of the urine are mixed with 5 c.c. of saturated sodium carbonate solution, and to the mixture are added 5 c.c. of Fehling's solution previously decolourised by the careful addition of sodium bisulphite solution. The Fehling's solution used contains 130 grms. of sodium hydroxide, 105 grms. of tartaric acid, 80 grms. of potassium hydroxide, and 40 grms. of copper sulphate per litre. The precipitate formed is collected after five minutes, washed several times with water, the filter and precipitate are placed in a beaker containing 150 c.c. of water, 10 c.c. of dilute sulphuric acid (1 : 1) are added, and the mixture is titrated with permanganate solution. If the latter contains 2·12 grms. of potassium permanganate per litre, each c.c. is equivalent to 0·1 grm. of uric acid per litre of urine. W. P. S.

ORGANIC ANALYSIS.

Identification of Acids. V. *p*-Halogen Phenacyl Esters. W. L. Judefind and E. E. Reid. (*J. Amer. Chem. Soc.*, 1920, **42**, 1043-1055.)—Organic acids may be identified by preparing their *p*-halogen phenacyl esters, many of which have destinctive m.-pts. The *p*-halogen phenacyl bromides, and especially *p*-bromophenacyl bromide, are the most useful reagents for this purpose, particularly in the case of monobasic aliphatic acids. The method of preparation is analogous to that used in the preparation of *p*-nitro-benzyl esters (ANALYST, 1917, **42**, 89), monobasic acids being heated for three-quarters to one hour with the reagents, dibasic acids for two hours, and tribasic acids for three hours. When possible, the alkali salts of the acids are used, otherwise the free acid is nearly neutralised with sodium carbonate prior to adding the reagent and alcohol. The resulting esters are recrystallised until a constant m.-pt. is obtained. The following m.-pts. were observed with the *p*-bromo-phenacyl esters of typical acids: Acetate, 85·0°; benzoate, 119·0°; butyrate, 63·0°; caprate, 66·0°; caprylate, 65·5°; citrate, 148·0°; lactate, 112·8°; palmitate, 81·5°; salicylate, 140·0°; stearate, 78·5°; succinate, 211·0°; thiocyanate, 146·5°; and valerate, 63·6° C. C. A. M.

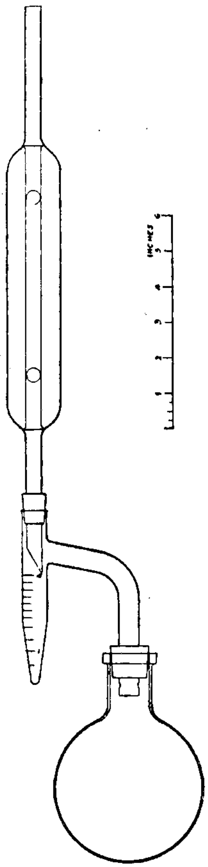
Estimation of Alcohol in Mixtures of Alcohol, Sulphuric Acid, and Water. G. S. Butler and H. B. Dunnicliff. (*J. Soc. Chem. Ind.*, 1920, **39**, 146T.)—The method described involves the estimation of the alcohol both as ethyl hydrogen sulphate and as free alcohol. If the free sulphuric acid is estimated by titration by the described method, the results show good agreement with those obtained by the precipitation of the free acid as barium sulphate, thus showing that during titration no appreciable hydrolysis takes place. Combined alcohol is estimated by determining the amount of acid which has undergone esterification. A weighed quantity of the alcoholic sulphuric acid is titrated against standard alkali; this "direct" titration gives (*b*) the percentage of acid present in terms of H_2SO_4—*i.e.*, the free sulphuric acid and the acid due to ethyl hydrogen sulphate. The "total" acidity is found by evaporating a weighed quantity of the alcoholic sulphuric acid to a pasty consistence with excess of standard caustic soda or potash, heating in an air oven at 120° C. for half an hour, and then, after extraction with distilled water, titrating the excess alkali with standard acid. From this is calculated the percentage acidity of the alcoholic sulphuric acid before any esterification took place. The value is expressed as percentage of sulphuric acid (*a*). Thus, the percentage of acid esterified = $2\,(a-b) \div a \times 100$. The weight of esterified alcohol in 100 grms. of the alcoholic sulphuric acid is $\frac{2\,(a-b)}{a \times 100} \times \frac{46}{98}$ grms. The free alcohol may be determined by weighing out 25 grms. of the alcoholic sulphuric acid, making faintly alkaline with sodium carbonate, and distilling until about 95 c.c. of distillate has been collected. This treatment does not hydrolyse the ester, and the distillate contains all the uncombined alcohol present. It is made up to 100 c.c., and its density at 60° F. determined. Analyses are appended of mixtures of known content which were determined with exactitude by the method described. H. F. E. H.

Butyl Alcohol as a Medium for the Determination of Saponification Numbers. A. M. Pardee, R. L. Hasche, and E. Emmet Reid. (*J. Ind. and Eng. Chem.*, 1920, **12**, 481.)—Normal butyl alcohol is found by the author to be superior to ethyl alcohol as a medium for quantitative saponification of fats and waxes, since satisfactory results are more readily obtained, and special precautions less often required. Substantially the same values result with both alcohols for the more readily saponified oils and fats, although the values in butyl alcohol are always somewhat higher. For substances which are difficult to saponify, such as wool fat, lanolin, and beeswax, considerably higher and more reliable values are obtained by using butyl alcohol than in the same volume of ethyl alcohol, though the latter values would doubtless have reached the higher figures had larger amounts of ethyl alcohol been employed or had the saponification been carried on longer. A table is given showing comparative values for twenty different kinds of oils, fats, and waxes, determinations in all cases being made on 1 grm. quantities, and 10 c.c. of the standard $\frac{N}{2}$ alcoholic alkali being employed for the heating on a steam bath for exactly one hour. Fifty c.c. of carbon dioxide free water were then added, and excess alkali titrated with $\frac{N}{2}$ hydrochloric acid; since the butyl alcohol was nearly anhydrous, 0·5 c.c of water was added to each flask containing this alcohol half an hour after heating had begun to provide for the saponification of the butyl ester which is first formed.

H. F. E. H.

Tanning Value of Vegetable Tanning Materials. J. A. Wilson and E. J. Kern. (*J. Ind. and Eng. Chem.*, 1920, **12**, 465-469.)—It has become customary to apply the name tannin to that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fibre which are resistant to washing. The remaining portion of the soluble matter is called non-tannin. A convenient amount of the tannin material is shaken with a definite amount of purified hide powder until all tannin has been removed from solution. This point is determined by filtering off a portion of the residual liquor and adding drop by drop, avoiding a large excess, a solution containing 10 grms. of gelatin and 100 grms. of sodium chloride per litre; if the solution becomes turbid or a precipitate forms, it shows that all tannin has not been removed from solution, in which case the mixture must be discarded and the test repeated, using less of the tannin material or shaking for a longer time, until the solution after filtration gives no visible reaction with the gelatin-salt reagent. The tanned powder is then washed free from soluble matter, including the non-tannin removed from solution by the hide powder, which is responsible for the large errors in the methods now in use. It is then carefully dried and analysed for tannin as in the regular procedure for vegetable-tanned leathers, and from this figure the percentage of tannin in the original material may be readily calculated. Since the results obtained for any one material, using different dilutions, agree closely, it is concluded that the hide powder removed practically all of the tannin from all solutions which gave no test with the gelatin-salt reagent after the shaking process. In each test, 12 grms. of hide powder (of known hide substance content) were put into a wide-mouth, rubber-stoppered, half-pint bottle, the tanning material dissolved in 200 c.c. of solution was added, and the whole was shaken in a rotating box for six hours. Whenever the liquor after the six-hour shaking gave a turbidity or precipitate with the gelatin-salt reagent, the test was repeated with less material. The smallest amount used for any material represents the least it was possible to use and still get reproducible results. The tanned powder was washed by shaking with 200 c.c. of water for thirty minutes, squeezing through a suitable cloth, and repeating the washing operation until the wash water showed no colour and gave no test with ferric chloride solution. The washed powders were dried at room temperature for twenty-four hours or longer, and then analysed for water, ash, fat, and hide substance. The difference between 100 and the sum of these percentages was taken as the percentage of tannin in the leather. The parts of tannin per 100 parts of hide substance in the leather divided by parts of tanning material used per 100 parts of hide substance gave the fraction of tannin in the original material. The principle of the official (American) method is similar to that of the new method as regards the shaking of a solution of the tanning material with hide powder, but differs in that the drop in concentration of the liquor upon shaking is taken as the measure of its tannin content, while the tanned powder is simply discarded. As might be expected, the greatest errors in the official method are obtained with those materials containing the greatest proportion of non-tannin to tannin. Quebracho, having least non-tannin, gives the smallest error. The analyses of eight common tanning materials by the new method and by the official method of the American

Leather Chemists' Association indicate that the latter method is in error to the extent of from 43 to 220 per cent. H. F. E. H.



Convenient Method for the Determination of Water in Petroleum and other Organic Emulsions. E. W. Dean and D. D. Stark. (*J. Ind. and Eng. Chem.*, 1920, **12**, 486-490.)—Experience has indicated that the method of distilling in the presence of an immiscible solvent is the most generally satisfactory scheme of estimating the water content of organic emulsions, particularly petroleum emulsions. The authors have found the most satisfactory solvent to be a so-called cleaner's naphtha derived from petroleum. A mixture of 80 per cent. of commercial xylene and 20 per cent. of commercial 90 per cent. benzol has also been found satisfactory. This mixture should not be saturated with water before using. The use of a charge of 100 c.c. of emulsion and 100 c.c. of solvent has proved satisfactory for oils containing between 0·5 and 10 per cent. of water. If an accurate determination of water content of less than 0·5 per cent. is desired, it is necessary to use 200 c.c. or more of both emulsion and solvent, employing, of course, a correspondingly larger distilling flask. If the emulsion to be tested contains more than 10 per cent. of water, the quantity taken should be some suitable fraction of 100 c.c. The method has been tried with a number of emulsions prepared by mixing known amounts of water with anhydrous oils. Results have almost invariably checked the theoretical water content within ±0·1 c.c., which apparently represents the normal magnitude of error. The applicability of the method for the separation of water from refractory emulsions has been questioned, and tests have been made to settle this point. Water was determined according to the procedure described. The flasks were allowed to cool somewhat, then connected with an ordinary distilling tube and condenser, and the distillation continued until a vapour temperature of 250° C. was reached. In no case was any additional water separated or observed, thereby indicating that distillation at the temperature existing in the presence of the solvent was adequate to "break" the emulsion. The apparatus consists of an electrical source of heat, a 500 c.c. short-necked distilling flask, a special device combining the functions of distilling tube and receiver and a condenser. The source of heat may be an alcohol or gas burner, but the authors prefer a special type of electric heater. The illustration appended sufficiently describes the apparatus employed; the distilling-tube receiver is usually made by attaching a proper side-tube to a stock type of tapered graduated test-tube; cork stoppers are used for the two junctions, and if of good quality require no luting.

H. F. E. H.

Estimation of Aromatic Hydrocarbons in Petrol. D. Florentin and H. Vandenberghe. (*Bull. Soc. Chim.*, 1920, **27**, 204-209.)—Twenty c.c. of the petrol are cooled in a flask immersed in cold water (or preferably ice and water) beneath a reflux condenser, and treated drop by drop, with continual shaking, with nitric acid (sp. gr. 1·5) until a brown tint is no longer produced. A few additional drops of the acid are then added, and the flask left for fifteen minutes, after which its contents are poured into a large excess of cold water, and neutralised with sodium or potassium hydroxide. Small quantities of the oxidation products of impurities in the petrol are removed by distillation in a current of steam, the petrol then decanted, the aqueous solution extracted twice with petroleum spirit, and the extracts added to the petrol. The whole is then made up to 50 or 100 c.c. with petroleum spirit, and the nitro derivatives estimated in an aliquot portion. This is evaporated over sulphuric acid under diminished pressure in a glass dish, which is weighed at intervals of ten minutes until constant in weight (or until the weight shows a constant decrease), and the amount of this residue multiplied by 0·634 gives the weight of hydrocarbons as benzene. Or the amount of nitro derivative may be estimated volumetrically by means of stannous chloride or titanous chloride, preferably the latter. For this purpose an aliquot portion of the liquid is heated with titanous chloride solution for two hours beneath a reflux condenser in a current of carbon dioxide, and the excess of the titanium salt titrated with ferric chloride solution. This method is preferable to the gravimetric method when the petrol contains constituents of higher b.-pt. Examined by these methods, commercial samples of petrol were found to contain considerable quantities of benzene hydrocarbons (31·25 to 61·5 grms. per litre), and especially of toluene (fraction boiling at 100° to 130° C.). C. A. M.

Physico-Chemical Method for the Analysis of Commercial Chlorobenzene. F. Bourion. (*Comptes rend.*, 1920, **170**, 990-993.)—The sample is fractionally distilled so as to obtain a fraction boiling below 130° C. and containing the whole of the benzene with a portion of the chlorobenzene, and another fraction (the remainder) containing the rest of the chlorobenzene, together with the *p*-dichlorobenzene. The sp. grs. of the two fractions are determined, and reference to tables showing the sp. grs. of known mixtures of benzene and chlorobenzene and of *p*-dichlorobenzene and chlorobenzene gives the composition of the fractions. W. P. S.

INORGANIC ANALYSIS.

Detection of Arsenic in Sulphur. H. S. Davis and M. D. Davis. (*J. Ind. and Eng. Chem.*, 1920, **12**, 479-480.)—Sulphur free from arsenic tested by Schaeppi's method (*J. Soc. Chem. Ind.*, 1881, **4**, 409) gave positive tests, and the authors describe a method of their own which obviates this. The method as described by Schaeppi consists essentially in first digesting the sulphur with dilute nitric acid for the purpose of removing calcium chloride, sulphate, and sulphide. The sulphur washed free from acid is then treated with dilute ammonia solution for fifteen minutes at 70° to 80° C. Schaeppi assumes that any arsenic present in the sulphur must exist as sulphide, mainly arsenious sulphide, and will be dissolved by the ammonia. The arsenic is then estimated indirectly through determination of the amount of sulphide by precipitation with silver nitrate in neutral solution. It was found, however, that sulphur continuously reacts with dilute ammonia at 70 to 80° C. to form sulphides, so that even arsenic-free sulphur will give a qualitative test for arsenic by this method. As is well-known, sulphur readily dissolves in hot solutions of the strong alkalis to form polysulphides, and it thus follows that a sample of arsenic-free sulphur will continue indefinitely to give a positive reaction by Schaeppi's method. The authors treat 10 grms. of the sample of sulphur with 30 c.c. of a mixture containing three parts of carbon tetrachloride and two parts bromine, and after standing for ten minutes, about 40 c.c. of strong nitric acid are added slowly in small quantities ; the mixture is taken to dryness in a steam bath, and the arsenic finally determined on the residue by the Gutzeit method. The carbon tetrachloride is employed to moderate the violence of the reaction and to prevent the precipitation of sulphur. H. F. E. H.

Separation of Chromium and Manganese. M. Herschkowitsch. (*Zeitsch. anal. Chem.*, 1920, **59**, 11-12.)—The method of separation described depends on the fact that permanganate is decomposed when heated with ammonia and ammonium salts, whilst chromates are not affected. After the two metals have been oxidised to permanganate and chromate respectively, their solution is treated with ammonium sulphate and an excess of ammonia, and heated for some hours on a water-bath. The precipitate formed is collected, washed first with 5 per cent. ammonium sulphate solution, then with water, ignited, and weighed as Mn_3O_4. W. P. S.

Colorimetric Method of Estimating Copper and Iron in Lead and Lead Oxides. C. R. Hardy. (*Chem. News*, 1920, **120**, 256.)—A weighed quantity (about 200 grms.) of the sample is dissolved in nitric acid (sp. gr. 1·2), sufficient water being added to prevent the separation of crystalline lead nitrate, and the solution treated with concentrated sulphuric acid (32 c.c. per 100 grms. of the sample). The liquid is filtered by decantation four or five times, and the filtrate treated with 10 c.c. of sulphuric acid, and evaporated nearly to dryness, cooled, diluted with water, and filtered from lead sulphate. The filtrate is evaporated to a small volume with a few drops of nitric acid, cooled, and treated with ammonia. The iron hydroxide is separated, washed, redissolved in nitric acid, reprecipitated, and thoroughly washed. The two filtrates, which will contain all the copper, are concentrated to a small volume, cooled, made up to definite volume, and 50 c.c. treated with 5 c.c. of a 0·4 per cent. solution of potassium ferrocyanide and 5 c.c. of 10 per cent. ammonium nitrate solution, and the coloration compared with that given by a standard copper solution (0·393 grm. of copper sulphate per litre). The iron precipitate is dissolved in a little nitric acid, the solution made up to 250 c.c., and 25 c.c. treated with 9 c.c. of 25 per cent. hydrochloric acid and 5 c.c. of 5 per cent. ammonium thiocyanate solution, and the coloration compared with that given by a standard iron solution (0·210 grm. of ferrous ammonium sulphate per litre) under the same conditions. C. A. M.

Iodic Acid as a Reagent for the Microchemical Identification of Soluble and Insoluble Calcium, Strontium, and Barium Compounds. G. Denigès. (*Comptes rend.*, 1920, **170**, 996-998.)—Characteristic crystals are obtained, in many cases almost immediately, when a particle of a calcium, strontium, or barium compound is treated with a small drop of 10 per cent. iodic acid solution. With calcium, the crystals have the form of sharp octahedra; with strontium, short octahedra mixed with rhombic prisms; with barium, needle-like prisms in groups. The crystals may be obtained with calcium oxalate, calcium fluoride, and strontium sulphate; barium sulphate must be reduced to sulphide (by heating on a platinum wire in a reducing flame) before it reacts with iodic acid, and calcium iodate itself must be converted into iodide by heating before the test is applied. W. P. S.

Estimation of Mercury. C. M. Bouton and L. H. Duschak. (*U.S. Dept. of the Interior, Technical Paper*, No. 227, 1920, pp. 1-44.)—A method proposed for the estimation of small quantities of mercury consists essentially in separating the metal by distillation, dissolving it in nitric acid, and titrating the solution with thiocyanate. In the case of ores or other material containing but little sulphur or organic matter, 1 grm. of the finely divided sample is mixed with 0·5 grm. of dry powdered calcium oxide, and the mixture is introduced into a combustion tube, 22 cm. long and 10 mm. in diameter, closed at one end, and into which has already been placed a layer of coarse sand. A 1 cm. layer of calcium oxide is added to the tube, and on this a like layer of sand. After a plug of brass gauze has been pushed into the tube, the latter is placed horizontally in a furnace heated at 450° to 550° C. The furnace may consist of an iron block in which a number of holes have been bored. The tube is heated for fifteen minutes, then placed open end downwards in a test-tube containing 5 c.c. of hot concentrated nitric acid, the closed end of the tube is broken off, and the acid is sucked up the tube above the ring of condensed mercury, but the acid must not be allowed to reach the gauze plug. The solution is transferred to a beaker, the combustion tube washed in a similar way with 10 c.c. of water, the total mercury solution is oxidised with permanganate, the excess of the latter destroyed with hydrogen peroxide, 2 c.c. of 10 per cent. ferric sulphate solution are added, the mixture is cooled, and titrated with standardised thiocyanate solution. If the sample contains much sulphur and organic matter, cupric oxide and a small quantity of potassium chlorate are mixed with the sample in addition to the calcium oxide, and potassium chlorate is also mixed with the layer of sand at the closed end of the tube. This procedure may be adopted for distilling mercury from precipitates collected on filter-paper, but it is better to collect the precipitate on a film of clay previously deposited in an alundum filtering crucible; the use of potassium chlorate is then unnecessary. With about 40 mgrms. of mercury there is a fairly consistent loss of 0·3 mgrm. The presence of selenium and tellurium does not interfere with the method, and arsenic and antimony have no effect on the results when cupric oxide is used in conjunction with the calcium oxide. If chlorides or sulphates are present in the sample, iron filings may be used as a reducing agent in the distillation, but it is preferable to separate the mercury as sulphide and subject this to distillation. A bibliography of some 124 methods for the estimation of mercury is given. W. P. S.

Gravimetric Estimation of Molybdenum as Sulphide. J. Sterba-Böhm and J. Vostrebal. (*Zeitsch. anorg. Chem.*, 1920, **110**, 81-103.)—Molybdenum when in the form of molybdate may be quantitatively precipitated as molybdenum sulphide, MoS_3, by means of hydrogen sulphide in the presence of a sufficient quantity of formic acid, but any reduced molybdenum present should first be oxidised by means of nitric acid. The molybdate solution (0·1 to 0·3 grm. of molybdenum) is diluted with water to 200 to 300 c.c., and treated with sufficient formic acid to give an acidity of 5 per cent., whilst if the solution contains too small a quantity of electrolytes it is advisable to add from 0·5 to 0·75 per cent. (calculated on the volume of the liquid) of pure sodium chloride to prevent the formation of a colloidal solution. Immediately after the addition of the formic acid a rapid current of acid-free hydrogen sulphide is introduced, and after thirty minutes the temperature of the liquid is raised to 40° to 50° C., and the current of the gas continued for one to one and a half hours. Or the molybdate solution may be rendered alkaline with ammonia or potassium hydroxide, and the current of hydrogen sulphide passed through it for two hours, after which it is treated with formic acid, and heated for an hour on the water-bath. The molybdenum sulphide precipitate, obtained by either method, is washed by decantation, transferred to a Gooch crucible, and dried in a current of carbon dioxide at 100° C., and subsequently at 250° C., cooled in the current of gas, and weighed in a closed weighing-bottle. C. A. M.

Method for the Estimation of Sulphur in Oils. C. E. Waters. (*J. Ind. and Eng. Chem.*, 1920, **12**, 482-485.)—The author had previously worked out a method in which the total sulphur was estimated in rubber goods by decomposing that material with concentrated nitric acid saturated with bromine; the residue was then completely burned by heating with sodium and saltpetre. He now applies this method to the estimation of sulphur in oil. From 0·5 to 1·5 grms. of the oil are weighed in a 100 c.c. porcelain crucible, and 5 c.c. of concentrated nitric acid saturated with bromine are then added, a watch-glass covering the crucible; the crucible is placed on the steam-bath and carefully digested for half an hour or more; after cooling, 10 or 12 grms. of anhydrous sodium carbonate are added in small portions, the whole being thoroughly mixed with a glass rod; the resulting pasty mass is spread on the sides of the crucible, to which it should adhere, after which it is gently ignited. If more than 1 grm. of oil has been taken, there is a tendency for it to burn too briskly, but this is controllable by judicious use of the stirring-rod. It is never necessary to heat the crucible to redness. After cooling, the crucible and its contents are placed in a beaker and extracted with about 150 c.c. of water, filtered, and the sulphuric acid precipitated with barium sulphate in the presence of hydrochloric acid in the usual manner. Control experiments should be run with the reagents, and it is advisable to use a petroleum ether flame as a precaution against the presence of sulphur in gas. Duplicate analyses differ by less than 0·05 per cent., and the method has been compared with the bomb calorimeter and several other methods. The author considers it fair to claim his procedure is sufficiently accurate for all ordinary purposes, although it has not yet been applied to kerosene or gasolene. He admits that the conditions under which the barium sulphate is precipitated are far from ideal, involving as they do the occlusion of sodium salts; of these, the sulphate tends to low results, while the nitrate has an opposite effect, and only by chance will these errors cancel one another. Estimations made with double the usual amounts of reagents go to show that the net error due to occlusion is small. H. F. E. H.

Separation of Tin and Antimony and Estimation of Tin by Means of Cupferron. A. Kling and A. Lassieur. (*Comptes rend.*, 1920, **170**, 1112-1114.) —McCay's method of separating tin from antimony by precipitation with hydrogen sulphide from a hydrofluoric acid solution (ANALYST, 1909, **34**, 244) gives accurate results, and may be used for the estimation of the tin as stannic oxide after precipitation with cupferron. The antimony sulphide is dried at 300° C. in a current of carbon dioxide and weighed. The filtrate from the antimony sulphide is treated with boric acid (10 grms. for about 0·2 grm.), which effects a partial precipitation of stannous sulphide, and the liquid is then boiled with hydrogen peroxide to oxidise the stannous sulphide. The resulting clear liquid is cooled, and treated with a 10 per cent. solution of cupferron, and the precipitate washed with cold water, dried, ignited, and weighed as stannic oxide. C. A. M.

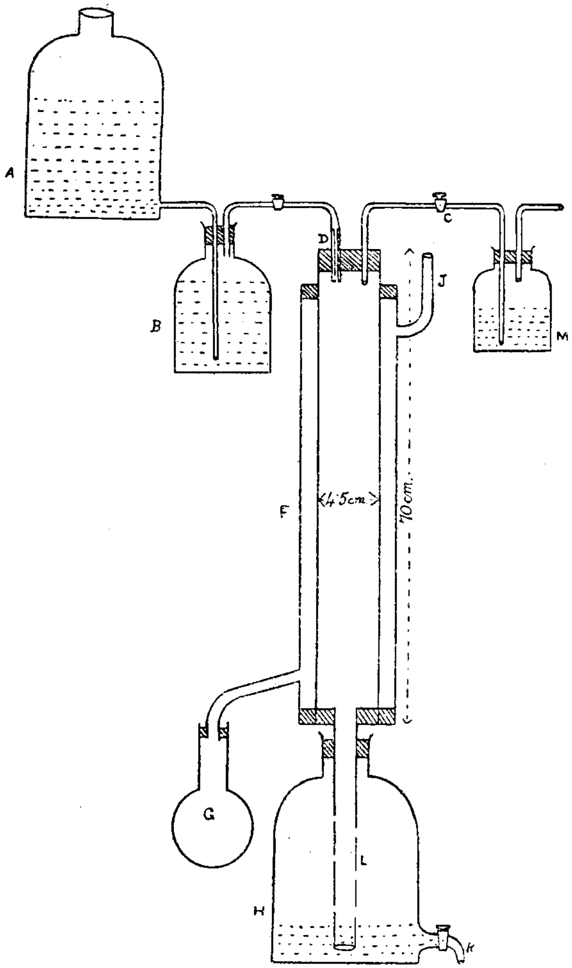
Analysis of Tungsten Ores. J. Erlich. (*Ann. Chim. anal.*, 1920, **2**, 102-103.) —From 1 to 2 grms. of the sample are heated for two hours on a sand-bath with 30 c.c. of 30 per cent. ferric chloride solution and 100 c.c. of hydrochloric acid; ammonium nitrate is then added, and the insoluble portion collected on a filter, ignited, and weighed. This portion is fused with sodium bisulphate and the mass dissolved in ammonia; the solution is oxidised with bromine, and elements other than tungsten are precipitated by the addition of ammonium carbonate. The precipitate is collected, ignited, and weighed. The difference between the two weights gives the weight of tungstic oxide (WO_3) present. In some cases the fusion with sodium bisulphate must be repeated to effect complete separation of the tungsten.

W. P. S.

Estimation of Uranium. R. Schwartz. (*Helv. Chim. Acta*, 1920, **3**, 330-346.)—Precipitation with ammonium sulphide or ammonia affords the most trustworthy means of estimating uranium; the precipitation should be made at 100° C., and in the presence of ammonium chloride. The precipitate should be ignited to U_3O_8 in a porcelain crucible, with free access of air; reduction of the U_3O_8 to UO_2 is unreliable (*cf.* ANALYST, 1902, **27**, 28). Precipitation of uranium by means of ammonium phosphate from an acetic acid solution is untrustworthy. Accurate results may be obtained by dissolving the U_3O_8 in sulphuric acid and titrating the solution with permanganate solution; uranous and uranyl sulphates are formed, and the former is titrated. Uranium may be separated from aluminium by precipitation, at 70° C., with an excess of ammonium carbonate in the presence of ammonium chloride; the precipitated aluminium hydroxide must be dissolved in hydrochloric acid and the precipitation repeated in order to separate all the uranium. To separate uranium from chromium, the latter should be converted into chromate by means of ammonium persulphate, and the uranium then precipitated with ammonia, but the precipitation must be repeated several times. By heating U_3O_8 for eight hours at 1122° C. in an atmosphere of carbon dioxide, an oxide having the composition U_2O_5 may be obtained. W. P. S.

APPARATUS, ETC.

New Hydrogen Sulphide Generator. B. D. Steele and H. G. Denham. (*J. Chem. Soc.*, 1920, **117**, 527-529.)—In the apparatus here shown, rapid evolution of the gas and complete neutralisation of the acid are effected. The steam-jacketed tube *F* is packed with lumps of iron sulphide, and the acid holders *A* and *B* charged with dilute (1 : 1) hydrochloric acid. Steam generated in the flask *G* is passed through the jacket until the sulphide is thoroughly hot, and the tap *C* opened so that the acid drips into the heated column through the capillary tube *D*. Each incoming



drop reacts immediately, and the acid is completely neutralised long before it reaches the bottom of the column, and falls into the reservoir *H* (25 litres in capacity), the displacement of air in the latter being facilitated by having a number of holes in the tube *L*. By attaching a short air-condenser to the side tube *J*, the condensation of the escaping steam is practically complete. C. A. M.

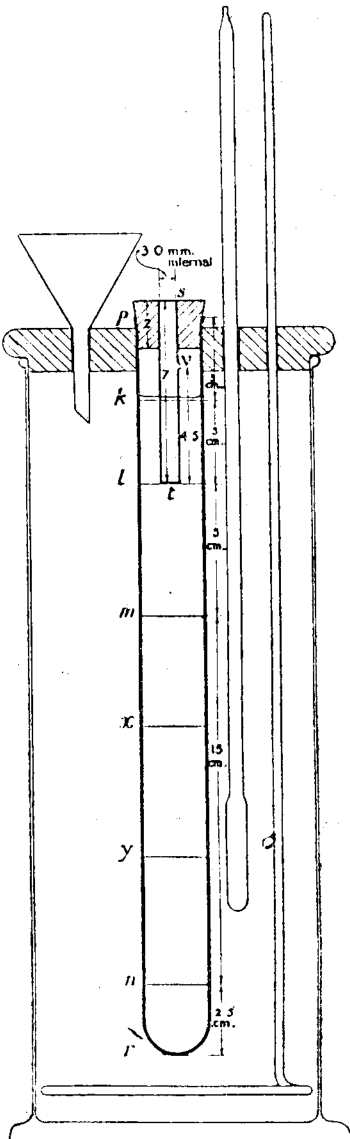
Falling Sphere Viscosimeter. W. H. Gibson and L. M. Jacobs. (*J. Chem. Soc.*, 1920, **117**, 473-478.)—In the form of apparatus shown in the diagram various errors associated with this type of viscosimeter are taken into consideration. The tube is 29 cm. long, with an internal diameter of 2±0·05 cm., and is divided into three lengths of 5 cm. for measuring the time of fall, and another 5 cm. for the ball to acquire its maximum velocity, whilst there is a graduation mark to determine the height of the liquid in the tube. The steel sphere (0·15 cm. in diameter) is delivered into the centre of the tube through a glass tube 7 cm. long and 3 mm. in internal diameter, which passes through the centre of a rubber stopper, and is adjusted to dip 3 cm. below the surface of the liquid. Applying the corrections for wall and end effects, Stokes' equation becomes—

$$9\eta s(1+2{\cdot}4x)\left(1+3{\cdot}3\frac{r}{h}\right)=2gr^2(s-\sigma)\mathrm{T},$$

where T represents the time of fall through a length *s*, *r* the radius of the sphere, and *h* the height of the liquid. If spheres of equal radius are used in tubes of the same dimensions, the viscosity of a liquid may be obtained by the equation—

$$\frac{\eta}{\eta_1}=\frac{(s-\sigma)\mathrm{T}}{(s-\sigma)\mathrm{T}_1},$$

when the time of fall for another liquid of known viscosity has been determined. The viscosity of castor oil ($\eta=9{\cdot}888$) determined by means of this instrument agreed closely with the value found by Kahlbaum and Raber. C. A. M.



Theory of Gravimetric Analysis, with Special Consideration of Sources of Error. L. Moser.

(*Zeitsch. anal. Chem.*, 1920, **59**, 1-10.)—A discussion dealing principally with sources of error in gravimetric analysis. Errors due to solubility of precipitate, induced precipitation, formation of solid solutions, absorption, and occlusion cannot be entirely eliminated, but those caused by impurities, action of gases (atmospheric oxygen, or carbon dioxide), mechanical losses, volatility, etc., may be avoided. In many cases the errors have a compensating effect. W. P. S.

Flask for the Distillation of Frothing Liquids. E. Lenk. (*Chem. Zeit.*, 1920, **44**, 330.)—In the distillation of certain liquids under reduced pressure, frothing takes place at the beginning of the operation. To avoid loss due to frothing, the lower end of a vertical reflux condenser is sealed into the side of the neck of an ordinary distillation flask at a point below and opposite to the usual side tube; the latter connects with a condenser and receiver. At the commencement, the air in the apparatus is exhausted through the reflux condenser; any froth formed rises in this condenser (this has a bulbed inner tube), breaks in the latter, and the liquid returns to the flask. When frothing ceases, the tap of the reflux condenser is closed, and the distillation proceeded with in the usual way. W. P. S.

Substitutes for Platinum Wire in Bead and Flame Tests. C. C. Kiplinger. (*J. Ind. and Eng. Chem.*, 1920, **12**, 500.)—To avoid waste of platinum wire or alloyed platinum wire, the author recommends the use of the "lead" in lead pencils for making bead tests. If not too large, the borax bead adheres firmly to the graphite, yet the cold borax glass may be readily removed by a knife; the reducing action of the carbon does not seem to interfere materially. Another device is the use of a clean iron nail, which can be easily cleaned and burned free from sodium; in general, the spectra of the iron salts do not interfere. A modification is described of a method used by Ehringhaus in which a strip of filter-paper is wetted with the solution to be tested and held in the flame, or one end of the paper is placed in the solution and the other in the flame. It is possible to eliminate the carbon flame which interferes with direct-vision work by supporting the burner horizontally on a stand and bringing the upper edge of the paper wick barely within the bottom portion of the flame; the salt solution is thus vaporised and colours the flame with a minimum consumption of paper. H. F. E. H.

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REPORTS.

MINISTRY OF FOOD: OILS AND FATS BRANCH.

Report by the Committee of Analysts on Standard Methods of Analysis of Seeds, Nuts and Kernels, Fats and Oils, and Fatty Residues.—A Committee of Analysts was appointed by the Director of Oils and Fats in November, 1918, to consider the settlement of standard methods of analysis of oil-seeds, fats and oils. The terms of reference of the Committee were as follows:

1. To determine the ingredients affecting the value of any of the scheduled articles.

2. To consider the usual limits of constants for good merchantable quality of the scheduled articles.

3. To arrange standard tests for all the scheduled constants for scheduled articles, and special tests.

The following took part in the deliberations of the Committee: Otto Hehner (Chairman), John Allan, G. H. Appleyard, E. R. Bolton, J. L. Buchanan, Alfred Smetham, E. W. Voelcker, W. Ellard Woolcott.

11, Billiter Square, E.C.,
February 26, 1919.

The Director of Oils and Fats, Ministry of Food.

Sir,—The Committee of Analysts appointed by you have considered the questions embodied in the terms of reference conveyed to them at the meeting on November 13 last, and beg to submit herewith for the consideration of the Ministry of Food their report on the standard methods of analysis for oilseeds, nuts and kernels, fats and oils, and fatty residues. They present separately schedules of the data essential in defining the commercial value of particular oils, and of some of the standards governing "good merchantable quality." Other data will probably have to be added later.

The Committee have held fourteen meetings, and those members who have not been able to be present at the meetings have collaborated by correspondence.

I am, sir,
Your obedient servant,
(*Signed*) Otto Hehner
(*on behalf of the Committee of Analysts*).

Part I.—Determination of Oil in Seeds, Nuts and Kernels.

1. Extract a weighed quantity of the sample prepared for analysis with petroleum ether* in a suitable apparatus for two hours. Remove the partially extracted material, dry, grind in a mortar (grinding may be facilitated by the addition of 1 grm. of fine sand), and again extract until exhausted. If the sample contains a large percentage of oil it is advisable to grind twice, extracting after each grinding. Evaporate off the solvent, dry at 100° C., and weigh. In the case of oils liable to rapid oxidation, like linseed, drying should be conducted in an inert atmosphere.

2. The extracted oil must be free from solid matter and completely soluble in petroleum ether.

3. In the case of woolly cotton-seed special attention must be paid to obtaining an average sample. The seed must either be crushed by being passed through steel rollers and then thoroughly ground in an iron mortar, or well broken and ground in a mortar.

4. Owing to the variation both in the amount and composition of the oil in cross sections of the "meat" of copra, it is essential that the portion taken for analysis from the original sample be cut from the pieces at right angles to the rind.

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* Petroleum ether, volatile without residue at or below 60° C.

The copra must therefore be reduced by shredding or grating at right angles to the rind, or small pieces must be completely shaved down.

5. In the case of castor-seed the clean seed with the shell is ground in a mortar, which is covered to prevent loss of husk. The extraction must be more prolonged than is the case with other seeds, and is, as a rule, complete in eight hours.

Part II.—Fats and Oils.

6. In the sample of fat or oil the following constituents are first determined: moisture, organic dirt, ash, fatty matter (by difference)—total 100.

7. Upon the clear filtered fatty matter the following determinations are made: acid value, saponification value, unsaponifiable matter, iodine value.

8. The estimations and determinations shall be carried out according to the methods described below.

MOISTURE.—9. A U-tube, one limb of which is an ordinary narrow-bore glass tube, and the other a tube about 3 feet long and from 1¼ to 1½ inches in diameter (see appended sketch), is charged in its wider limb with soft blue Cape asbestos, which has been dried at 100° C. The wide limb is provided with a rubber stopper through which passes a narrow tube bent at right angles. The tube, without the stopper, accurately weighed, suspended by a wire, and about 2 grms. of the well-mixed sample of oil or fat are dropped on to the asbestos, and the whole reweighed. The stopper is then inserted, and the tube which passes through the stopper is connected with a Kipp apparatus supplying hydrogen, thoroughly dried by passage through strong sulphuric acid.

10. A U-tube, such as is used in elementary analysis, and provided with two glass taps, is filled with glass beads which are afterwards moistened with strong sulphuric acid. This tube is accurately weighed, after having previously been filled with dry hydrogen, and is then connected with the narrow limb of the asbestos-charged tube, the latter being suspended in a beaker containing water kept at a temperature about 10° C. above the m.-pt. of the fat. A slow current of hydrogen is now passed through the whole. When no trace of condensed moisture can be seen in the horizontal limbs of the oil tube and of the weighing tube, which is generally the case after one hour, the latter is weighed, then again attached, and a current of hydrogen allowed to pass for another hour. Minute traces of volatile organic matters, as a rule, produce a slight darkening of the sulphuric acid.

11. The asbestos may advantageously be used in the form of a very porous felt paper produced by pulping the asbestos and running the pulp into a centrifugal which is lined with linen.

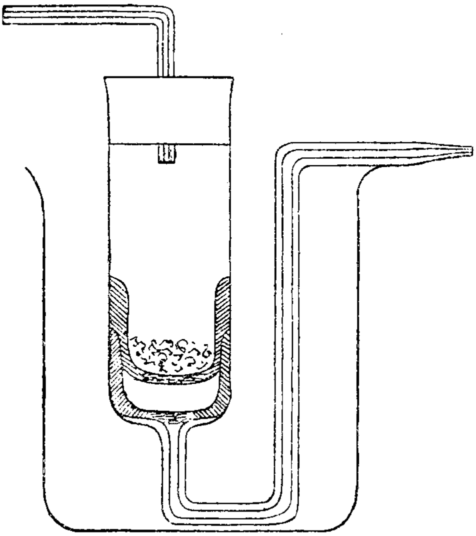
12. As an alternative method capable of dealing with a number of samples in one operation, stoppered weighing bottles of about the dimension of the wider limb of the U-tube used in the standard method may be charged with asbestos, or alternatively with strips of pleated blotting-paper or with paper pulp. These tubes are dried in a vacuum desiccator containing sulphuric acid, and kept at a pressure of 2 to 5 mm. After weighing, about 2 grms. of the fat or oil are placed in each tube, which is again weighed. The tubes are warmed till the fat is melted, and then

replaced into the vacuum desiccator. The air is exhausted and the desiccator is kept in an incubator at 20° C. for at least forty-eight hours. The weight after that time remains practically constant.

13. The standard method is applicable to all fats and oils, whether readily oxidisable, like linseed oil, or containing high percentages of free fatty acid of low molecular weight, such as lauric.

14. In the case of fats and oils which are free from uncombined fatty acid and not readily oxidisable, the ordinary methods of drying on sand in a water-oven may often be used, provided the results are in agreement with those furnished by the standard method.

Dirt and Ash.—15. The percentage of "dirt" in a sample of oil should be arrived at by direct estimation, and not by difference.



Apparatus for estimating Moisture in Oils and Fats.

16. In the case of a sample containing dirt of such a nature and size as to render it impossible to incorporate the whole of it uniformly throughout the sample, the whole of the sample should be strained through a 25 mesh wire sieve and the solid fragments picked out, weighed, and separately examined.

17. At least 10 grms. of the thoroughly mixed fat or oil is treated with about ten times its volume of hot paraffin oil (kerosene), the insoluble matter filtered off through a weighed filter, washed with hot kerosene, then with petroleum ether. The filter is dried in the water-oven to constant weight, incinerated, and the ash weighed.

18. The percentage of ash in the strained oil is determined.

19. The ash in the insoluble matter in the oil is deducted from the ash found in the oil, and this figure is taken as "soluble mineral matter."

Acid Value : *Definition.*—20. The acid value of a fat or oil is a measure of the free fatty acids present, and is defined as the number of mgrms. of potassium hydroxide required to neutralise the free fatty acids in 1 grm. of the fat or oil—*i.e.*, parts of potassium hydroxide which are required to neutralise the free fatty acids in 1,000 parts of the fat or oil.

Chemicals Required.—21. (*a*) Alcoholic alkali solution, $\frac{N}{10}$ and $\frac{N}{2}$ potassium or sodium hydroxide, accurately standardised. (*b*) Neutral alcohol, 94 to 95 per cent. (by volume), containing 0·2 grm. of phenolphthaleïn per litre. This may be conveniently prepared by redistilling industrial methylated spirits free from mineral oil over sodium hydroxide, adding the phenolphthaleïn, and subsequently neutralising.

The Test.—22. The necessary quantity of the fat or oil is carefully weighed into a 250 c.c. flask, and about 50 c.c. of the alcohol are added. The mixture is gently boiled, well shaken to thoroughly dissolve out the free fatty acids, and titrated while still warm, and with constant agitation, with $\frac{N}{10}$ alkali till the pink colour is permanent on shaking for ten seconds. Towards the end of the titration the alkali should be added drop by drop in order to avoid excess until the end point is reached.

23. As a rule, 5 grms. of the sample will be found a suitable quantity, but in the case of refined fats or oils this should be increased to 10 grms. If more than 10 c.c. $\frac{N}{10}$ alkali solution are required for the test, it should be repeated with $\frac{N}{2}$ alkali.

Then if X = number of c.c. of $\frac{N}{10}$ solution,
F = weight of fat or oil taken,

$$\text{Acid value} = \frac{X \times 5{\cdot}61}{F}.$$

24. In order to express the acidity in percentages of oleic acid, the following formula should be used:

$$\text{Oleic acid per cent.} = \frac{X \times 2{\cdot}82}{F}.$$

25. In the case of fats obtained from the kernels of the coconut group, such as coconut oil, palm, kernel oil, tucum, babassu, cohune, etc., the acidity is calculated as lauric acid, when the following formula should be used:

$$\text{Lauric acid per cent.} = \frac{X \times 2{\cdot}0}{F}.$$

SAPONIFICATION VALUE: *Definition.*—26. The saponification value represents the amount of potassium hydroxide required to neutralise the free and combined acid constituents of a fat or oil, and is expressed in terms of parts of potassium hydroxide per 1,000 parts of the fat or oil.

Solutions Required.—27. (*a*) $\frac{N}{2}$ hydrochloric acid accurately standardized. (*b*). An alcoholic solution of potassium hydroxide or sodium hydroxide, approximately $\frac{N}{2}$, prepared by dissolving 18 to 20 grms. of stick potassium hydroxide in not more than 10 c.c. of distilled water, and making up to 500 c.c. with 94 to 95 per cent. (by volume) alcohol, which may be prepared as in par. 21 (*b*). The solution is allowed to stand for twenty-four hours, and the clear liquid siphoned off for use. Potassium hydroxide may be replaced by sodium hydroxide, but this substitution is not desirable. The alcohol must be free from mineral oil and of such a purity as to yield a nearly colourless solution after twenty-four hours. (*c*) An alcoholic solution of phenolphthaleïn, 1 per cent.

The Test.—28. About 2 grms. of the clear filtered fat are accurately weighed into a 200 c.c. flask of resistance glass, 25 c.c. of neutral alcohol added, and 25 c.c. of the alcoholic potassium hydroxide solution accurately measured run in. A like quantity of the same solution is run in, in exactly the same way, into a similar flask, together with 25 c.c. of the neutral alcohol. The flasks are connected to reflex condensers and heated, preferably in a water-bath, so that the alcohol boils briskly for thirty minutes. The flask containing the fat should be shaken with a rotary movement from time to time during the period. The contents of the flasks are then titrated while hot with the $\frac{N}{2}$ acid, after the addition of 1 c.c. of the phenolphthaleïn solution.

If F = grms. of fat taken,
X = c.c. of acid required in the control experiment,
Y = c.c. of acid required to neutralise the excess of alkali in the test,

$$\text{Then saponification value} = \frac{X - Y \times 0{\cdot}02805 \times 1{,}000}{F}.$$

$$\text{N.B.—The saponification equivalent} = \frac{561000}{S},$$

Acid Value and Saponification Value (Combination Method).—29. The acid value and saponification value may, if so desired, be determined upon the same weight of the sample in the following manner:

30. About 4 grms. of the clear filtered fat or oil are accurately weighed into the saponification flask, and 25 c.c. of hot alcohol containing 1 c.c of phenolphthaleïn solution, and previously neutralised, are added. The free fatty acids are titrated from a burette with the alcoholic alkali solution as used for the saponification value, warming if necessary during the titration. The number of c.c. required by the free fatty acids having been noted, such a further quantity of alcoholic alkali as will make a total of 50 c.c. is added, and the process continued as described above.

31. A blank test is made with 50 c.c. of the alcoholic alkali delivered from the identical burette, using similar quantities of all the reagents. The exact value of the alcoholic alkali having been determined with $\frac{N}{2}$ hydrochloric acid, the acid value and saponification value may be respectively calculated.

Unsaponifiable Matter.—32. Unsaponifiable matter in fats and oils includes all substances which are insoluble in water but soluble in the fat solvents specified below after alkali saponification of the fats and oils.

33. Saponify 5 grms. of the sample with 50 c.c. approximately normal alcoholic KOH, boiling under a reflux condenser for sixty minutes with occasional shaking. Transfer the alcoholic solution to a separating funnel; rinse the flask successively with 50 c.c. of methylated ether, 50 c.c. of petroleum ether, and 50 c.c. of water. Transfer the rinsings to the separating funnel, shaking well after each addition. Allow to separate, and withdraw the soap solution. Repeat the extraction of the soap solution twice, using ether and petroleum ether as before, omitting the treatment with water. The combined ethereal extracts are washed by shaking with slightly alkaline water, allowing to settle, and run through a filter into a tared flask. Wash the filter

with petroleum ether, distil off the solvents, dry at 100° C., and weigh the saponifiable matter.

IODINE VALUE: 34. *Reagents Required:* (*a*) *Iodine Solution.*—35. This is conveniently prepared by dissolving 7·5 grms. of iodine trichloride in acetic acid (minimum strength 95 per cent.), and solution may be hastened by warming on a steam bath. When dissolved, add to the solution 8·2 grms. of resublimed iodine, assist solution by heating as before, and make up to 1,000 c.c. with acetic acid (95 per cent.) The solution is standardised by means of a blank test carried out at the time that it is used, which should be at least twenty-four hours after it is made up. If the solution is heated for a short time by immersion in boiling water, it may be used immediately after cooling.

(*b*) *Sodium Thiosulphate Solution.*—36. Dissolve 24·8 grms. of the pure salt in 1 litre of distilled water. It is advisable to add 0·5 grm. per litre of sodium bicarbonate to the solution as a preservative. This solution must be standardised by titrating it against pure dry resublimed iodine, but where this is inconvenient the iodine may be liberated from potassium iodide by a known amount of potassium dichromate in the presence of hydrochloric acid. As the oxidising value of potassium dichromate does not always correspond accurately with that of an equivalent amount of iodine, the potassium dichromate to be used as described below shall first be set against pure dry iodine. The titration is carried out as follows: Weigh 0·20 grm. of pure recrystallised $K_2Cr_2O_7$ into a 200 c.c. stoppered bottle, dissolve in 25 c.c. distilled water, add 20 c.c. 10 per cent. potassium iodide solution and 10 c.c. pure HCl, moisten the stopper with the KI solution, and allow to stand five minutes. Wash down the stopper with distilled water, dilute to about 100 c.c. volume, and titrate the liberated iodine with the sodium thiosulphate solution, using starch solution as indicator. A blank test, using the potassium iodide solution and hydrochloric acid alone, should be carried out, and the necessary deduction, if any, made from the previous titration.

$$0{\cdot}2 \text{ grm. } K_2Cr_2O_7 = 0{\cdot}51768 \text{ iodine.}$$

(*c*) *Potassium Iodide Solution.*—37. A 10 per cent. solution of the pure salt in distilled water.

(*d*) *Solvent.*—38. Chloroform or carbon tetrachloride to be used as a solvent for the oil. A blank test on the solvent must not show an absorption of iodine equal to more than 0·2 c.c. of the thiosulphate solution.

(*e*) *Starch Solution.*—39. Use a 1 per cent. solution of soluble starch.

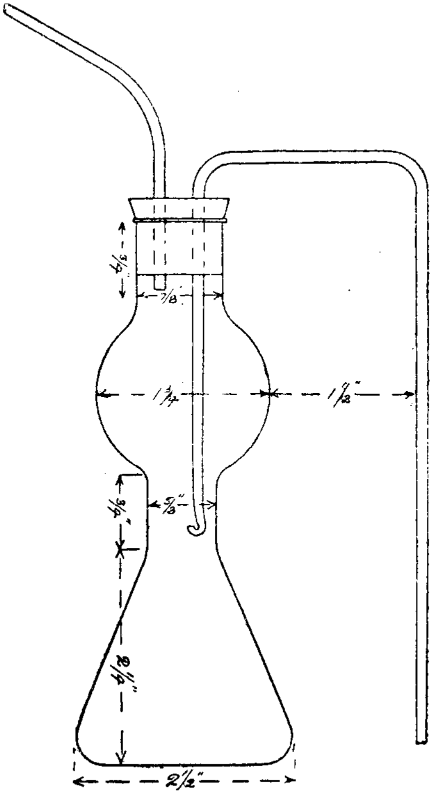
Method.—40. 0·15 to 1 grm. of the sample is weighed into a wide-necked stoppered bottle of about 200 c.c. capacity; 0·15 grm. of a strongly drying oil and a proportionately larger amount for oils or fats of lower iodine value, up to approximately 1 grm. for such fats as coconut and the like. Dissolve the weighed quantity of fat or oil in 10 c.c. of the solvent (*d*) and add 25 c.c. of the iodine solution, moisten the stopper with potassium iodide solution, and allow to stand for one hour. In the case of fats having a very high iodine value like linseed, allow to stand for three hours.

41. After standing, wash the stopper and neck of the bottle down with 15 c.c. of

the 10 per cent. potassium iodide solution, mix, and add 100 c.c. of distilled water, and titrate the excess of iodine with the sodium thiosulphate solution. Towards the end of the titration add about 2 c.c. of the starch solution, and shake vigorously after each addition of the thiosulphate solution until the contents of the bottle are colourless.

42. A blank test, using 10 c.c. of fat solvent and 25 c.c. of the iodine solution, must be done with each set of estimations, or at least once daily.

43. The result is expressed as per cent. of iodine reacting with the fat.



SEPARATING FLASK

44. N.B.—Where a large number of liquid oils have to be tested it may be convenient to weigh them by dropping them from a small lipped tube and ascertaining the weight taken by difference, while solid fats can be arranged in small cubes on a suitably-sized glass plate and picked up with a pin which has been tared along with the whole, in this case also the weights of the successive pieces are determined by difference until the last piece has been weighed.

SPECIFIC GRAVITY AND VISCOSITY.—45. It cases where it is desirable to determine the specific gravity or the viscosity of an oil or fat, the specific gravity shall be determined by the ordinary standard methods and viscosity by the Redwood viscometer.

TITER TEST.—46. In cases where it is desirable to determine titer the method to be adopted is that prescribed by the Seventh International Congress of Applied Chemistry. This method is given in full in J. Lewkowitsch's "Chemical Technology of Oils and Fats," fifth edition, 1913, vol. i.

Part III.—Fatty Residues: Evaluation of Soap Stock, Acid Oils and Fatty Acids, Cotton Oil, Black Grease and Mucilage.

47. A weighed quantity of the sample (sufficient to give from 1 to 2 grms. of fatty extract) is introduced into a separating flask as illustrated, 10 to 20 c.c. of hot water are added, followed by one drop of methyl orange and a sufficient excess of hydrochloric acid to insure the decomposition of soap; 5 grms. of salt are added, and the mixture is heated gently until the acids separate in a clear layer.

48. The contents of the flask are allowed to cool to about 30° C., and 20 c.c. of petroleum ether and the liquors are gently agitated, and water is added until the junctions of the water and ether rises to the bottom of the centre constriction. When the separation is complete the ether is blown off by means of a siphon and, if necessary, filtered into a weighed flask, 10 c.c. of petroleum ether are introduced into the separating vessel, and again siphoned off. Two further portions of 10 c.c. of petroleum ether are then used, and in these latter cases the flask is closed with a stopper, and gently inverted two or three times after each addition of ether.

49. The mixed ethereal extracts are distilled and the residue dried at 100° C. and weighed.

Report by the Committee of Analysts on Standards of Good Merchantable Quality.—Members of the Committee of Analysts: Otto Hehner (chairman), John Allen, G. H. Appleyard, E. R. Bolton, J. L. Buchanan, Alfred Smetham, E. W. Voelcker, W. Ellard Woolcott.

11, BILLITER SQUARE, E.C.
March 5, 1919.

TO THE DIRECTOR OF OILS AND FATS, MINISTRY OF FOOD.

SIR,

1. In the terms of reference submitted to us by you at our first meeting on November 13, 1918, we were asked to arrange standard tests for all constants and all schedules for oil seeds, nuts and kernels, and oils and fats. We have already communicated to you the results of our deliberations on this point.

2. We now forward for your consideration our report on the two other terms of reference which we have interpreted as follows: (i.) To determine the ingredients affecting the value of any of the scheduled articles; (ii.) to consider the usual limits of constants for good merchantable quality of the scheduled articles.

3. STANDARDS FOR VEGETABLE OILS.—An official schedule for vegetable oils, home manufactured, good merchantable quality, was submitted to us embodying a blank schedule for the insertion of standards and constants under several headings. After due consideration we decided that although all of these particulars are of interest to analytical chemists it would not be practically useful to insert the whole

of these in a contract. We therefore decided to limit our recommendations to those characteristics which have an immediate bearing on the commercial value of the oil.

4. We recommend the following standards for oil of "good merchantable quality" on the understanding—(i.) that such oils shall be free from foots and foreign matter (a mere compliance with the standard prescribed does not furnish proof of purity). (ii.) That an allowance should be made to the buyer or the seller for any deviation from these standards.

The figures are based on records covering, in some cases, a considerable period of years, and have been selected as representing a fair average, and as tending to raise rather than lower the existing standard.

5. We realise that other considerations actually enter into the value of different oils, specially those required for edible purposes. There is at present a very great difficulty in defining systematically such qualities as colour, turbidity and odour, but it might be possible eventually to secure such a definition.*

6. SEEDS, NUTS AND KERNELS ("GOOD MERCHANTABLE QUALITY").—We have also considered the definition of "good merchantable quality" in the case of seeds, nuts and kernels. In this case, too, we have selected the figures from records which different firms have been kind enough to make available, and have sought to establish an average which will tend to the general improvement of the product. In some cases, where the same kind of produce is imported from widely differing sources, there is necessarily a good deal of variation. Moreover, produce coming from the same source is liable to differ in standard from year to year, and at different periods of the same year.

7. We have, nevertheless, come to the conclusion that it would be a great advantage to have standards that might be applied with an allowance, over or below, to the seller or to the buyer, for all kinds of produce. We think that such standardisation, even in the case of crops varying so much as cotton-seed and linseed from place to place and year to year, would tend to the improvement of the produce, and to better conditions of storage and transport. We have therefore given standards for one or two classes with a view to simplification.

8. The standards which we suggest are calculated on the pure produce, and assume that the determination of shell and dirt has already been carried out. The question whether the oil content of any oleiferous admixture which is not pure produce should be estimated depends on the terms of the contract, and is a commercial matter on which we are not competent to offer a recommendation. As, however, impurities are usually the same kind from the same country of origin, it might be possible to fix an average oil content, if this were required, for the foreign oleaginous admixture.

9. The data in the schedule which we propose conform to those already adopted for the West African Contract, but we have included data for other seeds, nuts and kernels which are not covered by that document. The schedule is as follows:

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* We understand that a Sub-committee of the Oils and Fats Committee of the Food Investigation Board are now considering the question of palatability of edible oils, and that further research into the general question is in contemplation.

Schedule.

(Oil of "good merchantable quality" shall be free from foots or foreign matter, and shall conform to the following standards.)

Oil.	Percentage of Free Fatty Acids (Oleic, except where otherwise stated).	Percentage of Moisture not exceeding—	Percentage of Unsaponifiable Matter.	Other Standards.
Linseed Oil—				
Raw	2	0·25	1	Iodine value (Wijs) 185.
Refined	2	0·25	1	,, ,, ,,
Cotton Oil—				
Crude, Indian ...	2·5	0·25	1·5	
,, Egyptian ...	4			
Technical Refined ...	0·3			
Common edible ...	0·3			
Fine edible ...	0·15			
Ground-nut Oil—				
Crude	4	0·25	1	
Fine edible ...	0·15			
Sesame Oil—				
Crude	3·5	0·25	1	
Fine edible ...	0·15			
Rape Oil—				
Crude	1	0·25	1	Specific gravity, 0·915. Viscosity, Redwood standard.
Technical Refined ...	1			
Fine edible ...	0·1			
Palm-kernel Oil—				
Technical	5 lauric	0·25	1	
Fine edible ...	0·1 ,,			
Castor Oil—				
Pharmaceutical ...	1	0·25	1	Specific gravity, 0·963.
Firsts	1			
Seconds	4			
Soya Oil—				
Crude	2·5	0·25	1	
Fine edible ...	0·15			
Maize Oil—				
Crude	3	0·25	2	
Fine edible ...	0·15			
Coconut Oil (Technical)—				
Cochin quality ...	1 lauric	0·25	1	
Ceylon	2			
Copra	4			
Fine edible ...	0·1			

SCHEDULE OF STANDARDS FOR SEEDS, NUTS AND KERNELS.

	Oil Content.	Percentage of Free Fatty Acids* in Extracted Oil.
Babassu	66	2 (lauric).
Castor-seed	47	1
Copra	66	2 (lauric).
Cotton-seed, Egyptian type	22	3
,, Indian ,, ...	18	2
Benni-seed, gingelly or sesame ...	54	3
Decorticated ground-nuts	48	6
Undecorticated ground-nuts	37	2
Linseed	38	1·5
Mowrah	58	—
Palm-kernel	52	6 (lauric).
Rape-seed	43	2
Shea-nuts	46	10
Soya	17	2

* Calculated as oleic unless otherwise stated.

10. ANALYSIS OF FEEDING STUFFS.—The method of analysis of oil-cake is prescribed under the Fertilisers and Feeding Stuffs Act. As the use of petroleum ether as a solvent has been agreed upon for oleaginous seeds, nuts and kernels, we should like to suggest that the Board of Agriculture be invited to consider the use of the same solvent for oil-cake on the ground that ether at present prescribed as the solvent has a tendency to extract from oleaginous materials non-fatty substances.

11. The schedules referred to us did not include animal fats, but we are willing to investigate these if desired.

We are, Sir,
Your obedient servants,
(*Signed*)
(*The Committee of Analysts.*)

* * * * *

REVIEWS.

Quantitative Analysis by Electrolysis. By Alex. Classen, with the co-operation of H. Cloeren. Revised, rearranged, and enlarged English edition by W. T. Hall. Pp. xiii + 346. New York: J. Wiley and Sons, Inc.; London: Chapman and Hall, Ltd., 1919. Price 17s. 6d. net.

The appearance of a new English edition of Classen's well-known book will be generally welcomed. The present edition is a revision by W. T. Hall of a translation of his which was published about six years ago.

To the majority of English readers Classen's book is probably known from B. B. Boltwood's translation of the fourth German edition, and to these the present volume will appear practically as a new book. The theoretical introduction has been entirely rewritten. It occupies about a third of the book, and gives a good account of the subject. The apparatus is clearly described, and details of most of the methods of rapid electrolytic analysis are supplied, the apparatus in use in the author's laboratory being more fully dealt with. In the practical part it will be found that in agreement with the results of modern work on the subject simple electrolytes have, wherever possible, been given the preference over complex ones. The methods of determination and separation of metals based upon the control of the potential of the cathode are dealt with both in the theoretical and the practical part. The processes emanating from Edgar F. Smith's laboratory for the determination and separation of the metals of the alkali and alkaline earth groups and for the simultaneous estimation of anions have been included. A special part is devoted to the analysis of commercial products. The work of the translator has been well performed throughout, and several additions have been made by him. Thus in the practical part a number of new methods will be found, and the more important data, such as equilibrium and over-voltage, are stated at the head of the section dealing with each element. In the theoretical part the history of electrolytic analysis has been extended by a short account of the history of theoretical electrochemistry, in which the modern views of the structure of the atom and of the process of ionisation are discussed. A theoretical chapter has also been added dealing with electrometric titrations and the applications of potential and conductivity measurements; the matter is, however, not again referred to in the practical part. The book may be thoroughly recommended to technical and teaching laboratories. H. J. S. Sand.

The Chemistry of Coal. By John B. Robertson. London: Gurney and Jackson, 1919. Price 3s. 6d. net.

This little monograph is divided into two distinct sections; in the first it has been the aim of the author to show the chief methods by which the problems of coal constitution have been attacked, and to outline some of the more interesting results obtained. In the first five chapters a useful summary is given of the theories of coal formation and the work which has been done by the aid of solvents, by oxidation, and by destructive distillation, with a view to throwing light on the constitution of coal.

Chapters VI. to IX. deal with sampling, analysis, and calorimetry of coal. There is nothing novel in this section, but the methods are well described, and the author has found them successful in practice, and attention is drawn to sources of error which are sometimes overlooked. The calorimetric bomb method is described very clearly, but exception must be taken to the author's statement that the *technical heat value* differs from the determined calorific value by the latent heat of the steam condensed to water in the bomb. The result so obtained (the net value) is a mere convention; it takes no account of the sensible heat in the water vapour escaping at flue-gas temperature in practice—an amount different in every boiler plant. In his concluding chapter he deals briefly with "The Properties of Coal on Combustion." Altogether the book is well written, and is a useful little addition to the books on coal.

J. S. S. BRAME.

FUEL PRODUCTION AND UTILISATION. By H. S TAYLOR, D.Sc. London: Baillière, Tindall and Cox, 1920. Price 10s. 6d. net.

Dr. Taylor has certainly produced a book which, as he states in his preface, shows points of divergence from the standard textbook on "Fuel." He is modest in his claim, for his book is conceived on quite different lines to the ordinary textbook, and has been admirably arranged. The textbook, on orthodox lines, serves a most useful purpose; it is indispensable to the ordinary student, and Dr. Taylor's book as a supplementary treatise on fuel dots the i's and crosses the t's. It is largely compiled from the valuable publications on fuel resources and their efficient utilisation which have been issued by the United States and the Canadian Bureau of Mines, and from other authoritative sources.

One may safely say that every phase of the fuel problem receives adequate treatment, particularly the minor fuels and the utilisation of waste fuels. These may appear to be more fully treated than their present importance warrants, but in view of their undoubted future importance, with the great rise in price of the more staple fuels, this full discussion is to be welcomed.

The chapter on synthetic fuels, which concludes the volume, will be found of very considerable interest, dealing as it does with acetylene, "the synthesis of liquid hydrocarbons from coal," synthetic alcohol and benzol. Hexamethylene (cyclohexane), referred to in an earlier chapter, might well have been included here.

Dr. Taylor has in many cases drawn at considerable length from his authorities, but his selection of material has been excellent, and it is no disadvantage to have the statements in the words of the responsible authors. In one direction only has the author made what may be regarded as a mistake, and that is in sometimes quoting costs and estimates based on pre-war figures. Unfortunately, prices like one shilling per thousand cubic foot for coal-gas and the same price for a gallon of petrol are to-day but reminders of a happy state of things which existed "once upon a time"—a phrase we learn in childhood to associate with fairy tales!

J. S. S. BRAME.

MANUAL OF THE CHEMICAL ANALYSIS OF ROCKS. By HENRY S. WASHINGTON, PH.D. Third Edition, revised and enlarged. 1919. New York: John Wiley and Sons, Inc, London: Chapman and Hall, Ltd. Price 11s. 6d. net.

This well-known work now appears in its third edition. It describes in detail the analysis of a typical silicate-rock, and the methods employed will give results as accurate as is possible with our present-day knowledge. The introduction is followed by a general discussion on apparatus and reagents, sampling, and methods. Then the procedure needed for determining the individual constituents is treated in detail. These methods can now be regarded as having been more or less standardised by use.

There are many traps in the analysis of silicates, and it is only with the confidence of ignorance that these analyses have been undertaken by skilful analysts unprepared for the peculiar errors to which the analyses are susceptible. The $100 \pm x$ per cent. total is not necessarily a satisfactory check, since if one constituent is high, another will be proportionally low. As a result, a comparatively large percentage of published analyses, even where conscientiously performed, are altogether useless. Here are two recent analyses of the same dried clay reported upon commercially by two independent men. The figures are rounded to the first decimal:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	Loss on Ignition.
(1)	73·6	—	12·5	4·1	0·04	0·01	2·12		7·7
(2)	51·9	1·1	17·5	8·4	4·4	3·2	3·9	1·4	7·8

Here is another pair of analyses of another dried clay reported by the same two independent sources:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	Loss on Ignition.
(3)	63·0	—	6·8	3·9	3·2	5·6	1·9		15·6
(4)	35·3	0·6	14·4	3·7	8·3	12·9	3·5	0·9	20·2

The writer can guarantee that analyses (2) and (4) were conscientiously performed, but the differences between (1) and (2) and (3) and (4) are so great that it is inconceivable that even Washington's book would be of any assistance to one of them, for these numbers must have been obtained by a parasite on the profession—namely, the *guessing analyst.*

Although silicate analyses can be conducted with a high degree of accuracy, the methods unfortunately occupy an inordinately long time—four or five days. A great deal of platinum ware also is needed for the operations. This all accentuates the cost of a commercial analysis. The cost of platinum for chemical and other important work is now so high that it is time the demand for this indispensable metal was relieved by prohibiting its use in the manufacture of jewellery for ornamenting the fair sex.

J. W. MELLOR.