THE ANALYST.

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

AN ordinary meeting of the Society was held on Wednesday evening, May 2, in the Chemical Society's Rooms, Burlington House. The President, Mr. G. Embrey, F.I.C., occupied the chair.

The minutes of the previous ordinary meeting were read and confirmed.

A certificate of proposal for election to membership in favour of Captain N. M. Comber, B.Sc., A.R.C.Sc., was read for the second time; and certificates in favour of Messrs. Charles V. Bacon, 3, Dey Street, New York, analytical and consulting chemist; and Kapilram Hardevram Vakil, B.A. (Bombay), B.Sc., Tech. (Manchester), Ivyhurst, Burlington Road, Altrincham, analyst and consulting chemist, were read for the first time.

The following papers were read: " A Rapid Method for Estimating Nickel and Cobalt in Alloys," Part I., by W. R. Schoeller, Ph.D., and A. R. Powell; " Note on Opium-Poisoning Cases," by John Webster, F.I.C.; and " Determination of Unsaponifiable Matter in Oils, Fats, and Waxes," by John M. Wilkie, B.Sc., F.I.C.

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A RAPID METHOD FOR ESTIMATING NICKEL AND COBALT IN ORES AND ALLOYS.—PART I.

BY W. R. SCHOELLER, PH.D., AND A. R. POWELL.

(Read at the Meeting, May 2, 1917.)

THE present investigation, referred to in the reply to the discussion on the authors' previous paper (Analyst, 1916, **41**, 124), is an endeavour to elaborate a quick method for assaying materials containing nickel and cobalt. Though the experimental work on the new method is not yet concluded, we consider the encouraging results so far obtained justify the publication of this paper, as the information may be of use to analysts dealing with the metals in question. An account of the complete investigation will be given later.

We do not lay claim to having discovered the reaction on which the process is based, it having been shown some years ago that potassium iodide precipitates

nickel in ammoniacal solution; this reaction was stated to afford a means of separating nickel from zinc.   The idea occurred to us that nickel, and cobalt also, might be separated from other metals by this method.   Apart from a patent claiming the separation of nickel from zinc, copper, etc., by means of an excess of alkali chloride and ammonia added to a solution of the mixed chlorides (*J. Chem. Soc.*, 1904, **85**, ii., 128), nothing could be found in the technical literature concerning such separation. Qualitative tests proved that nickel solutions treated with excess of strong ammonia and potassium chloride, bromide, or iodide, gave pale mauve crystalline precipitates; cobalt solutions under the same conditions yielded similar, flesh-coloured precipitates.   By their mode of formation, these precipitates were presumably compounds of the metallic halides with two, four, or six molecules of ammonia, the description of which may be found in Gmelin-Kraut's " Handbuch der anorganischen Chemie " (7th ed., vol. v., part 1, 95, 265).   We have adopted Werner's nomenclature (Werner, " Neuere Anschauungen auf dem Gebiete der anorganischen Chemie ") in referring to these substances, the composition of which was ascertained (in the case of the iodides) by dissolving the precipitate, obtained from a known weight of metal and washed free from ammonia with alcohol, in excess of $\frac{x}{5}$ acid, and titrating back with $\frac{x}{5}$ alkali.

$$\text{Ratio NH}_3 : \text{Ni found} : 6\cdot04 : 1.$$
$$\text{,,} \quad \text{NH}_3 : \text{Co} \quad \text{,,} \quad : 5\cdot94 : 1.$$

These figures prove the precipitates to consist of hexamminenickelous iodide, $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$, and hexamminecobaltous iodide, $[\text{Co}(\text{NH}_3)_6]\text{I}_2$.

An endeavour was made to substitute the cheaper alkali chlorides for the iodide, but the attempt had to be abandoned, as the precipitation was very incomplete. Potassium bromide in sufficient quantity gave a more complete precipitation, but the best results were obtained with iodide.   This is shown in Table I., in which the figures indicate the quantities of nickel and cobalt that passed into the filtrate after adding varying amounts of halide to 0·1 grm. of metal in 100 c.c. of solution containing 80 c.c. of strong ammonia.

TABLE I.

Halide added.	Nickel Solution.		Cobalt Solution.	
	+ KI.	+ KBr.	+ KI.	+ KBr.
1 grm.	0·0153 grm.	0·0406 grm.	Considerable.	Considerable.
2 grms.	0·0028 ,,	0·0076 ,,	0·0066 grm.	,,
3 ,,	0·0007 ,,	0·0053 ,,	0·0026 ,,	0·0155 grm
4 ,,	0·0005 ,,	0·0047 ,,	trace	0·0115 ,,
5 ,,	0·0002 ,,	0·0040 ,,	,,	0·0086 ,,

The figures show that, in presence of excess of iodide, the precipitates are sufficiently insoluble to · be utilised for quantitative purposes.   This excess of iodide

required was not recognised for some time, and much delay occurred before the cause of our low results was discovered.   Sufficient iodide must be added over and above the quantity required for precipitation (0·6 grm. KI per 0·1 grm. Ni + Co) to yield a solution containing 4 per cent. of the precipitant.   Table II. gives the minimum amount of potassium iodide required for complete precipitation.   It is added to the assay in cold saturated solution immediately after the ammonia, to avoid oxidation of the cobalt.

TABLE II.

Volume of Ammoniacal Solution.	Grms. Ni + Co in Solution.				
	0·05	0·10	0·15	0·20	0·25
60 c.c.	2·7	3·0	3·3	3·6	3·9
80 ,, ...	3·5	3·8	4·1	4·4	4·7
100 ,, ...	4·3	4·6	4·9	5·2	5·5

Other experiments proved that the concentration of the ammonia need not be regulated so strictly as that of the iodide ; but the volume of strong ammonia (sp. gr. 0·88) should be at least two-thirds of the total.   The authors always aim at four-fifths.   The bulk of solution should be kept as low as possible, and not greatly exceed 80 c.c.   Under these conditions the loss of metal in the filtrate is inappreciable.

With quantities of nickel or cobalt exceeding a few mgrms., the precipitation appears to be almost instantaneous; in all the test assays the solutions were never left to stand for more than ten to fifteen minutes before filtering.   Though very small quantities (e.g., less than 2 mgrms.) fail to precipitate within that time, precipitation may be induced by adding a small quantity of strong sodium sulphate solution, which, by double decomposition with the potassium iodide, causes a precipitate of potassium sulphate, more or less insoluble in strong ammonia.   This precipitate will carry down the metallic iodide.   Working in this manner, 0·00066 grm. of cobalt was recovered from 75 c.c. of solution containing 60 c.c. of ammonia, 4 grms. of potassium iodide, and 0·00088 grm. of cobalt; from a similar solution containing 0·00103 grm. of nickel, 0·00086 grm. was obtained.   The method is therefore not suitable for detecting or estimating traces of nickel or cobalt.

In filtering the iodide precipitate, the use of a filter pump would be of advantage, but we purposely carried out all filtrations at ordinary pressure, using a very loose filter-paper (Whatman No. 4) and carefully selected funnels.   In spite of the high filtering speed thus attained, the precipitate, being crystalline, never ran through the filter.   Water decomposes the precipitate with formation of basic salts; hence washing must be effected with a cold solution containing 800 c.c. of strong ammonia

and 40 grms. of potassium iodide per litre. A filtering flask fitted with a Bunsen valve is suitable as a wash-bottle, the side-tube being closed with the finger whilst blowing.

For the separation and estimation of nickel and cobalt, the washed precipitate is rinsed back with water, without removing the filter-paper from the funnel, through a short-stemmed funnel into the precipitation flask; the filter is washed with dilute hydrochloric acid and a small quantity of sulphurous acid to bleach the filter coloured by iodine, the washings being allowed to run into the flask containing the precipitate. The latter is now dissolved in a small excess of hydrochloric acid, more sulphite being added if required. The solution is then filtered through the same filter into a 300 c.c. beaker to remove any gangue or other insoluble material; it is now ready for the precipitation of cobalt ammonium phosphate, which may be titrated according to the authors' alkalimetric method (cf. our previous paper, loc. cit.). The ammoniacal filtrate containing the nickel is titrated with cyanide, no indicator being required, as the liquor already contains iodide; the small amount of sulphite, if not previously destroyed in the boiling, has not been found to interfere with the nickel titration.

The property of forming complex iodides insoluble under the conditions here described is not confined to nickel and cobalt, being common to several bivalent metals. The behaviour of the latter and of the commoner elements, when present in an assay based on this method, will now be considered.

Iron.—In presence of sufficient tartaric acid to prevent precipitation of the hydroxide (i.e., ten times the amount of iron present), ammoniacal solutions of ferrous salts yield a white precipitate of hexammineferrous iodide, $[Fe(NH_3)_6]I_2$; the ratio NH_3 : Fe found in duplicate titrations was 5·78 and 5·59 : 1. The figures are low because the white precipitate cannot be washed with alcohol without decomposition and oxidation, the colour gradually changing to rust-brown. Ferric salts in ammoniacal tartrate solution are not precipitated by iodide; and, provided the necessary excess of tartaric acid has been added (as shown by the pale green colour of the ammoniacal solution), a quantitative separation from cobalt and nickel by a single precipitation can be effected in this manner (see Ore A).

Manganese.—Manganous salts are precipitated in ammoniacal tartrate solution in the form of white pentamminemanganous iodide, $[Mn(NH_3)_5]I_2$; the estimation of the ratio NH_3 : Mn gave 5·00 and 5·13 : 1. The precipitate is more stable than the ferrous salt, but begins to decompose, with separation of manganic hydroxide, on removing the excess of iodide and ammonia by washing with alcohol.*

Manganese is not precipitated so readily as nickel or cobalt, hence a small quantity (e.g., 5 mgrms. or less) by itself fails to precipitate within the time allowed before filtration (ten to fifteen minutes); but in presence of nickel or cobalt much smaller quantities of manganese are carried down by the iodide precipitate. The problem of overcoming the interference of manganese is still under investigation;

* As far as the authors are aware, the ferrous and manganous iodides described above have not before been obtained by precipitation. Hexammineferrous iodide (Moissan, "Chimie minérale," tome iv., 339) and hexamminemanganous iodide (Abegg, "Handbuch der anorganischen Chemie," vol. iv., part 2, 711) have been prepared by the interaction of the anhydrous iodides and gaseous ammonia. Most polyammine iodides decompose on drying or by contact with water.

for the present the simplest procedure seems to be solution of the mixed iodide precipitate in a small excess of dilute acid, addition of excess of sodium acetate, and precipitation of nickel and cobalt by hydrogen sulphide.

Copper is not precipitated under the conditions of the assay (*i.e.*, in ammoniacal 4 per cent. iodide solution), though with a much higher concentration of iodide (about 10 per cent.) blue crystalline tetramminecupric iodide, $[Cu(NH_3)_4]I_2.H_2O$, is precipitated (Gmelin-Kraut, *loc. cit.*, vol. v., part 1, 953). In presence of nickel or cobalt, however, co-precipitation of copper takes place, and this is indicated by the blue colour of the precipitate; the precipitation of the copper is incomplete, as the filtrate always exhibits the familiar deep blue colour. Unlike manganese, very small amounts of copper (about 0·01 grm.) are not co-precipitated.

On dissolving a cupriferous cobalt-nickel iodide precipitate in dilute hydrochloric acid, cuprous iodide is precipitated with liberation of iodine. In presence of a slight excess of sulphur dioxide or a sulphite, quantitative precipitation of the copper ensues (Crookes, " Select Methods," 4th ed., 1905, 324). The filtering properties of cuprous iodide are much improved by boiling the liquid containing it; but, as the hot solution has a solvent effect upon cuprous iodide, due to soluble iodides and chlorides, it should be cooled to room temperature before filtration. The washing is carried out with cold water. This separation of copper from cobalt and nickel has been found very satisfactory. If it is preferred to remove copper as cuprous thiocyanate previous to the precipitation of cobalt and nickel, the filtrate from the thiocyanate is oxidised with nitric acid, boiled down almost to dryness, and treated with tartaric acid, ammonia, and iodide, as prescribed (Ore D). Copper, if not removed, would cause high results in the nickel titration.

Cadmium.—This metal is precipitated as white, crystalline tetramminecadmium iodide, $[Cd(NH_3)_4]I_2$; titration gave an NH_3 : Cd ratio of 3·74 : 1. This low result is probably due to loss of ammonia in washing; the identity of the precipitate can hardly be in doubt, as a compound answering the above formula has been obtained by the action of strong ammonia on cadmium iodide solution (Gmelin-Kraut, *loc. cit.*, vol. iv., part 1, 878).

Like manganese, cadmium is co-precipitated even if present in small quantity, and interferes with the subsequent estimation of cobalt as phosphate; however, the rare occurrence of cadmium except in zinc ores, from which cobalt and nickel are almost invariably absent, makes the possibility of its interference a remote one. If present, cadmium could be readily eliminated by passing hydrogen sulphide through the solution of the iodide precipitate faintly acidified with sulphuric acid.

Zinc has not been found to give any insoluble compounds with ammonia and potassium iodide, nor has co-precipitation been observed to take place in presence of nickel or cobalt.

Alkaline Earth Metals.—Barium occurs most commonly as, or can be converted into, sulphate, and in this form is eliminated at the same time as the insoluble gangue. Soluble lime salts do not interfere, strictly speaking, but if in large quantities they slowly crystallise out as a complex tartrate, with attendant risk of contaminating the cobalt precipitate in the phosphate separation. It is therefore advisable, in such a case, to evaporate the solution of the ore with 1 c.c. of strong sulphuric acid

to fumes, and take up with a little water followed by an equal volume of methylated spirit. The anhydrous calcium sulphate is filtered off and washed with 50 per cent. spirit; the alcoholic filtrate is boiled down until about 5 c.c. remain (see Ore B). Smaller quantities of lime need not be thus removed (Ore C).—Magnesium is without influence on the assay (Ore B).

Lead, Mercury, Silver.—Lead iodide is soluble in ammoniacal tartrate solution, and appears to be harmless. In dealing with large quantities of lead, recourse can always be had to the separation as sulphate, avoiding the use of an excess of sulphuric acid (as for lime).—Mercuric salts yield a complex iodide (probably $[Hg(NH_3)_2]I_2$: Gmelin-Kraut, *loc. cit.*, vol. v., part 2, 796) which slowly crystallises out in long glistening needles decomposed by water and acids, leaving insoluble mercuric iodide. —Silver is thrown down as a curdy white precipitate, the composition of which is uncertain; it is converted by dilute acids or water into the normal iodide, in which form it is removed by filtration.

Trivalent Metals.—The non-interference of ferric salts has already been mentioned. Nor is the presence of aluminium, chromium, antimony, or bismuth, objectionable, provided sufficient tartaric acid has been added.

Arsenic is a very common constituent of cobalt and nickel ores; nitric acid converts it into arsenic acid, which, under the conditions attained by the ordinary procedure, is without influence (Ore A). The simultaneous presence in an ore of large amounts of arsenic and magnesium (*e.g.*, as dolomite)—an unusual case— would necessitate a preliminary reducing roast, or fusion with soda-sulphur or soda-nitre mixture; otherwise the addition of tartaric acid and ammonia would cause precipitation of magnesium ammonium arsenate, which, by remaining with the iodide precipitate, would interfere with the separation of cobalt as phosphate.

Sulphur.—Sulphides (unless capable of being decomposed by hydrochloric acid) are oxidised by nitric acid to sulphates. Though the presence of the latter presents no real objection, the addition of the strong ammonia to a solution containing much copper and an excess of sulphuric acid may produce a blue precipitate of tetramminecupric sulphate, $[Cu(NH_3)_4]SO_4 . H_2O$, while addition of potassium iodide to the ammoniacal liquor causes precipitation of potassium sulphate. The bulk of precipitate to be washed out is thus increased, while potassium sulphate is apt to slowly crystallise out in the filtrate, which might be mistaken for incomplete precipitation. On treating the mixed iodide precipitate with hydrochloric acid, any tetramminecupric sulphate is converted into cuprous iodide, provided enough nickel or cobalt iodide is present; if not, sufficient potassium iodide must be added to complete the precipitation of the copper. If an ore is treated with sulphuric acid, as little as possible should be used, or the excess almost completely expelled (see under lime). If sodium iodide be used instead of the potassium salt, no precipitation of sodium sulphate takes place.

Chlorine.—Ammonium chloride, in quantities exceeding 0·5 grm., has a slight but distinct solvent effect upon the iodide precipitates, especially that of nickel. Hence, if hydrochloric acid has been used for opening up an ore, the excess should be expelled by boiling, and the chlorides formed destroyed by one evaporation with nitric acid to small bulk, carefully avoiding separation of basic salts. The required

amount of tartaric acid is then added, together with a minimum of hot water neces-
sary to dissolve it; the assay is cooled and treated with ammonia and iodide.

Citric Acid should not be used instead of tartaric, because it leads to low results;
it probably exerts a retarding effect on the precipitation.

Several examples will now be given of the application of the method to some
ores and metallurgical products of known composition, together with a brief descrip-
tion of the procedure followed in each case. A complete analysis of each sample
was made, disregarding elements present in minute quantities. The separation and
estimation of the nickel and cobalt in the complete analyses was carried out by various
standard methods other than electrolytic. In order to obtain an additional and
independent check on their results by the new process, we secured the co-operation,
with the courteous permission of Messrs. D. C. Griffith and Co., Assayers to the Bank
of England, of their chief chemist, Mr. Charles E. Barrs, who estimated the sum of
nickel and cobalt by electrolysis. The errors in the test assays of samples A to D
are calculated on the figures supplied by Mr. Barrs.

A.—SPEISS (TABLE III.).

One grm. was treated with nitric acid in a 200 c.c. flask and the excess of acid
boiled off. Five grms. of tartaric acid and 65 c.c. ammonia (sp. gr. 0·88) were added,
the solution being kept cool, and 4 grms. potassium iodide added in saturated solu-
tion. Filtered after ten minutes, washed with ammoniacal iodide solution till free
from iron; dissolved the precipitate in dilute hydrochloric acid, adding a little sodium
sulphite; filtered off insoluble matter through the same filter into a beaker. The
filtrate was then ready for nickel-cobalt separation. The time required for com-
plete assay in duplicate was two to two and a half hours.

TABLE III.

Ni + Co (C. E. Barrs): 12·31%.

Composition (per Cent.): Ni, 4·53; Co, 7·75; Fe, 54·03; As, 20·33;
S, 8·57; Insol., 4·06; Total, 99·27.

Exp.	Ni %.	Co %.	Sum %.	Error %.
46a	4·53	7·68	12·21	− 0·10
46b	4·61	7·80	12·41	+ 0·10
46c	4·58	7·33	11·91	− 0·40
50a	4·56	7·51	12·07	− 0·24
51a	4·56	7·74	12·30	− 0·01
51b	4·61	7·68	12·29	− 0·02

B.—BASIC ORE (TABLE IV.).

One grm. was dissolved in nitric acid in a porcelain basin, evaporated with 1 c.c. of strong sulphuric acid until fumes were given off, and taken up with 20 c.c. of water and 25 c.c. of methylated spirit. Filtered after half an hour, and washed with 50 per cent. spirit; the filtrate was boiled down to 5 c.c., adding 2 grms. of tartaric acid; cooled, and added 60 c.c. of strong ammonia and 4 grms. of iodide (saturated solution). Filtered after ten minutes, and washed with ammoniacal iodide solution. The precipitate was rinsed back and dissolved in dilute hydrochloric acid, and cuprous iodide filtered off as described under copper; the filtrate was then ready for cobalt-nickel separation. The time required was about four hours.

TABLE IV.

$Ni + Co$ (C. E. Barrs): 9·07%.

Composition (per Cent.): Ni, 6·66; Co, 2·40; Cu, 9·40; Fe, 3·00; Zn, 0·05; S, 13·72; SO_4, 4·54; $CaCO_3$, 32·36; $MgCO_3$, 26·80; Insol., 0·92; Total, 99·85.

Exp.	Ni %.	Co %.	Sum %.	Error %.
77h	6·61	2·41	9·02	− 0·05
78d	6·53	2·44	8·97	− 0·10
78e	6·43	2·50	8·93	− 0·14
78f	6·47	2·65	9·12	+ 0·05
78g	6·59	2·50	9·09	+ 0·02
80c	6·72	2·43	9·15	+ 0·08
80d	6·72	2·47	9·19	+ 0·12

C.—SULPHIDE CONCENTRATE (TABLE V.).

0·5 grm. was dissolved in nitric acid, the excess of acid removed by boiling, and 2 grms. tartaric acid, 60 c.c. strong ammonia, and 4 grms. of iodide were added. The subsequent treatment was similar to that described under B. The time required was about three hours.

Examples of low results due to insufficiency of potassium iodide are shown in Tables V. and VI.

TABLE V.

Ni + Co (C. E. Barrs): 21·12%.

Composition (per Cent.): Ni, 15·50; Co, 5·01; Cu, 21·03; Fe, 8·41; Zn, 0·48;
S, 44·52; CaCO$_3$, 2·86; MgCO$_3$, 0·97; Insol., 0·72; Total, 100·10.

Exp.	Grms. KI added.	Ni %.	Co %.	Sum %.	Error %.
57a	3	15·25	5·28	20·53	− 0·59
57b	3	15·25	5·10	20·35	− 0·77
83a	4	15·50	5·49	20·99	− 0·13
83b	4	15·50	5·65	21·15	+ 0·03
83c	4	15·47	5·65	21·12	0·00
83d	4	15·41	5·65	21·06	− 0·06

D.—MATTE (TABLE VI.).

0·4 grm. was dissolved in nitric acid, and the copper precipitated with thio-cyanate and sulphur dioxide. The excess of thiocyanate in the filtrate was destroyed by nitric acid; after boiling down to a very small bulk, 1 grm. tartaric acid, 60 c.c. strong ammonia, and 4 grms. iodide, were added. The precipitate was filtered off and washed with ammoniacal iodide solution, dissolved in hydrochloric acid, and titrated with cyanide without separating the minute quantity of cobalt, the brown colour of which was very conspicuous in all the titrations.

TABLE VI.

Ni + Co (C. E. Barrs): 41·74%.

Composition (per Cent.): Ni, 41·55; Co, 0·22; Cu, 37·50; Fe, 0·45;
S, 16·80; Insol., 2·91; Total, 99·43.

Exp.	Grms. KI added.	Ni + Co %.	Error %.
66a	3	41·36	− 0·38
66b	3	41·18	− 0·56
66c	4	41·78	+ 0·04
66d	4	41·75	+ 0·01
68a	4	41·82	+ 0·08
68b	4	41·78	+ 0·04

The method was further tested on three nickel-silicate ores, with the following results:

% Ni by—	Iodide Method.	Other Method.
Ore E	1·46	1·44
,, F	1·85	1·85
,, G	1·89	1·90

The experimental evidence proves that the new method is applicable to ores containing iron, copper, lime, magnesia, arsenic, or sulphur, and that it results in a considerable saving of time as compared with any other process. We trust in due course to be able to publish another paper dealing with the assay of manganiferous, lead-zinc, and argentiferous ores from Cobalt (Ont.), etc., as well as cobalt-steel and non-ferrous alloys; we are also working out a process for recovering the iodide from the ammoniacal filtrates and washings.

The greater part of the experimental work, which so far has necessitated over 300 estimations of cobalt and nickel, was carried out at the Sir John Cass Technical Institute.

APPENDIX.

Since the above paper was written, we were informed by Mr. J. H. Wells, who formerly assisted Mr. L. Parry, that the latter was the originator of the separation of nickel and zinc by potassium iodide and ammonia, the method having been published in the *Mining Journal*. The following is an abstract of the two brief communications by Parry dealing with the process (*Min. J.*, 1909, **85**, 728, 805):

In the course of a general analysis, the metals of the first two groups are precipitated by hydrogen sulphide; the filtrate is oxidised and precipitated with bromine, ammonia, and ammonium carbonate. The acidified filtrate is boiled down to 30 c.c., cooled and neutralised with ammonia; an excess of 10 c.c. is added, followed by 10 grms. of potassium iodide in 20 c.c. of water. The nickel precipitate is redissolved and the solution titrated with cyanide. In the filtrate from the nickel zinc is titrated with ferrocyanide.

Parry merely mentions that cobalt is also precipitated, and remarks that this separation of nickel and zinc affords a means of estimating them, in solutions free from metals of the preceding groups and from cobalt, which, for quickness and accuracy, cannot be surpassed. He also states that copper is co-precipitated, in which case the precipitate is blue instead of violet.

We submit that the method elaborated by us represents a considerable advance on that given by Parry, inasmuch as we separate both nickel and cobalt at the outset as hexammine iodides without a preliminary treatment by hydrogen sulphide or bromine and ammonia, the latter procedure for removing iron and manganese being quite unsatisfactory, as it gives low results, especially for cobalt. We have

also ascertained the best conditions for the quantitative precipitation of nickel and cobalt and the behaviour of the commoner elements in the assay, and have converted the original nickel-zinc separation into a method of general applicability for the estimation of nickel and cobalt.

DISCUSSION.

Mr. G. N. HUNTLY said the fact that the presence of iron did not interfere with the process was important, as the estimation of nickel and cobalt in the presence of iron was admittedly difficult, and although dimethyl-glyoxime gave a satisfactory separation of the nickel the reagent was expensive. With regard to the errors shown in the tables, perhaps the authors would say what was the unavoidable experimental error in the phosphate titration corresponding to one drop of the standard solution.

Dr. SCHOELLER said that the differences mainly arose in the separation of the nickel and cobalt from one another by the phosphate method, this being really more difficult than the iodide separation of nickel and cobalt from other metals; but in the phosphate method any cobalt that might be lost in the filtrate would count as nickel, while any nickel co-precipitated with the cobalt would count as cobalt. Although they preferred the phosphate separation as being much the quickest, the glyoxime and other methods might also be used, provided that a satisfactory separation of nickel and cobalt from other metals was obtained in the first place.

Mr. C. E. BARRS said that in estimating nickel and cobalt in the presence of iron he had usually resorted to the ether separation, which was fairly well known and satisfactory. In order to make sure of obtaining all the nickel and cobalt, a little iron might be allowed to go through also, as that did not interfere with the satisfactory carrying out of the electrolytic process. With regard to the phosphate method, the separation of the cobalt required practice, and even in experienced hands small errors were likely to occur, unless the addition of ammonia was carefully regulated. But, as the authors worked, nickel and cobalt replaced one another, so that the sum of the two could be taken, and confirmation of the separate amounts obtained in another way. The dimethyl-glyoxime precipitation also had its difficulties. Indeed, on one occasion he had failed to get a satisfactory separation, and had since been told that this was probably due to the fact that he was using an isomer of dimethyl-glyoxime which did not effect a separation.

Dr. SCHOELLER said that, as Mr. Huntly had remarked, the most satisfactory result of their work was the separation of iron from nickel and cobalt. In fact, provided sufficient tartaric acid was used, any trivalent metal would without difficulty be obtained in the filtrate, leaving the precipitate quite free.

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THE ESTIMATION OF UNSAPONIFIABLE MATTER IN OILS, FATS, AND WAXES.

By JOHN M. WILKIE, B.Sc., F.I.C.

(Read at the Meeting, May 2, 1917.)

IN spite of the simplicity of the underlying reactions, the estimation of unsaponifiable matter in an ordinary oil or fat is very often a troublesome operation. Usually 5 grms. of the oil or fat are saponified with about 50 c.c. of $\frac{N}{2}$ alcoholic alkali, and after evaporation to remove alcohol the resulting soap is dissolved in hot water and the unsaponifiable matter extracted with ether. But emulsification may occur, and a long period may elapse before satisfactory separation occurs. Archbutt and Deeley in a comprehensive treatment of the subject (" Lubrication and Lubricants," pp. 250-252) give useful directions as to the treatment to be adopted when emulsification has occurred; but it would obviously be much better to eliminate the factors that produce emulsification.

Assuming that the soap solutions are clean and free from suspended matter, the emulsification is mainly dependent on two factors—alcohol concentration and the volume ratio of ether and soap solution—and, to a minor degree, on temperature. Mitchell (J. Ind. and Eng. Chem., 1915, 7, 217-218 ; ANALYST, 1915, 40, 247) has pointed out that the alcohol water ratio should be 1 : 4, and that at this concentration the separation is almost instantaneous.

A constant alcohol concentration may be obtained by saponifying, evaporating to dryness, dissolving the soap in a known volume of water, and then adding a definite amount of alcohol. Alternatively one can eliminate evaporation by saponifying under a reflux condenser with $\frac{N}{2}$ alcoholic alkali of known composition, diluting with a definite volume with water, and extracting with ether in the usual manner, but the large volume of ether required renders this method unpractical.

To eliminate evaporation and the use of large volumes of ether, saponification with 2N alcoholic alkali under a reflux condenser was adopted.

The alcoholic alkali was prepared by dissolving stick potash in absolute alcohol and adjusted to 2N, saponification was carried out under a reflux condenser, and enough water was added to give a concentration of 20 per cent. by volume before addition of ether. It will perhaps be useful to give the method.

Weigh 5 grms. into a flask, add 12·5 c.c. 2N alcoholic potash, heat one hour or half, transfer to a separator with 50 c.c. of water, extract with 40, 30, 30 c.c. ether, unite the ether extracts in a separator containing about 20 c.c. of water. Without shaking, run off completely the wash water, and wash the ethereal solution by shaking vigorously with 2, 5, and 30 c.c. water; evaporate and weigh the residue.

In the ordinary way separation is as rapid as when ether and water are shaken together, though in cold weather it may be more sluggish; but, if the soap solution after drawing off from the first and second extractions is heated on the water-bath

until the dissolved ether obviously commences to distil, no trouble is experienced. In very warm weather it is sometimes an advantage to allow the separation to take place under reduced pressure by placing in running water for a few minutes.

The washing of the ethereal solution to remove adherent soap deserves more attention than is usually given. In my opinion it is best to wash with gradually increasing volumes of water; and it is a good plan to have a relatively large volume of water in the separator into which the ether extracts are decanted, this preliminary wash water being rejected without shaking; shaking with such a large volume of water results in the formation of an opalescent liquid which does not separate cleanly.

An experienced worker is able to carry out the operation from the completion of saponification in about thirty minutes, a period which is considerably reduced if a number of estimations are carried out simultaneously.

Sperm and similar oils may be treated as above, with the modification that a fourth treatment with 30 c.c. of ether should be given to ensure extraction.

The estimation of the unsaponifiable matter of a solid wax, such as beeswax, by the wet method presents great difficulty. The unsaponifiable matter is only sparingly soluble in ether, while the soaps of the wax acids are extremely easily hydrolysed, and, together with their products of hydrolysis, possess only a limited solubility in dilute alcohol.

So long as the proper precautions are observed to ensure that a small quantity accurately represents the bulk, it adds to rather than detracts from the accuracy to work on 0·5 grm. of beeswax, etc., rather than on a larger quantity. The experimental error involved in extracting, drying, and weighing 0·25 grm. of unsaponified matter, including the blank correction for the castor oil, is of an order which is small compared with the variations caused by increasing the weight taken; this is obvious, because the errors are not those of weighing, but of separation and manipulation, and these are less in proportion with a small than with a larger quantity.

Although the alcohol concentration and the volume of ether were varied, satisfactory separations could not be obtained. This behaviour of the beeswax soaps is well known and referred to in the standard books (Lewkowitsch, Allen, Archbutt and Deeley, etc.). As the difficulty is mainly of a mechanical nature, there was a possibility that, in the presence of sufficient soaps of the fatty acids usually occurring in oils, the beeswax soaps would behave normally. In the selection of the oil, weight was given to the property possessed by linseed and castor oils of dissolving hydrocarbons.

A mixture of 0·5 grm. beeswax and 4·5 grms. of castor oil was saponified with 12·5 c.c. 2N alcoholic potash. With a slightly higher alcohol concentration and increased quantities of ether, excellent working conditions were attained. Details of the method I used may be useful.

Saponify 0·5 grm. of the beeswax (truly representative of the bulk) and 4·5 grms. of castor oil with 12·5 c.c. 2N alcoholic potash for one hour, complete precisely as the ether method (already described), but use 40 c.c. water at 30° C. instead of 50 c.c. cold water, and extract with 50, 40, 40, 30 c.c. ether. Wash with 2, 5, 30 c.c. water, evaporate, and weigh. Apply a correction for the known unsaponifiable

content of the castor oil. Other solid waxes and lanolin (wool wax) may be treated precisely as beeswax.

A paper by Richardson and Bracewell ("The Analysis of Waxes, with Special Reference to Beeswax and Woolwax," *J. Soc. Chem. Ind.*, 1916, **35**, 161) illustrates the difficulties experienced when the conventional methods are followed in the estimation of unsaponifiable matter in waxes, which are avoided by the method above described.

During the last seven years, estimations of the unsaponifiable matter by this process have been made in a large number of samples of most of the ordinarily occurring fats and oils.

It will be seen that the figures obtained are in good agreement with those usually accepted for normal oils. It might be mentioned here that the unsaponifiable matter obtained from medicinal cod-liver oil is often distinctly crystalline.

	Percentage of Unsaponifiable Matter.	Number of Samples.
Castor oil	10·4 to 0·7	3
Cod-liver oil, medicinal	0·8 to 1·4	100
Lard	0·2 to 0·4	3
Linseed oil	1·0 ,, 1·5	13
Neat's-foot oil	0·5 ,, 1·2	23
Olive oil	0·7 ,, 1·5	62
Palm oil	0·5	1
Poppyseed oil	0·4 to 0·6	3
Rape (colza) oil	0·8 ,, 1·2	32
Whale oil	0·8 ,, 1·4	12
WAXES:		
Sperm oil	34·3 to 43·6*	22
Spermaceti	51·0 ,, 52·5	2
Beeswax, yellow	52·3 ,, 55·5	10
,, white	50·0 ,, 54·4	13
Lanolin (wool wax)	41·0 ,, 51·8†	19

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

* Recently samples have been met with unsaponifiable matter in the neighbourhood of 30 per cent. and saponification numbers about 140 to 150. Normal oils are distinctly difficult to obtain at present.
† These figures refer to samples obtained since the outbreak of war. Recently the composition has been more constant.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Analysis of Acetylsalicylic Acid (Aspirin). M. François. (*J. Pharm. Chim.*, 1917, **15**, 213-222.)—Acetylsalicylic acid should volatilise completely when heated; the odour of the vapours given off during heating will often indicate the presence of such substances as sugar, tartaric acid, quinine, etc., if these be contained in the sample under examination. Pure acetylsalicylic acid melts at 132° C.; owing to the fact that the acid tends to decompose and show a false melting-point when heated for some time in the neighbourhood of its melting-point, the oil-bath should be heated to 125° C. before the capillary containing the substance is introduced, and the temperature then raised at the rate of 1° per minute. When added to water containing ferric chloride, acetylsalicylic acid should not give a violet coloration during the first minute (absence of free salicylic acid). The quantity of acetylsalicylic acid in a sample may be found by determining the acid or saponification value, or both. Two samples of aspirin examined recently by the author contained—Magnesium sulphate, 53·2 and 46·4 per cent.; lactose, 38·9 and 46·6 per cent.; acetylsalicylic acid (mixed with free salicylic acid), 7·8 and 7·9 per cent., respectively.

The acetic acid residue in acetylsalicylic acid may be identified by treating the substance with an excess of calcium hydroxide and a small quantity of water filtering the mixture, evaporating the filtrate to dryness, igniting the residue thus obtained to destroy any traces of salicylate, and then applying the usual tests for acetic acid.   W. P. S.

Qualitative Identification of the Drugs containing Emodin. G. D. Beal **and R. Okey.** (*J. Amer. Chem. Soc.*, 1917, **39**, 716-725.)—Cascara, Rumex, Rhubarb, Frangula, Senna, and Aloes, are all supposed to owe their medicinal properties to the presence of some derivative of a methyl anthraquinone such as emodin, chrysophanic acid, or their homologues and isomers, or glucosides yielding these compounds on hydrolysis. The extracts of the drugs used in testing were as a rule made by shaking one part of the fluid extract, or of a solution made by extracting a solid drug preparation with boiling 50 per cent. alcohol, with four parts of an immiscible solvent, allowing the mixture to settle, and drawing off the solvent for use. Ethyl ether, benzene, and amyl alcohol, were the most satisfactory for this purpose. The following tests were then applied: (1) Directly to the solutions in the above solvents: the nitration, mercurous nitrate, nickel acetate, lead subacetate, iodine, and borax tests. (2) To the residues obtained by evaporating the solutions described above: the nitration test. (3) To the resins precipitated by adding the concentrated alcoholic extracts of the drugs to an excess of water: the sodium peroxide test. All the colours obtained in these tests were named according to the Milton Bradley Company scheme found in Mulliken's " Identification of

Pure Organic Compounds." The authors have devised colour tests that will serve to detect rhubarb, senna, and freshly prepared fluid extract of cascara, in almost any proportion likely to be present in a commercial mixture. The mercurous nitrate test has been successfully applied to aloes. Pure extracts of frangula and rumex, and frangula in mixtures free from cascara and rhubarb, can be identified; but in other mixtures a comparison of a series of colour tests will be required. Phenolphthaleïn, if present, responds to the group reaction with the alkaline hydroxides; but when the concentrations of fixed alkali exceeds 10 per cent. the colour disappears, whereas the emodin drug colours are unaffected by concentrated alkali.

H. F. E. H.

Non-Existence of Lecithin in Egg-Yolk. N. A. Barbieri. (*Gazz. Chim. Ital.*, 1917, **47**, 1-37.)—The so-called lecithin separated from egg-yolk is commonly accepted to be a compound of distearylglycerophosphoric acid with one molecule of choline. The author, however, has found that the whole of the fat may be extracted from egg-yolk by successive treatment with neutral solvents, and that when saponified it yields nothing but glycerol and fatty acids. Nitrogenous substances, colouring matter, and phosphates, are dissolved or suspended in this fat, and may be quantitatively separated by dialysis, hydrolysis with very dilute acid, or by treating their alcoholic solution with water. The fat from which they have been separated shows no sign of decomposition, not a trace of glycerol being liberated. The phosphorus in egg-yolk is entirely present as phosphoric acid combined with alkalis (potassium, sodium), alkaline earth bases (calcium), and magnesium. Glycerophosphoric acid cannot be isolated by means of neutral solvents, but only by saponification, and the soap when decomposed with acids yields glycerol and the phosphoric acid derived from the phosphates. No trace of choline can be detected in egg-yolk, and the conclusion is drawn that the alleged choline constituent of the supposed lecithin is a putrefaction product or is derived from the hydrolysis of ovocromin. The author considers that these facts prove that egg-yolk does not contain lecithin. The principal constituents isolated from egg-yolk were as follows:

	Per Cent.
Ovovitellin	20·73
Paravitellin	0·73
Egg oil (17·31 per cent.) ⎱	21·09
Egg oil and tristearin ⎰	
Ovine	0·078
Cholesterol	10·01
Ovocromin	0·20
" Lecithin " mixture: Tripalmitin, oleopalmitin, ovocromin, mineral phosphates	9·48
Lipochrome or lutein mixture: Tripalmitin, oleopalmitin, ovocromin, cholesterol	1·96
Sodium chloride	1·96
Water (by difference)	47·45

C. A. M.

Specifications for and Methods of Testing Soaps. Circular No. 62, December 16, 1916, Bureau of Standards, Department of Commerce, U.S.A., 1-25.—(1) *Milled Soaps:* Matter volatile at 105° C. must not exceed 15 per cent.; free alkali (as NaOH), 0·1 per cent.; alkali as alkaline salts (Na_2CO_3), 0·3 per cent., not more than half of which shall be silicate; sulphate as Na_2SO_4, 0·1 per cent.; chlorides as NaCl, 0·3 per cent.; substances insoluble in water, 0·1 per cent.; unsaponified saponifiable matter, 0·1 per cent. No rosin, sugar, or foreign matter must be present. The mixed fatty acids must solidify not lower than 37° C. (titer test), and have a neutralisation value within the limits 203 and 212. Constituents other than moisture are to be calculated upon a material containing 10 per cent. of volatile matter, and a deduction of 2 per cent. shall be made from the weight of soap delivered for each 1 per cent. of volatile matter in excess of 10 per cent.   (2) *White Floating Soap:* Matter volatile at 105° C., 34; free alkali as NaOH, 0·1; alkali as alkaline salts (Na_2CO_3), 0·5; chloride as NaCl, 1; and substances insoluble in water, 0·1—per cent. No rosin, sugar, or foreign matter, must be present. Melting-point of fatty acids to be not less than 35° C., and neutralisation value not less than 212. The basis for the calculations is to be 28 per cent. of volatile matter, and 2 per cent. to be deducted from the weight of soap to be paid for for each 1 per cent. of volatile matter over 28 per cent.   (3) *Liquid Soap:* This must be a clear solution of a vegetable oil potash (or potash and soda) soap containing not less than 20 per cent. of soap. Free alkali (as KOH) must not exceed 0·05; alkali as alkaline salts (K_2CO_3), 0·3; and chloride as KCl, 0·3—per cent.; and no sugar or sulphates must be present. (4) *Salt Water Soap* must have been made exclusively from coconut oil, without removal of glycerol, and must contain no-filling materials, rosin, or sugar. Matter volatile at 105° C. shall not exceed 55 per cent. (basis for calculation of other constituents); free alkali as NaOH, 0·5; alkali as alkaline salts (Na_2CO_3), not less than 2 nor more than 4; mineral matter, 0·5—per cent.; neutralisation value of fatty acids, not less than 256. In calculating the weight of deliveries, ½ pound of matter not volatile at 105° C. shall be considered 1 pound of soap.   (5) *Special Grade Laundry Soap* (intended for use with soft water): Moisture must not exceed 20; matter volatile at 105° C., 34; free alkali as NaOH, 0·2; alkali as alkaline salts (Na_2CO_3),1; chloride and sulphate together, 1; insoluble substances, 0·1; and rosin, 15—per cent.; solidification-point of fatty acids, not less than 35° C. Constituents other than volatile matter are calculated on basis of substance containing 28 per cent. of volatile matter. In calculating the weight to be paid for $\frac{4}{5}$ pound of matter not volatile at 105° C. represents 1 pound of soap, and a deduction of 2 per cent. is made from the weight for each 1 per cent. of volatile matter in excess of 28 per cent. up to the limit of 34 per cent.   (6) *Ordinary Grade Laundry Soap* (for use with moder-ately hard waters): Water must not exceed 20; matter volatile at 105° C., 34; free alkali as NaOH, 0·5; alkali as alkaline salts (Na_2CO_3), not less than 2 nor more than 6 (of which not more than half shall consist of sodium silicate); chloride as NaCl, 1; sulphate as Na_2SO_4, 1; substances insoluble in water, 0·5; and rosin, 25—per cent.; solidification-point of. mixed fatty acids, not less than 33 per cent. Constituents other than volatile matter are to be calculated on a basis of 28 per cent., and the weight of soap to be paid for in the same way as for No. 5.   (7) *Chip Soap* must be

suitable for use with soft water in high-grade laundry work. Matter volatile at 105° C. must not exceed 15; free alkali as NaOH, 0·5; alkali as alkaline salts (as Na_2CO_3), 0·5; chloride as NaCl, 0·5; and substances insoluble in water, 0·1—per cent.; basis for calculations, 10 per cent. of volatile matter. Nine-tenths of a pound of non-volatile matter is taken as 1 pound of soap to be paid for, and a deduction of 2 per cent. from the weight is made for each 1 per cent. of volatile matter exceeding 10 per cent., up to the limit of 15 per cent. *Sampling Deliveries*—(a) *Cake Soap*: One cake is taken at random from every 1,000 cakes, or, if weighing less than 1 pound, additional cakes (not less than three) to give a sample of not less than 1 pound are taken. (b) *Liquid Soap*: One quart is taken from each 100 gallons of the thoroughly mixed consignment. (c) *Chip Soap*: Not less than 1 pound is taken at random from each 1,000 pounds of a consignment, and should fill completely a dry air-tight receptacle. *Preparation of Laboratory Sample—Cake Soap*: A cake of medium weight is divided diagonally, and representative layers are cut from the fresh surfaces. Two cakes of medium weight are reserved in air-tight containers for check analyses if necessary. *Liquid Soap*: In cold weather the main sample should stand for at least one hour at 20° to 30° C., before taking samples for analysis. *Chip Soaps*: Rapid mixture of the sample before weighing the portions for analysis is necessary. *Methods of Analysis*—(a) *Matter volatile at 105° C.*: Two grms. are dried for one hour at 60° C. in a porcelain dish 3 inches in diameter, 50 c.c. of absolute alcohol then added, the liquid evaporated, and the residue dried for one hour at 60° C., and then for two hours at 105° C. (b) *Free Alkali or Acid (except for Liquid Soaps)*: Five grms. are dissolved in 200 c.c. of hot freshly boiled neutral 95 per cent. alcohol, the solution filtered through a tared Gooch crucible, and insoluble matter washed with the hot alcohol. The filtrate and washings are cooled and titrated with standard acid or alkali. (c) *Method for Liquid Soaps*: Ten grms. of the sample are treated with 200 c.c. of the alcohol as described. Free alkali is returned as potassium hydroxide, and free acid as oleic acid. (d) *Alkali as Alkaline Salts*: The insoluble residue from (b) or (c) is extracted with hot water, and the solution titrated with standard acid (methyl orange as indicator). Carbonates, borates, and silicates, are included in the result as Na_2CO_3 or K_2CO_3. (e) *Silicate*: The titrated solution from (d) is evaporated with excess of hydrochloric acid in the usual way, and the silicate found is calculated into the equivalent sodium carbonate. (f) *Sulphate*: The filtrate from (e) is used for the estimation. (g) *Substances insoluble in Water*: The Gooch crucible containing the insoluble matter from (d) is dried for two hours at 105° C. (h) *Unsaponified Saponifiable Matter*: Five grms. of the soap are dissolved in 100 c.c. of 50 per cent. alcohol, any free fatty acids neutralised with standard alkali, and the solution skaken in a separating funnel with 100 c.c. of ether. The ethereal extract is washed with water, evaporated, and the unsaponified matter weighed. It is then boiled for one hour beneath a reflux condenser with 25 c.c. of alcoholic potassium hydroxide solution, evaporated to dryness, and the residue dissolved in water and shaken with ether. The ethereal extract is washed and evaporated, and the residue of unsaponifiable matter dried and weighed. The weight is deducted from the unsaponified matter, and the difference is added to the amount of free fatty acids, to obtain the total quantity

of unsaponified saponifiable matter. (*i*) *Preparation of Fatty Acids from Toilet Floating or Salt-Water Soaps:* A solution of 50 grms. of the soap in 300 c.c. of hot water is treated with 150 c.c. of about 2N sulphuric acid, cooled, and shaken with 120 c.c. of ether. The ethereal extract is washed with a strong solution of sodium chloride until free from acid, then shaken with 20 to 30 grms. of anhydrous sodium sulphate, allowed to stand until clear, filtered, and evaporated in a current of dry air below 50° C. (*j*) *Fatty and Rosin Acid: (Method for Laundry and Chip Soaps):* A solution of 50 grms. in 500 c.c. of hot water is heated with 100 c.c. of 30 per cent. sulphuric acid, and the resulting clear layer of fatty and rosin acids is washed with hot water, filtered through a hot water funnel, and dried for twenty minutes at 100° C. (*k*) *Solidification-point of Fatty Acids:* About 25 c.c. of the melted fatty acids are cooled to about 50° C. and introduced into a glass tube 100 mm. long, 25 mm. in diameter, and 1 mm. thick, which is fitted through a cork into a bottle about 150 mm. high by 70 mm. in diameter. The mass is slowly stirred with a thermometer until the mercury is stationary for thirty seconds, when the thermometer is suspended with its bulb in the middle of the material and the rise of temperature noted. (*l*) *Neutralisation Value of Fatty Acids:* Two to five grms. of the fatty acids are treated with 50 c.c. of neutral alcohol (free from carbon dioxide), and the solution titrated with standard alcoholic alkali (phenolphthaleïn as indicator). (*m*) *Total Alkali (Method for All except Liquid Soaps:* A solution of 5 grms. in 100 to 150 c.c. of hot water is heated with 40 c.c. of $\frac{N}{2}$ sulphuric acid on the water-bath until a clear layer of fatty acids is obtained. The beaker is cooled, the aqueous layer filtered, and the filtrate and washings titrated with standard alkali (methyl orange as indicator). (*n*) *Method for Liquid Soaps:* The acid aqueous liquids obtained in the estimation of total soap are heated to remove ether, and the excess of acid titrated as in (*m*). (*o*) *Chloride:* The neutral solution from the titration of the total alkali is titrated with $\frac{N}{10}$ silver nitrate solution (potassium chromate as indicator). (*p*) *Rosin:* As a qualitative test the fatty acids are heated with acetic anhydride, and a few drops of the liquid treated with a drop of sulphuric acid (sp. gr. 1·58), when a transient violet coloration indicates rosin. For the estimation of rosin, a hot 5 or 10 per cent. aqueous solution is treated with 40 c.c. of $\frac{N}{2}$ sulphuric acid, and the fatty acids washed with ice-water, dried for an hour at 105° C., and dissolved in 20 c.c. of absolute alcohol. The solution is mixed with 10 c.c. of a mixture of sulphuric acid and alcohol (1 : 4), boiled for four minutes beneath a reflux condenser, then treated with five to seven times its volume of 10 per cent. sodium chloride solution, and extracted with ether. The extraction is repeated two or three times, the united extracts washed with sodium chloride solution, and the rosin acids titrated with standard alcoholic sodium hydroxide solution (1 c.c. N alkali = 0·346 grm. rosin). (*q*) *Total Soap (Method for Liquid Soaps):* A 10 per cent. solution is heated with 40 c.c. of $\frac{N}{2}$ sulphuric acid, the fatty acids separated, the acid aqueous layer shaken twice with ether (20 c.c. each time), the fatty acids dissolved in the same ether, and the solution washed until no longer acid to methyl orange. The aqueous washings are united and shaken with 20 c.c. of ether, and this extract washed free from mineral acid and added to the other ether, the whole being then evaporated below 50° C. The residue is dissolved in

neutral alcohol (free from carbon dioxide), the solution neutralised with standard alcoholic potassium hydroxide solution and evaporated to dryness, and the residue of soap dried at 105° C. and weighed. Any unsaponified or unsaponifiable matter is deducted from the result. (r) *Sugar—Qualitative Test :* The soap solution is heated on the water-bath for fifteen minutes with an excess of hydrochloric acid, cooled and filtered from fatty acids, and the filtrate boiled for two minutes with an equal volume of Fehling's solution.   C. A. M.

Adsorption of Tin by Proteins, and its Relation to the Solution of Tin by Canned Foods. B. C. Goss. (*J. Ind. and Eng. Chem.,* 1917, **9,** 144-148.)—It is shown that the solution of tin by canned foods is not dependent on, or proportional to, the acidity of the foods alone, and that, in foods of relatively slight acidity which dissolve large amounts of tin, the greater part of the metal is converted into an insoluble and stable complex. When it is dissolved from the lining, the tin is constantly removed from solution by the proteins, carbohydrates, and other substances present, and, whether this is due to adsorption of tin ions or to hydrolysis of the tin salts, in either case the acid is regenerated and capable of dissolving more tin. Since tin is taken up by proteins, etc., even from concentrated acid solutions, the former explanation of the reaction appears to be the more probable. The reaction differs, however, from a true adsorption in that it is not reversible. Results of artificial digestion experiments show that by far the greater part of the tin in canned goods is in an insoluble form, and is so firmly adsorbed that it will be eliminated directly from the body, and not have the characteristic physiological action of soluble tin salts.   W. P. S.

Qualitative Test and Colorimetric Method for the Estimation of Vanillin. C. Estes. (*J. Ind. and Eng. Chem.,* 1917, **9,** 142-144.)—A violet coloration is obtained when vanillin is heated to boiling with acid mercuric nitrate solution; the latter is prepared by dissolving mercury in twice its weight of nitric acid (sp. gr. 1·42), and diluting the solution with twenty-five times its weight of water. The coloration is characteristic of vanillin, and its intensity is directly proportional to the amount of vanillin present. To estimate vanillin in alcoholic vanilla extracts, 5 c.c. of the sample are placed in a 50 c.c. flask, 6 c.c. of water and 1·5 c.c. of the reagent are added, and the mixture is heated in a boiling water-bath for twenty minutes. A standard is prepared at the same time by mixing 5 c.c. of a 1 per cent. vanillin solution, 6 c.c. of water, and 0·5 c.c. of the reagent, and this mixture is also heated for twenty minutes. After cooling, both mixtures are diluted to 50 c.c., filtered, and the colorations compared. The procedure is the same for non-alcoholic vanilla extracts, except that in this case only 1 c.c. of the reagent need be added to the sample. The results obtained by the method agree with those found by the ordinary gravimetric method.   W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Direct Microscopical Counting of Bacteria in Water. B. E. Nelson.

(*J. Amer. Chem. Soc.*, 1917, **39**, 515.)—Direct methods of counting bacteria in waters without preliminary " plating out " or growth in selected and selective media have many advantages; two ways are described in the present paper, both of which involve the use of zinc hydroxide precipitated *in situ* as a " flocking " reagent, in the first case followed by filtration and centrifugation, and in the second by centrifugation alone. For the microscopical examination of the organisms a magnification of from 450 to 500 diameters is quite sufficient, the most convenient concentration of the water being from 1,000 c.c. to 1 c.c. Of all the " flocking " materials employed, zinc hydroxide was found most satisfactory, mainly because, when followed by strong ammonium chloride solution, it could be dissolved away after use, and a sufficiently clear medium left in which to make the count. In the filtration method, 1 c.c. of 5 per cent. dried zinc sulphate solution followed by 0·7 c.c. of $\frac{N}{1}$ caustic soda is added to the litre of water, filtration being effected in a Sedgwick-Rafter type of filter consisting of a cylindrical glass percolator having a one-inch neck tapering inward to receive a perforated cork, glass trap tube, and attached rubber tube and screw clamp to control the rate of flow. The inner face of the cork is covered with a coarse linen cloth on which rests a little fine angular white sand which should fill the neck of the filter. The precipitate is transferred to a centrifuge and concentrated, then treated with saturated ammonium chloride at the rate of 0·8 to 0·9 c.c. for each c.c. of zinc solution originally used, and finally stained with alkaline methylene blue or clear carbol-fuchsine, the organisms being counted in a Thoma-Zeiss or similar cytometer. If the second method is employed, the whole litre of water is treated with 5 c.c. of zinc solution and 3·7 c.c. $\frac{N}{1}$ soda, and directly centrifuged in a special pear-shaped container with a double tap at the narrow end, the zinc coagulum, carrying with it the bacteria, being transferred to a centrifuge as before, or directly collected in the centrifuge tube attached to the narrow end of the large container. Using this method, it is usually possible to complete a water count in from twenty to forty minutes. The following are a few typical values obtained by plating out and by the direct method; the figures are organisms per c.c.:

			Agar Plates.	Gelatine Plates.	Direct Count.
River water (raw)	..	..	800	650	2,100
,, ,,	..	..	650	550	900
,, ,,	..	..	450	500	960
,, ,,	..	..	9,000	Liq.	16,000
,, (filtered)	..	..	12	10	25
,, ,,	..	..	18	12	30
,, ,,	..	..	111	10	20
Reservoir water	..	..	1,300	1,400	2,000
Shallow well	..	..	12	8	15
Deep well	..	..	7	—	30

H. F. E. H.

Detection of Traces of Mercury Salts for Toxicological Purposes. K. C. Browning. (*J. Chem. Soc.*, 1917, **111**, 236-240.)—Traces of mercury salts too minute for detection by the ordinary standard methods may be deposited by electrolysis, and detected on the cathode by spectroscopic examination in a Dupré tube.   Experiments were made on solutions containing about 1 part of mercuric chloride in 100 millions of water.   Of the various cathodes investigated, gold-foil was found to be most delicate, and next to this, silver gauze.   In every case the electrodes were heated before use to about 900° C. in a small electric muffle, and then examined spectroscopically for mercury.   As regards the size of the cathode, a piece of gold-foil 1·5 cm. long and 0·65 cm. broad was found satisfactory, the gold-foil being welded autogenously to a platinum wire.   Electrolysis of 10 c.c. of a solution of the above order with 0·2 ampère for ten minutes was found to be sufficient; a very slight improvement was found with a current of 0·8 ampère.   With 200 c.c. of solution, the current may be increased up to 2 ampères if the liquid be powerfully stirred, but with high current densities loss of mercury takes place as the time is prolonged, and the delicacy of the test is reduced.   When the electrolyte becomes warm, even at 50° C. the loss of mercury is considerable; as regards the composition of the electrolyte, it is well to acidify it with a few drops of nitric acid.   After the electrolysis is finished, the cathode is washed with water only, without interrupting the current, and placed in one limb of a Dupré tube.   This limb is immersed in an electric oil-bath at 200° to 250° C.   The tube is exhausted by a Gaede rotary oil-pump, and well washed out with hydrogen; it is then exhausted again and the tap closed.   The spectrum may be examined end-on to the capillary by a Hilger direct-vision spectroscope.   A moderately powerful coil (15 cm. spark) is suitable.   Under these conditions the mercury spectrum can be detected when 200 c.c. of a 1 per 1,000 million solution of mercuric chloride are electrolysed with 2 ampères for ten minutes with violent stirring.   When only small quantities of fluid are available (*e.g.*, 10 c.c. of urine), it is convenient to electrolyse without stirring in a small quartz dish for ten to fifteen minutes, using 0·2 ampère; it is thus possible to detect 1 part of mercuric chloride per 100 millions.   It has not yet been possible to obtain quantitative results.   Very weak solutions of mercury salts do not keep well in glass or quartz vessels, the mercury apparently being adsorbed by the quartz walls.   Attempts to concentrate the solutions by evaporation have not been satisfactory, and it is best to employ a large volume for the electrolysis while stirring vigorously.   J. F. B.

Utilisation of Pentoses and Pentosans by Fungi. L. A. Hawkins. (*Amer. J. Botany*, 1915, **2**, 375-388.)—Seillière (*Compt. rend. Soc. Biol.*, 1908, **64,** 941-943; *ibid.*, 1909, **66,** 691-693), Lindsey and Holland (*Ann. Rep. Mass. Agr. Exp. Sta.*, 1894, 175-188), Swartz (*Trans. Conn. Acad. Arts and Sci.*, 1911, **16**, 247-382), and others, have shown that pentosans as such disappear in passing through the alimentary canal of the higher animals; but it is doubtful whether such animals secrete any enzyme capable of hydrolysing them, this work probably devolving upon their intestinal bacteria.   Some invertebrates, such as certain Mollusca, and Coleopteral larvæ, can utilise pentoses readily, and appear to be able to hydrolyse some pentosans; while pentoses have been found to be a good source of carbon for certain fungi,

some kinds of which can break down pentosans by means of the enzymes they secrete. The resulting products of such action have not hitherto been identified, and the present work describes experiments showing that, as a result of the action of the fungus *Glomerella cingulata* on rotten apples, the amount of furfural-yielding material is reduced, the alcohol-soluble pentose cleavage products formed from the apple pentosans being split off and used by the fungus. The fungus can utilise dextose, xylose, arabinose, araban, and xylan, as a sole source of carbon, xylose being probably the most useful, while xylan is preferred to araban. The filtered extract of the fungus mycelium is able to produce xylose from pure xylan, a capacity lost if the extract is boiled; crystalline xylose was obtained as a result of such action, showing the presence of a xylanase in the fungus. The method employed for testing the growth of the fungus on the various sugars, etc., employed was to make a nutrient solution consisting of ammonium nitrate (1 grm.), potassium dihydrogen phosphate (0·5 grm.), magnesium sulphate (0·25 grm.), and water (100 c.c.). To this was added the carbohydrate in sufficient quantity to make about a 1 per cent. solution, which was inoculated by transferring conidiospores from the stock cultures. The mycelium containing the enzyme was extracted with water and a little chloroform after grinding up the dried mass, the neutral extract being then added to small portions (0·2 or 0·3 grm.) of the xylan substrate, and digested at 30° C. for varying periods under aseptic conditions. H. F. E. H.

New Microscopic Stains derived from Methylene Blue. L. Tribondeau and J. Dubreuil. (*Comptes rend.*, 1917, **164**, 551-553.)—Methylene azure blue and methylene violet may be prepared by treating a 1 per cent. aqueous solution of methylene blue with 5 to 10 per cent. of ammonia solution, heating the mixture just to boiling-point on the water-bath, and filtering it from the abundant precipitate which forms. The filtrate is evaporated in a shallow dish at 37° to 40° C., and leaves a practically pure deposit of methylene violet. The precipitate on the filter and in the flask is exposed to the air for twenty-four hours in a cold place to avoid evaporation of the liquid, and then assumes an intense blue-black colour. It is dissolved in water, the solution filtered and evaporated, and the residue of methylene azure blue collected. Approximately equal quantities of the two dye-stuffs should be obtained. From these the following microscopic stains may be prepared: (1) A 1 per cent. aqueous solution of *Azure blue*. This is useful for staining liquids or organic products in the fresh condition. (2) *Polychrome blue*. This is a mixture of 1 per cent. aqueous solutions of azure blue and methylene violet in the proportion of 1:3, and is useful for the examination of sputum, pus, etc., alcohol being used as the fixative. (3) *Azeo*, which is a mixture of 1 per cent. solutions of azure blue and eosin in a mixture of absolute alcohol and glycerol (75:25). It is used in the same way as Giemsa's staining bath, and absolute alcohol is used for fixing the preparations. C. A. M.

ORGANIC ANALYSIS.

Free Carbon of Wood-Tar Pitches. H. K. Benson and L. L. Davis. (*J. Ind. and Eng. Chem.*, 1917, **9**, 141.)—The so-called " free carbon " in wood-tar pitches cannot be estimated by using carbon disulphide as the solvent, but acetone is suitable for the purpose. The solubilities of various bitumens in acetone and carbon disulphide are given in the following table; in each case the residue insoluble in one solvent was again extracted with the other solvent:

	Insoluble in Carbon Disulphide.		Insoluble in Acetone.	
		Residue Insoluble in Acetone.		Residue Insoluble in Carbon Disulphide.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Douglas fir pitch ..	67·7	59·7	57·7	57·8
,, ,, ...	62·5	30·1	31·6	31·1
,, ,, ...	93·1	35·3	34·6	34·4
,, ,, ...	60·2	22·0	21·5	21·3
Hardwood pitch ..	18·7	3·1	2·9	2·7
,, ,, ..	59·9	18·0	17·5	17·4
Coal-tar pitch	27·4	27·4	57·5	27·1
,, ,, ...	22·7	22·6	37·1	22·3
,, ,, ...	18·4	18·0	35·3	18·5
,, ,, ...	17·4	17·1	33·3	16·9
Petroleum asphalt ..	4·1	4·0	27·1	3·9
Trinidad asphalt ..	42·6	42·1	69·0	41·8

Coal-tar pitches may be classed with the native and manufactured asphalts as regards the estimation of free carbon.   W. P. S.

Estimation of Phenol in Tar Oil Phenols. R. Masse and H. Leroux. (*Bull. Soc. Chim.*, 1917, **21**, 2-8.)—When a tar oil is distilled, the phenol content can be estimated in each fraction by determining the crystallisation temperature, since the effect of an admixture of cresols has a definite effect on the setting-point. A table is given connecting percentage of phenol and crystallisation temperature for mixtures containing between 66 and 100 per cent. of carbolic acid. The method of distillation is as follows:

Three kgrms. of crude phenols are placed in a four-litre copper flask attached to a Vigreux column 60 cm. in length. Condensation is effected by a condenser cooled with a current of water so that the vapours are cooled below 180° C. After this point the cooling water is reduced, and the distillation so adjusted that 6 to 8 c.c. pass over per minute.

Three fractions are collected: (1) Water and phenols passing over up to 180° C.;

(2) distillate collected between 180° and 203° C.; (3) about 100 c.c. distilling above 203° C.

Sufficient sodium chloride is added to fraction (1) to precipitate the dissolved phenols. Fraction (2) together with the phenols from (1) are placed in a flask and again distilled, using the same apparatus as before, but for the condenser is substituted a thin glass tube. On gentle warming the water is driven off. After further distillations and fractionations the crystallisation-point of each fraction is determined, and the phenol content determined by reference to the table. The method is sufficiently accurate for all ordinary purposes, but great accuracy is not claimed for it. H. F. E. H.

Action of Aromatic Amines on Fatty Acids. E. de Conno. (*Gazz. Chim. Ital.*, 1917, **47**, 93-132.)

—A method of identifying the constituents of a fat, and possibly of estimating their proportions, is based upon the fact that, when glycerides are heated in a sealed tube at 230° C. with an aromatic amine, they are hydrolysed, and yield the amides of the fatty acids present. Although the decomposition is not quantitative, the amounts of the amides formed appear to be proportional to the quantities of fatty acids in the fat, and they may be separated from one another by fractional distillation under reduced pressure (10 mm.), their boiling-points differing by about 10° C. for the different members of a series. When heated with strong hydrochloric acid in a sealed tube for three hours at 150° C., they are decomposed, and the corresponding fatty acids are liberated. The fatty acid amides of aniline, substituted anilines, and naphthylamines were prepared by heating the fatty acids with equimolecular proportions of the respective amines in a sealed tube, the yields being from 85 to 87 per cent. of the theoretical amounts. The amides are insoluble in water, sparingly soluble in petroleum spirit, readily soluble in acetone and hot acetic acid, and very soluble in ether, chloroform, and benzene. The best medium for the crystallisation of anilides is hot alcohol or methyl alcohol; while the *p*-phenylenediamides, which are insoluble in those solvents, may be crystallised from hot amyl alcohol. The melting and boiling points (10 mm. pressure) of typical amides of saturated and unsaturated fatty acids are given in the following table:

Fatty Acid Radicle.	Anilides.		p-Methyl-anilides.		p-Methoxy-anilides.		a-Naph-thylamides.		β-Naph-thylamides.		p-Phenylene-diamides.	
	M.P.	B.P.	M.P.	B.P.	M.P.	B.P.	M.P.	B.P.	M.P.	B.P.	M.P.	B.P.
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Myristic	81·5	113·0	84·0	121·5	101·5	215·5	110·0	162·5	108·0	179·0	162·5	186·5
Palmitic	88·5	132·5	93·5	140·0	108·0	238·0	112·0	182·0	109·0	198·5	181·5	208·0
Stearic	88·0	153·5	95·5	161·5	104·0	259·0	110·8	205·0	109·0	220·5	179·5	229·5
Arachidic	91·5	172·0	96·0	189·5	106·0	281·5	99·0	221·0	112·0	239·0	139·8	250·0
Oleic	41·0	143·5	42·5	156·5	67·0	262·0	60·0	199·5	169·2	215·5	158·7	224·5
Erucic	55·0	181·5	57·5	192·5	85·0	287·0	73·0	230·0	87·0	247·5	151·0	263·0
Linolenic	liq.	—	liq.	—	—	—	—	—	—	—	—	—

Linolenic anilide is a limpid yellow liquid which is readily soluble in organic solvents, but is insoluble in water. The sample prepared by the author had an iodine value of 211·14 (theory=215·86), and an elementary composition corresponding with the formula $C_6H_5NH.CO.C_{17}H_{29}$.   C. A. M.

Duclaux Method for the Estimation of the Volatile Fatty Acids. F. W. Upson, H. M. Plum, and J. E. Schott.

(*J. Amer. Chem. Soc.*, 1917, **39**, 731-742.) —The Duclaux method (*Ann. Chim. Phys.*, 1874, **2**, 289; *Ann. Inst. Pasteur*, 1895, **9**, 265) has been used by its author for the estimation of the acids in wine, and by other workers on the composition of corn silage and cheese acids (see also Richmond, ANALYST, 1895, **20**, 193; 1906, **31**, 324; 1908, **33**, 305).   •

The present authors in an exhaustive investigation into the method conclude— (1) That small variations in the experimental results within the limits of error of the method may cause such wide variations in the calculated results as to render them valueless; (2) that, as might be expected, when more than two acids are present in an unknown mixture, several calculations may be made to fit the analytical results, and in the case of three or more acids more than one combination of the same acids may be calculated to correspond with the Duclaux series as determined; and (3) that the method erroneously assumes that each acid will follow its own law of distillation even when present in a mixture, thus tacitly assuming that the vapour pressure of one substance is not affected by the presence of others. Again, results which indicate the presence of one acid may just as well be calculated in terms of three or more acids, and small amounts of acids may be distributed just as well between the acids next higher and lower in the series. Moreover, the theory of the method is not sound, and it does not serve either quantitatively or qualitatively for determining the composition of unknown mixtures of fatty acids. Tables are given in which values obtained by other workers are recalculated in terms of acids other than those actually present, the agreement in both cases being within the experimental error of the method. (*Cf.* ANALYST, 1917, 149, also following abstract.)
                                                                              H. F. E. H.

Note on the Duclaux Method for Volatile Fatty Acids. A. R. Lamb.

(*J. Amer. Chem. Soc.*, 1917, **39**, 746.)—The author criticises the adverse opinion formed of the method by Upson, Plum, and Schott (see preceding abstract), and gives figures showing that, when carefully standardised precautions are taken to insure uniformity of heating and absolute purity of the acids used, great accuracy may be obtained. He considers that it is impracticable to estimate more than two or three acids in the same fraction, but by proper fractional distillation the acids in the mixture may be quite well separated, thus obviating the necessity of calculating as many as four acids from a single distillation. The precaution of preparing carefully purified acids by repeated crystallisation of their salts, followed by frequent distillation of the acids liberated from them, was apparently neglected by these three workers, resulting in values which, though agreeing well among themselves, were not the true values for the purified acids. (*Cf.* ANALYST, 1917, 149.)   H. F. E. H.

Identification of Acids—II. J. A. Lyman and E. E. Reid. (*J. Amer. Chem. Soc.*, 1917, **39**, 701-711.)—In continuation of the previous work of one of the authors (ANALYST, 1917, 89), some thirty further *p*-nitrobenzyl esters of organic acids have been prepared. The methods already described were chiefly used, but *p*-nitrobenzyl chloride and iodide were used as well as the bromide. With *m*-toluic acid, however, the chloride yields only 62 per cent. of the calculated weight of ester,. whereas the bromide gave 97 per cent. In the case of diethyl-, dipropyl-, and benzyl-malonic acids, the iodide gives better yields than those obtained for other substituted malonic acids with the bromide, suggesting that the iodide is better than the bromide for dibasic acids, the di-*p*-nitrobenzyl esters of which are very insoluble, making it easy to free them from any unchanged iodide. A table is given showing the halide used, the yield obtained, the melting-points, and the solubilities of the esters in hot and cold alcohol. Levulinic and mucic acids failed to yield esters, and attempts to prepare mono- as well as di-esters of dibasic acids were usually unsuccessful, as the monosodium salt of the dibasic acid gave in all but one case the di-ester. Malic acid gives both mono- and di-esters. H. F. E. H.

Estimation of Gasoline Vapour in Air. R. P. Anderson. (*J. Ind. and Eng. Chem.*, 1917, **9**, 142.)—Attention is directed to the difficulty of obtaining complete combustion, in the ordinary combustion method, of the gasoline when this is present in air to the extent of more than 5 per cent. by volume. In such cases,. Burrell and Robertson's method of separating the gasoline by condensation with liquid air (*cf.* ANALYST, 1914, **39**, 414; 1915, **40**, 246) is more trustworthy. W. P. S.

Notes on Oil Testing. A. H. Gill. (*J. Ind. and Eng. Chem.*, 1917, **9**, 136.)— *Test for Oils by salting out their Soaps:* The test depends on the amount of sodium chloride required to " salt out " a soap from its aqueous solution. Two grms. of the oil are saponified by heating with 5 c.c. of 10 per cent. sodium hydroxide solution, adding alcohol if necessary; the mixture is then evaporated to dryness, and the soap dissolved in warm water. The solution is neutralised with hydrochloric acid, using phenolphthaleïn as indicator, and diluted to 50 c.c. Ten c.c. of this solution are then titrated with sodium chloride solution (420 grms. per litre), as in determining the hardness of a water, until the lather obtained fails to exist for five minutes. From the quantity of hydrochloric acid used for the neutralisation, and this titration with sodium chloride, is calculated the grms. of sodium chloride necessary to precipitate the soap from 1 grm. of oil. The following results were obtained with various oils, the figures expressing grms. of sodium chloride per grm. of oil: Olive oil, 2·2; cottonseed oil, 8·3; linseed oil, 13·7; oleomargarine, 2·8; butter, 1·3. In the case of coconut oil an end-point could not be obtained.

Test for Gelatinous Matter in Linseed Oil: Ten grms. of the oil are saponified by boiling with 20 c.c. of 10 per cent. sodium hydroxide solution, and the soap is diluted to 225 c.c. with warm water. Twenty-five c.c. of this solution are now placed in a six-inch by one-inch test-tube, shaken with 8 c.c. of petroleum spirit, and then submitted to centrifugal action (1,800 revolutions per minute) for three minutes. The quantity of flocculent matter which appears between the aqueous and petro-

leum spirit layers is then observed. Ordinary linseed oils give a sludge layer about 10 mm. in thickness, whilst artists' oils yield a layer of less than 5 mm. The largest amounts of flocculent matter are given by the slower-drying, inferior oils. W. P. S.

Crampton-Simons Colour Test for Palm Oil. A. H. Gill. (*J. Ind. and Eng. Chem.*, 1917, **9,** 136-139.)—This reaction (ANALYST, 1905, **30,** 250), which depends on the formation of a green colour when palm oil is treated with acetic anhydride containing a trace of sulphuric acid, is really one for carotin, and is quite untrustworthy for the detection of palm oil, since the coloration is given by any other oil which contains carotin—for instance, by butter, sesame oil, etc. W. P. S.

" Nitron " as Gravimetric Reagent for Analysis of Substances used in Explosives. W. C. Cope and J. Barab. (*J. Amer. Chem. Soc.*, 1917, **39,** 504-514.)—Busch, who discovered " nitron " (1·4-diphenyl- 3·5-endoanilodihydrotri-azol), showed that the picrate was even less soluble than the nitrate, and the perchlorate almost as insoluble as the nitrate. He also recommended its use for the estimation of nitric esters, nitrocellulose, for example, which yield good results when saponified with caustic soda, using hydrogen peroxide to overcome the tendency of the other products of the saponification to reduce nitrate to nitrite, then acidifying with dilute sulphuric acid, heating to boiling, and precipitating the nitric acid with nitron. The authors find this method yields good results with nitromannite and nitrostarch. With nitroglycerin Busch's original method gives low results, but satisfactory analyses may be made as follows:

The nitroglycerin is weighed out in a 100 c.c. conical flask to which an air condenser 25 cm. long is attached by means of a ground joint. About 5 c.c. of 30 per cent. sodium hydroxide and 5 c.c. of 3 per cent. hydrogen peroxide are added, and then about 15 drops of 30 per cent. hydrogen peroxide. The mixture is heated on the water-bath for ten minutes, by which time the gas evolution has moderated considerably, and then 10 to 15 drops of 30 per cent. peroxide are again added. This operation is repeated over a period of two hours, and twice at half-hour intervals. As saponification is still incomplete the condenser is removed, 10 to 15 drops of 30 per cent. hydrogen peroxide are added, a splash head is attached to the flask by means of a rubber stopper, and the flask heated for a few minutes over a free flame. The addition of hydrogen peroxide and the heating are repeated twice and the solution is finally boiled down to a volume of about 3 c.c. Water (40 c.c.) and 10 c.c. of 3 per cent. hydrogen peroxide are added, the liquid heated to 50° C., acidified with 40 c.c. of 5 per cent sulphuric acid, and 12 c.c. of 10 per cent. " nitron " added.

Trinitrocresol and dinitrophenol can be directly precipitated with " nitron," the addition compound of trinitrocresol with " nitron " being the most insoluble known compound of trinitrocresol, as nitron picrate is the most insoluble known compound of picric acid. G. C. J.

Aniline Method for the Estimation of Mineral Fillers in Rubber. O. H. Klein, J. H. Link, and F. Gottsch. (*J. Ind. and Eng. Chem.*, 1917, **9,** 140-141.)—One grm. of the finely divided (twenty-mesh) sample is extracted for four hours with

acetone, then dried at a low temperature, and transferred to a weighed 100 c.c. centrifuge tube. After the addition of 50 c.c. of pure aniline and 5 c.c. of nitro-benzene, the contents of the tube are heated at 160° C. for about eighteen hours, or until the rubber has dissolved; in some cases complete solution is obtained in about four hours. The mixture is then cooled, the tube is filled with ether and centrifuged for fifteen minutes at 1,500 revolutions per minute. The supernatant liquid is now decanted, the residue is centrifuged with four successive quantities of ether, using 25 c.c. each time, then dried at 100° C., and weighed. The decanted liquids are united, and the residue obtained on evaporation is ignited and weighed, the weight being added to that of the fillers in the tube. The small quantity of nitrobenzene added causes more rapid solution of the rubber. W. P. S.

Wet Combustion in the Nitrosite Combustion Method for the Direct Estimation of Rubber. L. G. Wesson and E. S. Knorr. (*J. Ind. and Eng. Chem.*, 1917, **9**, 139-140.)

—The nitrosite is prepared as described previously by Wesson (ANALYST, 1914, **39**, 368), and the chloroform solution is filtered through asbestos into a round-bottomed flask and evaporated. The portion of the substance insoluble in chloroform is meanwhile dried and extracted many times with small quantities of dry ethyl acetate, the extracts being filtered into the same flask. After the ethyl acetate has been evaporated, the residue in the flask is heated in a boiling water-bath for fifteen minutes; 15 c.c. of water containing 1 drop of hydrochloric acid are added, and evaporated rapidly by the use of a boiling calcium chloride bath and a current of air. The heating is then continued for at least thirty minutes after the residue is apparently dry. The residue in the flask is now oxidised by the gradual addition of a mixture of 10 grms. of powdered potassium bichromate dissolved in 75 c.c. of concentrated sulphuric acid, and the gases evolved are conducted through a series of absorption tubes containing, successively, sulphuric acid and bichromate, water containing a drop of the preceding mixture, granulated zinc, calcium chloride, soda-lime (weighed), and soda-lime and calcium chloride (weighed). The flask is heated to complete the combustion, and the last traces of carbon dioxide are driven over into the absorption vessels by means of a current of air free from carbon dioxide. If 0·5 grm. of rubber is taken for the estimation, the weight of carbon dioxide found is multiplied by 61·8181 to obtain the percentage quantity of $C_{10}H_{16}$ in the sample.

W. P. S.

Colorimetric Test for the Determination of Organic Impurities in Sands. D. A. Abrams and O. E. Harder. (*Chemical Engineer*, 1917, **25**, 9-11.)

—It is recognised that the presence of organic matter, derived mainly from surface loam, is extremely deleterious to the value of sands used for concrete. Methods for the estimation of organic matter based on combustion or on loss of weight by ignition are open to the objection that they fail to discriminate between organic matter and carbonates or combined water. The colorimetric method depends on the production of a coloured extract ranging from pale yellow to deep red, almost black, when the sand is digested with sodium hydroxide solution at the ordinary temperature. Two hundred grms. of dry sand are treated with 100 c.c. of 3 per cent. solution of

ɔdium hydroxide, and digested with occasional stirring for twenty-four hours. The extract is filtered through a paper filter and refiltered if necessary, since it is absolutely essential that a clear filtrate be obtained. Ten c.c. of the filtrate are placed in a Nessler cylinder, diluted to 50 c.c. with water, and shaken. The colour of the solution is compared with that of a standard alkaline solution of sodium tannate, freshly prepared. Ten c.c. of a 2 per cent. solution of tannic acid in 10 per cent. alcohol are added to 90 c.c. of 3 per cent. solution of sodium hydroxide, and allowed to stand for twenty-four hours. From 1 to 10 c.c. of this are measured into Nessler cylinders, and diluted to 50 c.c. with water. The colour value in parts of tannic acid per million of sand is 100 times the number of c.c. of alkaline tannate solution taken to match the colour. It is best to compare the solutions in good sunlight, looking through the whole column of liquid. Investigations have shown that all natural sands which have been found defective on account of organic impurities have responded to the colorimetric test, and that all sands which have shown high colour values have shown low values in mortar tests. Defective sands may be improved by the removal of organic matters either by extraction or ignition; and if the sodium hydroxide extracts from defective sands be deposited on high-grade sands, the mortar strength of the latter is considerably reduced. Exact values cannot be given for the relation between the colour value of a sand and the strength of mortars made from it, but approximate estimations show that a colour value of 250 may correspond to a loss of compressive strength in a 1:3 mortar of 10 to 20 per cent.; a colour value of 500 to a loss of 15 to 30 per cent.; 1,000 to a loss of 20 to 40 per cent.; 2,000 to a loss of 25 to 50 per cent.; and 3,000 to a loss of 30 to 60 per cent. J. F. B.

Polarimetric Estimation of Starch in the Presence of Other Optically Active Substances. C. Baumann and J. Grossfeld. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1917, **33**, 97-103.)—A method is proposed for the estimation of starch in substances which, in addition to starch, contain gelatinised starch, dextrins, and sugars. It is based on the fact that starch, even when gelatinised by heat, is precipitated completely by lead tannate, provided that this compound is formed in the solution containing the starch. Ten grms. of the substance to be analysed are shaken for one hour (fifteen minutes is sufficient if dextrins are absent) in a 100 c.c. flask with 75 c.c. of water; 5 c.c. of 10 per cent. tannin solution and 5 c.c. of basic lead acetate solution are then added, the mixture is diluted to 100 c.c. with sodium sulphate solution, and filtered. Fifty c.c. of the clear filtrate are mixed with 3 c.c. of 25 per cent. hydrochloric acid, and heated in a boiling water-bath for fifteen minutes; after cooling, 20 c.c. of 25 per cent. hydrochloric acid and 5 c.c. of sodium phosphotungstate solution (12 grms. of sodium phosphate and 20 grms. of sodium tungstate per 100 c.c.) are added, the mixture is diluted to 100 c.c., filtered, and the filtrate is polarised in a 200-mm. tube. A separate portion of 5 grms. of the sample is now heated directly with the addition of water and hydrochloric acid (see Ewers' method, ANALYST, 1908, **33**, 481), then cooled, treated with an additional quantity of 20 c.c. of hydrochloric acid and 5 c.c. of sodium phosphotungstate, the mixture is diluted to 100 c.c., and polarised after filtration. The difference between the two

polarimeter readings is multiplied by 5·444 to obtain the percentage quantity of starch in the sample; the factor is deduced from the average rotatory power of various starches, this average being $[a]_D = +183.7°$. Owing to the presence of acetates in the solution, it is necessary, for the first inversion, to add 3 c.c. of hydrochloric acid, instead of 2 c.c. as recommended by Ewers, in order to bring the acidity to the required concentration. Sodium phosphotungstate does not precipitate certain organic bases, alkaloids, etc., from a dilute hydrochloric acid solution, hence an additional quantity of the acid is introduced after the inversion part of the process. In dealing with products containing from 10 to 60 per cent. of starch together with relatively large amounts of cane-sugar, dextrose, dextrins, milk, etc., the error of the method does not exceed 0·2 per cent.   W. P. S.

INORGANIC ANALYSIS.

Analysis of Aluminium Dust. J. E. Clennell. (*Eng. and Min. J.*, 1917, **103**, 496-499 ; through *J. Soc. Chem. Ind.*, 1917, **36**, 506.)—One grm. is dried at 100° C. to constant weight and the loss reported as moisture. The dried material is transferred to a dry 2C0 c.c. beaker and washed with ether till free from grease. The filtered extract is evaporated in a tared flask and the grease weighed. The residue from the extraction is transferred to a 300 c.c. flask and dissolved in dilute hydrochloric acid ; the hot acid solution is filtered through the filter previously used into another flask, and the filter washed with hot water. The insoluble residue is washed back and treated with nitric acid: this solution is filtered through the same filter into a separate flask. The ignited insoluble residue consists of silica mixed with some carbon which resists ignition very persistently. It is fused with a small quantity of sodium peroxide and the silica separated as usual; this is calculated to silicon. The nitric acid filtrate is evaporated with sulphuric acid and added to the main hydrochloric acid filtrate. This is precipitated with hydrogen sulphide, and the precipitate digested with hot 50 per cent. hydrochloric acid to separate copper and lead. The residual copper sulphide is dissolved in nitric acid and the copper titrated with cyanide. The lead solution is neutralised with ammonia, acidified with acetic acid, and precipitated with bichromate. The filtrate from the hydrogen sulphide precipitate is oxidised and treated with excess of caustic soda ; the precipitate is dissolved and re-precipitated with ammonia; the filtrate from the ferric hydroxide is used for the estimation of magnesium. The alkaline filtrate containing aluminium and zinc is precipitated with sodium sulphide, and the zinc sulphide estimated with $\frac{N}{10}$ iodine and thiosulphate. The aluminium may be roughly estimated by acidifying the last filtrate, expelling hydrogen sulphide by boiling, making up to 500 c.c. and titrating 100 c.c. with $\frac{N}{1}$ alkali first with methyl orange, and then with phenolphthaleïn as indicator. The interval between the two end-points is proportional to the aluminium; the alkali is standardised against pure aluminium. Special methods for the separate estimation of the impurities are also described.

Penfield Test for Carbon. **W. G. Mixter and F. L. Haigh.** (*J. Amer. Chem. Soc.*, 1917, **39**, 374-375.)—The authors state that the method now described does not appear anywhere in the literature, although the late Professor Penfield's very similar method for the estimation of water in minerals and rocks is widely known. As in the test for water, the apparatus consists of a narrow hard glass tube closed at one end. It is convenient to have a small bulb blown near the open end for the accommodation of the reagent, a solution of barium hydroxide. The substance to be examined is mixed with lead chromate and introduced into the far end of the tube. One drop of a clear solution of barium hydroxide is introduced into the bulb near the open end, which is then closed with a short piece of rubber tubing carrying a small bulb tube containing solid potassium hydroxide. The chromate mixture is then heated, when, if 0·003 mgrm. or more carbon is present, a distinct white film w.ll appear on the surface of the barium hydroxide solution. The test is so sensitive that the tubes must be scrupulously freed and kept free from dust, and the lead chromate prepared and preserved with care, and tested before use and from time to time after storage. Lead chromate precipitated from the nitrate, washed by decantation, and dried in a beaker covered with a clock glass, has been found to be free from carbon; if exposed to air in preparation, it will react for carbon. A bad sample may be freed from carbon by heating in an atmosphere of oxygen.   G. C. J.

Improvements in Calorimetric Combustion: The Heat of Combustion of Toluene. **T. W. Richards and H. S. Davis.** (*J. Amer. Chem. Soc.*, 1917, **39**, 341-354.)—In this paper there are described improvements in various details of the procedure of calorimetric combustion, notably means of effective closing with less risk of injury to the platinum lining and cover of the bomb, means of burning volatile liquids without loss, a method of automatically controlling the temperature of the environment about the calorimeter so as to make the combustion more convenient and more truly adiabatic, and means of evaluating the incompleteness of combustion if any volatile carbon compounds should remain unburned.

New determinations of the heat of combustion of toluene are recorded. The mean value obtained was 10,158 18°-calories or 42·47 kilojoules per grm. weighed in vacuum.   G. C. J.

Iodimetric Estimation of Sulphur Dioxide and Sulphites. **J. B. Ferguson.** (*J. Amer. Chem. Soc.*, 1917, **39**, 364-373.)—For the very accurate estimation of large or small amounts of sulphur dioxide in a gas mixture, the best method is solution of the sulphur dioxide directly in an excess of iodine solution, and titration of the excess iodine with thiosulphate, using starch as indicator. The Reich method (drawing the gas mixture through starch iodide solution of known iodine content until the solution is decolorised) may be used for either small or large proportions, but yields results of satisfactory accuracy only when sufficiently large samples are taken to render the uncertain end-point a negligible source of error. When carbon dioxide and sulphur dioxide are to be estimated on the same sample, the sulphite method can be used with advantage. The sulphur dioxide is absorbed in caustic alkali solution, and the sulphite determined either (*a*) by adding the sulphite solution

from a burette to a measured volume of standard iodine solution, acidified with hydrochloric acid, until the colour of the starch indicator is discharged; or (*b*) by adding the sulphite solution to a measured and more than sufficient volume of acidified standard iodine solution, and titrating the excess of iodine with thiosulphate. The accuracy of this method falls off sharply when the percentage of sulphur dioxide in the gas mixture exceeds 3 or 4 per cent.

The following general observations are offered: For accurate work, the gas sample must not come in contact with even a trace of moisture before reaching the absorbent. The apparatus must be free from rubber connections if 10 per cent. or more sulphur dioxide is present in the gas to be analysed. It is best to avoid them in all cases, but when the proportion of sulphur dioxide does not exceed 3 per cent. the error from this source is negligible. Mixtures of sulphur dioxide and air when dry do not react appreciably, but when moist, slow oxidation takes place.

For the analysis of soluble sulphites the following method is recommended, on the ground that it eliminates several sources of error due to oxidation of the salt by agents other than the iodine used to measure it. The solid salt is dissolved directly in an excess of iodine solution containing sufficient hydrochloric acid, and the excess iodine is determined by titration with thiosulphate.   G. C. J.

Estimation of Small Quantities of Free Sulphuric Acid in the Presence of Sulphates. E. Vulquin and M. Entat. (*Ann. Chim. anal.*, 1917, **22**, 61-66.)— An electrometric method is proposed for the purpose, measurements being made of the difference in potential between a polarised platinum electrode and a normal calomel electrode, both placed in the solution, while the latter is titrated with barium hydroxide solution. The curve plotted from the quantities of barium hydroxide used and the differences in potential observed exhibits a distinct break at the point where all the free sulphuric acid present has been neutralised. The method may be used for solutions containing 0·005 grm. of free sulphuric acid in addition to sulphates, other inorganic salts, and free organic acids.   W. P. S.

Determination of Gelatinisation Temperatures of Starches by Means of an Electrically-heated Chamber on the Microscope Stage. A. W. Dox and G. W. Roark junior. (*J. Amer. Chem. Soc.*, 1917, **39**, 742-745.)—The method used is similar in principle to that adopted by Francis and Smith (ANALYST, 1916, **41**, 248), but using electric in place of water heating. The apparatus consists of a special electric incubator for the microscope stage, which a simple change in the wiring converts from an incubator into an oven. A thin "hanging drop" slide is used, the gelatinisation temperature being taken as that at which anisotropy disappears in all the grains large enough to show the characteristic shape and markings. The proper amount of water in the drop must be used, too much leading to "clumping," and too little to premature evaporation. A correction is necessary, due to the fact that the thermometer bulb is nearer the source of heat than the sample tested, and this is found by checking the instrument with pure substances of known melting-point. A deduction of 3·8° C. was found necessary in the apparatus employed in

order to obtain the true melting-point. Thirteen different maize varieties were examined for the purpose of determining the melting-points of the starches prepared from them, the values (corrected) varying from 64·1 to 71·1, the average being 68, the figures found by other workers being 62·5 (Lippmann), 62·2 to 67·5 (Reichert), 70-71 (La Wall and Graves), and 70·9 (Francis and Smith *loc. cit.*).

<div align="right">H. F. E. H.</div>

Preparation of Sulphurous Acid. E. Hart. (*J. Amer. Chem. Soc.*, 1917, 39, 376.)—The cheapest and most convenient way of preparing small amounts of sulphurous acid for the laboratory consists in warming fuming sulphuric acid (30 per cent. SO_3) with sulphur. The acid need not be pure, and the evolution is slow and regular provided only lump sulphur in not too large amount is used. The sulphur dissolves, forming a blue solution from which, on warming, sulphur dioxide is given off mixed with some trioxide. If sulphuric acid is objectionable, the resulting solution must be boiled and the gas again absorbed. Evolution of sulphur dioxide ceases when the free sulphur trioxide of the oleum has been acted on and the sulphur melts. If the acid remaining is allowed to cool, it contains only a small amount of dissolved sulphur, and is still fit for many uses. The present high price of copper recommends the process.

<div align="right">G. C. J.</div>

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REVIEW.

CHEMICAL DISCOVERY AND INVENTION IN THE TWENTIETH CENTURY. By Sir
William A. Tilden, F.R.S. London: G. Routledge and Sons, Ltd., 1917.
Price 7s. 6d. net.

For many years chemists have had only too good cause to deplore the losses
which this country has suffered through the ignorance of the methods, the aims, and
the achievements of chemistry which pervades all classes of the community. It
must be admitted, however, that chemists themselves are not altogether free from
blame in the matter, because for the most part they have been content to carry on
their work, and have not sought to arouse a general interest in the subject among
the unscientific public. Yet there is urgent need—more urgent now, perhaps, than
at any previous time—that the nation should be led to appreciate the paramount
necessity for the "intensive cultivation" of chemistry in all its branches. Of
course, there are many books dealing with different parts of the science, but those—
written as a rule for the student—are necessarily too technical for the general reader;
on the other hand, books in which the methods and results of chemical research are
described in a manner calculated to awaken the interest and hold the attention of
the unscientific are few and far between. For this reason a cordial welcome will be
given to Sir William Tilden's " Chemical Discovery and Invention in the Twentieth
Century," a book of outstanding merit, in which the difficulties which must be faced
in writing a truly scientific and yet at the same time a popular account of the sub-
ject have been successfully overcome.

The first section of the book includes a description of several general and special
laboratories, and of some of the principal instruments used in analysis and research.
To the chemist this may seem somewhat superfluous, but no doubt the author was
right in deciding to give the unscientific readers (who, it is to be hoped, will be num-
bered by multitudes) some idea of the accommodation and equipment which are
indispensable in a modern chemical institute. The second part of the book is a
veritable *tour de force*, for in the space of little more than a hundred pages we find
a comprehensive, succinct, and eminently lucid account of modern discoveries and
theories. There follow a most interesting section dealing with the modern applica-
tions of chemistry, and finally a section on recent progress in organic chemistry.
Here the mass of material at the disposal of the author must have made the task of
selection very troublesome, but few will be disposed to cavil at his choice of subjects.
A few portraits and a large number of excellent illustrations enhance the attractions
of a delightful volume, which, if read as widely as it deserves, should do yeoman
service in helping to impress upon the minds of our countrymen the madness of their
past indifference to the work of the chemist.

G. G. HENDERSON.

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