

THE ANALYST:

THE ORGAN OF THE

Society of Public Analysts and other Analytical Chemists

A MONTHLY JOURNAL DEDICATED TO THE ADVANCEMENT
OF ANALYTICAL CHEMISTRY

Publication Committee :

G. EMBREY, F.I.C. (PRESIDENT).

L. ARCHBUTT, F.I.C.

BERTRAM BLOUNT, F.I.C.

E. RICHARDS BOLTON, F.I.C.

A. CHASTON CHAPMAN, F.I.C.

CECIL H. CRIBB, B.Sc., F.I.C.

BERNARD DYER, D.Sc., F.I.C.

OTTO HEHNER, F.I.C.

E. HINKS, B.Sc., F.I.C.

C. A. KEANE, Ph.D., D.Sc., F.I.C.

ARTHUR R. LING, F.I.C.

P. A. ELLIS RICHARDS, F.I.C.

J. AUGUSTUS VOELCKER, Ph.D., F.I.C.

E. W. VOELCKER, F.I.C.

Editor: JULIAN L. BAKER, F.I.C.

Abstractors:

J. F. BRIGGS, A.C.G.I.

H. F. E. HULTON, F.I.C.

G. C. JONES, A.C.G.I., F.I.C.

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

W. P. SKERTCHLY, F.I.C.

VOL. XLII.

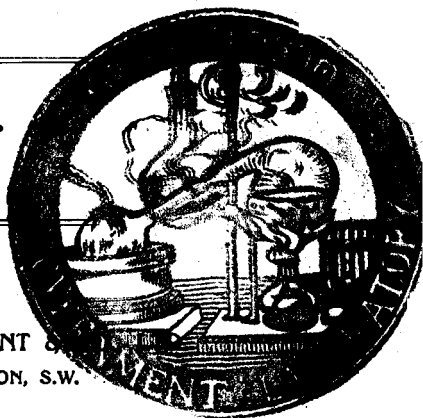
1917

639

TRADE AGENTS:

SIMPKIN, MARSHALL, HAMILTON, KENT &
2, 4, 6, 8, ORANGE STREET, LONDON, S.W.

1917



THE ANALYST.

INTERNATIONAL ATOMIC WEIGHTS, 1917.

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminium ...	Al	27.1	Molybdenum ...	Mo	96.0
Antimony ...	Sb	120.2	Neodymium ...	Nd	144.3
Argon ...	A	39.88	Neon ...	Ne	20.2
Arsenic ...	As	74.96	Nickel ...	Ni	58.68
Barium ...	Ba	137.37	Nitron (radium emanation)	Nt	222.4
Bismuth ...	Bi	208.0	Nitrogen ...	N	14.01
Boron ...	B	11.0	Osmium ...	Os	190.9
Bromine ...	Br	79.92	Oxygen ...	O	16.00
Cadmium ...	Cd	112.40	Palladium ...	Pd	106.7
Cæsium ...	Cs	132.81	Phosphorus ...	P	31.04
Calcium ...	Ca	40.07	Platinum ...	Pt	195.2
Carbon ...	C	12.00	Potassium ...	K	39.10
Cerium ...	Ce	140.25	Praseodymium ...	Pr	140.9
Chlorine ...	Cl	35.46	Radium ...	Ra	226.0
Chromium ...	Cr	52.0	Rhodium ...	Rh	102.9
Cobalt ...	Co	58.97	Rubidium ...	Rb	85.45
Columbium ...	Cb	93.1	Ruthenium ...	Ru	101.7
Copper ...	Cu	63.57	Samarium ...	Sa	150.4
Dysprosium ...	Dy	162.5	Scandium ...	Sc	44.1
Erbium ...	Er	167.7	Selenium ...	Se	79.2
Europium ...	Eu	152.0	Silicon ...	Si	28.3
Fluorine ...	F	19.0	Silver ...	Ag	107.88
Gadolinium ...	Gd	157.3	Sodium ...	Na	23.00
Gallium ...	Ga	69.9	Strontium ...	Sr	87.63
Germanium ...	Ge	72.5	Sulphur ...	S	32.06
Glucinum ...	Gl	9.1	Tantalum ...	Ta	181.5
Gold ...	Au	197.2	Tellurium ...	Te	127.5
Helium ...	He	4.00	Terbium ...	Tb	159.2
Holmium ...	Ho	163.5	Thallium ...	Tl	204.0
Hydrogen ...	H	1.008	Thorium ...	Th	232.4
Indium ...	In	114.8	Thulium ...	Tm	168.5
Iodine ...	I	126.92	Tin ...	Sn	118.7
Iridium ...	Ir	193.1	Titanium ...	Ti	48.1
Iron ...	Fe	55.84	Tungsten ...	W	184.0
Krypton ...	Kr	82.92	Uranium ...	U	238.2
Lanthanum ...	La	139.0	Vanadium ...	V	51.0
Lead ...	Pb	207.20	Xenon ...	Xe	130.2
Lithium ...	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
Lutecium ...	Lu	175.0	Yttrium ...	Yt	88.7
Magnesium ...	Mg	24.32	Zinc ...	Zn	65.37
Manganese ...	Mn	54.93	Zirconium ...	Zr	90.6
Mercury ...	Hg	200.6			

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

An ordinary meeting of the Society was held on Wednesday evening, December 6, 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 Mr. G. W. Baker was read for the second time; and a certificate in favour of Professor Alfred Francis Joseph, D.Sc., A.R.C.Sc. (Lond.), F.I.C., 296, Willesden Lane, N.W., Professor of Chemistry, Ceylon Medical College, was read for the first time.

The President announced that the Decennial Index of the ANALYST, 1906-1915, was now ready, and could be obtained from Messrs. Billing and Sons, Ltd., Railway Esplanade, Guildford, the price being one guinea. He hoped that all members of the Society would make a point of purchasing it.

The following papers were read: "Copying-Ink Pencils and the Examination of their Pigments in Writing," by C. A. Mitchell, M.A., F.I.C.; "Brazilian Oil Seeds," by E. Richards Bolton, F.I.C., and Dorothy G. Hewer, B.Sc.; "Army Sanitation," by Captain C. G. Moor, M.A., F.I.C.; and "The Analysis of Honey and Other Substances containing Lævulose," by W. R. G. Atkins, Sc.D.

The list of the Council's nominations of Officers and Council for 1917 was read as follows:

President.—G. Embrey, F.I.C.

Past-Presidents serving on the Council (limited by the Society's Articles of Association to eight in number).—L. Archbutt, F.I.C.; Edward Bevan, F.I.C.; A. Chasten Chapman, F.I.C.; Bernard Dyer, D.Sc., F.I.C.; Otto Hehner, F.I.C.; R. R. Tatlock, F.I.C.; E. W. Voelcker, A.R.S.M., F.I.C.; J. Augustus Voelcker, M.A., B.Sc., Ph.D., F.I.C.

Vice-Presidents.—Harold G. Colman, D.Sc., Ph.D., F.I.C.; J. T. Dunn, D.Sc., F.I.C.; C. A. Hill, B.Sc., F.I.C.

Hon. Treasurer.—E. Hinks, B.Sc., F.I.C.

Acting Hon. Treasurer.—E. W. Voelcker, A.R.S.M., F.I.C.

Hon. Secretaries.—P. A. Ellis Richards, F.I.C., and E. Richards Bolton, F.I.C.

Other Members of Council.—W. T. Burgess, F.I.C.; T. W. Glass, B.Sc., F.I.C.; H. G. Harrison, M.A., F.I.C.; G. N. Huntly, B.Sc., A.R.C.Sc., F.I.C.; P. H. Kirkaldy, F.I.C.; S. J. C. G. Macadam, F.I.C.; W. Macnab, F.I.C.; W. Partridge, F.I.C.; W. H. Roberts, M.Sc., F.I.C.; E. Russell, B.Sc., F.I.C.; H. L. Smith, B.Sc., F.I.C.; J. Webster, F.I.C.



**COPYING-INK PENCILS AND THE EXAMINATION OF THEIR
PIGMENTS IN WRITING.**

By C. A. MITCHELL, B.A., F.I.C.

(Read at the Meeting, December 6, 1916.)

THE nature of the pigments in copying-ink pencils might seem, on first thoughts, to be of little interest to anyone except the manufacturer and the consumer, who naturally would not buy an unsuitable article; but when I mention that during the last few years I have had to examine these pigments in connection with two criminal trials and one civil action, the importance of the subject in forensic chemistry will be recognised.

One of the earliest applications of aniline dyestuffs was in the preparation of inks which could be used for copying purposes. Unlike iron-gall copying inks, which form an insoluble pigment on oxidation, and so will only yield good copies for a short time after writing, concentrated solutions of aniline dyestuffs will produce writing which does not undergo any material alteration on exposure to the air for a relatively long period, and from which, therefore, a copy may be taken at any subsequent time.

Most of the commercial inks of this type contain sugar, glycerol, or deliquescent salts, to give consistency, and to prevent their drying up in open bottles. Methyl violet has long been the favourite dyestuff for this purpose, and is given as the main constituent in the earlier formulæ for such inks.

This copying quality of solutions of aniline dyestuffs suggested the incorporation of the pigment with the graphite of a lead pencil, which would then be capable of producing characters from which one or more copies could be taken on damp paper in a copying press.

The earliest reference to copying-ink pencils which I have been able to discover is a description of their composition by Viedt in 1875 (*Dingler's polyt. J.*, 1875, 216, 96). It is there stated that the pigment consists of a mixture of kaolin clay, graphite, and methyl violet, and that gum arabic is not a suitable binding material. A year previously a patent was taken out by Petit (Eng. Pat., 4090, 1874) for the manufacture of pencils of this type, but it was abandoned before completion.

It is probable that at the present time such pencils are but seldom employed for copying purposes, but are commonly used for producing writing which cannot be erased so readily as the marks of a lead pencil. Hence they are also frequently termed "indelible pencils," although the description is only relatively correct. Lehner (Eng. trans. from 8th Germ. Ed. *Ink Manufacture*, 1902, p 125) gives the composition of the pigments in four kinds of ink pencils then being made by Faber in Bavaria. I have calculated his figures into the corresponding percentage amounts:

					Aniline Dyestuff.	Graphite.	Kaolin Clay.
1	50.0	37.5	12.5
2	44.2	32.6	23.2
3	30.0	30.0	40.0
4	25.5	24.5	50.0

The pencil containing No. 1 is stated to be very soft, that containing No. 4 very hard. Neither of the specimens of Faber's pencils which I examined gave results corresponding with any of these formulæ (*vide infra*).

Pencils containing methyl violet are still the most popular, although those containing blue and red pigments are also made by most manufacturers. Two examples of blue copying-ink pencils are included in the subjoined table of analyses.

The following is an outline of the methods I used to estimate the constituents of these pigments:

Moisture.—From 0.25 to 0.3 gm. of the finely powdered pigment was dried in the water-oven until constant in weight.

Dyestuff.—The dried pigment was treated with successive small quantities of warm 95 per cent. alcohol, each extract being decanted on to a small filter until no further colour was extracted. In some instances the combined alcoholic filtrates were evaporated, and the residue dried in the water-oven, but in most cases the amount of dyestuff was estimated by difference.

A colorimetric method was also tried, an aliquot portion of the alcoholic extract being compared with a solution of 0.05 gm. of methyl violet in 50 c.c. of alcohol diluted to the required extent. The objection to a colorimetric method is that neither the standard dyestuff nor that in the pigment of the pencil are necessarily of the same degree of purity.

Substances Insoluble in Alcohol.—The filter-paper through which the alcoholic extracts had been filtered was lightly brushed with a camel's-hair brush dipped in alcohol, so as to remove all fine particles of graphite and kaolin clay. These brushings were added to the insoluble residue in the basin, which was then heated in the water-oven until constant in weight.

Carbon.—The dried residue was heated in a wide platinum basin covered with a flat lid. Occasionally the graphite burned away quite readily, but more often it was necessary to accelerate the ignition by introducing small quantities of ammonium nitrate from time to time. By keeping the basin covered it was possible to avoid all loss during the deflagration.

The Residue from the Ignition.—This was boiled with hydrochloric acid, and any iron or aluminium present in the solution was estimated in the usual way.

The results thus obtained with the pigments of twenty-one pencils typical of those on the market since 1907 to the present year are given in the following table: From these results it appears that the proportion of dyestuff used in these pencil pigments ranges from less than 25 per cent. (Nos. 13 and 17) to about 50 per cent. (Nos. 12 and 19).

As part of the ash is derived from impurities in the original graphite, it is only possible to make an approximate estimation of the relative proportions of graphite and kaolin clay from these figures. Impure graphite may contain only about 50 to 70 per cent. of carbon, but the better kinds used for pencils generally contain not more than 3 or 4 per cent. of impurities (iron oxide, silica, etc.).

When the amount of ash is less than 5 per cent., as in the case of Nos. 4, 12, 13, 16, 17, 20 and 21, it is probable that the mineral matter was derived solely from the graphite. The ash of No. 14 (8.76 per cent.), consisting largely of ferric oxide, was also probably due to the graphite.

COMPOSITION OF PIGMENTS OF COPYING-INK PENCILS.

	Description.	Origin.	Date.	Moisture (Loss at 100° C.).		Residue in Insoluble Alcohol.		Dye stuff.		Loss on Ignition (Graphite, etc.).		Ash (Kaolin, etc.).		Remarks.
				Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.			
1	American Pencil Co., Duplex, Blue	U.S.A.	1911	2.35	76.45	21.20	27.09	47.36	Red ash, Fe ₂ O ₃ = 14.54%					
2	Do. Duplex, Violet	U.S.A.	1916	3.96	59.28	36.76	27.36	31.92	White ash, Al ₂ O ₃ = 2.19%				Trace Fe	
3	Do. "Ink Eau," No. 160	U.S.A.	1916	7.48	51.53	40.99	25.48	26.36	Al ₂ O ₃ and Fe ₂ O ₃ = 0.59%					
4	Do. Venus, No. 167	U.S.A.	1916	2.30	60.89	36.81	56.84	4.05	Slight iron reaction					
5	Eagle Pencil Co., Atlas, No. 823	London	1907	4.86	66.69	28.45	35.78	30.91	Buff-coloured ash, Al ₂ O ₃ = 1.21%				Trace of Fe	
6	Do. Copying Eagle Ink, No. 1522	U.S.A.	1911	4.53	67.77	27.70	11.66	56.11	White ash, Al ₂ O ₃ = 2.52%				Trace of Fe	
7	Do. Do. No. 824	U.S.A.	1911	3.75	63.95	32.30	13.90	50.05	White ash					
8	Do. Leads, No. 119	U.S.A.	1911	3.55	57.14	36.84	22.18	34.96	Putty-coloured ash, Fe ₂ O ₃ = 3.0%					
9	Faber, Copying X	Bavaria	1907	3.72	64.48	31.80	11.86	52.86	Al ₂ O ₃ + Fe ₂ O ₃ = 5.31%					
10	Do. X	Bavaria	1911	2.64	71.27	26.09	23.50	47.77	Al ₂ O ₃ + Fe ₂ O ₃ = 13.27%					
11	Do. Blue, No. 2251	Bavaria	1907	1.82	58.68	39.50	29.34	29.34	Ash, mainly Fe ₂ O ₃					
12	Hardmuth, "Mephisto"	Austria	1907	3.56	47.14	49.94	44.14	3.00	Trace of Fe					
13	Hessin, Copying Ink, No. 74	Bavaria	1911	3.74	72.92	23.34	68.12	4.80	Red ash. Good Fe reaction					
14	"Ink and Copying"	U.S.A.	1911	5.36	61.40	33.24	52.64	8.76	Ash, mainly Fe ₂ O ₃					
15	Kurz	Bavaria	1907	3.83	57.59	38.58	40.01	17.58	Trace of Fe					
16	Lapis Tinta, No. 180	—	1911	2.04	69.36	28.60	64.86	4.50	Buff-coloured ash. Good Fe reaction					
17	Rowney	Britain	1911	4.53	73.05	22.42	69.17	3.88	Reddish ash. Good Fe reaction					
18	Swan Copying, No. 1039	Bavaria	1907	6.33	59.83	33.84	7.61	52.22	White ash, Al ₂ O ₃ = 19.37%				Trace of Fe	
19	Do. No. 1039	Bavaria	1911	2.05	46.43	51.52	5.50	40.93	Do.					
20	Wolff's "British Preference"	London	1916	2.72	65.48	31.80	62.08	3.40	Red ash, mainly Fe ₂ O ₃					
21	Do. "Royal Sovereign"	London	1916	2.91	65.35	32.74	62.56	2.79	Do.					

The total amounts of mineral matter range from 2.79 per cent. in No. 21 to 56.11 per cent. in No. 6. By attributing about 5 per cent. (calculated on the entire pigment) to the graphite, and adding this to the loss on ignition, a result approximating to the proportion of impure graphite originally used would be obtained.

These pigments may therefore be classified into four main groups—viz. (1) those composed of graphite and dyestuff only; (2) those in which the dyestuff has been incorporated with approximately equal proportions of kaolin and graphite (Nos. 2, 3, 5 and 8); (3) those in which the kaolin is largely in excess (Nos. 1, 6, 7, 9, 10, 18 and 19); and (4) one case (No. 15) where the graphite predominates.

The amount of iron oxide left on igniting the pigment ranged from *nil* to 14.54 per cent. in No. 1, in which it constituted about a third of the total ash.

The alumina extracted from the ash by means of hydrochloric acid ranged from 0.59 per cent. in the case of No. 3 to 19.37 per cent. in No. 18. Where alumina was present in quantity it acted as a mordant, so that about 5 per cent. of the total dyestuff was not extracted by alcohol, and the residue was of a pale mauve colour. Its presence affected the behaviour of the pigment in the solution tests, and probably accounted for the inferior copying properties of some of the pencils (notably Nos. 18 and 19).

The variations in the pigments in pencils of the same type made by the same manufacturers at different periods are shown in Nos. 10 and 11 and 18 and 19. Making allowance for the variations in the grades of graphite, the two pencils manufactured by Faber were probably made from the same formula. But there is a pronounced difference in the proportions of dyestuff in the two Swan pencils, made in 1907 and 1911 respectively.

COPYING PROPERTIES.—Two consecutive copies on moist paper were taken of writing done with most of these pencils. The best results were obtained with No. 3 “Ink Eau” and No. 12 Hardmuth’s; the worst with No. 16 “Lapis Tinta” and Nos. 18 and 19 (Swan).

The copying properties thus appear to depend not only on the proportion of dyestuff, but also on the influence of the substratum on the solution of the dyestuff in water. For instance, No. 19 (Swan), which contained a larger proportion of dyestuff than any of the other pencils, but had a large amount of alumina in its pigment, gave only a very faint copy, whereas No. 14, with a medium proportion of dyestuff, but no alumina, gave a fairly good copy. The nature of the graphite in the pigment also appears to have an influence on the copying properties. For example, No. 4 (“Venus”), in which the substratum was mainly graphite, gave a relatively poor copy compared with No. 2 (“Duplex”), which contained about the same amount of dyestuff incorporated with a mixture of graphite and kaolin; while one of the best copies was given by No. 12, in which the basis was graphite only.

The behaviour of the written characters on treatment with a drop of water, or, in other words, their copying properties in miniature, may thus be used as one of the tests for distinguishing between the pigments of different pencils in writing.

DIFFERENTIATION OF THE PIGMENTS IN WRITING.—It is possible to distinguish between many of these pigments by the difference in the colours of the writing. For example, pigments which contain a large proportion of kaolin clay are of a much

brighter tint than those in which graphite predominates, and even the intermediate colours may be differentiated to some extent with the aid of the microscope.

For such colour comparisons, and also for following the parallel action of reagents upon two specimens of writing, the comparison microscope devised by Mr. A. S. Osborn, of New York, will be found of the greatest use. This instrument, which is made by Messrs. Bausch and Lomb, has two separate body-tubes, the upper ends of which are fitted into a prism-box containing a double prism. The objects to be compared are placed side by side below the respective objectives, and when viewed through the single eyepiece each appears to occupy one-half of the field, owing to the effect of the double prism.

In each tube is a slot with a movable shutter intended for the introduction of Lovibond's tintometer glasses, so that it is possible to obtain a numerical record of the colour of any pigment placed under either objective.

SOLUTION TESTS.—The behaviour of the pigments on treatment with different solvents is frequently characteristic.

If a drop of water be placed on part of the writing and allowed to remain undisturbed for a few minutes, pronounced differences will be observed with different pigments. In some cases (*e.g.*, Nos. 2, 3, 4, 5, 6 and 12) there is immediate solution of the dyestuff, while in others (*e.g.*, Nos. 10, 11, 17, 18 and 19) the drop remains colourless, or practically so, for five minutes or longer. As has been mentioned already, the amount of dyestuff which can be absorbed by applying filter-paper to the drop affords a rough indication of the copying capacity of the pigment. Again, the behaviour of ether may prove distinctive. There is usually a pronounced centrifugal action, but in some cases the dyestuff is diffused over the whole area (Nos. 4, 5, 8 and 13), while in others the core is left much paler or nearly colourless, and a dark zone is formed (Nos. 9, 12 and 15). A similar test with a drop of acetic acid will sometimes distinguish between two closely similar pigments.

The residue left after removal of the dyestuff by means of acetic acid should be examined microscopically. When much graphite is present, the carbon particles will be seen scattered plentifully all over the field, while pigments poor in graphite will show only a scanty sprinkling of carbon. The difference between Nos. 13 and 18 in this respect was quite pronounced.

CHEMICAL TESTS.—A consideration of the analytical results given in the table indicates that chemical tests of differentiation may be based on the nature and quantity of the dyestuff, on the influence of the graphite or kaolin clay on the course of colour reactions given by the dyestuff, and on the presence of iron, alumina, or other mineral impurities in the pigments.

The Dyestuff.—The dyestuff in these pigments may be readily extracted by placing a drop of acetic acid or alcohol on a portion of the writing, and then applying filter-paper. To prevent any chance of reduction, the solvent should be allowed to evaporate spontaneously.

The colour reactions of violet dyestuffs thus transferred as spots to filter-paper differ somewhat from those given by the same dyestuffs on sized paper, owing to the more rapid diffusion of the reagent in the former case. The influence of any impurities in the dyestuff on the course of the reaction is much more pronounced in the tests on the non-absorbent paper.

For example, I obtained the following results with samples of methyl violet and with crystal violet:

REACTIONS OF METHYL VIOLETS ON SIZED PAPER.

	Methyl Violet Extra III. N. (B.A.S.F.).	Methyl Violet O. (B.A.S.F.).	Crystal Violet (B.A.S.F.).
Strong nitric acid ..	Bright yellow with green zone, changing to green	Yellow to brownish-yellow, changing to dark green with purple core	Bright yellow, thin green zone
Sulphuric acid (50%)	Bright yellow, paler in centre	Yellow to greenish-yellow or brown	Bright yellow
Stannous chloride ..	Grass-green with dark green centre	Bluish-green	Pale green, darker zone
Sodium nitrite with acetic acid	Blue with dark blue zone, subsequently bleached	Blue with dark blue zone	Violet blue centre, light blue and dark blue zones
Titanous chloride ..	Bright yellow with green zone	Dirty yellow with faint green zone	Bright yellow, thin green zone
Sodium hypochlorite with acetic acid	Blue - green centre, dark blue zone, before bleaching	Blue core, white inner zone, dark blue outer zone	Pale blue, dark blue zone, before bleaching

REACTIONS OF METHYL VIOLETS ON FILTER-PAPER.

	Methyl Violet Extra III. N.	Methyl Violet O.	Crystal Violet.
Nitric acid	Green with orange zone	Dark green with orange zone	Bright yellow, then green with yellow zone
Sulphuric acid ..	Bright yellow	Dull yellow	Bright yellow
Hydrochloric acid ..	Bright yellow	Dull yellow	Bright yellow, darkening
Stannous chloride ..	Deep green with darker centre	Deep green, forming plum-coloured centre	Grass-green with darker centre
Sodium nitrite with acetic acid	Blue with darker zone	Blue with darker zone	Violet-blue with darker zone
Titanous chloride ..	Yellow, darkening	Dirty yellow	Deep yellow

The sodium nitrite was applied in the form of a minute particle of the salt, which was then moistened with 80 per cent. acetic acid.

The titanous chloride was the ordinary commercial solution, which had been kept for some years, and did not react as strongly as when fresh.

In the tests applied to the filter-paper stains the differences in the colorations given by Methyl Violet Extra III. N. and O. were mainly in the brilliancy of the former, and they were hardly sufficiently distinctive to differentiate between the two dyestuffs.

The alcoholic extracts from most of the pencil pigments left stains which gave very similar colour reactions.

In the case of the two blue pencil pigments, however, there was a pronounced difference. The blue Duplex pencil (No. 1) contained a water-soluble blue aniline dyestuff, while in Faber's blue pencil (No. 11) the soluble dyestuff to which it owed its copying properties was methyl violet, and its blue colour was due to Prussian blue.

In applying these reagents to the pigments of the pencils in writing, the course of the colour reactions should be followed under the microscope. Speaking generally, they will resemble the reactions of the residues from the extracts, but will vary in their speed and intensity with the proportion of the dyestuff, while the purity of the colour will be affected by the other constituents of the pigment.

Another useful reagent is 5 per cent. potassium ferrocyanide solution, which is applied to the spot from which the pigment has been extracted by means of acetic acid. In some cases (*e.g.*, No. 21) a pronounced green coloration was obtained immediately, while in others there was only the faintest indication of iron after a long period (*e.g.*, No. 5).

I attempted to adapt F. Atack's alizarine red test (*ANALYST*, 1915, **40**, 511) for alumina, using a specimen of the dyestuff which he kindly placed at my disposal. Unfortunately, the test was unsuitable for this purpose, as a blood-red coloration was obtained with certain papers to which no pigment had been applied, apparently owing to the presence of alum in the paper.

Silver nitrate solution may be employed as an additional test, a drop being applied to the writing either before or after treatment with acetic acid. The presence of chloride is shown by the growing opalescence of the drop, as seen under the microscope.

In this way it was possible to distinguish between the pigments in the two violet pencils made by Faber (Nos. 9 and 10).

By way of illustration, the case of *Rex v. Wood*, tried in 1907, may be cited. Some fragments of partially burned paper, on which were words written in copying-ink pencil, were found in the grate of a room where a woman had been murdered. The resemblance of the writing to that upon a postcard led to the arrest of the man Wood, and in his pocket was found a Swan copying-ink pencil. The question was thus raised whether the pigment of this pencil could have been used in writing the words on the fragments.

The colour of the pigment when applied to paper matched exactly, both in light and dark portions, the colour of writing on the fragments. It was a very deep purple, quite distinct from the colour of the ordinary Swan copying-ink pencil (No. 1039). The colour somewhat resembled that of the pigments in some of the pencils made by the Eagle Pencil Co., but the solution test with a drop of water sharply differentiated between the two pigments. The writing on the fragments and that produced by Wood's pencil repelled the water for a long time, and the drops remained practically colourless for five minutes.

Ether produced a fairly uniform stain with very little centrifugal effect, while acetic acid acted rapidly, producing zones and extracting much dyestuff. Two good copies could be taken on filter-paper of the acetic acid stains, while the residue still retained colour. This residue showed a larger proportion of graphite particles

than the Swan pencil (No. 1039), although these were scanty as compared with results given by pencils rich in graphite.

The ferrocyanide test applied to the residue from the acetic acid treatment showed no indications of green coloration at first, and only a slight green tint after drying. In this respect the pigment resembled that of the Swan pencil (No 1039).

The following colour reactions were given by this pigment in comparison with certain other pencil pigments:

	Wood's Pencil, and Writing on Fragments.	Swan Pencil 1039 (No. 18).	Hessin's Pencil (No. 13).	Faber's Pencil (No. 9).	Eagle Pencil (No. 5).
Nitric acid ..	Yellow to deep orange, according to amount of pigment. Greenish zone with tendency to form outer pale zone. Dried with dirty mauve or greenish centre	Very faint yellow, bleached	Very pale green, slowly darkened to olive-green	Pale green drop, with light-yellow zone	Pale green, darkening to olive-green
Stannous chloride	Dirty green	Light dirty green	Faint lemon-yellow	Faint straw tint	Faint straw tint
Sodium nitrite with acetic acid	Deep bluish-green, leaving pale green core, and dark blue narrow zone	Rapidly bleached, leaving narrow pale blue zone	Bleached, leaving pale blue zone	Deep blue zone, nearly colourless core	Deep blue zone, pale-blue core
Titanous chloride	Deep yellow, slowly bleached. Left pale green core, deep blue zone	Bright yellow, quickly bleached. Left very pale green core, with wide blue green zone	Yellow, then bleached	Bright yellow, slowly bleached	Dirty yellow
Sodium hypochlorite with acetic acid	Rapidly bleached. Deep violet-blue zone	Rapidly bleached. Light violet-blue zone	Bleached, leaving pale blue zone	Slowly bleached. Colourless ground	Rapidly bleached. Colourless area

The general course of the reactions of the pigment of Wood's pencil and of the writing on the fragments was similar to those given by the Swan pencil, but they could be readily distinguished when compared under the microscope.

After having denied that he had written the words on the fragments, Wood subsequently admitted that he had done so.

In another criminal case (*Rex v. Seddon*) the question was raised whether the entries of payments in a note-book over a period of fourteen months had been made on the corresponding dates. The pigment of the copying-ink pencil was of the same

character throughout the whole period, but it was, of course, impossible to express any opinion as to the age of any part of the writing.

The degree of permanence of methyl violet in association with graphite and kaolin clay has not been ascertained, although the dyestuff by itself is well known to be fugitive. It is possible that under certain conditions the degree of fading might enable an estimate of the age of writing to be formed.

In the case of *Macbeth v. King*, which was tried in July of this year (1916), the question of the fastness of copying pencils was raised. The steamship *Membrand* was presumably lost at sea early in 1915. Two months later the stave of a wooden bucket was washed ashore near Hornsea, and on this was written in copying-ink pencil the words "Membrand torpedoed engine-room port-side. Good-bye, dear."

If this were genuine, it would show that the vessel had been sunk by war risks, and one set of underwriters would be liable. Otherwise it was contended that the ship had fallen a victim to ordinary marine risks.

At the Board of Trade inquiry in 1915 it had been suggested that a copying-ink pencil pigment would not withstand the action of sea-water for two months. To determine this point I wrote words on pieces of oak with four kinds of copying-ink pencil, and placed these in a strong solution of salt and water in a glass basin, which was shaken at frequent intervals and exposed to strong sunlight. The writing on these slips remained quite legible after eight weeks, although the writing done with Hardmuth's pencil was less smudged than that done with the Eagle or Atlas pencil. The pigment from Faber's pencil was most affected by the treatment. There would therefore seem to be little doubt as to the possibility of writing done with a copying-ink pencil remaining relatively unaffected when immersed in sea-water for a long period.

In giving his decision, the judge held that conceivably the stave was genuine, but he was not convinced on the point; he decided, however, upon other grounds that the vessel had been lost by war risks. (See *Times Law Reports*, 1916, 32, 581.)

In conclusion, I would thank Messrs. Wolff and Sons for their kindness in supplying me with specimens of their pencils and details as to their manufacture; and the Bausch and Lomb Optical Company for the loan of instruments and information with regard to the construction of the comparison microscope.



THE ANALYSIS OF HONEY AND OTHER SUBSTANCES CONTAINING LÆVULOSE.

By W. R. G. ATKINS, Sc.D.

(*Read at the Meeting, December 6, 1916.*)

IN the course of some work on mixtures of the three reducing sugars, dextrose, lævulose, and maltose, met with in plant tissues, it was found necessary to devise means for the estimation of each. If maltose is hydrolysed by prolonged boiling with acid, so much lævulose is destroyed as to render the estimation worthless. The oxidising action of bromine in removing aldehydic sugars while leaving the ketonic sugar lævulose untouched, was finally made use of for the purpose of estimating one constituent of the mixture of the three sugars. While the work was in progress the researches of Davis and Daish (*ANALYST*, 1913, **38**, 504) were published.

These workers obtained very accurate results, but the preparation of cultures of pure yeasts is troublesome, and the length of time, about twenty-one days, required for complete fermentation is a drawback to the general usefulness of the method for technical analyses.

The bromine method of Wilson and Atkins (*ANALYST*, 1917, 19) does not give as accurate results as those obtained by Davis and Daish, but it is rapid.

If a mixture containing dextrose, lævulose, and maltose, to which has been added excess of bromine and enough sulphuric acid to render the solution decinormal, be allowed to remain for forty-two hours at room temperature, the lævulose only is unoxidised. To insure completion of the reaction the reaction flask must be shaken continuously during the period. This may be effected by causing it to rotate slowly with the long axis of the bottle at a small angle to the horizontal. Glass beads in the solution may also be used to assist shaking. The maltose leaves a mere trace of reducing power, dextrose leaves approximately 1 per cent. of the original reducing power, and lævulose falls off in reducing power approximately 1 to 2 per cent., owing to its decomposition, even in the cold, by the $\frac{N}{10}$ acid and by the hydrobromic acid formed during the oxidation of the other sugars.

The slight loss in the quantity of lævulose is roughly balanced by the reducing power remaining after the destruction of the dextrose and maltose. The excess of bromine is cautiously removed by gaseous sulphur dioxide, and finally by titration with solution of the gas in water. The acidity is just removed by the addition of potassium carbonate, care being taken to leave the liquid neutral or faintly acid, but not alkaline. The reducing power of an aliquot portion is then determined. For this we found Kendall's solution (*ANALYST*, 1912, **37**, 205) suitable, as it does not dissolve the cuprous oxide. Kendall did not give a table for lævulose, so one was constructed by the author (*ANALYST*, 1916, **41**, 285).

By this means lævulose may be estimated readily and with tolerable accuracy in the presence of dextrose and maltose, or either of them. If only dextrose and lævulose are present, as in natural honey, which contains about 36 per cent. of the latter, it is sufficient to determine the reducing power before and after oxidation

with bromine. The cane-sugar in the honey must be estimated separately by determining the reducing power before and after inversion. Oxidation should be effected on the inverted solution, due allowance being afterwards made for the dextrose and lævulose resulting from the inversion.

It is, of course, possible to estimate dextrose and lævulose in a mixture of the two by obtaining the total reducing power and the optical activity. From these data two equations can be constructed, and a solution of the simultaneous equations gives the values of each. In this procedure, however, errors are magnified, and the procedure is not so accurate as the determination of reducing power before and after oxidation.

It appears that oxidation with bromine may be of use in the technical analysis of honey, syrups, jams, and other articles containing these sugars, especially as it affords an easy method of detecting the presence of dextrose in abnormal quantities.

TRINITY COLLEGE,
DUBLIN.



ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Vitamines and Lipoids in Butter and Margarine. J. de Ruiter. (*J. Ind. and Eng. Chem.*, 1916, 8, 1020-1021.)—A method of estimating lipid substances in oils in fats was based on their solubility in concentrated acids, and precipitation on dilution with water. Results were most rapidly obtained by means of hydrochloric acid of sp. gr. 1.19, the lipid being subsequently separated by the addition of water, washed on a filter, dried at 100° C., and weighed. In this way the following results in grms. per 100 c.c. of fat were obtained: Sesame oil, 0.10; arachis oil, trace; olive oil, trace; cod-liver oil, trace; refined coconut oil, trace; filtered butter fat, trace; butter, 0.40; vegetable margarine ("Klappa"), 0.75; vegetable margarine ("Planta"), 0.475; margarine, 0.975; and "bran butter," 1.125. These results indicate that the lipoids in butter are not in the fat, but in the casein, and that they represent only a part of the total lipid content of milk (0.75 per cent.). The vegetable margarine and the margarine proper derived their lipoids mainly from the skimmed milk with which they were churned, while egg yolk in addition to skimmed milk may have caused the high result given by the margarine. It is suggested that albumin containing vegetable seeds may be used to increase the lipoids in margarine, as was done in the case of the "bran butter," which was prepared from arachis oil and coconut oil incorporated with a liquid obtained by steeping wheat bran in lime water and separating it from the deposit of starch.

C. A. M.

Detection of Excess of Shell in Cacao Powder. (*Chem. Zeit.*, 1916, **40**, 969-970.)—The following official (German) methods are given for the detection of an excess of cacao shell in cacao powder. If a preliminary microscopical examination of the cacao shows indications of an excessive proportion of shell particles in the sample, an estimation of the amount of crude fibre is made. In some cases, however, owing to the fineness to which the shell has been ground, the microscopical examination does not indicate plainly that excess of husk is present, and the insoluble phosphates must be estimated in addition to the crude fibre. Estimations of the moisture and fat are essential, since the results for crude fibre are expressed in terms of the dry, fat-free substance.

Estimation of Moisture.—Five grms. of the sample are mixed with 20 grms. of ignited sand, and the mixture is dried at 105° C., until practically constant in weight, but the heating should in no case be prolonged for more than four hours.

Estimation of Fat.—Five grms. of the cacao are placed in a tube 4 cm. in diameter and containing a small layer of asbestos supported on a porcelain plate having holes about 1 mm. in diameter; this filter tube is attached to a filter flask, and 10 c.c. of ether are poured on the surface of the layer of cacao. As soon as the ether begins to drop into the flask, suction is applied, and further quantities of 10 c.c. of ether are added, successively, until about 100 c.c. of ethereal solution have been collected. This solution is then evaporated and the residue of fat weighed.

Estimation of Crude Fibre.—The residue of cacao remaining in the filter tube is freed from ether, and, together with the asbestos (the asbestos used in this and the succeeding filters should have been boiled with dilute sulphuric acid, then with dilute potassium hydroxide solution, washed, dried, and ignited), is transferred to a flask and boiled for one hour under a reflux condenser with 200 c.c. of 1.25 per cent. sulphuric acid. The mixture is then filtered through an asbestos filter, washed with hot water, and the filter and its contents are returned to the flask and boiled for one hour with 200 c.c. of 1.25 per cent. potassium hydroxide solution. The mass is again collected on an asbestos filter and washed, and the treatment with sulphuric acid and alkali solution repeated. The washed mixture of asbestos and crude fibre obtained finally is transferred to a platinum basin, dried at 105° C., and weighed, then ignited, and again weighed. The difference between the two weights gives the quantity of crude fibre present. The fat-free, dry cacao should not contain more than 6 per cent. of crude fibre; if this limit is exceeded, the cacao contains an amount of shell in excess of that which is present in well-manufactured cacao powder.

Estimation of Phosphates.—Twenty grms. of the cacao are ignited at a low temperature, the carbonised mass is collected on a filter, washed with hot water, and the filter and its contents are ignited in a platinum basin to a white ash; the filtrate is now added to the basin and evaporated to dryness. The residue thus obtained is gently ignited, again evaporated with the addition of a few drops of hydrogen peroxide solution and 10 c.c. of 25 per cent. hydrochloric acid, the residue is taken up with hydrochloric acid and hot water, the solution is filtered, the filtrate nearly neutralised with sodium hydroxide solution, using methyl orange as indicator, then heated on a water-bath for five minutes, and treated with a further small quantity of alkali, so that the solution still remains slightly acid in reaction. The precipitated iron and aluminium phosphates are now collected on a filter and washed. The filtrate

is diluted to 100 c.c. The soluble phosphates are estimated by treating 10 c.c. of this solution with 30 c.c. of neutral calcium chloride solution, adding a few drops of phenolphthaleïn solution, titrating the mixture with $\frac{N}{10}$ sodium hydroxide solution until a distinct red coloration is obtained, then keeping the mixture at 15° C. for two hours, and titrating the slight excess of alkali added. Under these conditions 1 c.c. of $\frac{N}{10}$ alkali solution is equivalent to 4.75 mgrms. of PO_4 . To estimate the insoluble phosphates, the filter containing the precipitated iron and aluminium phosphates is transferred to a flask containing 30 c.c. of trisodium citrate solution (200 grms. of the salt dissolved in 300 c.c. of water) which have been previously cooled in ice-water and neutralised, using phenolphthaleïn as the indicator. The contents of the flask are heated on a water-bath for twenty minutes, then cooled in ice-water, and titrated with $\frac{N}{10}$ sodium hydroxide solution. Each c.c. of $\frac{N}{10}$ alkali solution is equivalent to 9.5 mgrms. of PO_4 . The results of both estimations are expressed as percentages of the cacao powder; in the case of a cacao free from an excessive quantity of shell, the proportion of insoluble PO_4 will not exceed 4 per cent. of the total PO_4 .

W. P. S.

Fermented Milk Products: the "Laben Raieb" of Egypt and the "Miciuratu" of Sardinia. A. Sanna. (*Staz. sperim. agrar. ital.*, 1914, 49, 773-788; through *Int. Rev. of the Science and Practice of Agriculture*, 1916, 7, 878-880.)—"Miciuratu" is prepared by boiling milk (cow's, ewe's or goat's, or a mixture of the three) for about six minutes, then cooling it to 37° C., and introducing the ferment diluted with milk; after seven hours the milk forms a doughy mass and is ready for consumption. The sugar, fat, and proteins undergo changes during the preparation, the sugar being converted into lactic acid; the acidity increases gradually up to the end of three days, after which time the product is unfit for use owing to butyric fermentation. Ethyl alcohol is also formed, the three-day-old product containing about 2 per cent. of this alcohol, and traces of acetaldehyde are present. The casein and albumin are partially peptonised and the fat is hydrolysed to a slight extent, traces of glycerol appearing in the product. "Laben raieb" is prepared in a similar manner, but the milk is evaporated at 80° C. until its volume is reduced by one-third before the ferment is introduced; the ferment in this case consists of a mixture of milk (also concentrated by one-third) and "laben raieb" prepared the day before. Allowing for the difference in concentration, its composition is similar to that of "miciuratu."

W. P. S.

Detection of Resorcinol. F. C. Krauskopf and G. Ritter. (*J. Amer. Chem. Soc.*, 1916, 38, 2182-2187.)—When as little as 1 mgrm. of resorcinol dissolved in 50 c.c. of water is treated with 1 c.c. of a dilute solution of cobalt chloride (0.4 gm. cobalt per litre), 0.25 c.c. of concentrated ammonia, and 3 c.c. of 95 per cent. alcohol, a dark green colour is developed. Phenol under similar conditions does not produce any colour, whilst catechol, quinol, and pyrogallol, when present in sufficient quantity, develop a brown colour. Nevertheless, the solution is green without a perceptible trace of brown if as much as 10 mgrms. of resorcinol are present in 50 c.c. of a solution containing 0.2 gm. of quinol or of pyrogallol. As little as 5 mgrms. of resorcinol

can be readily detected in presence of 0.2 grm. of catechol. Although phenol does not itself produce an interfering colour, it reduces the sensitiveness of the test for resorcinol to about 5 mgrms. in 50 c.c. of solution containing 0.3 grm. of phenol.

G. C. J.

Estimation of Salol and Acetanilide, or of Salol and Phenacetin, in their Mixtures. B. Salkover. (*Amer. J. Pharm.*, 1916, **88**, 484-485.)—The method depends on the relative insolubility of acetanilide or phenacetin in petroleum spirit, and on the solubility of salol in this solvent. A weighed quantity of the mixture under examination is shaken for thirty minutes in a closed flask with a measured volume of chloroform; an aliquot portion of the solution is then filtered into a weighed flask, the chloroform is evaporated, the residue dried at 60° C., and weighed. This estimation gives the combined amount of salol and acetanilide, or of salol and phenacetin, which may be present. Another portion of the sample is then extracted in a similar way with petroleum spirit; the residue obtained is dried at 50° C., and weighed. In this case the residue consists of salol alone, but its weight must be corrected for the slight solubility of acetanilide or phenacetin, depending on which of these is present in the mixture. One hundred c.c. of petroleum spirit (b.-pt. 40° to 45° C.) dissolve 0.015 grm. of phenacetin or 0.022 grm. of acetanilide. The accuracy of the method is not affected by the presence of talc, starch, acacia or tragacanth.

W. P. S.

Estimation of Sugar in Meat Products, particularly Extracts. W. B. Smith (*J. Ind. and Eng. Chem.*, 1916, **8**, 1024-1027.)—Five grms. of meat extract in about 25 c.c. of water (or the aqueous decoction from 50 grms. of the finely divided meat product) are treated with an excess (4 to 6 grms.) of solid picric acid and an excess (40 to 60 c.c.) of a 20 per cent. aqueous solution of phosphotungstic acid, and made up to 100 c.c. and filtered. An aliquot portion (60 c.c.) of the filtrate is treated with 3 c.c. (or more if necessary) of hydrochloric acid, made up to 66 c.c., and filtered rapidly, and the reducing sugar estimated without delay by means of Fehling's solution. In the presence of cane sugar the results will be accurate within 0.1 or 0.2 per cent., provided that the hydrochloric acid in the filtrate is neutralised at once; otherwise slow inversion will continue. Another portion of the filtrate is inverted with hydrochloric acid and the invert sugar estimated.

C. A. M.

Estimation of Strychnine in *Nux Vomica*. H. R. Jensen. (*Pharm. J.*, 1916, **97**, 458-461.)—The unnecessary manipulation and the hot (50° C.) nitration method prescribed in the British Pharmacopœia, 1914, for the separation of brucine from strychnine is unreliable, and gives results for strychnine which are from 5 to 11 per cent. too low. Nitration at 20° C. with "active" nitric or with nitric acid which has been "activated" with sodium nitrite is more trustworthy. Attention is drawn to the fact that when the nitrated mixture is treated with sodium hydroxide strychnine nitrate is liable to "salt out" before it is decomposed by the alkali; this strychnine nitrate is very slightly soluble in chloroform, but to an extent sufficient to influence the results. In a number of experiments the average contamination

of the alkaloid by strychnine nitrate was 8.8 per cent., and in each case the nitrate gradually crystallised from the chloroform extract. The alkaloid may also be contaminated by isomeric strychnine compounds formed during the nitration. It is recommended, therefore, that the residue of strychnine should be weighed, then dissolved and titrated, using cochineal as the indicator. The actual quantity of strychnine present is then found by calculation from the gravimetric and volumetric results obtained.

W. P. S.

Estimation of Vanillin in Vanilla Extract. A. W. Dox and G. P. Plaisance. (*Amer. J. Pharm.*, 1916, **88**, 481-484.)—The vanillin is precipitated by thiobarbituric acid in hydrochloric acid solution; the precipitate formed is the condensation product, 3-methoxy-4-hydroxybenzalmalonylthiourea. Twenty-five c.c. of the extract are evaporated to remove alcohol, and are then diluted to 50 c.c. with lead acetate solution; after standing for several hours at 37° C., the mixture is filtered, 40 c.c. of the filtrate are treated with concentrated hydrochloric acid in quantity sufficient to make the volume up to 50 c.c. and the acidity 12 per cent., the lead chloride formed is separated by filtration, and 40 c.c. of this filtrate are mixed with thiobarbituric acid in 12 per cent. hydrochloric acid solution. After about eighteen hours, the orange-coloured precipitate is collected on a filter, washed with 50 c.c. of 12 per cent. hydrochloric acid, then with 20 c.c. of water, dried at 98° C., and weighed. A correction of 2.6 mgrms. is added to the weight of precipitate found, this being the allowance for the slight solubility of the compound. The method cannot be applied to artificial extracts coloured with caramel, since this contains furfuraldehydic derivatives, and thiobarbituric acid is a precipitant for all aromatic aldehydes. The presence of caramel is denoted by the brown colour of the filtrate obtained after the treatment with lead acetate; this filtrate is straw-coloured in the absence of caramel. The latter may also be detected by the formation of a brown precipitate when the acidified filtrate is treated with phloroglucinol.

W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Comparative Study of the Proteins of the Colostrum and Milk of the Cow and their Relations to Serum Proteins. C. Crowther and H. Raistrick. (*Biochem. J.*, 1916, **10**, 434-451.)—The chief proteins of cow's colostrum and cow's milk were isolated, and analysed by the method of van Slyke, with the following results: Caseinogen, total lactoglobulin, and lactalbumin are sharply differentiated and distinct proteins, and have respectively the same composition whether prepared from colostrum or from normal milk. The presence in milk of a globulin in small quantities (0.03 per cent. isolated) was proved. Eulactoglobulin and pseudolactoglobulin are identical as far as the protein part of their molecules is concerned.

Lactoglobulin from either colostrum or milk is very closely allied to, and is probably identical with, serum globulin from ox-blood. Lactalbumin from either colostrum or milk is very different in composition from serum albumin from ox-blood.

H. F. E. H.

Reactions of Peroxidase purified by Ultrafiltration. A. Bach. (*Arch. Sci. phys. nat.*, 1916, [iv.], 42, 56-61; through *J. Chem. Soc.*, 1916, 110, i., 682-683.)—Whilst phenol, guaiacol, quinol, and pyrogallol were found to give the same colour reactions with an extract of horse-radish and when the same extract was subjected to ultrafiltration in presence of hydrogen peroxide, very different results were obtained with orcinol, aniline, dimethyl- and diethyl-aniline, benzidine, and *p*-phenylenediamine. When *o*-cresol and saligenin are treated with a mixture of purified peroxidase and hydrogen peroxide, a yellow colour is produced in both cases, which changes to brown and then to reddish-brown. Salicylaldehyde only reacts when the solution is made slightly alkaline with hydrogen-potassium phosphate. Salicylic acid gives no reaction. In the oxidation of *o*-cresol and saligenin, formic acid is produced, but no appreciable amount of carbon dioxide can be detected. Ethyl alcohol is not attacked. It is considered more probable that ethyl alcohol is oxidised by a mixture than by a specific "alcoholoxidase."

Examination of Certain Methods for the Study of Proteolytic Action. H. C. Sherman and D. E. Neun. (*J. Amer. Chem. Soc.*, 1916, 38, 2199-2216.)—The experiments recorded were all carried out with preparations of commercial pepsin and trypsin, the following methods being employed: (1) The Mett method; (2) the estimation of total nitrogen of digestion products; (3) the measurement of increase of amino nitrogen by the Van Slyke method; (4) the titration of the acidity of acid cleavage products (Volhard-Löhlein method); (5) the increase of electrical conductivity; (6) the polarimetric method; (7) the biuret reaction; (8) the triketo-hydrindene hydrate (Ninhydrin) method. In every case, with the exception of the Mett method, a casein substrate was used. In general terms it was found that the quantitative estimation of the total nitrogen (2), or of the amino nitrogen of the digestion products (3), or both, were more delicate methods of detecting proteolysis than either the biuret or the Ninhydrin reactions, and also more generally applicable as a means for its measurement than any of the other methods. All the results emphasised the importance in quantitative comparisons of so limiting the amount of enzyme preparation and the time of its action as to keep within the region in which the velocity of hydrolysis is directly proportional to the enzyme concentration.

As regards the popular Mett method, it was found to be quite unreliable for trypsin at all concentrations, owing to the action of the alkali upon the albumin, while with pepsin the action is only approximately proportional to the quantity of pepsin employed at the very lowest concentrations at which the length of column digested is too short for accurate measurement. With the second method described above it was found that the amount of digested nitrogen increased in direct proportion to the amount of enzyme used to about 20 to 25 mgrms. of nitrogen in the case of pepsin, or 40 to 60 mgrms. in the case of trypsin, quantities large enough to be determined by the Kjeldahl method with a high degree of accuracy. The nitrogen is estimated in the filtrate after precipitating the undigested casein by sodium sulphate and hydrochloric acid. For the estimations by the Van Slyke method the "micro" apparatus, using the new 3 c.c. gas burette, was employed. The polarimetric method was found to afford a delicate means of detecting the action of very small amounts of proteolytic enzyme, but the fact that the change in rotation

does not proceed progressively with the amount of enzyme or its time of action necessarily renders its use for quantitative work of little or no value. Neither the biuret nor the Ninhydrin reaction is susceptible of yielding more than rough comparisons of proteolytic power within the range covered by the colour changes, even when the greatly enhanced delicacy obtained by the Herzfeld modification of the latter is taken advantage of (*Biochem. Zeitsch.*, 1914, **59**, 249; *J. Biochem.*, 1915, **20**, 217; 1916, **24**, 503. See also Long and Barton, *ANALYST*, 1914, **39**, 551).

H. F. E. H.

General Method of Estimating the Relative Turbidity or Opacity of Fluid Suspensions including Bacterial Emulsions. G. Dreyer and A. D. Gardner. (*Biochem. J.*, 1916, **10**, 399-407.)—The procedure adopted embodies the main features of the method employed by Dreyer and Hansen in an investigation dealing with the effect of light on enzymes (*Compt. rend.*, 1907, **145**, 564). The method is of general application for all chemical and biological measurements of turbidity, and, as described in the present paper, is concerned specially with the standardisation of agglutinable cultures. A graduated series of dilutions of each fluid is made in miniature test-tubes of uniform bore, clean and free from scratches. By artificial light against a black background the turbidities of a number of tubes of one series are matched against a succession of tubes of the other series. Each reading provides figures from which the relative turbidities can be calculated, and by taking the average of a number of readings, an accurate ratio is obtainable. Special details are given of the method of calculation, and the method is shown to be capable of great accuracy in the estimation of silver in high dilutions when precipitated as silver chloride, as well as for the comparison of bacterial growths in broth, etc.

H. F. E. H.

ORGANIC ANALYSIS.

Methods for the Estimation of Mixtures of Four or More Carbohydrates involving Oxidation with Bromine. E. G. Wilson and W. R. G. Atkins. (*Biochem. J.*, 1916, **10**, 504-521.)—The five carbohydrates usually found in foliage leaves are starch, cane-sugar, dextrose, lævulose, and maltose, with, in addition, sometimes small quantities of pentoses. For the estimation of starch, see Davis and Daish (*ANALYST*, 1914, **39**, 312); and for pentoses, Davis and Sawyer (*ibid.*, 1915, **40**, 128) and Daish (*ibid.*, 1914, **39**, 555). The present work deals only with the four remaining sugars. Since all methods involving the use of Fehling's solution for the quantitative estimation of reducing sugars are liable to error, owing to the solvent action of the hot sodium hydroxide on cuprous oxide, it was decided to employ Kendall's method (*ANALYST*, 1912, **37**, 205). It was found that dextrose and maltose are quantitatively oxidised by bromine at room temperature when allowed to stand in a saturated solution; the liquid, however, still retains a small amount of its original reducing power towards alkaline copper solutions. Lævulose is not oxidised at all by bromine under these conditions, or only to a very small extent, while in the presence of $\frac{N}{10}$ sulphuric acid there is a slight loss of lævulose in sixty-six hours at room temperature.

A mixture of cane-sugar, maltose, dextrose, and lævulose may be analysed as follows: (a) The amount of cane-sugar is determined by polarisation and reduction before and after treatment with invertase. (b) The resulting mixture of reducing sugars is treated with bromine under standard conditions of acidity and temperature for a given time. The aldehydic sugars, dextrose (including the portion derived from cane-sugar) and maltose, are oxidised, and the ketonic sugar lævulose, (including the portion derived from cane-sugar), remains behind. The reducing power of the solution may then be taken as due to the lævulose only. (c) The rotations due to the lævulose and cane-sugar are then allowed for in the initially determined rotation. This gives the rotation due to dextrose and maltose. (d) The reduction due to lævulose is subtracted from the initial reduction. This gives the reduction due to dextrose and maltose. From these data two equations may be constructed, which, when solved, give the amounts of the two remaining sugars. When only dextrose and lævulose are present, the bromine method enables the latter to be estimated directly.

The addition of dilute alkali ($\frac{N}{2}$ or 2N sodium hydroxide) to a solution of dextrose, lævulose, or maltose was found to produce a large temporary increase in its reducing power. From a study of the electrical conductivity of a mixture of sodium hydroxide and dextrose some indication was obtained of the formation of a compound between these two substances. An attempt to modify Barfoed's solution (cupric acetate and acetic acid) for quantitative work, by reducing the reaction to the first order instead of the fifth, was found unsuccessful (Bunzel, *Amer. J. Physiol.*, 1908, **21**, 23).
H. F. E. H.

Modification of the Pratt Method for Estimation of Citric Acid. J. J. Willaman. (*J. Amer. Chem. Soc.*, 1916, **38**, 2193-2199).—Pectins are precipitated by adding twice the volume of 50 per cent. alcohol to the aqueous solution. The solution is filtered through paper on a Buchner funnel, and the precipitate washed with 65 per cent. alcohol. The filtrate is diluted until approximately of 30 per cent. alcoholic strength, and 5 c.c. of a 10 per cent. solution of barium acetate in 30 per cent. alcohol are then added. The barium citrate is filtered off on a Gooch crucible, washed once with 30 per cent. alcohol, dried, and dissolved in hot 6 per cent. phosphoric acid (60 c.c.), followed by about 40 c.c. hot water. The solution is transferred to a distilling flask, the side tube of which is connected to a condenser, whilst the cork in the neck carries a tap funnel or other arrangement for running in a 0.05 per cent. solution of permanganate. Precautions must be taken against bumping. The adapter of the condenser dips into 40 c.c. of Denigès' mercuric reagent for acetone, made by heating 50 grms. of mercuric oxide with 500 c.c. water and 200 c.c. sulphuric acid, making up to 1,000 c.c., and filtering. The citric acid solution is heated to boiling, and permanganate is run in at the rate of about 5 c.c. a minute, the distillation proceeding at a somewhat faster rate. When a deep pink colour has persisted for two minutes, the reaction is complete. The distillate is made up to 300 c.c., and if more bulky than this, 15 c.c. of Denigès' reagent are added for each additional 100 c.c. It is then boiled under a reflux condenser for forty-five minutes, after which the precipitate is filtered off and washed twice with hot water. The precipitate adhering

to the flask is dissolved in a small quantity of hot 5 per cent. hydrochloric acid, which is then used to dissolve the precipitate on the filter. The flask and filter are thoroughly washed with hot water, the solution nearly neutralised with 10 per cent. sodium hydroxide, made up to 100 c.c., and transferred to a burette. It is then titrated against a measured quantity of potassium iodide solution containing 28.02 grms. per litre, 1 c.c. of which equals 2 mgrms. of citric acid under the conditions of the experiment.

G. C. J.

Errors in the Estimation of Acid Values of Boiled Oils and Varnishes.

E. E. Ware and R. E. Christman. (*J. Ind. and Eng. Chem.*, 1916, 8, 996-997.)—

The presence of metallic linoleates and resinates in a boiled oil or varnish will cause the acid value to appear too high, since the potassium hydroxide will not only neutralise the free fatty acids of the soap, but also hydrolyse the metallic soaps. In test experiments the linseed oil soaps of lead, manganese, cobalt, calcium, and zinc were prepared, dried *in vacuo*, dissolved in alcohol-ether, and their "acid values" estimated in the usual way, the molecular equivalent of the acid radicle being taken as 280. The values obtained differed by only a few tenths from the calculated values, except in the case of the calcium soap, the hydrolysis of which had only been partial, so that the value was 79.5 instead of 186.8. In like manner the resinates of the same metals were partially hydrolysed in the test, the difference between the observed and calculated "acid values" indicating that from 81.3 to 94.0 per cent. were hydrolysed (calcium resinate, 49.1 per cent.). A sample of linseed oil with an acid value of 3.05 was heated with lead linoleate until a cloudy solution was obtained, and then contained 1.15 per cent. of ash and had an acid value of 10.20. The same oil heated alone under parallel conditions showed an acid value of 2.31 and contained 0.18 per cent. of ash, the decrease in the acid value being attributable to volatilisation of fatty acids. The difference between the amounts of ash indicated the presence of about 1 per cent. of lead oxide in solution, and this would cause an apparent acid value in the oil of 7.1, assuming that hydrolysis occurred to the same extent as in the experiments.

C. A. M.

Some Fatty Oils. S. Uchida (*J. Soc. Chem. Ind.*, 1916, 35, 1089-1093.)—

Para rubber tree seed (*Hevea braziliensis*) yielded on expression 32.88 per cent. of a pale yellow oil with weak drying properties. *Shiromoji seed oil*, from *Lindera triloba* (yield from kernels, 45.26 per cent.), is a pale yellow non-drying oil, with a higher saponification value than any other known vegetable oil. *Calophyllum oil*, from *Calophyllum inophyllum* (yield from kernels, 33.83 per cent.), is a dark green, viscous, semi-drying oil, the high acid value of which is due to the presence of resin. *Hernandia seed oil*, from *Hernandia peltata* (yield from kernels, 33.89 per cent.), is a reddish-brown oil, which dries to a soft brittle film when heated for six hours at 100° C. It is suitable for soaps and rubber substitutes and as a lamp oil. *Hakuunboku seed oil*, from *Styrax obassia* (yield from kernels, 30.51 per cent.), is a semi-drying oil, containing a considerable amount of volatile fatty acids (butyric acid). *Akebi seed oil*, from the Japanese shrub *Akebia quinata* (yield from kernels, 17.69 per cent.), is a yellowish-brown non-drying oil, with an extremely high Reichert-

ABSTRACTS OF CHEMICAL PAPERS

Oil from	OIL.						FATTY ACIDS.					
	Sp. Gr. at 15° C.	Refractive Index.	Acid Value.	Saponification Value.	Reichert-Meissl Value.	Höbner Value.	Iodine Value (Hbbl).	Melting Point C.	Solidification Point C.	Neutralisation Value.	Iodine Value.	Mean Molecular Weight.
Para rubber tree seed	0.9239	1.4720 (27.5° C.)	4.21191.9)	0.3095.37	130.8	—	—	27.0	185.0	116.5	303.3	
Shiromoji seed	0.9361	1.4732 (27.3° C.)	0.63282.0	2.0385.72	11.68	—	—	14.0	287.1	12.19	105.4	
Calophyllum seed	0.9452	1.47925 (26.8° C.)	45.91194.1	0.3893.61	95.49	37	28.29	190.1	95.4	295.1		
Hernandia seed	0.9380	1.47735 (27.2° C.)	7.39193.7	1.7793.17	126.1	—	—	12.13	185.7	130.0	302.1	
Hakuimboku seed	0.9610	1.48925 (27.5° C.)	1.73181.8	16.4592.94	115.4	—	—	14.13.5	166.1	114.7	337.8	
Akebi seed	0.9340	1.46145 (27.5° C.)	25.45246.4	39.7685.80	78.38	38.39	31	191.7	77.8	292.7		
Kuromoji seed	0.9401 (at 30°/30° C.)	1.4680 (27° C.)	18.78255.6	2.5386.22	65.29	—	—	9.5	262.0	37.0	214.1	
Aburachan seed	0.9348	1.4550 (27° C.)	2.60273.6	1.3989.21	20.53	—	—	13.0	277.2	18.28	202.4	
Magnolia whole fruit	0.9315	1.4739 (26.8° C.)	13.43224.4	4.9393.11	109.2	35.5	28.28.5	201.9	99.66	277.9		
" fruit flesh	0.9239	1.4693 (27° C.)	13.59205.0	4.6791.83	89.53	36.5	32.32.5	205.1	86.16	273.5		
"	0.9288	1.4754 (27° C.)	6.69207.4	0.1796.54	124.5	—	—	17.5-17.0	193.7	125.5	289.6	
Tea seed	0.9126 (30°/30° C.)	1.4669 (27.6° C.)	4.12193.8	0.1095.76	86.2	—	—	25.5	190.5	80.79	294.5	

Meissl value. It can be used for edible purposes and for the manufacture of soap and Turkey-red oil. *Kuromoji seed oil*, from *Lindera serica* (yield from kernels, 58.02 per cent.), has an aromatic odour. It is best suited for soap-making. *Aburachan seed oil*, from *Lindera præcox* (yield from kernels, 18.17 per cent.), is a dark brown non-drying oil. *Magnolia fruit oil*, from *Magnolia hypoleuca* (yield from seed and flesh, 31.51 per cent.), is a semi-drying oil suitable for burning and soap-making. The flesh alone yielded 35.34 per cent. of oil, and the seeds 7.74 per cent., but it would not be profitable to press them separately. *Tea seed oil* (*Thea Chinensis*) is a pale brown non-drying oil suitable for soap-making, lubrication, and burning. With strong sulphuric acid it gives an indigo-blue coloration, changing to greenish-brown on stirring. The following analytical values were obtained with these oils: (see p. 22).

C. A. M.

Rapid Volumetric Estimation of Indigo. S. M. Jones and W. Spaans. (*J. Ind. and Eng. Chem.*, 1916, 8, 1001-1002.)—This method, like that of Müller, is based on the reduction of indigo to indigo white. Instead, however, of working in presence of coal-gas, the authors use a current of hydrogen, which is found to be a great improvement. Formaldehyde sodium sulphoxylate also replaces the unstable sodium hydrosulphite as reducing agent; but as its action is slow, sodium bisulphite is added to set free sodium sulphoxylate and so accelerate the reaction.

The sample (1 gram. of powder, proportionately more of paste) is mixed to an even paste with 15 c.c. sulphuric acid, a further 15 c.c. of acid is added, and the mixture heated to 55° to 60° C. for three hours, when sulphonation should be complete. The cooled mixture is diluted to 300 c.c., again cooled, diluted to exactly 1,000 c.c., and filtered. One gram. of pure indigo is similarly treated to produce a standard for comparison.

Fifty c.c. of the standard solution and 50 c.c. of 35 per cent. sodium bisulphite solution are mixed in a flask of 300 c.c. capacity, and the flask is closed with a rubber stopper with four holes. Through one of these a thermometer dips into the liquid, two provide for the admission and exit of hydrogen, whilst the fourth accommodates the tip of a burette. The air is displaced by hydrogen, and the mixture heated to 75° C. Standard sodium formaldehyde sulphoxylate is then run in from the burette until the blue colour disappears. This solution is made by dissolving 1 gram. of the solid reagent in 1,000 c.c. of water. The sample to be analysed is treated in a similar manner.

G. C. J.

Estimation of Free and Combined Galactose. A. W. Van der Haar. (*Chem. Weekblad*, 1916, 13, 1204-1213.)—This method, which is a modification of that of Creydt (*Dissert.*, Erlangen, 1888), is based on the oxidation of galactose to mucic acid by means of nitric acid. In the case of free *d*-galactose, from 0.25 to 1 gram. is heated with occasional agitation with 60 c.c. of nitric acid (sp. gr. 1.15 at 15° C.) in a beaker 12 cm. in height and 60 mm. in diameter, which is placed in a boiling-water bath. When the contents of the beaker have been reduced to less than

20 grms., the mixture is cooled, made up to 20 grms. with water, and after the addition of 0.5 gm. of pure dry mucic acid (purified by recrystallisation from alcohol) the beaker is allowed to stand for forty-eight hours at a temperature of 15° C. The deposit of mucic acid is then collected on an asbestos filter in a Gooch crucible, washed with 5 c.c. of water, and dried in the water-oven until constant in weight, and the 0.5 gm. of mucic acid which was added to promote the crystallisation is deducted from the result. In the case of combined galactose 0.25 to 1 gm. of the anhydrous glucoside or polysaccharide is hydrolysed with 25 c.c. of 2 to 5 per cent. sulphuric acid. When insoluble products are formed they are filtered off, after twenty-four hours, and the filtrate and washings concentrated. The resulting solution of galactose is rendered slightly alkaline with sodium hydroxide solution, made up to 30 c.c., and after the addition of 30 c.c. of 50 per cent. nitric acid, and as much cane-sugar as corresponds to the non-sugar portion of the glucoside (*e.g.*, saponogenins), the mixture is oxidised as described above. The following tables give the quantities of galactose corresponding to the weights of mucic acid obtained:

I. GALACTOSE ALONE.

Mucic Acid.	Galactose.	Mucic Acid.	Galactose.	Mucic Acid.	Galactose.	Mucic Acid.	Galactose.
Mgrms.	Mgrms.	Mgrms.	Mgrms.	Mgrms.	Mgrms.	Mgrms.	Mgrms.
- 4	0	187	260	383.8	520	597	780
+ 0.8	10	194	270	392.7	530	606	790
5.6	20	201	280	401.6	540	615	800
10.4	30	208	290	410.5	550	623	810
15.2	40	215	300	419.4	560	631	820
20	50	223.1	310	428.3	570	639	830
27	60	231.2	320	437.2	580	647	840
34	70	239.3	330	446.1	590	655	850
41	80	247.4	340	455	600	663	860
48	90	255.5	350	462	610	671	870
55	100	263.6	360	469	620	679	880
64	110	271.7	370	476	630	688	890
73	120	279.8	380	483	640	695	900
82	130	287.9	390	490	650	703.5	910
91	140	296	400	497	660	712	920
100	150	303	410	504	670	720.5	930
108.4	160	310	420	511	680	729	940
116.8	170	317	430	518	690	737.5	930
125.2	180	324	440	525	700	746	960
133.6	190	331	450	534	710	754.5	970
142	200	338	460	543	720	763	980
149.6	210	345	470	552	730	771.5	990
157.2	220	352	480	561	740	780	1,000
164.8	230	359	490	570	750		
172.4	240	366	500	579	760		
180	250	374.9	510	588	770		

II.—GALACTOSE MADE UP TO 1 GRM. WITH SACCHAROSE.

Mucic Acid.	Galactose.	Mucic Acid.	Galactose.	Mucic Acid.	Galactose.	Mucic Acid.	Galactose.
Mgrms.	Mgrms.	Mgrms.	Mgrms.	Mgrms.	Mgrms.	Mgrms.	Mgrms.
- 4	0	173	260	376	520	582	780
+ 2.4	10	181	270	384	530	591	790
8.8	20	189	280	392	540	600	800
15.2	30	197	290	400	550	609	810
21.6	40	205	300	408	560	618	820
28	50	212	310	416	570	627	830
34.9	60	219	320	424	580	636	840
41.8	70	226	330	432	590	645	850
48.7	80	233	340	440	600	654	860
55.6	90	240	350	447	610	663	870
62.5	100	248.8	360	454	620	672	880
70	110	257.6	370	461	630	681	890
77.5	120	266.4	380	468	640	690	900
85	130	275.2	390	475	650	699	910
92.5	140	284	400	483	660	708	920
100	150	292.2	410	491	670	717	930
106.6	160	300.4	420	499	680	726	940
113.2	170	308.6	430	507	690	735	950
119.8	180	316.8	440	515	700	744	960
126.4	190	325	450	523	710	753	970
133	200	332	460	531	720	762	980
139.4	210	339	470	539	730	771	990
145.8	220	346	480	547	740	780	1,000
152.2	230	353	490	555	750		
158.6	240	360	500	564	760		
165	250	368	510	573	770		

C. A. M.

Extraction of Lactic Acid for its Estimation. E. Ohlsson. (*Skand. Arch. Physiol.*, 1916, **33**, 231-234; through *J. Chem. Soc.*, 1916, **110**, ii., 542-543.)—In the estimation of lactic acid according to Von Fürth-Charnass, as modified by Embden, the extraction with ether is a troublesome and lengthy process. For the isolation in a pure state the author finds ethyl acetate a better solvent, and when the acid is merely to be estimated, amyl alcohol is much better. The liquid containing lactic acid is saturated with ammonium sulphate, filtered after twelve hours, and mixed with $\frac{1}{10}$ volume of 50 per cent. sulphuric acid. It is then shaken with 2 volumes of amyl alcohol, which are then freed from the acid by shaking with sodium carbonate, and used similarly for four more successive extractions of the fluid. Traces of amyl alcohol are removed from the sodium carbonate extracts by three extractions with benzene, and the estimation is then carried out in the usual way.

Differentiation of the Two Naphthols by Means of Titanic Acid dissolved in Sulphuric Acid. G. Denigès. (*Ann. Chim. anal.*, 1916, 21, 216-217.)—A solution of titanic acid in sulphuric acid (*cf.* ANALYST, 1916, 41, 343) gives a bright green coloration when mixed with a small quantity of α -naphthol, whilst a blood-red coloration is obtained with β -naphthol. If the mixtures are diluted with acetic acid, the green coloration given by α -naphthol changes to red-violet, but in the case of β -naphthol the blood-red colour remains unchanged. The reaction may be applied as a ring test, the naphthol being dissolved previously in acetic acid. The esters of the two naphthols yield similar distinctive reactions with the reagent. W. P. S.

INORGANIC ANALYSIS.

Estimation of Calcium in Ash of Forage Plants and Animal Carcasses. S. B. Kuzirian. (*J. Amer. Chem. Soc.*, 1916, 38, 1996-2000.)—Phosphorus is removed from the acid solution of the ash as ammonium phosphomolybdate. Calcium is precipitated as oxalate, the solution containing the precipitate is boiled for half an hour, the oxalate filtered off on a Gooch crucible, and ignited to render molybdenum compounds insoluble. The ignited precipitate is treated with dilute hydrochloric acid, the solution filtered, iron and alumina separated as hydroxides, and the calcium in the filtrate finally precipitated as oxalate. G. C. J.

Efficiency of Calcium Chloride, Sodium Hydroxide, and Potassium Hydroxide as Drying Agents. G. P. Baxter and H. W. Starkweather. (*J. Amer. Chem. Soc.*, 1916, 38, 2038-2041.)—Experiments are described which show that potassium hydroxide at 25° C. is as efficient a desiccating agent as sulphuric acid, the vapour pressure of the lowest hydrate being about 0.002 mm. That of sodium hydroxide is 0.15 mm., and of calcium chloride 0.34 mm. at 25° C. The temperature coefficients are high, the vapour pressure of sodium hydroxide being 0.04 mm. at 0° and 1.15 mm. at 50°, and that of calcium chloride 0.07 mm. at 0° and 1.34 mm. at 50°. That of potassium hydroxide at 0° was unmeasurable by the methods used; at 50° it is 0.007 mm. G. C. J.

Estimation of Hydrogen Sulphide in Water. L. W. Winkler. (*Zeitsch. angew. Chem.*, 1916, 29, 383-384.)—The water is collected in a 500 c.c. stoppered bottle containing about 20 grms. of marble free from any trace of sulphide, and the bottle should be filled completely with the water. The stopper of the bottle is removed and replaced by a rubber stopper carrying the stem of a bulb tube which is provided with a side tube; a tapped funnel containing hydrochloric acid is attached to the top of the bulb tube, and the side tube is connected with a U-tube containing cotton wool, and then with an absorption vessel containing acid-free bromine water. The hydrochloric acid is admitted gradually into the bottle, and the liberated carbon dioxide passes over into the absorption vessel, carrying with it the hydrogen sulphide contained in the water. The contents of the absorption vessel are then evaporated until all free bromine and hydrobromic acid have been expelled, and the residual solution is titrated with $\frac{N}{100}$ borax solution, using methyl orange

as the indicator. The oxidation of the hydrogen sulphide proceeds according to the equation: $\text{H}_2\text{S} + 4\text{Br}_2 + 4\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 8\text{HBr}$, and each c.c. of $\frac{N}{100}$ borax solution is equivalent to 0.1705 mgrm. of hydrogen sulphide. Alternatively, the free bromine alone may be expelled by boiling, and the hydrobromic and sulphuric acids then titrated with $\frac{N}{10}$ borax solution; in this case 1 c.c. of $\frac{N}{10}$ borax solution (19.11 grms. of the crystallised salt per litre) corresponds to 0.341 mgrm. of hydrogen sulphide.

Hydrogen sulphide in relatively strong aqueous solution may be estimated as follows: A stoppered flask containing 100 c.c. of $\frac{N}{10}$ permanganate solution and 1 grm. of pure sodium hydroxide is weighed; a few c.c. of the hydrogen sulphide solution are now introduced, and the flask is again weighed. After one hour the mixture in the flask is acidified with sulphuric acid, potassium iodide is added, and the liberated iodine titrated with $\frac{N}{10}$ thiosulphate solution. Each c.c. of $\frac{N}{10}$ permanganate solution is equivalent to 0.4263 mgrm. of hydrogen sulphide.

W. P. S.

Method of Extraction as affecting the Estimation of Phosphoric Acid in Soils. H. Hale and W. L. Hartley. (*J. Ind. and Eng. Chem.*, 1916, 8, 1028-1029.)

—Experiments are recorded which show that two hours' digestion with 2N nitric acid extracts as much phosphoric acid as ten hours' digestion with hydrochloric acid of sp. gr. 1.115. It is also shown that the ten hours' digestion with hydrochloric acid brings down much more interfering substances than the shorter digestion with nitric acid.

G. C. J.

Reagents for Use in Gas Analysis. V.—Relative Advantages of Sodium and Potassium Hydroxides in Preparation of Alkaline Pyrogallol. R. P. Anderson.

(*J. Ind. and Eng. Chem.*, 1916, 8, 999-1001.)—A criticism of the conclusions of Shipley (*ANALYST*, 1916, 41, 349), who advocated the use of sodium hydroxide. It is agreed that when the best practicable solutions of sodium and potassium pyrogallate are compared, the specific absorption of the sodium reagent is the higher, and the cost of the sodium reagent is less, even in normal times. But the author does not agree that the use of sodium hydroxide effects any real economy, even at present prices of potassium compounds, as the loss of time when using the sodium reagent much more than counterbalances its lower cost. He gives figures showing that a saving of three shillings in cost of chemicals involves the expenditure of some thirty additional hours in manipulation, each analysis with sodium pyrogallate taking about two and a half minutes longer than would be the case were potassium hydroxide substituted for sodium hydroxide.

G. C. J.

Solution of Red Lead. G. Torossian. (*J. Ind. and Eng. Chem.*, 1916, 8, 1076.)—Dilute (1:5) nitric acid containing 0.5 per cent. of tartaric acid is an excellent solvent for red lead. The hot mixture dissolves red lead instantly. Stronger solutions are sometimes convenient, but do not keep well.

G. C. J.

Volumetric Estimation of Tin. R. L. Hallett. (*J. Soc. Chem. Ind.*, 1916, 35, 1087-1089.)—The following modification of the method of Pearce and Low (Low, *Technical Methods of Ore Analysis*, p. 208) gives results accurate to within 0.1 per cent. in about one and a half hours. It is based on the oxidation of stannous chloride to stannic chloride by means of iodine in the presence of cold hydrochloric acid. Sulphuric acid in small amount does not interfere with the titration, but nitric acid or nitrates must not be present. When tin is dissolved in hydrochloric acid it will require complete reduction to the stannous condition before titration. The final solution should contain between 25 and 40 per cent. of strong hydrochloric acid, and during the reduction and titration a current of carbon dioxide should be passed through the flask. From 0.5 to 2 grms. of the sample are dissolved in about 50 c.c. of hydrochloric acid, and the solution is diluted to 200 c.c. with water, and gently boiled for thirty minutes in a flask in which is suspended a nickel coil made by rolling 6 sq. inches of heavy sheet nickel into a loose roll, while the mouth of the flask is covered with a watch-glass. The reduction is indicated by the change in the colour of the liquid from yellow to pale green, and the flask is then left to cool, after the introduction of two small cubes of crystalline marble to produce an atmosphere of carbon dioxide. The nickel coil is withdrawn and washed with dilute hydrochloric acid (1:3) during its withdrawal, and the solution is at once titrated with standard iodine solution, with starch as indicator. A convenient strength for the iodine solution is 10.7 grms. in 1,000 c.c. of water containing 20 grms. of potassium iodide (1 c.c.=1 per cent. of tin). Nickel, cobalt, manganese, molybdenum, uranium, chromium, aluminium, zinc, lead, calcium, magnesium, sulphates, phosphates, bromides, iodides, and fluorides, have no effect on the results, unless present in sufficient quantity to mask the colour of the indicator. Arsenious and antimonious acids have also no influence in the presence of hydrochloric acid of the strength used in this estimation. Precipitation of metallic antimony by the nickel coil may be prevented by the addition of an extra 25 c.c. of strong hydrochloric acid. Traces of copper do not influence the results, but if more than 0.05 gm. be present it should be removed beforehand by treatment with nitric acid, as in the case of titanium (*infra*). Bismuth is precipitated in metallic form in the reduction process, but the precipitate does not materially affect the titration. Tungsten is also precipitated as a blue oxide. In small quantities the effect of this is negligible, but, if necessary, the solution may be filtered, and again reduced before the titration. Titanium is best removed by converting the tin into oxide by evaporation with nitric acid, fusing the residue for five minutes with potassium acid sulphate, dissolving the melt in dilute sulphuric acid, and filtering the solution. Any tungsten present may then be separated from the tin by treatment with ammonium carbonate solution, in which the tin is insoluble. Ferrous chloride is not oxidised during the titration, unless a large amount of iodine is added and allowed to stand for some time.

C. A. M.

APPARATUS, ETC.

Melting-Point of Fats. (*Giorn. di Farm. e di Chim.*, 1916, 4, 151-153; through *Chem. Eng. and Manufac.*, 1916, 24, 188.)—To the thermometer employed is attached a platinum wire of a thickness of 0.3 to 0.4 mm., the free end of which is formed into a loop of 8 to 9 mm. diameter. The wire is attached in such a manner that the loop assumes a vertical position immediately in front of, but not touching, the mercury bulb. The fat to be examined is melted at a gentle heat, and when it is almost cool enough to solidify, the platinum loop is dipped parallel to the surface into the liquid and quickly withdrawn, leaving a thin film of fat, completely filling the loop. This is allowed to cool for an hour, the wire attached to the thermometer, which is then immersed in a wide-necked glass flask of about 250 mm. capacity filled with distilled water, which is slowly heated on an asbestos card, until the film of fat in the platinum loop becomes completely transparent just before breaking up. The temperature of complete transparency is the melting-point of the fat.

H. F. E. H.



REVIEW.

ELEMENTARY QUALITATIVE ANALYSIS. By BENTON DALES, Ph.D., and OSCAR LEONARD BARNEBEY, Ph.D. Pp. viii+205. John Wiley and Sons, New York; Chapman and Hall, Ltd., London. 1916. Price 5s. 6d. net.

The authors state in their preface that this book is intended to act as a guide in qualitative analysis for students who have previously carried out a year's course of work in general chemistry.

The book, as its title implies, deals with the subject in quite an elementary manner, but with some innovations that would seem to have little to recommend them. For instance, it is difficult to see anything but disadvantage in the arrangement of the special reactions for bases, not under the names of the latter, but in paragraphs headed with the formulæ of the reagents giving characteristic precipitates.

The authors also suggest that the acids present in a mixture should be detected before the bases; and although occasionally such a procedure may be found desirable, this is not usually the case.

The descriptions of the various reactions and tests are given concisely and clearly, but the detection tables are rather lacking in this respect, and, together with the general arrangement referred to above, this fact will probably militate against the general use of this book in teaching laboratories in this country.

P. A. E. RICHARDS.