MARCH, 1930. Vol. LV., No. 648.

THE ANALYST

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

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, February 5th, the President, Mr. Edward Hinks, being in the chair.

The President announced the names of those who had been nominated as Officers and Members of Council for the coming year.

Certificates were read for the first time in favour of:—Leslie Mansfield Adams, James Charles Harral, Donald Frank Harrington Button, A.R.C.S., A.I.C., Hugh Childs, B.Sc., F.I.C., John William Corran, B.Sc., Ph.D., F.I.C., Archibald Orton Jones, M.A., F.I.C., James Bruce Eric Patterson, M.Sc., A.I.C., Frank James Smith, B.Sc., A.I.C., Alfred Tingle, B.Sc., Ph.D.

Certificates were read for the second time in favour of:—Ronald Gilbert Baskett, B.Sc., Hugh Charles Loudon Bloxam, F.I.C., Claud McClellan Bottomley, B.Sc., John Butler, B.Sc., F.I.C., Robert Ellison, A.M.C.T., George Noel Grinling, F.I.C., Albert Houlbrooke, M.Sc., A.I.C., Philip Henry Jones, F.I.C., Raymond Mallinder, Sydney Norman Herbert Stothart, B.Sc., Ph.D., A.I.C., Hubert Threadgold, B.Sc., A.I.C.

The following were elected Members of the Society:—Noel Lionel Allport, A.I.C., James Gilbert Lunt, B.Sc., A.I.C., Fred Morris, F.I.C., Albert William Peters, Juda Hirsch Quastel, D.Sc., Ph.D., A.R.C.S., A.I.C., and Joseph Harold Totton, B.A., B.Sc., F.I.C.

The following papers were read and discussed:—"The Determination of Minute Amounts of Iodine in Soils and Waters," by R. L. Andrew; "Preliminary Studies in the Bacteriology of Wheat and Flour," by D. W. Kent-Jones, Ph.D., B.Sc., F.I.C., and A. J. Amos, B.Sc., A.I.C.; "The Separation of Metals by 'Internal Electrolysis'," by H. J. S. Sand, D.Sc., Ph.D., F.I.C.; "The Rapid Determination of Bismuth and Copper in Lead Bullion by Internal Electrolysis," by Ella M. Collin, B.Sc., A.I.C.; and "Notes on the Thiocyanate Method of Determining Iron. Influence of Different Classes of Phosphates," by G. Winthrop Leeper, M.Sc.

NORTH OF ENGLAND SECTION OF THE SOCIETY OF PUBLIC ANALYSTS.

THE Fifth General Annual Meeting was held on February 15th, in Manchester.

The Chairman (Mr. S. E. Melling) presided, and twenty-four members were present.

The accounts for the year ending December 31st, 1929, were passed, and Messrs. U. A. Coates and W. Marshall were elected Honorary Auditors for the coming year. The following officers and committee were elected :—*Chairman :* G. D. Elsdon; *Vice-Chairman :* C. J. H. Stock; *Committee :* H. M. Mason, H. T. Lea, J. Miller, E. G. Jones, A. Lees, and A. R. Tankard ; *Hon. Secretary and Treasurer :* J. R. Stubbs.

After the election of officers, the following papers were read and thoroughly discussed : "Cattle Drinking Waters," by T. McLachlan, F.I.C., and "The Freezing Point of Milk as the means of Detecting added Water," by G. D. Elsdon, B.Sc., F.I.C., and J. R. Stubbs, M.Sc., F.I.C.

The Identification of Pigments Used in Painting at Different Periods, with a Brief Account of other Methods of Examining Pictures.

BY A. P. LAURIE, M.A., D.Sc., LL.D.
(*Professor of Chemistry to the Royal Academy of Arts*).

(*Lecture given at the Meeting, December* 4, 1929.)

IF the pigments used from the earliest times are examined, some are found in common use from the beginning. The natural red and yellow ochres, chalk, and charcoal black are of the earliest pigments. Minerals, such as native cinnabar and orpiment, the blue and green carbonates of copper, and a green earth, such as terra verte, are necessarily found early. The Egyptians may probably claim to have been the first to manufacture an artificial pigment—the Egyptian blue—and Pliny describes the making of white lead, vermilion, and lakes.

The following account of tests for pigments is confined to the pigments principally used for illuminating MSS. from the seventh century, with some consideration of modern pigments, and an account of Egyptian blue, but leaving out the earth pigments, yellow and red ochres, terra verte, and umbers. Those selected are the pigments used not only for illuminated MSS., but also for painting pictures, and are of special interest, as in many cases they are not to be found at all periods, and are therefore of value in dating MSS. and pictures.

The most reliable way of fixing the date of a picture, and detecting forgeries and repaintings, is by the identification of the pigments, as different pigments have been used at different periods in the history of painting.

The identification of pigments includes the examination of the picture surface itself under the microscope, and the examination of minute fragments of pigment by optical means with a polarising microscope, by chemical reactions on the particle of pigment itself, and by the solution of the particle and its identification by microchemical tests.

EXAMINATION OF THE PICTURE ITSELF UNDER THE MICROSCOPE.

For this purpose a low power only is required, about 90 diameters' magnification being ample. The microscope is mounted on a long rod, with rack and pinion motion, the rod being supported with adjustable supports at the two ends. The picture is laid on a table close to a window with a north light. Artificial illumination is not satisfactory, and is not necessary at the low magnification employed. The filling up of old cracks by repaint is easily detected; the coarseness of grinding of the pigments, and mineral pigments consisting of sharp-edged coarse particles, like ultramarine, or azurite, and the glassy conchoidal fragments of smalt, are at once recognised.

SAMPLING.—For sampling, a hypodermic needle which has been cut down in length and repointed should be used. A needle of the usual length is too springy. A drop of xylol having been placed on a slide, the needle is moistened with a solution of Canada balsam, waved in the air until the Canada balsam is sticky, a small fragment dug out of the picture and the point of the needle then dipped in the drop of xylol, when the fragment will float off. While doing this, Zeiss stereoscopic magnifying glasses should be worn.

To take a section right through a picture, the hypodermic needle, reduced to a length of about a sixteenth of an inch, is cut off and sharpened like a cork borer, pressed on the picture with a slow screwing motion, and the sample ejected with a fine wire. From a comparatively modern picture a continuous cylinder is obtained. The medium of old pictures is more brittle, and the sample usually breaks up, but remains on the slide in the order of the layers. The sample can, if required, be mounted in paraffin wax and sections cut, but this is not usually necessary.

The medium of old pictures being fairly brittle, after washing away the Canada balsam with xylol, the fragment can usually be crushed on the slide with another glass slide; thus, for instance, separating from the white lead fragments of a pigment like azurite, and enabling them to be optically examined.

Liquids of different refractive index can be used to mount the fragments, but the most generally useful is oil of cassia. When pigments are to be dissolved and the solutions evaporated, the fragment should be placed near one corner of the slide. The top of a water-oven is convenient for evaporation. Slides with a quarter-inch flat depression, sunk to a depth of the thickness of a cover glass, are useful, and when the fragment is to be ignited a quartz slide can be used. Usually, by slightly warming, a reaction will take place in spite of the presence of the medium, but, if necessary, the medium can largely be removed by warming the fragment with a little caustic soda.

CHEMICAL TESTS.—A drop of the particular reagent is applied to the particle upon the slide, which may, if necessary, be slightly warmed to start the reaction. When the reaction is likely to be violent, as when strong nitric or hydrochloric acid is to be used, it is advisable to coat the surface of the particle with collodion, and to apply the reagent over the collodion; it will then diffuse through gradually, and its action will be concentrated on the particle. Such protection is essential when treating lakes with nitric acid or applying the Reinsch test for an arsenic green.

OPTICAL EXAMINATION.—It is often necessary to examine the particles with polarised light, and for this purpose a mineralogist's microscope is required. If the particle is mounted in oil of cassia, it may show a characteristic refraction. For example, the refractive indices of blue and green verditer are below that of the oil, whereas the refractive indices of azurite and malachite are above. Liquids of higher refractive index are useful, such as methylene iodide and brom-naphthalene.

THE PROPERTIES AND REACTIONS OF CERTAIN ANCIENT PIGMENTS FOUND IN ILLUMINATED MSS. AND PICTURES.

WHITE LEAD.—The account given by Pliny of the preparation of the basic carbonate of lead by the corrosion of lead plates in presence of the acid vapour of vinegar does not differ in principle from the modern stack process. It has been used as a pigment from classical times to the present day. It is not resolved into particles under a microscope of 90 diameters' magnification, but is readily identified by its effervescence, with acids, and by turning black, with sodium sulphide, and its presence can be confirmed by the triple nitrite test. When mounted in brom-naphthalene and examined between crossed Nicols it is seen to consist of transparent doubly refracting crystals.

GOLD.—This is used in the form of gold leaf, powdered gold leaf, or (on certain English MSS.) in rounded granules which were probably obtained from river washings. These can be readily distinguished under the microscope from the sharp-edged particles of gold leaf. A modern forgery may contain imitation gold leaf which at once yields to acid.

VERMILION (Plate, Fig. 2).—The natural mercuric sulphide cinnabar differs but little from artificial vermilion in brilliancy, if finely ground, but its colour is more brick-red. Under the microscope vermilion appears as translucent glowing deep-red particles. Modern vermilions are more finely ground, but the coarser lumps resemble cinnabar too closely to be distinguished microscopically. A film from the picture containing vermilion is not attacked by hydrochloric or nitric acid. Pliny describes vermilion as minium, which is now used to describe certain lead compounds. It must be dissolved in *aqua regia* and identified by the formation of cobaltous mercuric thiocyanate.

RED LEAD is usually slightly discoloured here and there from the formation of lead sulphide. It may be distinguished from vermilion by moistening the

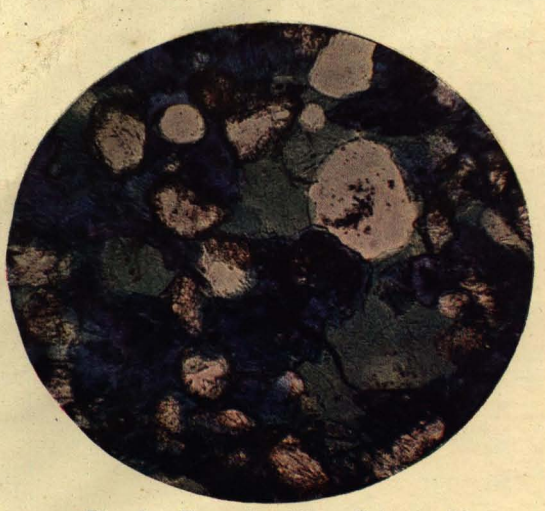


Fig. 1. Egyptian Blue, Frit, × 50.

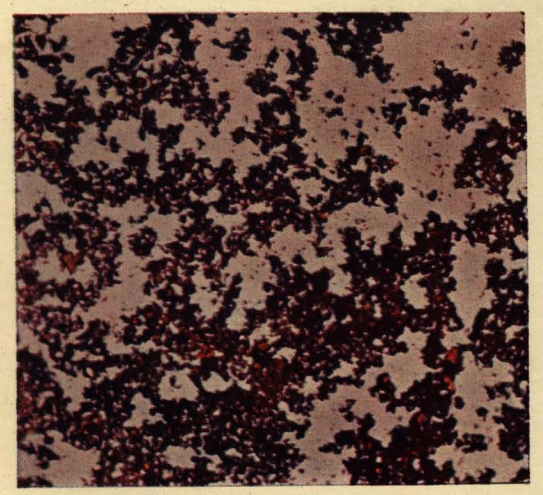


Fig. 2. Vermilion, × 200.

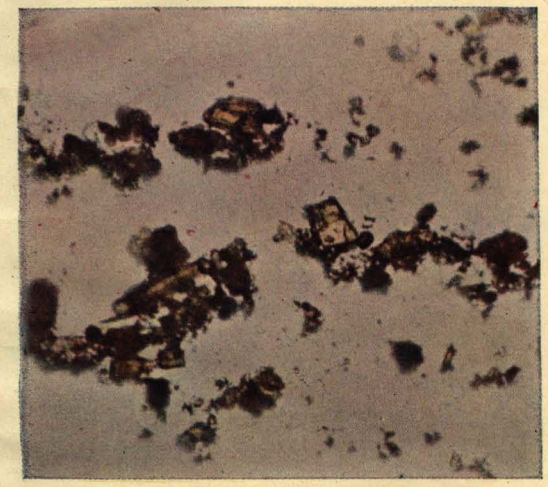


Fig. 3. Orpiment, × 300.

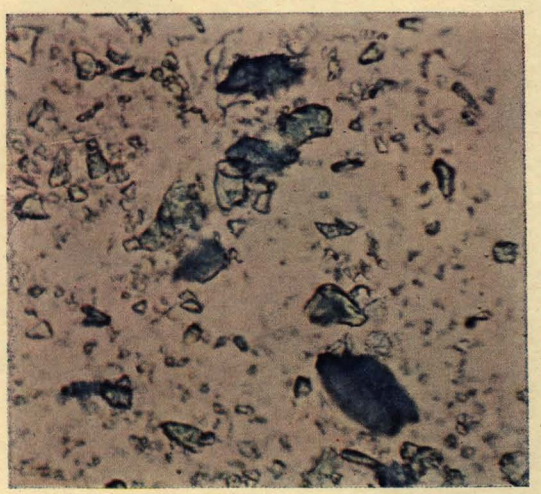


Fig. 4. Azurite, × 300.

Fig. 5. Ultramarine from Lapis Lazuli, × 200.

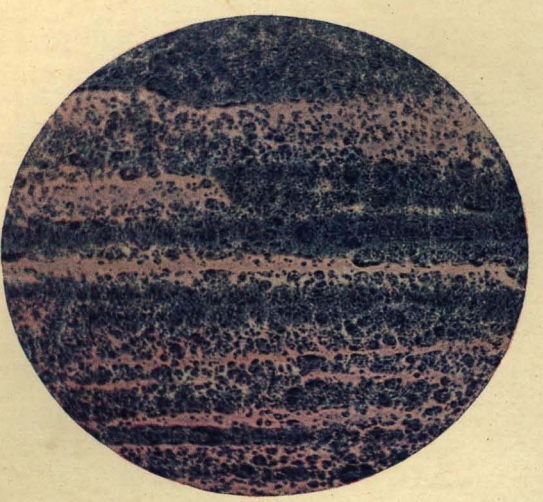


Fig. 6. Artificial Ultramarine, × 200.

PHOTOMICROGRAPHS OF PIGMENTS TAKEN ON LUMIÈRE PLATES.

particle with sodium sulphide, when it will at once turn black. Also, on treatment with strong nitric acid, red lead gives a dirty brown colour due to lead peroxide.

Lead compounds give very characteristic crystals of lead nitrate when dissolved in nitric acid, and can be confirmed by the formation of the triple nitrite of copper, potassium and lead.

ORPIMENT (Plate, Fig. 3).—The brilliant yellow colour and tint on a MS. are usually unmistakable. When moistened with sodium sulphide it does not blacken, like lead compounds, but dissolves; it is also soluble in caustic potash solution, in which respect it differs from the cadmium yellows. Microchemical methods for the identification of arsenic can be applied for confirmation (Charnot's *Chemical Microscopy*, p. 395). This pigment is found in late Egyptian painting and on illuminated MSS. De Wild did not find it on any of the Dutch pictures he examined (fifteenth—nineteenth century). Orpiment in oil is a brilliant yellow in ultra-violet light, while the chromes, cadmiums, and lead oxides are greenish or brownish-black.

MASSICOT YELLOW.—This is a yellow oxide of lead not used by modern artists. It blackens with sodium sulphide and is dissolved from an oil film by acetic acid. The triple nitrite test can be used to confirm the presence of this yellow.

NAPLES YELLOW.—For centuries this consisted of a compound of lead and antimony oxides, but the modern pigment is a mixed yellow which imitates the tint. The oil film is turned a dirty brown by sodium sulphide, is not attacked by acetic or hydrochloric acid, but dissolves in nitric acid. It is very similar in appearance to massicot and difficult to distinguish. De Wild advises fusion with potassium chlorate, the massicot giving the brown of lead peroxide. The presence of antimony can be confirmed by setting free the hydride and noting its action on silver nitrate. This can be conveniently done in the slide with a drilled recess, covered with a cover glass with a piece of filter paper attached, moistened with silver nitrate.

YELLOW LAKE (DUTCH PINK).—These are yellow lakes made from Persian berries or quercitron bark. They are soluble in acetic acid, become deep orange on treatment with caustic potash, and are bleached by chlorine water.

GAMBOGE.—The transparent deep orange particles can usually be recognised on a manuscript. It is dissolved by acetic acid and turns deep orange with caustic potash.

MALACHITE.—The native green copper mineral has a characteristic appearance under the microscope, and can usually be identified on a manuscript by matching. It differs from the artificial copper carbonate, green verditer, in being crystalline, and when examined with the polarising microscope usually shows a few doubly-refracting particles.

When green verditer is mounted on a slide in cassia oil and examined with the light stopped down, the white fringe which appears at the boundary between the oil and fragment moves from the fragment to the oil when the objective is raised,

whereas with malachite it moves from the oil to the fragment. The reason is that the refractive index of verditer is well below 1·6 (the refractive index of cassia oil), whereas that of malachite is much above it (1·9). Both these greens, being carbonates, effervesce with acids.

All these copper compounds turn red when moistened with a slightly acid solution of potassium ferrocyanide, and can be confirmed by the triple nitrite reaction.

VERDIGRIS.—Verdigris was prepared by the action of fermenting grape skins on sheets of copper. This is a basic acetate, containing some doubly refracting crystals, with a refractive index below oil of cassia. By treating this salt with a little water it is partly decomposed, leaving behind a still more basic salt, not readily soluble, which seems to have been used in illuminating fifteenth century MSS. It is a pale emerald green and contains a few doubly refracting particles.

The ordinary basic acetate was used in oil painting. It does not effervesce with acids, is below cassia oil in refractive index, and gives the usual copper reactions. Moistened with slightly acid potassium ferrocyanide it turns red, and when dissolved in acetic acid can be confirmed by the triple nitrite reaction.

TRANSPARENT COPPER GREEN.—This appears as a uniform transparent layer without crystalline structure. It can be matched by dissolving verdigris in Venice turpentine, or cedar balsam. This green can be used either after dilution with oil of turpentine, or after being dried to a powder and mixed with gum or white of egg, or after emulsification with egg.

Particles from early MSS. gave a brown-violet discoloration with tin bromide, thus indicating the presence of a resin, but on treatment with sulphuric acid the copper green from the MSS. and the copper green mixed with gum resisted the action of the acid for a long time, whilst the copper green I prepared was at once attacked. These facts support the conclusion that the green was painted on after emulsification with egg or admixture with gum or egg. A recipe for its preparation is given by De Mayerne (Sloan MS. 2052). The presence of copper can be confirmed by the usual reactions.

EGYPTIAN BLUE.—Experiments made by Russell, Fouqué, and myself indicate that this is a definite crystalline silicate, with the approximate formula $CaO, CuO, 4SiO_2$, though some of the metals can be partly replaced (Plate, Fig. 1). The crystals are double-refracting, and in convergent polarising light show the cross and ring characteristic of uniaxial minerals; they exhibit pleochroism, changing from deep blue to rose.

The blue is insoluble even in boiling hydrochloric acid. When treated with potassium ferrocyanide it gives here and there a reddish reaction, probably due to uncombined copper. It is readily distinguishable from ultramarine by its properties and by the presence of quartz fragments with which it is mixed. I have found it both on Egyptian and Roman paintings, and on the paintings in the Palace of Knossos. It is not found after the early centuries of the Christian era.

De Wild ignites on a platinum spatula with strong sulphuric acid and ammonium fluoride to dissolve the blue, then applying the usual reactions for copper.

ULTRAMARINE REAL.—Lapis Lazuli, from which the natural pigment is prepared, contains several other minerals, usually including iron pyrites, to which the golden spicules in the stone are due, and calcite (Plate, Fig. 5). Some of the colourless associated minerals are double-refracting, such as calcite, so that the appearance of ultramarine under crossed nicols is characteristic. It is bleached by dilute acids, but its optical behaviour distinguishes it from artificial ultramarine, which is also bleached by acids. The production of hydrogen sulphide on moistening with an acid can be confirmed by coating the particle with a thin film of collodion and then moistening with an acid solution of a lead salt. The particle turns black. When mixed with white lead, discoloration of the white lead on treatment with acid is obtainable. I cannot confirm De Wild's statement that it is insoluble in acetic acid; it dissolves very slowly in strong acetic acid, but readily in more diluted acid.

AZURITE.—This is a basic copper carbonate, which, on the illuminated MSS. and pictures that I have examined, is always of a very fine crystalline variety (Plate, Fig. 4). The crystals are usually slightly green, double-refracting, and in convergent polarised light show figures characteristic of a biaxial mineral; the refractive index is about 1·8. Azurite effervesces with acids and gives the copper reaction with acid potassium ferrocyanide, and can be confirmed by the triple nitrite reaction.

BLUE VERDITER.—The old "azures" were made by various methods, including the treatment of a copper salt with lime or potash, and the introduction of a certain amount of sal-ammoniac. Analysis shows blue verditer to consist of a basic copper carbonate which sometimes contains calcium sulphate, and sometimes copper sulphate. Like azurite, it gives a copper reaction with acid potassium ferrocyanide, gives the triple nitrite reaction, and effervesces with dilute acids, but it can be distinguished from azurite by the facts that it is not double-refracting, and that it has a refractive index lower than that of oil of cassia.

GREEN VERDITER.—This is also a basic copper carbonate. It can be distinguished from malachite by its refractive index being lower than that of oil of cassia. It can be identified as a copper carbonate by the methods already given.

LAKES.—*Kermes* is the product of a small insect, resembling the cochineal insect, which is found on the prickly oak of the shores of the Mediterranean. It forms lakes similar to cochineal lakes, but not quite so brilliant.

Sapan Wood (a dye from Ceylon) contains a violet colouring matter which forms fugitive lakes.

Lac Lakes (from *Coccus lacti*), crimson lakes from the *cochineal* insect (*Coccus cacti*), and *madder lakes* from the madder root are made by a similar process of precipitating the colouring matters in association with hydrated alumina.

Lakes from cochineal or kermes seem to be sufficiently permanent for use on illuminated MSS. which are seldom exposed to light, and, if locked up in a resinous medium, such as Venice turpentine, are quite permanent.

If small particles of the lakes are exposed to the action of moist sulphur dioxide gas, madder and Brazil wood lakes are quickly bleached, whilst cochineal and lac lakes are much more resistant than the others.

On treatment with ammonia all the lakes are rendered very purple in tone, but with cochineal lakes a very deep violet solution is formed surrounding the particles. If Brazil wood lake is treated with a weak acid, such as acetic acid, it is bleached to a yellow colour, whilst the other lakes are but little affected.

The best means of distinguishing madder lake from the others is to cover the particle on the slide with a thin film of collodion, and then to treat with dilute nitric acid. All the lakes are apparently bleached, but if the slide is then immersed in ammonia solution, the madder lake at once turns purple, whilst the other lakes are unaffected. The identification of faded lakes immersed in a medium like oil is well nigh impossible, but I have been successful in identifying madders which have borne the test of time remarkably well.

TYRIAN PURPLE.—The pigment obtained from the secretions of *Purpura haemastoma* and *Murex brandonis* by the action of sunlight has been investigated by Friedländer (*Ber.*, **1909**, **42**, 765), and found to be a dibromindigotin. To prepare the lakes used in early MSS. the secretions were probably mixed with a suitable paste and exposed to the sun.

The dyestuff is insoluble in water, alcohol or ether, and sparingly soluble in boiling benzene or glacial acetic acid, but dissolves readily in boiling aniline.

A purple lake is found on Byzantine MSS. which is probably Tyrian purple. Parchment was also stained purple. Scot–Irish MSS. have a purple pigment which is probably from the *Purpura capillus*.

SMALT.—This is a glass coloured by cobalt. Examined under the microscope it can be seen to consist of minute fragments of glass, which have a quite characteristic appearance under the microscope on the surface of a picture. Its spectrum shows two absorption bands in the red and in the yellow, while a certain amount of red is transmitted. A fragment is not decomposed by acetic acid, but if the fragment is warmed with hydrochloric acid the smalt is decomposed. De Wild finds decomposition by hydrochloric acid difficult and advises incineration with sulphuric acid and ammonium fluoride. A test is made for cobalt with mercuric thiocyanate.

THE PROPERTIES AND REACTIONS OF CERTAIN MODERN PIGMENTS.

PRUSSIAN BLUE.—This may be identified by moistening the section with potassium hydroxide solution; the colour will be destroyed at once, but can be restored by adding acetic acid. This pigment is too finely divided to be resolved by a magnification of 90 diameters.

COBALT BLUE is a compound of the oxides of cobalt and alumina. It is very insoluble and is not affected when warmed with strong hydrochloric acid.

Examined with the micro-spectroscope, it shows the bands characteristic of smalt, and the presence of cobalt may be confirmed by means of a borax bead.

In the case of Egyptian blue, smalt, and cobalt blue, De Wild advises heating on a platinum spatula with sulphuric acid and sodium fluoride, identifying them by the usual reactions.

ARTIFICIAL ULTRAMARINE.—This differs from lapis lazuli in showing no double-refracting particles. It is readily destroyed by a weak acid, such as acetic acid. A further test is to coat a particle with collodion and then moisten it with a mixture of acetic acid and lead acetate, when the particle becomes black. The appearance under the microscope is quite different from that of real ultramarine, consisting of fine amorphous, instead of coarse crystalline, particles (Plate, Fig. 6).

LEAD CHROME.—The lead chromes are lead chromates usually containing lead sulphate, and often other substances, such as calcium sulphate and calcium carbonate. If particles are left in contact with a solution of silver nitrate and acetic acid, they are gradually converted into the red silver chromate. They are blackened by sodium sulphide, and converted into a white mass by hydrochloric acid.

BARIUM CHROMATE AND STRONTIUM CHROMATE.—These are also used in painting. They are dissolved from an oil film by hydrochloric acid, and give the same reactions as lead chromate with silver and mercury salts.

CADMIUM YELLOWS (compounds of cadmium and sulphur) are dissolved from the oil film by hydrochloric acid or nitric acid. The film is unchanged by sodium sulphide, and turns black if wetted with a solution of silver nitrate containing a little acetic acid. The presence of cadmium is confirmed by microchemical tests applied to a solution of the film.

COBALT YELLOW is the double nitrite of cobalt and potassium. The oil film is not attacked by acetic, hydrochloric or nitric acid; it turns black with sodium sulphide, and dark brown with caustic soda. The presence of cobalt is confirmed by microchemical tests.

SCHEELE'S GREEN (copper arsenite) can be distinguished under the microscope from the copper carbonate greens by its greater brilliancy; it differs from emerald green in being non-crystalline and not doubly refracting. For its identification in an unknown specimen, samples of verditer and Scheele's green are put on the slide beside the unknown sample, and the whole coated with collodion and immersed in a bath of stannous chloride dissolved in strong hydrochloric acid. On heating the bath gently to 60° C. the verditer dissolves, but the arsenic green becomes brownish-black. Arsenic can be confirmed by the usual microchemical tests (Charnot, *loc. cit.*, p. 395).

CHROME GREENS are mixtures of Prussian blue with chrome yellow. If the oil film is treated with caustic soda, the Prussian blue is destroyed, leaving the yellow pigment unattacked, which can then be identified as a lead chromate.

EMERALD GREEN is a copper aceto-arsenite, consisting of green crystals which are doubly refracting and have a refractive index above that of oil of cassia.

With copper ferrocyanide it gives the brown coloration of a copper green, and with stannous chloride and hydrochloric acid the brown colour reaction for arsenic. As confirmation, the usual microchemical tests (Charnot, *loc. cit.*, 388) are applied.

VIRIDIAN OR GREEN OXIDE OF CHROMIUM.—This is a chromium hydroxide; it appears transparent when examined under the microscope. The oil film is not attacked by acetic, hydrochloric or nitric acid, or by caustic soda. A fusion is necessary to confirm the presence of chromium.

ZINC WHITE is not resolved under 90 diameters. It appears a bright yellow in ultra-violet light, whilst white lead is a bluish white. It dissolves in acids without effervescence, is not blackened by sodium sulphide, its deliquescence on the slide of the nitrate crystals is very characteristic (De Wild), and it gives a white feathery precipitate with mercuric thiocyanate.

The following tables give a summary of the most suitable reactions of the various pigments, even when embedded in a dried linseed oil film, with the exception of the lakes and white lead and zinc white. The most common pigment to be found mixed with them is white lead; this can be removed by repeated treatment with dilute acetic acid, where the pigment is insoluble in weak acetic acid, but many of the selected reactions are not affected by the presence of white lead. Where both pigments are present in solution and cannot be separately identified, Charnot's *Elementary Chemical Microscopy* should be consulted.

TESTS FOR RECOGNISING MICROSCOPIC FRAGMENTS OF CERTAIN PIGMENTS IN A DRIED OIL FILM, TO BE FOLLOWED BY DISSOLVING A PARTICLE OF THE PIGMENT, AND CONFIRMING IN SOLUTION WITH MICROCHEMICAL TESTS.

ORANGE.

	Nitric acid.	*Sodium sulphide.*
Red lead	Dirty brown	Black
Orange chrome	Bright yellow	Black
Orange cadmium	Dissolves	No change

GREENS.

	Acid potassium ferrocyanide	*Hydrochloric acid with stannous chloride.*	*Optical properties.*	*Acetic acid.*
Verdigris	Deep red	—	Double refracting; R.I. below cassia oil	—
Malachite	Deep red	—	Double refracting; R.I. above cassia oil	Effervesces
Green verditer ..	Deep red	—	Not double refracting; R.I. below cassia oil	Effervesces
Scheele's green ..	Deep red	Black	Not double refracting	—
Emerald green ..	Deep red	Black	Double refracting	—

NOTES. *Cobalt green* dissolves in acetic acid and gives cobalt borax bead. Confirm by tests for cobalt.

Viridian is insoluble in, and unchanged by, acetic, hydrochloric or nitric acid. Confirm by fusion.

Chrome green turns yellow with sodium hydroxide.

YELLOWS.

	Acetic acid.	*Hydrochloric acid.*	*Sodium sulphide.*	*Caustic potash.*	*Silver nitrate and acetic acid.*
Lead chrome ..	Unchanged	Turns white	Black	Dissolves	Red slowly
Barium chrome ..	Unchanged	Dissolves	Unchanged	—	Red slowly
Orpiment	Unchanged	Unchanged	Dissolved	Dissolves	—
Cadmium sulphide ..	Unchanged	Dissolves	Unchanged	—	Black
Yellow lake	Dissolves	Dissolves	Unchanged	Orange	—
Gamboge	Dissolves	Dissolves	Unchanged	Orange	—
Naples yellow ..	Unchanged	Unchanged	Brown	—	—
Lead oxide	Dissolves	Dissolves	Black	—	—
Cobalt yellow ..	Unchanged	Unchanged	Black	Brown	—

BLUES.

	Acetic acid.	*Acid potassium ferrocyanide.*	*Strong hydrochloric acid.*	*Caustic soda.*	*Chlorine.*	*Optical properties.*
Ultramarine—real	Bleached	—	—	—	—	Colourless, double-refracting crystals
Ultramarine—artificial ..	Bleached	—	—	—	—	—
Azurite	Dissolves	Deep red-brown	—	—	—	Double-refracting. R.I. above cassia oil
Blue verditer	Dissolves	Deep red-brown	—	—	—	Not double-refracting R.I. below cassia oil
Prussian blue	Unchanged	—	—	Bleached	—	—
Indigo	Unchanged	—	—	—	Bleached	—
Smalt	Unchanged	—	Dissolves	—	—	—
Cobalt blue	Unchanged	—	Unchanged	—	—	—

NOTE. Prussian blue and indigo hardly resolved when magnified 150 diameters.
To confirm ultramarine, cover particle with collodion and moisten with acetic acid plus lead acetate. The particle turns black. Confirm cobalt blues and greens by microchemical tests for cobalt.

Two of the most useful methods for confirmatory tests are as follows:—

(1) CONFIRMATORY TESTS FOR LEAD COPPER AND COBALT AND ZINC REACTIONS WITH POTASSIUM MERCURIC THIOCYANATE.—This reagent is prepared as follows:—To a saturated solution of mercuric nitrate containing 1 part by volume of concentrated nitric acid to 100 parts of water, add a 5 per cent. solution of potassium thiocyanate as long as precipitate is formed. Wash till no reaction is obtained with potassium iodide or ferric chloride solution. To a 5 per cent. solution of potassium thiocyanate, add the mercury thiocyanate thus obtained until the solution is saturated. This takes some time. Filter; add a few drops of potassium thiocyanate solution; evaporate and crystalise; re-dissolve and re-crystallise.

This reagent gives with zinc salts, white feathery crystals; with copper salts, radiating acicular prisms of a yellowish green colour; and with cobalt salts, deep blue-black orthorhombic prisms (Chamot).

(2) THE TRIPLE NITRITE REACTION.—When testing for copper, add dilute acetic acid, and a crystal of lead acetate; then a small fragment of potassium nitrite. The black triple nitrite of potassium, copper and lead is formed.

In testing for lead, add acetic acid, sodium acetate, and copper acetate. Then add a fragment of potassium nitrite.

In using these confirmatory tests, the pigment should first be dissolved in a suitable acid on the corner of the slide, and evaporated to dryness on the top of the water-bath, and then redissolved. When evaporated, the crystals should be examined. Both lead and zinc nitrates, for instance, crystallise in a very definite manner, easily recognisable. Mercury can be detected in solution by potassium thiocyanate and cobalt nitrate.

In conclusion to this part of my paper may I acknowledge my indebtedness both to Dr. Chamot and Dr. de Wild for several observations, reactions and methods additional to those originally published by me?

ILLUMINATED MANUSCRIPTS.

Egyptian blue was manufactured so far back as the fourth dynasty, and was universally used throughout the Roman Empire up to, at all events, the second century A.D., but by the seventh century it seems to have disappeared completely, possibly as a result of the conquest of the Empire by the Mohammedans. It was found on certain early MSS. by Church, but its occurrence there may have been due to its being scraped off old Roman frescoes. I have never once found it on any manuscript.

BYZANTINE MANUSCRIPTS.—The earliest MS. examined (Add. 5111, ff. 10, 11, Brit. Mus.) consists of two leaves from a Gospel book, supposed to be of the sixth or seventh century; they are entirely covered with gold leaf paint. The pigments used were a green resembling malachite, and a rich coloured lake which matches a modern madder carmine, but was probably a preparation from the Tyrian purple. The blue present is a badly washed ultramarine, *i.e* containing colourless minerals.

Other early Byzantine manuscripts contained vermilion, orpiment, malachite, or a dull green, badly washed ultramarine and Tyrian purple. This palette occurs again and again in these manuscripts from the seventh to the fourteenth centuries. The Tyrian purple apparently disappears in the thirteenth century, its place being taken by a poor faded lake. The Byzantine ultramarine used in the thirteenth century MSS. is inferior to that used in those of the seventh century, and not to be compared with European ultramarine of the thirteenth century.

SCOT-IRISH MANUSCRIPTS.—The earliest manuscript examined was the Lindisfarne Gospels (Brit. Mus., Nero D.IV) of the eighth century. Red lead is used in place of the vermilion of the Byzantine manuscripts. Other pigments identified on Irish MSS. include malachite green, badly washed ultramarine, vermilion, orpiment, and a fine purple which is peculiar to Irish and early English manuscripts. Presumably this was derived from *Purpura capillus*, which is found round the Irish and English coasts. The same pigments are found on the Book of Kells.

Some earth colours, such as yellow ochre, and a deep brown, which may be sepia, also occur.

With the replacement of red lead by vermilion, these pigments were characteristic of Scot–Irish MSS. up to the thirteenth century.

In an interesting Irish Psalter in the Edinburgh University Library (A. Ca. 44), which is supposed to be not later than the eleventh century, malachite has been replaced by the transparent copper green described above.

ENGLISH MANUSCRIPTS.—The transparent copper green occurs on a Canterbury Psalter of about A.D. 700 (Vespasian A.I); the ultramarine is fair or poor, and there is vermilion, as well as red lead; a poor purple lake is used instead of the Tyrian purple of the Irish MSS.

River-washed gold separated and prepared as a pigment appears to have been used on a Canterbury Gospel of the late eighth century. The result of using these coarse particles is to give a raised surface.

A beautiful mauve pigment, probably made by mixing ultramarine ash with a little lake, also occurs on this manuscript.

King Edward's Charter to Chichester (A.D. 966) is covered with a wash of pink, probably pink lake, and the pigments used include a very bright blue azurite, a transparent copper green, and a badly washed ultramarine, while the gold lettering consists of river-washed gold. The azurite was probably added at a later date; it does not appear again on any manuscript until the thirteenth century.

Other early English MSS. examined contained vermilion, red lead, orpiment, malachite green, badly washed ultramarine, red and purple lakes (probably made from kermes), transparent copper green and burnished gold leaf on gesso (first found on a Westminster Psalter of the late twelfth century). Azurite is of frequent occurrence on manuscripts from the middle of the thirteenth to the end of the fourteenth century.

A very brilliant azurite appears on late fifteenth and sixteenth century manuscripts, and was probably obtained from a different source, its first occurrence being noted on the Culross Psalter (A.D. 1470).

There is no indication of the use of madder lakes on earlier manuscripts, but there is justification for concluding that they were used in the fifteenth century.

CONTINENTAL MANUSCRIPTS.—An examination of early French, Flemish, German and Italian manuscripts has shown that the changes of palette show considerable agreement in different countries on passing through the centuries. Certain pigments, such as gold, vermilion, red lead and orpiment, are common throughout the period ending with the fifteenth century, whilst malachite, either as a natural or artificial preparation, appears at various dates. Purple dye from the murex is to be found on European MSS. of about 800 A.D., but later this purple remains peculiar to Irish manuscripts up to the thirteenth century.

Unlike the ultramarine on Irish and Byzantine manuscripts, the ultramarine on European manuscripts shows a steady improvement in the washing process, and from 1200 A.D. onwards the ultramarine is nearly always a fine pigment. Hence the condition of this pigment affords an approximate idea of the date of a European manuscript. With the improved washing of ultramarine, ultramarine ash began to be used for delicate backgrounds. The earliest date I have noted is on a thirteenth century French manuscript.

About the middle of the thirteenth century a dark blue azurite began to be used and continued into the fourteenth century. No instances of its use in the first half of the fifteenth century have been found, but towards the end of that century a very brilliant azurite was employed, and is also to be found in the sixteenth and seventeenth centuries.

Verdigris and transparent copper green are common to manuscripts of all countries from the eighth to about the middle of the fourteenth century, but in the fifteenth century the older verdigris is replaced by a brilliant verdigris which continues to be the principal green in use during the fifteenth and sixteenth centuries, whilst the transparent green is no longer to be found. This brilliant verdigris was probably made by the action of vinegar on azurite, and was subsequently mixed with a yellow pigment, probably gamboge. Under the microscope this mixture appears as a brilliant green in which nothing is visible but the crystalline structure of the verdigris.

The common type of lake used in the later thirteenth and fourteenth centuries can be matched by lac lakes, and there can be little doubt as to the use of madder lake, at all events on the later fifteenth century manuscripts.

The use of gold leaf and gold leaf ground down into a paint is found from the earliest to the latest times, but the use of raised burnished gold letters on bole seems to have come in towards the end of the twelfth century.

The coarse, apparently river-washed, gold has not been found on any manuscript outside the British Islands.

THE VENETIAN DUCALI.—The illuminated Venetian Ducali in the British Museum cover the period between the beginning of the sixteenth century and 1700,

and offer the advantage of being documents the date of which is approximately known.

With one or two doubtful exceptions, the pigments used on the documents are the same as those found on the fifteenth century missals. The use of azurite continues from 1500 to 1647, which is some twenty years later than its disappearance from the English legal rolls. The next manuscript is dated 1700, and on this the blue is certainly an artificial copper blue. It is interesting to note that although smalt was used by painters from the later half of the sixteenth century onwards, it does not occur on any of these documents.

THE CORAM REGE ROLLS.—The Legal Rolls preserved in the Record Office were formerly recorded on long strips of parchment, sewn together at the top, and from about 1500 to 1700 the first page was ornamented with gilt letter and painted miniatures. This series of rolls is of great interest as showing the gradual deterioration from the pigments used by the fifteenth century illuminator. In the seventeenth century there occurs first the replacement of verdigris by the non-crystalline artificial copper carbonate, and then the replacement of azurite by the inferior blue verditer. This is the most important change in the artist's palette, and the presence of azurite (re-introduced about 1470) in a picture may be regarded as evidence that it was painted before the middle of the seventeenth century, and probably later than 1470.

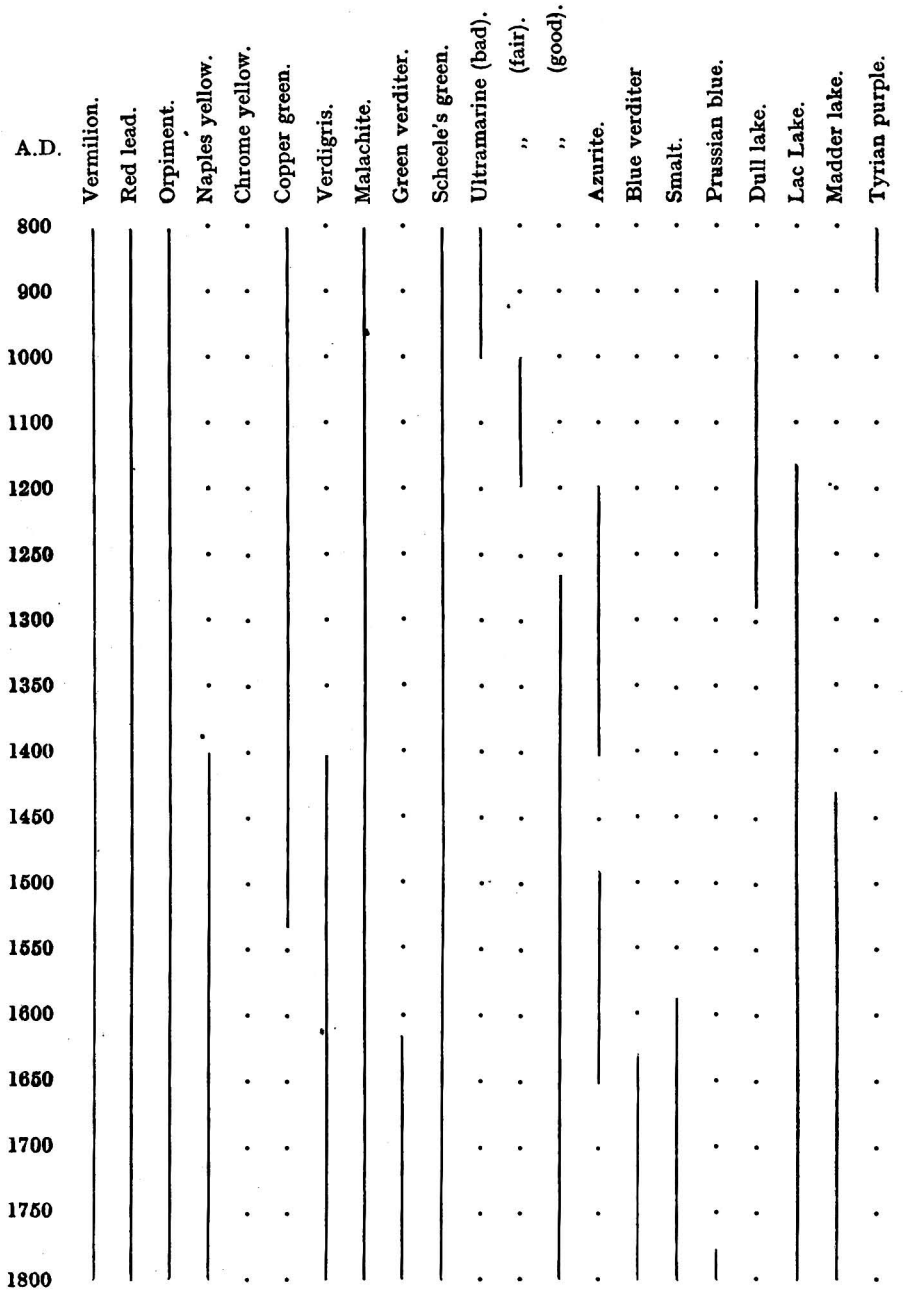
PIGMENTS ON PICTURES.

The results obtained by the examination of the pigments used on paintings in the National Gallery, Edinburgh, dating from the fifteenth to the beginning of the nineteenth century, confirm the evidence obtained from the Venetian Ducali and the Coram Rege rolls as to the disappearance of azurite from the artist's palette before 1650 and its replacement by blue verditer; the remaining blues in common use from 1650 onwards were ultramarine, blue verditer and smalt. Mixtures of azurite and ultramarine were not uncommon in the fifteenth and early part of the sixteenth century. In Watteau's pictures rich effects were obtained by the interpainting of verdigris and ultramarine. Prussian blue occurs in the late eighteenth century.

The first appearance of smalt is on a picture in the Hamilton Bruce Collection, which must have been painted about 1600. The Rokeby Venus contains a mixture of smalt and azurite. Green verditer first appears soon after 1600, and blue verditer, in place of azurite, in 1660. As regards yellows, reds and lakes, there is nothing new to record. Scheele's green and chrome yellow were discovered in the closing years of the eighteenth century, but there is no evidence that they were used or sold until early in the nineteenth century.

The tendency of an artist always to use the same palette is important when examining doubtful pictures supposed to be painted by him. Thus Teniers used smalt; Boucher blue verditer; and Watteau, as mentioned above, a mixture of verdigris and ultramarine.

The following table summarises the periods during which the various pigments were used for manuscripts and paintings:—



IDENTIFICATION OF MEDIUMS.

The most important point is the distinction between egg or size mediums and oil or varnish mediums, so as to determine whether a picture is to be classified as an example of tempera or of oil painting.

If a minute fragment of the material is moistened with strong sulphuric acid, it will be found that pigments which have been mixed with size or egg are not readily changed in colour, whereas if an oil varnish or resin is the medium a dark brown coloration is produced.

A more reliable test is to immerse the section in slightly warmed methyl violet stain for about 30 minutes, after which it is washed with alcohol. If egg or size is present the fragment will be permanently stained, whereas in the case of oil or varnish the stain is washed out by the alcohol.

The method can be applied to mixtures of the two kinds of mediums, the microscopic particles of egg or size showing a spotted appearance after the staining.

It is possible that the enamel-like medium used by Van Eyck and his immediate followers was an emulsion of a little yolk of egg with oil or varnish. The brilliant Van Eyck green is matched by the resin copper green, and the preparation of this pigment involves the use of a balsam; it would either have to be emulsified with egg or mixed with a small amount of oil to make it suitable for painting (and oil by itself would probably be too sticky), or oil and egg, or possibly dried, ground, and mixed with mediums.

The evolution in the methods of painting from the tempera of Italy and the triumph of the oil medium of the North was partly due to the preparation in commercial quantities of such thinning agents as turpentine and petroleum, towards the close of the fifteenth century. The earliest date at which I have found definite evidence of the use of spirits of turpentine (to dissolve beeswax) is on the MS. (18.1.7) in the Advocates' Library, Edinburgh (1465–1489).

EXAMINATION OF BRUSHWORK.

It is possible, in some cases, to identify the painter of a picture by means of his characteristic brushwork. For this purpose it is best to examine the canvas with a Zeiss stereoscopic magnifier, giving a magnification up to about 3 diameters. For comparison of two pictures, however, the best plan is to use a camera by means of which enlarged photomicrographs of small selected portions of the surface can be taken. For most purposes a magnification of 2 diameters is the most useful for securing minute details in the handling of the paint.

It is questionable whether the method could be of much service for typical sixteenth century Italian pictures, in which the brushwork was, to a large extent, concealed, but there can be no doubt as to its value when applied to pictures of a later period when brushwork was shown. For example, the pictures of Watteau show a softness and characteristic modelling process; whilst the work of Pater (who was Watteau's most successful pupil) shows a completely different technique,

the paint being laid smoothly on the face and then modelled up with one or two obvious shadows.

Again, the work of Mabuse shows no indication of brushwork, but the magnification brings out the accuracy of detail and finish, which a forger would hardly be likely to reproduce.

As an instance of the application of the method, an examination into the authenticity of a Teniers in a private collection may be cited. The brushwork of a characteristic Teniers is seen in a photomicrograph to consist of short broad straight strokes, with here and there fine slightly curved lines. Another admittedly genuine picture was found to show essentially the same type of brushwork, so that whilst Teniers modified the external character of his work, his method of applying the paint did not alter.

In the picture in the private collection, however, although evidently painted from the same model, the brushwork was distinctly different in character, although in places it showed touches resembling the work of Teniers. Hence the picture was either painted in his studio and retouched and signed by him, or was a forgery.

In the case of landscape painters the foliage of trees is usually characteristic of the artist, the methods of applying the paint varying greatly in complexity and detail. This point can be clearly seen in the paintings of Crome and of Constable, whilst the foliage of Corot, Courbet and Maris is equally distinctive.

When the brushwork of a reputed picture differs from that in an admitted one of the same master, it is, of course, necessary to collect authentic examples of the painter's work at different periods of his career, since an artist may completely change his technique in later life.

X-RAY EXAMINATION.

The application of *X*-ray examination to pictures has provided additional means of forming a judgment on their authenticity, as well as of ascertaining whether a picture has been painted over another painting or has been retouched at a later date.

It has been found experimentally that those paints in which pigments containing lead and mercury are present show a greater degree of absorption for *X*-rays than those in which the elements in the pigments (*e.g.* ultramarine) are of lower atomic number. For this reason an *X*-ray photograph of a picture may reproduce more or less distinctly the outlines of an old painting in which these heavier pigments were used to a predominating extent (*cf.* Glocker, *Materialprüfung mit Röntgenstrahlen*, Berlin, 1927).

The *X*-ray photograph may also show the structure of the canvas of a picture, owing to the difference in the absorption of the strands of the fabric and the priming (of white lead, chalk, etc.) which has been used to provide the painting surface. If, however, the priming is too thick, it may interfere with the absorption of the pigments used for the picture itself. This is not so likely to happen with paintings on wooden panels, for which much less priming was generally used.

In taking an *X*-ray photograph the painted surface is placed on the top of the photographic plate, and exposed at the selected angle of incidence to the rays, with precautions to prevent the access of light. The time of exposure and the distance at which the *X*-ray tube is to be focused on the picture will obviously depend upon the nature of the pigments present, and the details which it is desired to bring out; these points must be determined experimentally.

Several striking examples of the information to be gained by the use of the method were shown by Dr. Kaye in his Cantor Lecture to the Royal Society of Arts (1922). One of these was a portrait of a knight near a waterfall, which was painted on a wooden panel, and the *X*-ray photograph showed that, originally, the waterfall had been much larger and in a different position.

In another picture an *X*-ray photograph by Heilbronn of the Crucifixion by Cornelis Engelbrectsen revealed the fact that the figure of a monk in surplice and stole had been replaced at a later period by the figure of a woman, presumably the donor of the picture.

Equally striking evidence of later work having been imposed on the artists' original picture is that furnished by an *X*-ray examination of the picture by Frans Hals, "The Toper" (Catalogue No. 1200) in the National Gallery of Scotland. It was proved by De Wild that the red bonnet on this picture had been painted over the original uncovered hair, and that a goblet had been substituted for the original jawbone held in the hand of the sitter. In 1928 the over-painting was removed, and the portrait was restored to the condition in which it had left the hands of the artist.

ULTRA-VIOLET RAYS.—The use of ultra-violet rays in the examination of a picture is not without value, certain pigments being easily distinguished, zinc white becoming a light chrome yellow tint, and orpiment alone of the yellows reflecting a bright yellow, the cadmiums and chromes being greenish or brownish black. It also shows up repairs very distinctly.

SHORT LIST OF BOOKS SUITABLE FOR REFERENCE.

The leading authorities.
THE HISTORICAL DATA.
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EASTLAKE. *Materials for a History of Oil Painting.*
EIBNER. *Wandmalerei.*
HENDRIE. *Translation of Theophilus.*
HERRINGHAM. *The Book of the Art of Cennino Cennini.*
LAURIE. *Materials of the Painter's Craft.*
MACLEHOSE. *Vasari on Technique.*
MERRIFIELD. *Original Treatises on the Arts of Painting.*

ANALYTICAL METHODS.

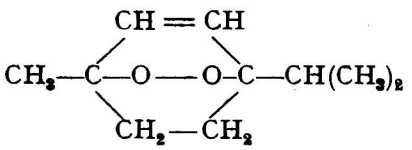
CHARNOT, E. M. *Elementary Chemical Microscopy.* (London: Chapman & Hall.)
DE WILD, M. *The Scientific Examination of Pictures.* (London: G. Bell & Sons.)
LAURIE, A. P. *The Pigments and Mediums of the Old Masters.* (London: Macmillan.)
RAEHLMANN, *Ueber die Maltechnik der Alten.*
— *Ueber die Farbstoffe der Malerei in den verschiedenen Kunstperioden.*
Report to the International Congress on Illumination. New York, 1928 (0–4).
Monsieur F. Cellerîer, Directeur du Laboratoire d'Essais du Conservatoire National des Arts et Métiers, Paris (Researches on the application of colour filters, ultra-violet rays and *X*-rays to the examination of the pictures in the Louvre).

The Determination of Ascaridole in Chenopodium Oil.

By T. TUSTING COCKING, F.I.C., and F. C. HYMAS, B.Sc., A.I.C.

Ascaridole is the chief constituent of chenopodium or American wormseed oil, in which it occurs to the extent of 60–75 per cent.

The formula below has been ascribed to it by Wallach (*Annalen*, **1912**, **392**, 59); this shows it to be a peroxide, and, as such, it reacts very vigorously with reducing agents—



Three methods have been used for the determination of ascaridole in chenopodium oil:—

(1) Separation of ascaridole by repeated fractionation *in vacuo*.

(2) Solution of the ascaridole by shaking the oil with 60 per cent. acetic acid and subsequently measuring the unabsorbed portion of the oil, the ascaridole being taken by difference. This method was first suggested by Nelson (*J. Amer. Pharm. Assoc.*, 1921, **10**, 836), and has been adopted by the United States Pharmacopoeia. It suffers from the disadvantage that adulterants such as cineole are also soluble in 60 per cent. acetic acid.

(3) Reduction of the ascaridole by means of excess of titanous chloride with subsequent titration of the excess with ferric alum. This method was introduced by Paget (Analyst, 1926, **51**, 170), and, while it is much superior to the other methods, inasmuch as it is not affected by the usual adulterants, it suffers from the inconvenience that the whole determination must be carried out in an atmosphere of carbon dioxide.

In the hope of finding a more convenient method than Paget's titanous chloride reduction, experiments were tried with a number of reducing agents. Stannous chloride and ferrous thiocyanate were found to react readily with the oil, but the reagents themselves are rapidly oxidised by atmospheric oxygen, and the methods therefore suffer from the same objection as the titanous chloride process.

Eventually the reducing effect of potassium iodide in acid solution was tried, and found to result in an immediate liberation of iodine. As this reagent is relatively stable towards atmospheric oxygen, the following series of experiments was instituted:—

An approximately 5 per cent. (w/v) solution of chenopodium oil in 90 per cent. acetic acid was prepared, and 5 c.c. of this solution, referred to as "Solution A," measured from a burette, were taken for each test.

(1) Five c.c. of solution A were mixed with 15 c.c. of glacial acetic acid and 10 c.c. of approx. $N/1$ potassium iodide solution.

An immediate liberation of iodine occurred, which increased on standing; after remaining at laboratory temperature for $2\frac{1}{2}$ hours, it was titrated with $N/10$ thiosulphate solution; there were required 23·5 c.c. per grm. of oil.

(2) As (1), but the solution was alternately warmed in a steam-bath and titrated until a permanent end-point was reached; time about 20 minutes; required 31·5 c.c. per grm. of oil.

(3) As (1), but with the addition of 5 c.c. of hydrochloric acid; required 31·7 c.c. per grm. of oil.

(4) A stronger solution of potassium iodide was now tried; 5 c.c. of solution A were mixed with 10 c.c. of glacial acetic acid and 3 c.c. of approx. $5N$ potassium iodide solution. This was alternately warmed in the steam-bath and titrated as before; required 32·2 c.c. per grm. of oil.

To the solution were now added 10 c.c. of hydrochloric acid, when a further liberation of iodine took place, and titration with thiosulphate corresponded to a further 22·0 c.c. per grm. of oil, or a total of 54·2 c.c. per grm.

At the completion of the titration, the liquid had a slight yellow colour which was not removed by more thiosulphate, in contradistinction to the end-point when acetic acid only was used, when the liquid was colouress.

(5) Five c.c. of solution A were mixed with 3 c.c. of approx. $5N$ potassium iodide solution and 5 c.c. of concentrated hydrochloric acid. A copious liberation of iodine occurred immediately, and this was titrated at once; required 72·3 c.c. per grm. of oil.

(6) As in (5), but the mixture was allowed to stand at laboratory temperature for $1\frac{1}{2}$ hours before titrating; required 64·0 c.c. per grm. of oil.

In this case, after titrating there was a dark oily scum, and it is evident that, on standing, some of the iodine was absorbed by the oil.

(7) In this experiment the same quantities were used, but the potassium iodide and hydrochloric acid were mixed together before adding solution A, and then titrated immediately; required 70·5 c.c. per grm. of oil.

(8) The acid was increased to 10 c.c., that is:—Three c.c. of approx. $5N$ potassium iodide solution were mixed with 10 c.c. of concentrated hydrochloric acid; 5 c.c. of solution A were added, and the mixture titrated immediately; required 78·1 c.c. per grm. of oil.

(9) The same as (8), but with the addition of 5 c.c. of carbon tetrachloride to the acid mixture before adding solution A; required 80·8 c.c. per grm. of oil.

(10) As in (9), but with 5 c.c. of benzene instead of carbon tetrachloride; required 61·7 c.c. per grm. of oil.

The layer of benzene appeared to have the effect of delaying the reaction, and it was found that the highest results were obtained when the mixing was as rapid as possible.

In these last four experiments it was noticed that the mixture became appreciably warm on the addition of solution A; the effect of cooling the acid mixture before adding the solution of the oil, was therefore tried.

(11) Three c.c. of approx. 5*N* potassium iodide solution were mixed with 10 c.c. of concentrated hydrochloric acid and 5 c.c. of carbon tetrachloride, and cooled in freezing mixture, and then 5 c.c. of solution A were added and the mixture titrated immediately; required 94·5 c.c. per grm. of oil.

(12) As (11), but without the carbon tetrachloride; required 97·5 c.c. per grm. of oil.

These last conditions appeared to give the best results, and a number of experiments were carried out by three different observers, with the following results:— 97·9, 98·2, 95·8, 98·9, 98·9, 98·2 c.c. per grm. of oil.

When the reaction mixtures were allowed to stand a long time before titrating, low results were invariably obtained; the appearance of the liquid at the end of the titration was also different. After a titration carried out under the best conditions, the liquid appeared uniformly white and very turbid; if the titration was delayed, or the conditions not adhered to, then the final liquid was yellowish, turbid and with a dark oily scum, and the lower the result, the darker the scum. Excess of thiosulphate did not remove the yellow colour, and the titration was very liable to be over-run.

At this point, it was decided to test the method on pure ascaridole itself, and Dr. T. A. Henry, of The Wellcome Chemical Research Laboratories, kindly supplied us with some ascaridole of 96 per cent. purity, as tested by the titanous chloride method. With this ascaridole, the method as outlined above was tried, and a result was obtained, which, on the assumption that ascaridole liberated 2 atoms of iodine per molecule, corresponded to 110 per cent. This was not entirely unexpected, as our figures for the chenopodium oil itself indicated a percentage higher than that of a normal oil.

Further experiments were carried out in an attempt to discover the conditions under which a theoretical figure would result.

On the assumption that ascaridole reacts like a normal peroxide and liberates 2 atoms of iodine per molecule, we found that by altering the quantities of the reagent it was possible to get results approximating very closely to the theoretical

figure, but, unfortunately, very slight variations of the conditions were sufficient to vitiate the tests and send the results either up or down, mostly up.

Our experiments seem to indicate that there are three separate reactions taking place: the first is the normal peroxide liberation of 2 atoms of iodine per molecule from acidified potassium iodide; the second is a further liberation of iodine, and we cannot at present explain the mechanism of this; while the third is the re-absorption of the iodine after its liberation; this takes place when the reaction mixture is diluted.

We were unable to find the conditions under which the several reactions would balance and give concordant results which could be expressed by a simple equation. We, therefore, turned our attention to discover the conditions that would allow a reasonable amount of latitude in working, and then to employ a factor standardised on pure ascaridole.

The reaction between the last-named reagent (Expt. No. 12) and the oil was extremely rapid, being completed in less than 30 seconds. Our next step was to delay this reaction by the addition of glacial acetic acid, and at the same time we reduced the amount of hydrochloric acid.

Our experiments showed that unless an excess of hydrochloric acid over the equivalent of the potassium iodide was present, the reaction did not proceed very far. Eventually it was found that identical results could be obtained when 3 c.c., 4 c.c., or 5 c.c. of the hydrochloric acid were used, but other observers found the results with 5 c.c. the most nearly uniform.

METHOD OF DETERMINATION.—The method finally adopted is as follows:— About 2·5 grms. of the oil, accurately weighed, are dissolved in sufficient 90 per cent. acetic acid to produce 50 c.c., and this solution is placed in a narrow burette. Three c.c. of potassium iodide solution, approximately 5*N* (83 per cent. w/v) and 5 c.c. of concentrated hydrochloric acid (31·8 per cent. by weight) are placed in a stoppered tube of about 60 c.c. capacity, and 10 c.c. of glacial acetic acid are added. The tube is cooled in a freezing mixture to about −3° C. (permissible limits 0° to −3°), then removed, and 5 c.c. of the acetic acid solution of the oil run in from a burette, this being mixed with the reagent as quickly as possible and due allowance being made for the draining of the burette. The tube is stoppered and allowed to stand in a cool place for 5 minutes. The reaction appears to be complete in 2 minutes, but we found that 5 minutes gave slightly more concordant results; and, provided the final temperature of the reaction mixture does not exceed 10° C., it may be left safely for 10 minutes. The contents of the tube are next titrated directly with *N*/10 thiosulphate solution, and, if the conditions have been adhered to, a sharp end-point will be obtained and the final titration liquid will be quite white and very turbid, the turbidity being due to fine oil globules in suspension.

A blank test on the reagents is carried out at the same time and under the same conditions, except that the mixture is diluted with 20 c.c. of water before titrating, and the reading subtracted from that obtained in the test.

Each c.c. of *N*/10 thiosulphate solution is equivalent to 0·00665 grm. of ascaridole.

Seven determinations by the above method were carried out on the sample of 96 per cent. ascaridole supplied by Dr. Henry, and the results showed a variation corresponding to an ascaridole equivalent per c.c. of $N/10$ thiosulphate solution of 0·00660 to 0·00670 grm., with a mean result of 0·00665 grm.

Twenty-eight tests on a sample of chenopodium oil by the above method were carried out by ourselves and four other observers, each of the latter doing from two to four tests each. These results, which have been tabulated in ascending order, show a maximum divergence of 2 per cent., that is, an experimental error of ± 1 per cent.

3	results	72·0	per cent.	ascaridole
1	,,	72·1	,,	,,
5	,,	72·3	,,	,,
2	,,	72·5	,,	,,
5	,,	72·7	,,	,,
4	,,	73·0	,,	,,
1	,,	73·3	,,	,,
1	,,	73·5	,,	,,
5	,,	73·7	,,	,,
1	,,	74·0	,,	,,

It was found that, if the reaction mixture were diluted before titration, low results were invariably obtained and the end-points were bad. The following diluents were tried: water, iced water, brine, iced brine, 10 per cent. hydrochloric acid, solutions of sodium sulphate, ammonium sulphate, ammonium acetate, ammonium chloride, and potassium iodide. With the exception of potassium iodide solution, all gave low and very variable results; with potassium iodide solution, most of the results were slightly low; but, in several instances, results identical with those given by undiluted mixtures were obtained. It is possible that dilution with potassium iodide solution might be successful, provided the exact conditions were worked out.

It seems apparent that, when the reaction mixture is diluted, a further reaction sets in, and a portion of the liberated iodine is re-absorbed into the molecule. In order to see if this reaction took place to any extent during the time occupied by the titration, in which the reaction liquid is progressively diluted with the thiosulphate solution, a special titration was carried out, the volumetric solution being run in, drop by drop, the time taken being 6 minutes, against a normal time of 1 to $1\frac{1}{2}$ minutes. The result was only very slightly lower, showing that in a normal titration the dilution effect was negligible.

A small quantity of iodine was liberated in the cooled reagent itself, and it was found impossible to titrate a blank in this strong acid solution without first diluting it; when diluted with water it required only a few drops of thiosulphate; but, without dilution, several c.c. were required, and the liquid was still slightly yellow, though the colour was not due to iodine, as it gave no blue colour with starch. The same phenomenon occurs when an attempt is made to titrate the free iodine in concentrated hydriodic acid; no definite end-point can be obtained,

even with a large excess of thiosulphate, but if the acid is diluted with water first, the end-point is sharp and definite.

APPLICATION OF THE METHOD TO OTHER ESSENTIAL OILS.—While this had no bearing on an actual titration when the oil was present, as the dilution with the volumetric solution was sufficient to overcome this difficulty, it made the testing of the action of the reagent on other essential oils and essential oil products, a little uncertain. The following substances were tried: turpentine, cineole, terebene, copaiba oil, paracymene and bay terpene (myrcene); in each case 1 c.c. of the oil was dissolved in 5 c.c. of glacial acetic acid, and added to the cooled reaction mixture and titrated under the same conditions as set out above. A second series was diluted with potassium iodide solution before titration. With the exception of the cineole, which did not liberate any iodine, the first series of tests all gave very similar results, averaging 5 c.c. of $N/10$ thiosulphate solution per grm., whilst the second series took only about 2 c.c. per grm. A small reading was expected, as peroxides, in traces, are normal constituents of essential oils. This small liberation of iodine by non-ascaridole constituents of essential oils may safely be ignored.

EFFECT OF ADULTERANTS.—Tests carried out on mixtures of chenopodium oil and other essential oil constituents show that the method holds good in presence of common adulterants. Mixtures of the oil with cineole, *p*-cymene, and turpentine were made, each containing 58·9 per ccnt. of ascaridole; on testing these, the following figures were obtained:

PER CENT. OF ASCARIDOLE.

	Diluent: Cineole.	Diluent: *p*-Cymene.	Diluent: Turpentine.
1	59·3	58·0	59·4
2	59·7	57·0	59·6
3	59·7	57·0	59·6
4	59·3	57·5	59·7
Mean	59·5	57·4	59·6
Error	+ 0·6	− 1·5	+ 0·7

The method has been communicated to Dr. T. A. Henry; and Mr. Paget has kindly carried out a series of tests on a pure chenopodium oil, and on the oil diluted with its decomposition products and terpenes.

Mr. Paget's results are appended, and show that good agreement is obtained between this method and that of the titanous chloride reduction.

RESULTS BY MR. PAGET.—*A* is an ordinary chenopodium oil of good quality;

B is an adulterated commercial sample containing cineole;

C is a mixture of about 55 per cent. terpenes, 22 per cent. ascaridole and 23 per cent. ascaridole-α-glycol;

D is a mixture of about 26 per cent. terpenes, 37 per cent. ascaridole and 37 per cent. ascaridole-glycol anhydride.

The α-glycol and its anhydride are most likely to be present in chenopodium oil of poor quality, being produced by bad methods of distillation. The terpenes used in making up samples *C* and *D* are terpenes of chenopodium oil.

PERCENTAGE OF ASCARIDOLE BY THE IODINE AND TITANOUS CHLORIDE METHODS.

	Oil *A*.		Oil *B*.		Oil *C*.		Oil *D*.	
	Iodine.	$TiCl_3$.	Iodine.	$TiCl_3$.	Iodine.	$TiCl_3$.	Iodine.	$TiCl_3$.
	72·7	73·5	48·1	48·1	22·9	21·7	37·6	37·4
	73·6	73·0	47·8	47·9	23·2	21·4	38·1	37·9
	74·4	74·1	49·0	47·2	24·8	22·4	37·8	36·1
Mean	73·6	73·5	48·3	47·7	23·6	21·8	37·8	37·1

SUMMARY.—A new method for the determination of ascaridole in chenopodium is proposed. The method consists in titrating with thiosulphate solution the iodine liberated by the ascaridole from an acidified solution of potassium iodide. The reaction is complex, and an empirical factor is necessary to calculate the results.

The conditions necessary to ensure uniformity have been worked out.

The reactions of other essential oil constituents under these conditions have been studied.

The experimental error should not exceed ±1 per cent.

We wish to acknowledge our indebtedness to Dr. T. A. Henry, of The Wellcome Chemical Research Laboratories, for kindly providing us with the sample of ascaridole on which our method has been standardised, and to him and Mr. Paget for carrying out the tests enumerated above, and for their permission to incorporate them in this paper.

The work entailed by the above has been carried out in the laboratories of The British Drug Houses, Ltd., to the Directors of which we are indebted for permission to publish these results.

The Determination of Small Amounts of Copper in the Presence of Iron.

By LESLIE JAMES CHALK, M.Sc., A.I.C.

Elvehjem and Lindow (*J. Biol. Chem.*, 1929, **81**, 435) encountered two difficulties in the determination of small amounts of copper in biological materials by the pyridine thiocyanate method: (1) The presence of a few mgrms. of iron produced a brownish (ferric iron) or greenish (ferrous iron) colour in the chloroform layer. (2) Calcium phosphate remained undissolved by the acetic acid, causing the subsequent extraction of the copper pyridine thiocyanate to be incomplete.

In these circumstances Elvehjem and Lindow (*loc. cit.*) recommend a preliminary separation of the copper by precipitation as sulphide, ferric iron, if present, being first reduced to the ferrous condition. It has now been found possible to avoid the sulphide separation by the substitution of tartaric acid for glacial acetic acid, the method being practicable in the presence of up to 40 mgrms. of iron.

The solution (volume 35 ml.) to be tested for copper containing up to 0·1 mgrm. of copper is made slightly alkaline to phenolphthalein with *N* caustic soda, and sufficient *N* sulphuric acid added to dissolve the precipitate of ferric hydroxide to a clear light yellow solution in the cold. Three ml. of *N* sulphuric acid are sufficient to dissolve 40 mgrms. of iron as ferric hydroxide. Where the iron content of the solution is unknown it is best to avoid using excess of acid, by adding to it one ml. at a time, and allowing the solution to stand, with occasional shaking, for about five minutes after each addition, until the solution is clear and light yellow in colour. It is then transferred to a 60 ml. separating cylinder with the stem cut off close to the tap, and with the 50 ml. mark etched on the glass. One ml. of a 10 per cent. solution of tartaric acid is added, followed immediately by 1 ml. of 10 per cent. potassium thiocyanate solution, 0·5 ml. of pyridine, and 5 ml. of chloroform, the last accurately measured. The liquid is then made up to 50 ml., shaken for about 15 seconds, and the chloroform layer run off into a 25 ml. Nessler glass.

Preparation of Standards.—The standards are prepared in a similar manner, using up to 10 ml. of a solution of copper sulphate containing 0·01 mgrm. per ml., the quantity taken being varied until an exact match is obtained on comparison with the sample. The amount of free sulphuric acid present is best limited to 2 ml. of *N* acid, since, when this figure is exceeded, 0·5 ml. of pyridine is insufficient to render complete the extraction of the copper pyridine thiocyanate. The solutions of copper pyridine thiocyanate in chloroform are quite stable, and a series of standards showed no sign of fading or discoloration after being corked and left for several days.

All reagents used should be tested to ensure that they are free from copper, and the distilled water used should be redistilled through glassware. Any evaporations or ashings that may be necessary in the preliminary preparation of the sample should be carried out in silica apparatus, since porcelain is a frequent source of contamination. With these precautions the blank should be practically colourless, and no difficulty experienced in detecting 0·001 mgrm. of copper.

INFLUENCE OF FERROUS IRON.—Aqueous solutions of ferrous salts, when treated with an alkali thiocyanate and excess of pyridine, were found to give a yellowish precipitate of ferrous pyridine thiocyanate (Grossman and Hunseler, *Z. anorg. Chem.*, **1905, 46, 361**). The composition of this substance, together with its possible application to the gravimetric determination of ferrous iron, is being further investigated.

Chloroform dissolves ferrous pyridine thiocyanate, 1 mgrm. of ferrous iron giving an intensely green solution resembling that produced by copper, but distinguishable from it in that the addition of a few drops of thioglycollic acid causes practically no change in colour, whereas copper pyridine thiocyanate is reduced to the white cuprous thiocyanate. Following the procedure described for copper, however, 1 mgrm. of ferrous iron gives a comparatively faint colour in the chloroform layer. Further addition of pyridine increased this considerably, although complete separation of the ferrous iron could not be effected with one chloroform extraction. As a consequence of the above experiments, attempts to determine copper in the presence of more than 1 mgrm. of ferrous iron were discontinued.

In cases where the solution to be analysed is known to contain ferrous iron, oxidation is best effected with ammonia and hydrogen peroxide, excess of the reagents being removed by boiling.

INFLUENCE OF FERRIC IRON.—Solutions of ferric alum and ferric chloride, containing approximately 10 mgrms. of iron/ml., were prepared and used throughout the experiments. Four ml. of each solution were made up to 35 ml., a few drops of phenolphthalein added, and *N* sodium hydroxide solution run in until the indicator changed to red. Sulphuric acid, tartaric acid, potassium thiocyanate, pyridine and chloroform were then added, as previously described, and the chloroform extracts separated and matched against the standards.

The amount of copper found was 0·004 mgrm. with the ferric chloride solution, and 0·005 mgrm. with the iron alum solution. With one, two and three ml. of the iron solutions the colours were proportionally smaller. The experiments were then repeated, omitting the phenolphthalein, and, after careful separation from the aqueous solution, the extracts were tested for the presence of iron with thioglycollic acid (Lyons, *J. Amer. Chem. Soc.*, **1927, 49, 1916**). Not more than a very pale pink colour developed with any of the extracts, showing the absence of more than a trace of iron, which would be insufficient to account for a colour equivalent to 0·005 mgrm. of copper. The trace of iron present in some of the extracts was probably due to the difficulty in separating completely the chloroform

from the aqueous solution. All the ferric salts used were found to contain minute amounts of copper.

A further series of experiments was then made to test the recovery of copper from ferric iron solutions. Sufficient standard copper solution was added to one, two, three and four ml. of ferric chloride and ferric alum solutions, contained in separate vessels, to bring the copper content in each solution up to 0·1 mgrm. The solutions were then made up to 35 ml. and analysed in the described manner. No difference could be detected between the chloroform extracts obtained in this way and a 0·1 mgrm. standard. As a similar result was obtained when using a total copper content of 0·05 mgrm. and 0·02 mgrm., it was concluded that the method given above was satisfactory in the presence of up to 40 mgrms. of iron. With more than 0·1 mgrm. of copper the colour of the solution becomes too deep for accurate colorimetric comparison.

If, after the removal of copper from solutions containing iron, further additions of pyridine (1 ml.) are made, followed by chloroform extraction, faintly green extracts are obtained in every case. Closer examination showed this to be due to ferrous pyridine thiocyanate, and it was assumed that tartaric acid exerted a slight reducing action on the ferric salt present. The amount of ferrous iron thus formed was much less than 1 mgrm., but could be substantially increased by allowing the ferric salt to remain in contact with tartaric acid for several hours. Ferrous iron was then found to be present in the first chloroform extract, when only 0·5 ml. of pyridine was used. For this reason it is essential, when analysing a solution for copper, to complete the operation within a short time of the addition of tartaric acid. Further, the amount of pyridine must be limited to 0·5 ml., since the addition of a large excess will cause the partial extraction of any ferrous iron present.

Attempts to prevent the reduction of the iron by addition of such oxidising agents as hydrogen peroxide, ammonium persulphate and nitric acid were unsuccessful.

Hydrochloric acid may be substituted for sulphuric acid if not more than 10 mgrms. of iron are present. With more than this amount 3 ml. of *N* hydrochloric acid either fails to dissolve the precipitate or gives a red solution from which ferric hydroxide is reprecipitated on addition of tartaric acid. This does not occur when the ferric chloride solution is yellow.

Acetates must be absent in all cases. Small amounts of calcium phosphate do not interfere, but for larger quantities (0·1 grm.) it is necessary to modify the method. The extraction of copper from a solution containing 0·1 grm. of calcium phosphate was found to be satisfactory when 4 ml. of *N* sulphuric acid, 4 ml. of tartaric acid, and 1 ml. of pyridine were substituted for the usual amounts of these reagents.

Influence of Other Metals.—Nickel and cobalt give a blue and pink pyridine thiocyanate, respectively, and consequently interfere with the green colour produced by copper. Silver and mercurous salts must also be absent, as these

give thiocyanates insoluble in water and chloroform, and the presence of a precipitate makes the extraction of copper liable to be incomplete. Addition of potassium cyanide prevents the formation of copper pyridine thiocyanate. In the presence of lead and barium, hydrochloric acid must be substituted for sulphuric acid. Other metals do not interfere, provided that their concentration is not so great that:

(1) Three ml. of *N* sulphuric acid fail to dissolve the precipitate obtained on making the solution alkaline to phenolphthalein. (2) Five ml. of chloroform are insufficient to dissolve completely the precipitate of pyridine thiocyanate formed (in the presence of manganese, zinc and cadmium). (3) A precipitate, insoluble in chloroform, is produced by 0·5 ml. of pyridine.

The following table shows the effect of various metal ions:

Metal.	Amount used. Mgrms.	Remarks.	
Aluminium	40	No interference	
*Antimony	10	No interference	
*Bismuth	10	No interference	
Cadmium	10	No interference	
Chromium	10	No interference	
Cobalt	1	Interferes	
Lead (see above)	5	No interference.	HCl used
Manganese	10	No interference	
Mercurous	1	Interferes.	
Mercuric	20	No interference	
Nickel	1	Interferes	
Silver	1	Interferes.	
*Stannous	10	No interference	
*Stannic	10	No interference	
*Titanium	5	No interference	
Uranium	10	No interference	
Zinc	10	No interference	

* These metals give with sodium hydroxide a precipitate which is difficult to dissolve in *N* sulphuric acid, but, apart from this, do not interfere. In the case of titanium it was necessary to warm to effect solution, and then to cool prior to the addition of tartaric acid. Tartar emetic was used in the case of antimony.

The method described in this paper is slightly less sensitive than that of Callan and Henderson (ANALYST, 1929, **54**, 650), where sodium diethyldithiocarbamate is used. It possesses the advantage, however, that, after oxidation, metals other than nickel, cobalt and silver do not interfere, since they give a colourless chloroform extract, whereas sodium diethyldithiocarbamate produces either a turbidity or coloration with a number of metals.

COPPER IN WATER.—The pyridine thiocyanate method here described has been applied to the determination of copper in river water. The two-litre sample is first evaporated to low bulk in a large silica beaker and organic matter destroyed by the addition of 5 ml. of concentrated nitric acid and 3 ml. of concentrated sulphuric acid (both redistilled in silica ware), and evaporation carried to the

fuming point. The solution is then transferred to a platinum dish, the beaker rinsed with warm dilute hydrofluoric acid (four drops of hydrofluoric acid per 25 ml.) and two ml. of hydrofluoric acid added. After volatilisation of the silica most of the sulphuric acid is removed by heating till fumes appear. The solution is then diluted, made just alkaline to phenolphthalein, and the determination carried out in the described manner. River water from Devon and Cornwall gave 1 to 4 parts copper per 100,000,000 water.

SUMMARY.—Small amounts of copper (0·1 mgrm. or less) may be determined in solutions of volume 35 ml. containing 40 mgrms. of iron, by addition of *N* sodium hydroxide solution, until alkaline to phenolphthalein, followed by 3 ml. of *N* sulphuric acid, and allowing the solution to stand until it is clear and light yellow in colour. It is then transferred to a small separating cylinder, 1 ml. of 10 per cent. tartaric acid, 1 ml. of 10 per cent. potassium thiocyanate solution, 0·5 ml. of pyridine, and 5 ml. of chloroform quickly added, the liquid made up to 50 ml. and shaken for 15 seconds. The chloroform extract is then compared colorimetrically with a standard prepared in a similar manner. For smaller amounts of iron the approximate proportionate quantity of sulphuric acid is added. Ferrous and mercurous salts interfere, and must be oxidised prior to the determination of copper, while nickel, cobalt and silver must be absent.

I wish to thank Sir Robert Robertson for permission to publish this paper, and Mr. B. A. Ellis for valuable advice.

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Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE OCCURRENCE OF ANTIMONY AND TIN IN FOIL-WRAPPED CHEESES.

ELTEN (*Chem. Ztg.*, 1929, **53**, 586; ANALYST, 1929, **54**, 552) reports the presence of tin in rindless cheeses which have been packed in metal foils containing 96 to 98 per cent. of tin and 2 to 4 per cent. of antimony. Recently, five half-ounce triangular portions of a Gruyère cheese, wrapped in foil, and contained in a circular box originally holding six such portions, were submitted to me for examination. In each case the underside of the foil and the cheese in contact with it were badly discoloured. On analysis, the foil proved to be an alloy of 96·8 per cent. of tin and 3·2 per cent. of antimony, with a trace of iron as impurity. Also, both tin

and antimony were detected in the cheese itself, and found to be present, in the case of two portions examined jointly, to the extent of:—Tin, 160 parts per million (1·12 grains per lb.); antimony, 17 parts per million (0·12 grain per lb.). Twelve other samples similarly wrapped, and including Cheddar, Cheshire and Gruyère types, were examined, and discoloration was found in all of the Gruyère cheeses (4), although it was only possible to estimate the degree of contamination in two of these, the tin found amounting to 15 and 160 parts per million, respectively. In the latter of these the wrapping was pure tinfoil, and discoloration was very pronounced, both on the foil and on the cheese.

In the qualitative analysis of the foil wrapping, after it was found that, apart from a trace of iron, only metals were present whose sulphides were soluble in ammonium polysulphide solution, some difficulty was experienced in detecting antimony in the hydrochloric acid solution, owing to the tin also being deposited by zinc on platinum foil in the existing concentration. As, however, after treatment of the foil with hydrochloric acid, there was always obtained a black residue which was soluble in *aqua regia*, this solution was freed from nitric acid by repeated boiling with hydrochloric acid, and from the resulting solution, after dilution, no difficulty was experienced in obtaining a deposit of antimony on platinum. Bromine water proved an efficient substitute for nitric acid, and was afterwards used in place of it. The presence of antimony was confirmed by solution in dilute nitric acid, followed by precipitation of the sulphide. The proportions of the two metals present in the cheese were determined as follows:

The surfaces of two weighed portions were scraped, and the removed pieces ignited. The ash obtained was treated with hydrochloric acid, and the solution filtered from undissolved solid. The antimony was then deposited on platinum by zinc, which had been proved to be free from antimony by a blank test. The black stain which resulted was dissolved off with warm hydrochloric acid, the antimony precipitated as the orange trisulphide, which was then ignited and the residue weighed as pentoxide. The tin was subsequently precipitated as the yellow stannic sulphide, and this was ignited and the residue weighed as dioxide. (*Cf.* Clarke, ANALYST, 1928, **54**, 373.)

In order to guard against a possible source of danger to the public health, and to maintain the original appearance of cheeses of the Gruyère type, it seems desirable that these should be protected from the action of metal foil.

CITY ANALYST'S LABORATORY, LEEDS. C. H. MANLEY.

A RAPID METHOD FOR THE DETERMINATION OF HALOGEN IN INSOLUBLE INORGANIC HALIDES.

THE necessity arose for a ready determination of halogen in mercuric iodide, and, as this compound sublimes from an alkali fusion mixture, the ordinary fusion process, followed by the Volhard estimation, was not possible. The following method gave excellent results and was adopted:

The finely divided halide (0·5 grm.) is triturated with 10 c.c. of water and 1 grm. of halogen-free zinc dust until no more of the unchanged material is visible. After standing for about 10 minutes, the supernatant liquor is decanted through a small filter, the insoluble material washed thoroughly, and the washings decanted through the filter and added to the main filtrate. The combined filtrate and washings are then titrated with $N/10$ silver nitrate solution, with potassium chromate as indicator.

Excellent results were also obtained with lead chloride and silver iodide. With mercurous chloride, however, even by varying the conditions, it was not found possible to obtain concordant results.

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Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports, would be submitted to the Publication Committee.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE FOURTH QUARTER, 1929.

DURING the quarter 1159 samples were submitted, 56 of which were bought formally and 1103 informally. Of the 520 informal samples of milk, 16 were adulterated, and of the 53 formal samples, 2 were adulterated. The total number of adulterated or incorrect samples was 35.

BOMBAY MACE SUBSTITUTED FOR GROUND MACE.—This sample contained at least 70 per cent., probably more, of Bombay mace, which is a cheap and worthless substitute for the genuine article, having neither flavour nor aroma. Its price is about 4½d. per pound, as compared with an average of 3s. 6d. per pound for genuine mace. The vendor had a warranty from his wholesale dealer, and he, when written to, denied the charge that the article supplied was worthless, but it is significant that he immediately withdrew the article from sale. The retail vendor has since ceased dealing with the firm.

MARGARINES.—A curious point arose with respect to a sample of margarine. Owing to a complaint the inspector visited a shop which had, exhibited in the window, a poster, stating, "To every purchaser of a half-pound of our 2s. presentation tea we will give a half-pound of margarine." The inspector bought a half-pound of the tea, and the margarine was handed to him without the necessary label in half-inch letters.

In addition, the statutory exposure labels were not attached to the parcels exposed in the shop. The vendor was cautioned, and promised that the omission should be rectified.

The question which arose is whether an offence was actually committed, since margarine was not sold; neither apparently was it exposed for sale. Actually it would appear that only when a sale takes place is the labelling legally necessary.

Another interesting point arose in the following way. A person called round at various houses to advertise a cheap brand of butter, and it was explained that a day or two later a traveller would call with a supply. When the purchase was made the article was discovered to be labelled "Margarine" in type of the usual size. The traveller, however, did not mention the word "butter," but simply stated that he represented the person who had called a day or two before. The

transaction would appear in the circumstances quite legal, but it certainly amounts to sharp practice on the part of the originator of the scheme.

HONEY.—This was an informal sample bought from a large stores. On analysis it proved to contain 40 per cent. of cane sugar, whereas no sample of genuine honey should contain more than about 8 per cent. The vendors had a warranty from the supplier, who was therefore communicated with and asked for an explanation of the facts. His reply indicated that, in his opinion, the excess of sugar was caused by artificial feeding of the bees on cane sugar syrup and also by the omission of the bees of their duty to inject the necessary acid, for inversion of the honey, into the cells of the comb.

It has been shown by several workers that bees, even when fed on nothing but cane sugar syrup, are still capable of producing genuine honey. Further, the sugar is inverted in the bees' bodies by a special enzyme, and not by the injection of acid into the cells after filling. Hence there could be little doubt as to its being a case of sheer adulteration. The Medical Officer of Health for the County where the honey was produced was written to and asked to investigate the matter, and to take samples, if necessary, directly from the hives.

SATIN HUMBUGS.—Two samples were taken from the same shop. After allowance had been made for the sulphur dioxide legally allowed to be present in the glucose syrup and cane sugar used, it was found that there was an excess of this preservative amounting to 180 parts per million. The vendor was communicated with, and he has stopped the sale of the article, and also arranged with his wholesaler to take back the whole of the goods supplied to him.

H. H. BAGNALL.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

BARYTES IN CHEESE.

ON January 30th a firm of provision merchants was fined £5, with £2 2s. costs, at Kingston for selling gorgonzola cheese which was not of the nature, substance and quality demanded, being adulterated with barytes and oxide of iron.

Mr. T. R. Ubsdell, prosecuting for the Surrey County Council, said that, since barytes was a heavy mineral, the purchaser of the cheese would suffer considerable loss. Similar prosecutions in 1910 (not against these defendants) had checked the objectionable practice, and it was necessary to prevent its being revived.

Mr. Ricketts, for the defence, said that an Italian firm had offered to supply the defendants with cheese which would continue to ripen on its journey to this country. That supplied, however, had rind containing the prohibited substance, and the firm's buyer had not heard of the proceedings of twenty years ago.

"CATTLE COD-LIVER OIL."

ON January 10, a Bristol firm was summoned under the Merchandise Marks Act, at Exeter, for having sold goods to which a false trade description was applied.

Mr. H. G. James, prosecuting on behalf of the Ministry of Agriculture, said that the defendants had sold to an Exeter firm twelve barrels of an oil which was described as "cattle cod-liver oil," but which was a mixture of sperm oil and cod-liver oil. The County Analyst (Mr. F. V. Dutton) had found the mixture to consist of 50 per cent. of each of the two oils, whilst the Government Chemist had judged it to contain 60 per cent. of sperm oil and 40 per cent. of cod-liver oil.

Counsel submitted that "cattle cod-liver oil" meant the grosser and less refined oil which was left after the best quality had been taken for human consumption. Sperm oil had no feeding value of any kind, and was very indigestible. The case was of considerable importance to the agricultural community and to those selling medicines for animals. The Act provided that it was not necessary to prove intention to defraud, and that it was sufficient to show that something had been done which was forbidden by statute. The maximum penalty was a fine not exceeding £20.

Mr. M. J. McGahey, for the defence, said that the defendants were an old-established firm, and it was with some regret that they pleaded guilty. They had never attempted to deny that the oil was a mixture of cod-liver oil and sperm oil. It had been found by farmers that pure cod-liver oil was too nauseous for the cattle to take, even when mixed with bran. Directly the Ministry took the sample and the firm's attention was called to the fact that the description might deceive the purchaser, they had stopped using the name, and they now sold the mixture under the name of "cattle-feeding oil," as they were entitled to do. They also stocked the pure cod-liver oil, which they now sold under the name of "cattle cod-liver oil," and this was sent to anyone who asked for cod-liver oil. As a result they were receiving scores of complaints from purchasers who said that their cattle would not take it, and asked for the old mixture to be sent instead. Other firms were doing the same thing, and counsel considered that it would have been more reasonable if the Ministry had called the attention of the firm to what they were doing instead of prosecuting them.

The Mayor said that the bench felt that they must convict, but the fine would be a nominal one of £1 and costs.

Department of Scientific and Industrial Research.

WATER POLLUTION RESEARCH.

SUMMARY OF CURRENT LITERATURE.*

THE abstracts from current scientific and technical literature dealing with water supplies, sewage, trade waste waters, river pollution and relevant subjects, were primarily compiled monthly for the information and guidance of the Water Pollution Research Board of the Department, and a limited number of copies were circulated in neostyled form.

In view of the value of the summaries to other authorities and to private persons interested in the subject, it has been decided to publish selected abstracts monthly, and to issue annual subject and author indexes.

* Vol. III, No. 1. Jan. 1930, pp. 36. Abstracts 1–119. H.M. Stationery Office, Kingsway, W.C.2. Price 1s. 3d. net. Annual subscription 15s. net, post free.

The abstracts are classified under the following six main headings: Water Supplies; Analysis and Examination of Water; Sewage; Trade Waste Waters; Pollution of Natural Waters; Miscellaneous.

The abstracts purport to be fair summaries of the original literature, but no responsibility is accepted either for the accuracy of the authors' statements or for their opinions.

Pharmaceutical Society of Great Britain.

PHARMACOLOGICAL LABORATORIES.

FOURTH ANNUAL REPORT, 1929.

THE work during the year comprised research and the examination by routine methods of samples submitted by manufacturers. The greater part of the research work has been directed to problems suggested by the revision of the British Pharmacopoeia, and one or two investigations have been carried out at the request of the Pharmacopoeia Commission itself.

PITUITARY (POSTERIOR LOBE) EXTRACT.—A simple method, in which a human subject is used, has been devised for measuring the anti-diuretic effect. Studies of the anti-diuretic, pressor figures and oxytocic figures of extracts showed that it is not safe to infer the value of any one property from the value determined for another property.

THE CARDIAC GLUCOSIDES.—*Strophanthin.*—A series of commercial samples of strophanthin has been examined to determine their relative potency. It was found that, out of 9 samples, the weakest had only 41 per cent. of the activity of the strongest, and that even among 8 of more or less uniform activity, the weakest was only two-thirds of the strength of the strongest. A suitable standard for strophanthin is obviously the international standard ouabain; and, expressed in relation to this, the average of these 8 samples was found to be 60 per cent. of the standard, and a margin of 25 per cent. just covered the deviations from this figure.

Strophanthus.—The average of 17 of 22 commercial samples of tincture of strophanthus was found equivalent in strength to a 0·42 per cent. solution of the international standard ouabain, and the strength of all the 17 lay within 25 per cent. of this average.

Digitalis.—A comparison of the result of examining 20 tinctures of digitalis by the frog method and by the cat method has been published. The results of the comparison were very unsatisfactory, inasmuch as the two methods only gave about the same result for 9 of the tinctures. The tinctures were not all freshly prepared, however, and it appeared that the age of the tincture was one important factor in determining the difference in the results by the two methods. The potency, estimated by the frog method, of some tinctures deteriorates at a much greater rate than that estimated by the cat method.

Digitalis lanata.—A sample of authenticated leaves of *Digitalis lanata* has been submitted to a careful examination, and has been found to possess 3·5 to 4·0 times the activity of the international standard powdered leaf.

ERGOT.—It has been found that there is a rapid loss of activity in extracts on keeping, and that this loss occurs in extracts made with either hydrochloric or

tartaric acids and with alcohol varying from 35 to 75 per cent. in strength. The rate of loss is affected by temperature, being much lower at lower temperatures. Even under the best conditions, however, half the activity may be lost in two or three months. Concentrated extracts are more stable, but they also lose activity at a rate which appears to vary considerably from one sample to another.

TOXICITY OF TETRA-IODOPHENOLPHTHALEIN SODIUM.—At the request of the Pharmacopoeia Commission an investigation has been made of the toxicity of different commercial samples of tetra-iodophenolphthalein sodium, the determinations being made by intravenous injection into the tail vein of mice. The dose of each preparation causing death of 50 per cent. of mice within three days was taken as a measure of the toxicity. It was found that the toxicity of seven different samples, prepared by different makers varied from 0·27 to 0·37 mgrm. per grm. weight of mouse.

EVIDENCE OF A NEW GROWTH FACTOR.—It has been found that rats fed on a diet theoretically sufficient for their needs, have produced young which, in successive litters, were less and less capable of normal growth, and which, when mature, were incapable of rearing their own young. When some of these young rats were given a diet deficient in vitamin *A*, they stopped growing very soon, and, most striking of all, responded very poorly to the addition of cod-liver oil to the diet, but promptly resumed growth when a commercial casein, known as "light white casein," was substituted for the casein ordinarily used in vitamin work.

Other substances which have been found to cause resumption of rapid growth, when added, are fresh milk, lettuce, fresh and dried grass, ox muscle, liver, and wheat embryo. Butter has very little effect. Extra dried yeast and marmite have none. Promising results have been obtained by treating wheat embryo with hot alcohol, and also with hot ether.

An examination of "light white casein" has shown that neither vitamin B_1 nor vitamin B_2, nor both, are concerned in these results, and the importance of using a casein like "light white casein" for vitamin *B* tests has been indicated.

CASEIN IN VITAMIN TESTS.—In making tests for vitamin *B* also, it has been found that the "light white casein" differs from the usual vitamin-free casein. Certain rats, prepared on a diet deficient in vitamin *B*, did not grow when amounts up to 10 per cent. of dried yeast were added to the diets. But when the "light white casein" was substituted for the "vitamin-free casein," the rats grew at once at rates proportional to the amount of yeast. These and other experiments have again indicated the unsuitability of the usual "vitamin-free" casein for tests for vitamin *B*.

VARIATION OF VITAMIN *D* IN COD-LIVER OIL.—Since all estimations of vitamin *D* are made in comparison with a standard preparation, it has been possible for the first time to provide information of the relative strengths of different substances, and of different samples of the same substance. Potency is expressed in units, the unit being defined as the amount of activity present in 0·0001 mgrm. of the standard preparation, which is a sample of irradiated ergosterol.

Cod-liver oil has been found to vary from 150 to 50 units per grm., 100 units per grm. being the potency of a good average sample. By comparison, butter is a poor anti-rachitic agent, samples containing about 0·8 to 1·0 per grm. Even more surprising, however, is the fact that milk often has no detectable anti-rachitic action, and the best samples examined were not found to contain more than 0·2 unit per grm.

VARIATION OF VITAMIN *D* IN IRRADIATED MILK.—Much irradiated milk is now sold, and an account of the potency of different samples has been given. Comparisons of the irradiated with the untreated milk have all shown that the

process has increased the amount of the vitamin, but the amount present in different irradiated samples is very variable, being as low as 0·1 or as high as 2·0 units per grm. The commonest potency appears to be about 0·2 unit per grm. The benefit which accrues to the child consuming this milk may be judged by comparison with the amounts of cod-liver oil ordinarily consumed. If the potency of the milk is 0·2 unit per grm., then half-a-pint is equivalent to 30 drops, or five and a half pints to two teaspoonfuls of cod-liver oil.

British Cast Iron Research Association.

RECOMMENDED METHODS FOR SAMPLING AND ANALYSIS OF FOUNDRY PRODUCTS.*

METHODS of sampling and analysis, intended solely for use in laboratories conducting acceptance tests on raw and other materials, are recommended, in order to reduce discrepancies to those dependent on the personal factor and on the heterogeneity of the material. In all cases the methods should be checked against a standard material of known composition.

The methods have not been drawn up with a view to use by those without proper training in chemical analysis, and hence have not been elaborated beyond the requirements of the trained works chemist. Neither is it suggested that they should be imposed upon chemists undertaking research or other work in which the chemist must be entirely free to choose the best methods for the particular conditions.

Tests should, of course, be conducted in duplicate, and the results should agree within limits which at present vary from laboratory to laboratory according to the nature of the work. Failing reasonable agreement, the test should be repeated.

The omission of a particular method from the report must not be taken to imply that the results obtained from it are unreliable.

In the text the unit of liquid volume is taken as the millilitre (ml.), and not the cubic centimetre (c.c.).

The Association has found the following order of elements most convenient in reporting analyses of cast iron, and the methods are given in this order: Total carbon; Graphite; Combined Carbon (by difference); Silicon; Manganese; Sulphur; Phosphorus; Other elements (if any). Ni., Cr., Va., Ti., Mo..

A method of sampling metallurgical coke is included pending the formulation of a suitable specification by the regional Coke Research Committees. The method of proximate analysis of coal dust, blackings, etc., are similar to those recommended in Report No. 9 of the Fuel Research Board on the Analysis of Coal. The requirements of the industry, however, enable these to be more briefly stated.

The methods of sampling and examination of foundry sands will be covered in subsequent reports.

J. G.

* Research Report No. 72. August, 1929. Obtainable at 24, St. Paul's Square, Birmingham. Price 10s. 6d. net.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Comparison of Reductase Tests. M. Lerner. (*Ned. Tijdschrift v. Hygiëne, Microbiologie en Serologie*, 1929, 45–86.)—The author has tested 1400 milks with a tablet form of Barthel's reductase reagent (*cf.* Straub, *Chem. Weekblad*, 1928, No. 11), which, when diluted to 200 c.c., gives a solution equivalent to 5 c.c. of saturated methylene blue solution in 195 c.c. of water. It is shown that when 0·15 c.c. is added to 0·15 c.c. of milk the reduction time is always less for the methylene blue solution than for the Barthel reagent, the differences varying continuously from 47 per cent. for milks having periods of the order of 1 to 5 minutes, to 4·8 per cent. when the period is 6 to 7 hours. In these two instances 31 and 10·5 per cent., respectively, of the samples examined had identical reduction times. J. G.

Chemical Treatment of Lemon Residues. Determination of Pectins. B. Melis. (*Giorn. Chim. Ind. Appl.*, 1929, **11**, 399–404).—Treatment of lemon residues with hot 80 per cent. alcohol removes sugars, starch, fats, proteins, etc., leaving a pectocellulose from which the pectins may be easily separated in a highly pure state. For the determination of the pectins, 1 grm. of the pectocellulose is macerated in a beaker with 25 c.c. of 1 per cent. chlorine water. After 30 minutes, the mass is heated nearly to boiling, with stirring, until it becomes decolorised and pasty, and is then boiled for 15 minutes with a further 25 c.c. of the chlorine water. It is next filtered through paper by suction and the residue, returned to the beaker, boiled for 15 minutes with 25 c.c. of chlorine water and again filtered. After a third similar treatment, the cellulosic residue is washed with hot water and the volume of the pectic liquid made up to 100 c.c. The cellulose is pressed on linen to remove absorbed water and treated with 95 per cent. alcohol until completely dehydrated, the alcohol being then pressed out and the cellulose dried at 60–70° C., detached from the cloth and weighed. The pectic extract, which contains about 0·37 per cent. of pectin, is neutralised with 5 drops of 16 per cent. ammonia solution, stirred, treated at once with 0·16 grm. of dry aluminium chloride dissolved in a few c.c. of water, heated to 80° C., and stirred vigorously. On further addition of 3 drops of ammonia, with stirring, the hydropectin separates as a heavy, gelatinous mass, whilst the mother liquor becomes clear and non-viscous. The liquid is decanted, and the hydropectin washed several times with distilled water and then pressed on linen, on which it is washed repeatedly with 95 per cent. alcohol, this being removed each time by pressing. The material is then dried at a temperature not exceeding 50° C., detached from the cloth, weighed in a platinum crucible, heated gently until it gives a porous charred mass, and then more strongly, until it is completely ashed. Subtraction of the weight of the ash from that of

the dry pectin gives the pure pectin. The mean percentage results given by various samples of pectocellulose are: pectin, 37·6; cellulose, 34·6; ash, 4·3; undetermined, 23·5. T. H. P.

Honey and Gingerbread. C. I. Kruisheer. (*Z. Unters. Lebensm.*, 1929, **58**, 282–300.)—The author's method of analysis (*id.*, 1929, **58**, 261) has been applied to a number of genuine, artificial and mixed honeys of known origins, and to gingerbreads prepared from ingredients of known compositions, and the results are tabulated in each case and discussed. The ratio 100 fructose/glucose varies from 110 to 140 for the genuine honeys examined (although there is no certainty that the figure must exceed 100), whilst for artificial honey it ranged from 0 to 90, and 90 is, therefore, provisionally fixed as the minimum figure for genuine honey. Similarly, Mees's ratio (ANALYST, 1929, 108)—100 fructose/extract, which is approximately constant at 50 for genuine honey, and varies from 0 to 44 for artificial honeys, should be at least 43. The extract is determined from the sp. gr. of the solution obtained by digestion of 20 grms. of ground gingerbread with 200 c.c. of water at 50° C. for 1 hour. The effects of baking on the compositions of gingerbreads prepared from genuine honey and from invert sugars, glucose syrup and sucrose were also compared, and it was shown that, whilst baking has little effect in the case of true invert and sucrose honeys, the glucose products show an increase in fructose, owing to the action of alkali. The extent of the change depends on the *p*H value and on the temperature and duration of heating. The sucrose content of gingerbread should not exceed 5 per cent. The Fiehe and oxymethylfurfural tests (see ANALYST, 1929, **54**, 748; Weiss, *id.*, 1930, 135) are only of value for the detection of invert sugar in honey so long as the *p*H value of gingerbread exceeds 5, for it has been found that oxymethylfurfural is not formed when sugars are heated, unless the *p*H value is less than 4·5. If the ratio 100 fructose/glucose exceeds 70, positive Fiehe and phloroglucinol reactions are reliable indications of the use of invert sugar. J. G.

Mineral Content of the Jujube or Chinese Date. M. P. Benoy. (*J. Agric. Res.*, 1929, **39**, 949–950.)—Analysis of two varieties of the dried ground pulp of the jujube or Chinese date, *Zizyphus jujuba* Mill., gave the following figures:—Total ash (on moisture-free basis), 1·84, 2·36 per cent.; percentage composition of ash: CaO, 5·42, 5·60; MgO, 4·46, 3·53; K_2O, 56·40, 54·78; Na_2O, 1·65, 1·29; P_2O_5, 1·04, 0·64; MnO, 1·11, 0·99; Fe_2O_3, 0·115, 0·115; SO_3, 1·85, 1·40; Cl, 4·08, 3·49; SiO_2 (soluble), 0·28, 0·27. From a nutritional point of view the two varieties of jujube compare favourably with dates and raisins with regard to phosphorus and calcium, but are markedly inferior in iron (date 0·47, raisin 0·576 Fe_2O_3 per cent. on the ash). D. G. H.

Separation of Maize Starch added as Adulterant to Egg Powder. Comte. (*Ann. Falsif.*, 1929, **22**, 600.)—When microscopic examination reveals the presence in egg powder of maize starch, this may be separated by placing 1 grm. of the powder in a centrifuge tube, adding a mixture of 3 vols. of carbon

tetrachloride with 1 vol. of ether to 1 cm. from the top of the tube, closing the latter with a piece of rubber sheet and shaking vigorously, and, finally, centrifuging for a minute at low speed. The starch forms a solid deposit, and the other solids (proteins) collect at the top of the liquid as a cake, which is readily removable. The liquid is then decanted and the residual starch washed with ether and allowed to dry spontaneously. After a few hours, the starch is easily removed and weighed.

T. H. P.

Detection of Fruit Wine in Grape Wine by the Sorbitol Process. A. Röhling and J. Richarz. (*Chem. Ztg.*, 1930, **54**, 61–62.)—The detection of fruit wine (cider, etc.) in grape wine by preparation of dibenzylidenesorbitol from the sorbitol present in most fruits of the natural order *Rosaceae*, but absent from grapes (*cf.* Werder, *Ann. Falsif.*, 1929, **22**, 260; Zach, *ibid.*, 261) may be complicated by the presence of mannitol, which reacts with benzaldehyde to form tribenzylidenemannitol. Sorbitol may be identified by conversion into its hexa-acetyl derivative, m. pt. 98–99° C., but this takes some time, and a more rapid distinction between sorbitol and mannitol may be effected by utilising the following characteristics. Sorbitol is amorphous, and its dibenzylidene compound has m. pt. 160–200° C. (mostly 170–180° C.), whereas mannitol crystallises in fine needles, and its tribenzylidene compound has m. pt. 214–217° C. Mannitol condenses with benzaldehyde less readily than sorbitol, and gives a product more easily soluble in alcohol and ether. Under the influence of the light from a quartz lamp, the sorbitol compound shows a white fluorescence with a yellowish-green tint, whereas the mannitol compound fluoresces with a deep violet colour (*cf.* ANALYST, 1929, **54**, 422, 603).

T. H. P.

Allanblackia Stuhlmannii Seeds and Oil from Tanganyika. (*Bull. Imp. Inst.*, 1929, **27**, 455–457.)—The nuts of the Msambo or Mkani tree, *Allanblackia Stuhlmannii*, of Tanganyika, have thin brittle reddish-brown shells (22·6 per cent.) closely adhering to the pale reddish-brown kernels (77·4 per cent.), and which proved difficult to separate. The dry kernels contained 70·7 per cent. of a white almost odourless and tasteless fat; this, when refined, should prove edible. The sample had the following characteristics:—Sp. gr. 100/15° C., 0·8549; $n_D^{40°}$, 1·457; m.pt. (open tube method), 40·0° C.; saponification value, 189·6; iodine value (Wijs), 39·6; unsaponifiable matter, 0·76 per cent.; solidif. pt. of fatty acids, 60·0° C. These figures closely resemble those for the fat of the Gold Coast Kisidwe nuts (*Allenblackia floribunda*). The residual meal contained:—Moisture, 13·9; crude proteins, 14·9; fat, 1·4; carbohydrates, 58·6; crude fibre, 7·7; and ash, 3·5 per cent. Tannin was present in the meal.

D. G. H.

Chicory Agglomerates and their Adulteration. L. Gobert. (*Ann. Falsif.*, 1929, **22**, 580–591.)—Powdered chicory does not command a ready sale in France, and is largely converted into artificial granules termed "agglomerates," which, according to the law, should contain no substance (other than starch) foreign to the chicory root, and not more than 10 per cent. of ash. Whitening of this

material by means of starchy products appears to have been discontinued, but the use of lupin grains for this purpose is now common. This procedure was regularised by the Congress of Paris in 1909, the amount of lupin flour permitted being not greater than 3 per cent. In many cases, however, chicory sold as "superfine," "extra pure," etc., contains lupin elements and also cider marc in the granules themselves. Samples in which the granules are packed with silicious particles are also not uncommon.

To separate the whitening powder, 2 grms. of the chicory grains are stirred with a mechanical stirrer in a porcelain dish with about 100 c.c. of water for a minute, the residue being collected on a sieve with about 17 meshes per cm., and washed with running water. The liquid passing the sieve is allowed to settle, and the supernatant liquid removed. The chicory remaining on the sieve is washed into a porcelain dish with about 150 c.c. of water, and boiled for 5 minutes after addition of 2 c.c. of a solution containing 10 c.c. of sodium hydroxide solution (36° Baumé) per 100 c.c., the grains being washed several times with water by decantation. Granules derived from the torrified root by pounding and bolting remain whole under this treatment, but are readily cut or penetrated by a needle; other agglomerates break down to form a broth, and others again retain their form, but disintegrate under the slightest pressure; some very hard ones cannot be broken by pressing. Information as to the origin of these different granules may be obtained by bleaching with hypochlorite solution, and by microscopic examination, and roughly quantitative results are obtainable if the relative numbers of granules of different types are determined. It is suggested that whitening of chicory by means of lupin powder be forbidden since chicory powder serves the same end; that addition of not more than 3 per cent. of lupin flour to powdered chicory to be whitened be allowed, such proportion being sufficient to prevent agglutination of the powder during wet weather; that the use of all other materials, especially apple and pear marc, as whitening agents, be prohibited; that the maximum permissible ash of chicory grains be 8 per cent. (on the dry product), of which at most 2 per cent. should be insoluble in hydrochloric acid; that "chicory agglomerates" should be sold under this name, and that not more than 10 per cent. of total ash or more than 3 per cent. of ash insoluble in hydrochloric acid, should be allowed. T. H. P.

Determination of Nicotine. F. D. Chattaway and G. D. Parkes. (*J. Chem. Soc.*, 1929, 2817–2820.)—The sample is dried and powdered, and 20 grms. ground with 10 c.c. of 55 per cent. alcohol containing 0·6 grm. of sodium hydroxide, and extracted to exhaustion in a Soxhlet apparatus. The residue left on evaporation is steam-distilled with 50 c.c. of 0·4 per cent. sodium hydroxide solution until the distillate (not less than 400 c.c.) is no longer precipitated by a solution of iodine trichloride in hydrochloric acid. The distillate is saturated with hydrogen chloride, cooled, and nicotine tetrachloriodide precipitated by addition of a 10 per cent. suspension of powdered iodine in hydrochloric acid saturated with chlorine. The yellow precipitate is collected on a tared Gooch crucible, washed

with a little concentrated hydrochloric acid and dried to a constant weight in a vacuum desiccator over phosphorus pentoxide and lime. It contains 23·077 per cent. of nicotine. In the presence of pyridine the sample is first steam-distilled with 50 c.c. of 15 per cent. acetic acid till a drop of distillate saturated with hydrogen chloride gives no precipitate with tetrachloriodic acid. Ammonia has no disturbing influence. A sample of tobacco was found to contain 0·05 per cent. less nicotine than by the silicotungstic acid method. The reagent will detect 1 part of nicotine in 100,000 parts of water, and the quantitative method is applicable to 1 : 5,000 solutions. J. G.

Quantitative Determination of the Composition of Potato Starch according to the Size of Granule. G. Bredemann and O. Nerling. (See p. 220.)

Quantitative Determination of Shell in Cocoa and Cocoa Preparations. M. Wagenaar. (See p. 221.)

Microchemistry of Berberine. M. Wagenaar. (See p. 222.)

Microchemistry of Brucine. M. Wagenaar. (See p. 223.)

Biochemical.

Colorimetric Method for the Determination of Sulphur and Sulphate in Biological Liquids. K. Lang. (*Biochem. Z.*, 1929, **213**, 469–474.)—The sulphate is precipitated as barium sulphate with a measured volume of $N/100$ barium chromate solution, and the excess of barium chromate is separated by rendering the solution alkaline with calcium hydroxide. The free chromate (liberated by the sulphate) is determined colorimetrically by the reaction with diphenylcarbazide (2 grms., dissolved in 10 c.c. of glacial acetic acid, and 90 c.c. of 96 per cent. alcohol added). Amounts of sulphate from 0·6–1·5 mgrms. were determined, with an error of less than 2 per cent. The best results are obtained when 20–80 per cent. of the added chromate are used in the reaction. Large quantities of salts of heavy metals affect the results, and not more than 0·17 mgrms. of iron per c.c. must be present in the colorimeter solution. The effect of iron is nullified by adding 1 c.c. of 20 per cent. hydrochloric acid to the colorimeter solution. J. W. B.

Arginase Method for Determination of Arginine and its use in the Analysis of Proteins. A. Hunter and J. A. Dauphinee. (*J. Biol. Chem.*, 1930, **85**, 627–665.)—Jansen (*Chem. Weekbl.*, 1917, **14**, 125; *Arch. néerl. Physiol.*, 1917, **1**, 618) first proposed the use of the enzyme arginase for the quantitative determination of arginine. His procedure, as applied to the analysis of proteins, involved the simultaneous addition, to a slightly alkaline hydrolysate, of arginase

and urease. By the first of these enzymes any arginine present was split into ornithine and urea, by the second the urea was converted into ammonium carbonate, and after 24 hours the ammonia thus produced was determined by the usual process of aeration and titration. A control conducted with urease alone gave the correction for pre-existing ammonia and urea. Many details of the method were left unmentioned. The authors have carefully studied the precautions and details necessary for the successful use of Jansen's principle, and recommend it as a strictly specific, highly accurate, trustworthy and convenient analytical procedure. Methods are described for the preparation and testing of highly active solutions of arginase. The source of the arginase was mammalian liver. Under the action of the enzyme urease, urea has been found by the authors to yield 99·4 per cent. of the theoretical amount of ammonia. Arginase has been shown to be capable of producing from arginine 99·1 per cent. of the theoretical amount of urea. By the successive use of the two enzymes, and with the application of a suitable correction, it is possible to determine arginine quantitatively with an error not exceeding 0·5 per cent. Methods are described for the application of this procedure to the accurate determination of arginine in proteins. The only special difficulty, occasionally associated with the use of arginase in protein analysis, was encountered in connection with the blank controls. Some liver extracts possess the property of liberating ammonia directly from some constituent or constituents of the hydrolysate. This deaminising action is discussed in detail, its nature, its effect upon the determination of arginine, and a method for the correction of that effect. Conditions for the hydrolysis of the protein are also discussed. Results are reported for the arginine content of gelatin and eight other proteins, and are compared with results obtained by other methods. The "direct" results by the authors for gelatin and fibrin are believed to be as close approximations as any yet made to the true arginine contents of these proteins.

P. H. P.

Milk of the Silver Fox. O. Laxa. (*Ann. Falsif.*, 1929, **22**, 598–600.)—This milk is white and very viscous, and has a penetrating, foxy odour, resembling that of asphalt. Owing to the smallness of the sample (8 grms.), special methods of analysis were necessary. The percentage results are: Total solids, **39·79**; fat, **12·25**; casein, **9·15**; albumin and globulin, **7·89**; sugar and extractives, **3·96**; soluble ash, **0·8**; insoluble ash, **1·54**. The fat, with saponification value **208**, remains liquid for some days at 26° C., but, later, deposits crystalline glycerides; it solidifies at 18° C. These results are similar to those obtained with dog's milk.

T. H. P.

Study of the Antimony Trichloride Colour Reaction for Vitamin *A*. E. R. Norris and A. E. Church. (*J. Biol. Chem.*, 1930, **85**, 477–489.)—The antimony trichloride colour reaction for vitamin *A* described by Carr and Price (*Biochem J.*, 1926, **20**, 497) is generally considered the most reliable colour test so far suggested for the vitamin. However, recently there has been considerable controversy as to the reliability and specific nature of the test, and so a critical study of it has been undertaken. Results obtained on this subject

by other workers are briefly mentioned. If the blue colour produced by antimony trichloride with a potent oil is a measure of the vitamin content of the oil, a correlation should exist between the colour test and the biological test of the oil. The blue colour produced should also be proportional to the active substance present and, consequently, to the amount of any one oil used. Work is now in progress to correlate the biological rat unit with the Lovibond blue unit, and a study has been made, and is described, of the colour reaction of the non-saponifiable substances of cod-liver oil with a chloroform solution of antimony trichloride, and the effect of various factors upon the colour developed. The results show that vitamin *A*, or the substance which produces the "blue" colour with antimony trichloride reagent, produces a greenish blue which fades to a colourless solution; the ratio of blue to yellow is approximately 1·0 to 0·4 Lovibond unit. The blue colour produced by an extract of the unsaponifiable portion of cod-liver oil with a chloroform solution of antimony trichloride is a linear function of the percentage concentration of the extract, and no red coloration develops on standing. The curve produced with a typical cod-liver oil is not a linear function. Traces of petroleum spirit and ethylene dichloride (which were present in the unsaponifiable extracts tested) are shown to have no effect upon the intensity of the colour produced. Varying amounts of these and other solvents were added to chloroform solutions of an extract, and colour tests were made in the usual manner. Of the solvents tried, chloroform gave the deepest blue colour, and alcohol, ether and acetone decreased the colour most markedly, but in no case was there any development of red coloration. The curve for cod-liver oil differs radically from that for the purified unsaponifiable fraction of the same oil, and the divergence of the concentration curve from a linear function varies with different cod-liver oils; it was therefore evident that some chemical compound common to all oils, but varying in amount in different oils, and which is removed by saponification and extraction, must have an inhibitory effect upon the observed blue colour. Oils differ in free fatty acids, oxidation products and impurities, depending upon the process of preparation and purification. Further tests showed that saturated fatty acids and oils have no effect upon the colour produced by the unsaponifiable portion of cod-liver oil with antimony trichloride reagent, whereas oleic acid and unsaturated oils accelerate the rate of fading of the blue colour. The red coloration developed is produced by some other substance present in oleic acid and unsaturated oils. Deviation of the observed blue colour, produced with varying amounts of cod-liver oil, from a linear function, is due to an increased rate of fading of the blue colour. Therefore, the colour change for vitamin *A*, if the colour is due to the vitamin, is not one from blue through yellow to red, as suggested by Wokes and Willimott. Quantitative comparison of the colour values between different oils or between colorimetric and feeding experiments can only be made at a value so low that the dilution curve approaches a linear function, or it can be made on the unsaponifiable portion. The colour tests must be very carefully controlled as to time, temperature and concentration of the reagent; the tests are best made in a constant temperature room. P. H. P.

Ratfish-Liver Oil as a Source of Vitamin *A*. E. R. Norris and I. S. Danielson. (*Ind. Eng. Chem.*, 1929, **21**, 1078.)—The liver oil of the ratfish (*Chimaera Colliei*) is a source of vitamin *A*. The oil is sold on the Pacific Coast, U.S.A., as a substitute for cod-liver oil; about 0·03 grm. of the oil is required daily to promote growth in rats. W. P. S.

Irradiation of Milk for the Increasing of its Antirachitic Potency. D. Nabarro and J. O. Hickman. (*Lancet*, 1930, Jan. 18, 127–129.)—The antirachitic potency of milk can be greatly increased by irradiation from a quartz mercury-vapour lamp, but prolonged treatment destroys the vitamin *A*; however, the fact that exposure of milk in thin films to a Hanovia lamp for a few seconds or not more than one minute, about doubles the antirachitic value of the milk, and apparently does not destroy the vitamin *A*, was shown by Supplee and Dow (*J. Biol. Chem.*, 1927, **75**, 227). Prolonged exposure imparts to the milk a disagreeable odour and taste, and any time longer than 8 minutes gives the milk a putrid odour; a slight change in flavour can be detected sometimes after only 30 seconds. The results are given of short-time exposures of milk (both whole and skimmed) to ultra-violet light under conditions which have definitely increased the antirachitic potency without apparently decreasing the vitamin *A* content of the milk or appreciably affecting its taste. The method of irradiation used was devised by one of the authors (J. O. H.). A thin film of milk on a cooler was exposed to the light from a Hanovia lamp, hung at a distance of 12 inches from the film; in no case was the exposure for longer than 30 seconds. Untreated milk, whether whole or skimmed, has very little antirachitic activity. The best sample examined had only 0·1 unit per c.c., and this was taken during a time when the cows were receiving the best "summer feed." Three samples taken during the winter and one taken during drought conditions at the same farm showed negligibly slight antirachitic potency. Where the potency of untreated milk could be measured, direct irradiation from a quartz mercury-vapour lamp for eight seconds increased it nine times, *i.e.* 0·1 unit of antirachitic activity per c.c. of untreated milk was increased to 1 unit. The capacity for activation of different samples of milk varies. An exposure of 30 seconds had no detectable influence on the vitamin *A* potency of the milk. Experiments have shown that irradiated milk can cure as well as prevent rickets in children and animals, and is of value in nutrition disorders and in other diseases. It is also shown that irradiation produces a marked decrease in the bacterial content of the milk. With the method of irradiation used by the authors the usual vitamin *D* content of the milk is about 1 to 2 units per grm. P. H. P.

Bacteriological.

Anaerobic Bacteria Causing Black-Rot of Eggs. R. M. Bohart. (*Amer. J. Hyg.*, 1930, **11**, 168–173.)—It is generally accepted as a fact that anaerobic bacteria of the genus Clostridium are the proteolytic agents which cause the putrefaction of protein foods such as meat. The author has attempted to correlate

the black-rot of eggs with this same group of bacteria which contaminate fresh eggs under natural conditions, and which, if given the right temperature and allowed sufficient time, will cause the decomposition of the eggs. Black rot is understood to be a state of reduction in proteins with the evolution of hydrogen sulphide gas. A dozen fresh clean eggs were inoculated with cultures of facultative proteolytic bacterial organisms, under aseptic conditions, and after 60 days of incubation only two eggs showed black-rot. *Clostridium putrificum* and *Clostridium sporogenes* were isolated from these two eggs. An attempt was made to isolate the bacterial organisms producing black-rot of eggs, to inoculate them into sterile eggs, and reproduce the black-rot under controlled conditions. Two dozen eggs, rejected after candling, were obtained from a wholesale market and incubated 10 days. Nine black-rot eggs were secured from these, and cultures of aerobic, facultative and anaerobic bacteria were isolated from them. The remaining eggs gave cultures of aerobic and facultative bacteria and moulds. The inoculation of sterile eggs was abandoned, since fresh eggs may not be sterile necessarily, and a "test egg" was prepared by placing small sections of a hard-boiled egg, both of the white and the yolk, in a test-tube, and covering to a depth of about 3 inches with plain nutrient agar, and sterilised. Cultures of the aerobic and facultative bacteria isolated from the rotten eggs, when re-inoculated into the test eggs, failed to evolve hydrogen sulphide, or to blacken or liquefy the egg sections during 60 days of incubation. The cultures of the anaerobic bacteria isolated from the same eggs, when re-inoculated into test eggs and incubated, evolved hydrosulphide and blackened the egg sections within 72 hours, and their liquefaction followed within 10 days. Cultures of 7 anaerobic bacterial organisms, from the laboratory collection, *viz. Clostridium putrificum, Clostridium botulinum, Clostridium tetani, Clostridium histolyticum, Clostridium Welchii, Clostridium tertium* and *Clostridium sporogenes*, were inoculated into test eggs, and within 72 hours of incubation six of the cultures evolved hydrogen sulphide associated with the blackening of the egg sections and produced complete liquefaction within 10 days. One culture, *Clostridium Welchii*, a known saccharolytic bacterial anaerobe, failed to evolve hydrogen sulphide or to blacken the egg fragments, though darkening did slowly occur, and it also failed to liquefy the egg sections. It is concluded that aerobic and facultative bacteria are unable to produce black rot in eggs, whereas the anaerobic spore bacteria occurring in eggs, and nearly all of the anaerobes from the laboratory collection, under the experimental conditions, if given the right time and temperature, will cause black-rot in eggs. P. H. P.

Studies with Methylene Blue. I. J. Fuchs. (*Woch. Brau.*, 1929, **46**, 437–439; *J. Inst. Brew.*, 1930, **36**, 32).—The concentration of methylene blue (1 in 10,000) generally used in testing yeast for dead cells should not be exceeded. Sufficient dyestuff should be added to render the yeast suspension blue, and not just greenish; and only those cells which take a deep stain at once should be considered as dead. The test is best carried out after removal of the wort or culture liquid; if the yeast is suspended in wort the colloids of the wort take up part of the dyestuff,

much more of which is thus needed. Cells which are only faintly coloured may still be capable of reproduction; probably the faint staining is due to a layer of mucilaginous matter on the cell walls. If a yeast suspension remains a long time in contact with an excess of the staining solution a number of cells which are at first uncoloured become stained in the course of hours or days, some gradually and others very suddenly, as if a rent had formed in the cell wall, and the number which thus die in the course of 1 or 2 days depends on the age of the original culture. Dead cells stained with methylene blue may, if suspended in water, become bleached again after a time, owing to the action of reductases which may remain active after the cells are dead. Owing probably to the acidity of wort, the bleaching is much more rapid in wort; it is equally rapid with a 0·2 per cent. lactic acid solution or a 2 per cent. monopotassium phosphate solution. P. H. P.

Toxicological.

Lead Poisoning from Tap Water. W. E. Cooke. (*Brit. Med. J.*, 1930, Feb. 1, 216)—Several cases of lead poisoning in the county areas of Lancashire have recently come under the notice of the author, in all of which the common factor is the habit of drinking hot water from the hot-water service in the home. The water supply of Lancashire comes chiefly from upland catchment areas, and in many cases is definitely plumbo-solvent; in hot-water systems, especially those with lead service piping from the hot-water cylinder, the solution of lead is accelerated. This matter is reported because these must be merely a few of the cases of lead poisoning existing in Lancashire, and they should be prevented.

P. H. P.

Organic Analysis.

Romijn's Formaldehyde Titration. R. Signer. (*Helv. Chim. Acta*, 1930, 13, 43–46.)—Experiments on the influence of time of reaction, and concentration and amount of the reactants, have shown that an accuracy of 0·1 per cent. is obtainable if 20 c.c. of a solution containing 20 mgrms. of formaldehyde are allowed to stand for 1½ hours with 20 c.c. of 0·2 *N* iodine solution and 5 c.c. of 2 *N* sodium hydroxide solution, and the excess of iodine is then titrated with 0·1 *N* sodium thiosulphate solution after addition of 2 c.c. of concentrated hydrochloric acid and 100 c.c. of water. Tests on pure trioxymethylene, depolymerised by the action of dilute hydrochloric acid for 30 hours at 100° C. in a sealed tube, showed that the accuracy falls off with an increase in the total volume of the reacting substances at a rate which increases rapidly when more than 0·04 grm. of formaldehyde is taken, or when the volume exceeds 90 c.c. J. G.

Distinction of Isoamyl, Isobutyl and *n*-Butyl Alcohols from one another, from the Lower Alcohols, and from Amyl and Butyl Acetates by means of Ammonium Cobaltothiocyanate. H. Weber. (*Chem. Ztg.*, 1930, 54, 61.)—These alcohols may be distinguished by means of their behaviour

towards a reagent made by mixing 10 c.c. of a solution of 12·5 parts of ammonium thiocyanate in 10 parts of water with 2 c.c. of 5 per cent. cobalt nitrate solution and 24 c.c. of water. After the alcohols have been isolated by fractional distillation and dissolved in mineral acids, the liquid to be tested is shaken with twice the volume of the reagent. The results are as follows: With isoamyl alcohol, upper layer blue, lower colourless; isobutyl alcohol, upper layer blue, lower greenish-blue, dilution with the reagent in the proportion 1: 6 resulting in a uniform blue liquid, to which addition of water gives a pink tint, causing no separation; *n*-butyl alcohol, uniform blue solution, giving an upper blue layer and a lower colourless one on dilution with water; amyl and butyl acetates, upper layer blue, lower pink, the upper layer becoming colourless and sometimes showing a white turbidity, and the lower layer becoming blue when the liquid is heated to boiling for a short time. Examples are given of the methods of separation to be followed when other solvents such as light petroleum or toluene are present, as is the case with lacquer or varnish solvents. T. H. P.

Tests for Isopropanol. H. Leffmann and C. C. Pines. (*Amer. J. Pharm.*, 1930, **102**, 39–43.)—The following tests, which are particularly useful for the detection of isopropanol in commercial alcohol or plain spirits, have been applied to the two types of the substance found in commerce. The *Dale Simonds* test depends on the formation of acetone furfural and the subsequent strong colour reactions with hydrochloric acid. Saturated solutions of disodium acid phosphate (1 c.c.) and potassium permanganate (3 c.c.) are added to 1 c.c. of sample, and, after warming, left till the permanganate is decomposed, when 3 c.c. of a 10 per cent. solution of sodium hydroxide and 1 c.c. of a 1 per cent. furfural solution are added, and the whole filtered. When a small quantity of this solution is poured into several c.c. of the strong acid, a very small proportion of isopropanol gives rise to a pink to cherry-red colour, but with large proportions erroneous inferences may be drawn from the deep red liquids. *Herstein's* test (*Pract. Druggist*, 1922, 38), like that with mercuric sulphate, appears to depend on the presence of some impurity. Three drops of strong sulphuric acid are added to the sample, followed by 1 c.c. of a 30 per cent. solution of sodium hydroxide or of 28 per cent. ammonium hydroxide, several c.c. of sodium nitroprusside solution and from 1 to 2 c.c. of glacial acetic acid, when a dark red colour is formed in the presence of iso-propanol. This test gave positive results with the isopropanol which did not react with mercuric sulphate, and a negative result with the one that did. If the industrial conditions governing the production of alcohols between ethanol and the pentanols (other than the isopropanols) should ever allow of their profitable use as adulterants, the tests available, while showing the presence of some substance other than ethanol or its natural accessory impurities, will not be sufficiently characteristic. D. G. H.

Presence of β-Ionone in a Natural Product. S. Sabetay. (*Bull. Soc. Chim.*, 1929, **45**, 1169–1171.)—A sample of essential oil of *Boronia megastigma*,

supplied by an Australian firm, was found to contain a considerable proportion of β-ionone, which has not previously been identified in a natural product.

T. H. P.

Cymbopogon Oils from India. (*Bull. Imp. Inst.*, 1929, **27**, 458–460.)—Samples of oils distilled in Burma from (1) *Cymbopogon clandestinus* and (2) *C.* (new species), are described. Both oils were clear pale yellow liquids with an odour resembling ginger grass oil, and had the following characteristics:—Sp. gr. at 15/15° C., (1) 0·9319, (2) 0·9734; α_D (1) +45·96°, (2) −48·67; n_D^{20}, (1) 1·495, (2) 1·497; acid value, (1) 3·0, (2) 4·9; ester value before acetylation, (1) 11·3, (2) 10·7; after acetylation, (1) 167·1, (2) 178·1; aldehydes and/or ketones, by the neutral sulphite method, (1) 18, (2) 11; solubility in 70 per cent. alcohol at 15° C., (1) soluble in 2·1 vol., (2) in 1·8 vols. Both oils bear a general similarity to ginger grass oil, although (1) has a more pronounced odour of, and contains more, carvone, and (2) has the stronger and pleasanter odour, and both could be classed as "ordinary commercial grades" of ginger grass oil. D. G. H.

Volumetric Determination of Certain Organic Acids with Ceric Sulphate. H. H. Willard and P. Young. (*J. Amer. Chem. Soc.*, 1930, **52**, 132–142.)—Ceric sulphate can be used for titrating the following organic acids (for, unlike permanganate, it is without effect on formic acid, one of the reaction products): tartaric, malonic, glycollic, malic, and citric acids. Formic, acetic, succinic, fumaric, and maleic acids are not oxidised. The oxidation of benzoic, phthalic, and salicylic acids is irregular. The solution to be titrated, containing 30 c.c. of sulphuric acid (sp. gr. 1·5) in a total bulk of 200 c.c., is treated with excess of 0·1 *N* ceric sulphate and kept at 90 to 95° C. for 30 minutes; the solution is cooled to 30° C. and the excess oxidant titrated electrometrically with ferrous sulphate. In the case of malonic acid, the ceric solution must be added before the sulphuric acid. The following factors were obtained:

1 c.c. of 0·1 *N* ceric sulphate:	Equivalents of oxygen per mol. of acid:
0·002084 grm. tartaric acid	7·2
0·001563 ,, malonic ,,	6·66
0·001923 ,, glycollic ,,	3·95
0·001449 ,, malic ,,	9·25
0·001211 ,, citric ,,	15·85

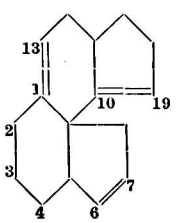
W. R. S.

Determination of Acidity of Oils and Fats by the Quinhydrone Electrode in Non-Aqueous Solutions. H. Seltz and L. Silverman. (*J. Ind. Eng. Chem.* (*Anal. Edition*), 1930, **2**, 1–2.)—The reference electrode was a platinum spiral, electroplated with silver, heated with moist silver oxide at 100° C., and then at 450° C. for an hour, and finally coated with a thin layer of silver chloride by electrolysis in dilute hydrochloric acid. The solvent for the oil (0·5 to 5·0 grms.) was *n*-butyl alcohol saturated with lithium chloride; to 125 c.c. of which was added 0·05 grm. of quinhydrone, and the titration carried out in an atmosphere of nitrogen with 0·05 *N* potassium hydroxide solution standardised electrometrically against

benzoic acid. A blank titration of the solvent was also made. Definite end-points were obtained for rosin, lard, arachis, neat's foot and transformer oils, and for butter-fat. J. G.

Influence of the Stability to Cold of Neat's Foot Oil on the Lubricating Properties of Compound Oils Prepared from it. P. Cuypers. (*Chem. Ztg.*, 1930, **54**, 30–31.)—Contrary to the conclusions of earlier workers (*cf.* Eckart, ANALYST, 1922, **47**, 521) cow neat's foot oil was found to contain small quantities of glycerides of linolic as well as of oleic, palmitic and stearic acids. The quality of the oil from the point of view of lubrication depends principally on the proportion of constituents with high setting-points, and, therefore, on the temperature (0° to 20° C.) at which the crude oil is pressed. Oils setting at −14·5° and −2° C. were found to contain linolic acid, 9 and 4·5 per cent.; oleic acid, 67·8 and 59·9 per cent.; and palmitic plus stearic acid, 18·7 and 30·7 per cent., respectively, and the influence of these acids on the lubricating properties of other oils is discussed. J. G.

Studies in the Sterol Group. Part VIII. The Reaction of *Iso*ergosterol. I. M. Heilbron and F. S. Spring. (*J. Chem. Soc.*, 1929, 2807–2810.)—The *iso*ergosterol acetate (m.pt. 129 to 131° C.) produced by the action of dry hydrogen chloride on ergosterol β-acetate is a mixture of an α- and β-acetate separable by fractional crystallisation and hydrolysed by a 5 per cent. alcoholic solution of potassium hydroxide to the respective α- or β-*iso*ergosterol (m.pt. 143 to 144° and 135° C., respectively). Since hydrogenation of both of these compounds at 20° C. in the presence of palladium produces dihydro*iso*ergosterol (III) and then α-ergostenol, it is inferred that the isomerisation of ergosterol (I) has not involved the shift of its inert double bond, which, according to Heilbron and Sexton (*id.*, 921), is probably situated in the 10: 19 position. Since, further, both *iso*-ergosterols (II) give Rosenheim's reaction, the ethenoid linkage 1: 13 is not involved, and it is concluded that isomerisation is due to a shift of the 6: 7 bond to the 2: 3 position. The authors' views are also in accordance with the fact that β- but not α-*iso*-ergosterol forms a yellow condensation product (m.pt. 159° C.) with maleic anhydride in benzene solution, after 6 hours at 20° C. α-*Iso*-ergosterol may be prepared quantitatively by the action on ergosterol of 10 per cent. alcoholic sulphuric acid for 1 hour under a reflux condenser, and recrystallised from acetone and then from a mixture of benzene and alcohol.



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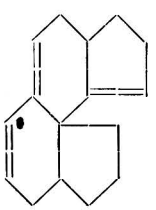
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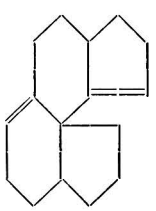

III

J. G.

Illipene and the Higher Alcohols in Commercial Illipé Butter. M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 365B.)—The illipé butter used had the following constants:—M.pt., 36–37° C., acid value, 4·5; saponification value, 198·3; iodine value, 5·49; unsaponifiable matter, 6·42 per cent. The unsaponifiable matter was treated with 95 per cent. alcohol. The higher alcohols dissolved, while the illipene remained undissolved. On isolating and distilling the illipene under 4·5 mm. pressure, it decomposed. It was a white powder with m.pt. 64° C., iodine value, 352; mol. wt. (Rast), 912, 899. It contained 86·40, 86·40 and 86·35 per cent. of carbon, and 11·86, 11·95 and 12·11 per cent. of hydrogen. The bromide is completely insoluble in ether. The author considers it to have the formula $C_{64}H_{106}$ or $C_{65}H_{108}$. The higher alcohols were isolated by concentrating the above-mentioned 95 per cent. alcoholic solution, white fibrous crystals being obtained. It had a m.pt. of 205° C., and gave no precipitate with digitonin. After being purified from 90 per cent. acetone the m.pt. was 210 to 211° C.; iodine value, 71·5, optical rotation $\alpha_D^{14} = +26·4$ in 2 per cent. ether solution. It contained 83·72 and 83·42 per cent. carbon and 12·01 and 11·94 per cent. hydrogen, mol. wt. 389 (Rast), 347 (cryoscopic). Its composition agrees closely with the formula $C_{27}H_{46}O$, isomeric with sitosterol or cholesterol. The author has named this higher alcohol *bassisterol*. R. F. I.

New Alcohol in Tarabakani Liver Oil. M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 362B.)—The unsaponifiable matter obtained from 5 kilos. of liver oil of Tarabakani (*Paralithodes Camtschatika* (Tilesius)) was dissolved in methanol and cooled by ice. The filtrate from the deposited solids, when freed from solvent, was found to consist of a dark yellow-orange viscous liquid with iodine value 153. This was acetylated and the 160 grms. of acetylated product was fractionally distilled under 5 mm. pressure. The largest fraction, distilling at 145 to 155° C., was purified by bromination at −10° C. in petroleum spirit. The filtrate from the insoluble products was freed from petroleum spirit and, the remaining brominated acetyl compound was debrominated with zinc and glacial acetic acid. Five grms. of this debrominated compound were again fractionated under 5 mm. pressure, the greater part distilling at 140–150° C. This was saponified, and the free alcohol isolated. It was a pale orange-yellow substance with the following characteristics:—Not solidified at −20°, sp. gr. at 20/4° C., 0·9553; iodine value, 145; n_D^{20}, 1·4740. It contained 70·40 (70·22) per cent. of carbon and 10·95 (11·41) per cent. of hydrogen. On hydrogenation, the percentages of carbon and hydrogen were 69·84 and 12·34, respectively. From these data it was concluded that its formula was $C_{10}H_{18}O_2$. It contains one non-acetylable oxygen atom in the molecule, thus resembling batyl and selachyl alcohols. The author proposes the name kanyl alcohol, from the Japanese "kani" (a crab). R. F. I.

Solubilities of Oils and Waxes in Organic Solvents. J. W. Poole. (*Ind. Eng. Chem.*, 1929, **21**, 1098–1102.)—Of a large number of solvents examined for the separation (extraction) of paraffin wax from mineral oil, butanol yielded

the most satisfactory results. Just below 30° C. mineral oil is completely miscible with butanol, and, even at 0° C. the solvent dissolves one-third of its weight of the oil. On the other hand, up to about 25° C. the solubility of paraffin wax in butanol is less than 2 per cent., and at 30° C. less than 40 per cent. The solubility of the wax increases rapidly above 30° C., and the point of complete miscibility is reached at 50° C. The solvent action of butanol is not improved by the addition of acetone. After butanol, ethyl acetate and butyl acetate appear to be the most suitable for commercial purposes. W. P. S.

Quantitative Separation of Phenol from the Cresols and Higher Phenols. J. N. Miller and O. M. Urbain. (*J. Ind. Eng. Chem.* (*Anal. Edition*), 1930, **2**, 123–124.)—The sample is divided into two 250 c.c. portions which are placed in the flasks of duplicate Kjeldahl distillation apparatus, 3 c.c. of concentrated sulphuric added to each, and 240 c.c. distilled. The apparatus is cleaned, the distillates returned to the flasks and 10 c.c. of a saturated solution of chromic acid crystals in concentrated sulphuric acid added to one, and 10 c.c. of sulphuric acid to the other. The solutions are raised to boiling in 45 minutes, maintained at this temperature without distilling, for 30 minutes, and 225 c.c. portions then distilled over. The former distillate contains no phenol (which has been destroyed), but all other similar substances, whilst the latter contains phenol, plus other phenolic substances. The difference between the total contents of phenol determined in terms of the same standard solution, distilled in the same way as the latter portion of the sample, gives the amount of phenol destroyed. This may be found by adding 4 c.c. of a mixture of an 8 per cent. solution of sulphanilic acid with 1 c.c. of concentrated sulphuric acid and 150 c.c. of water to 50 c.c. of distillate and 2 c.c. of 8 per cent. sodium nitrite solution. Five c.c. of 10 per cent. sodium hydroxide solution are then added, and the colour matched after 3 minutes. Permanent colour standards may be prepared from platinum and cobalt salt mixtures. The maximum error for 0·01 to 10 mgrms. of phenol in the presence of resorcinol, quinol or the cresols (or both) was $\pm$0·08 mgrm. per litre. J. G.

Knock Ratings of Aromatic Hydrocarbons. D. A. Howes and A. W. Nash. (*J. Soc. Chem. Ind.*, 1930, **49**, 16T.)—The knock ratings of some easily prepared aromatic hydrocarbons boiling in the usual petrol range were determined in the Standard Delco testing unit of General Motors Corporation, U.S.A., the engine being run at a constant speed of 500 rev. per min., and a cylinder head maintained at 140° F., fuel-air ratios being adjusted to give the maximum knock. Blends of the aromatic hydrocarbons were made with a Californian benzine of given properties, and these were then matched with blends of ethyl fluid in the same benzine, and the results of the engine tests expressed in terms of c.c. of ethyl fluid per gal. of standard benzine; 20 per cent. benzine, 2·1 c.c.; toluene, 2·75; *o*-xylene, 3·2; *m*-xylene, 4·0; *p*-xylene, 4·2; ethylbenzene, 3·8; *iso*-propylbenzene, 2·6; *p*-cymene, 4·2; *sec.*-butylbenzene, 1·8; *tert.*-butylbenzene, 3·2; *tert.*-butyltoluene, 3·8; *tert.*-amylbenzene, 3·2 c.c.; average value 20 per cent. aromatics=

3·2 c.c. of ethyl fluid per gal. In general, the *p*-di-substituted benzenes are the best anti-knocks, and tertiary groupings appear to be more effective than secondary.

D. G. H.

Determination of Labile Sulphur in Gelatin and Proteins. S. E. Sheppard and J. H. Hudson. (*J. Ind. Eng. Chem.* (*Anal. Edition*), 1930, **2**, 73–75.)—Labile sulphur is defined in terms of the method used for its determination, and in this instance is taken as the percentage of sulphur forming silver sulphide in the presence of ammonia under the conditions of the experiment. The sulphide is subsequently decomposed with acid, and the hydrogen sulphide determined by Almy's methylene blue method (ANALYST, 1925, **50**, 349). The gelatin is cut into 0·5 cm. strips, and 5 grms. allowed to swell for 1 hour in a tube in the presence of 25 c.c. of a 1 per cent. solution of silver chloride in ammonia. The tube is then heated, gently at first, for 2 hours, when the sample appears black owing to the formation of silver and silver oxide and sulphide. The liquid is evaporated to 10 c.c., the tube attached to an aerating train which is swept out with hydrogen sulphide-free and oxygen-free nitrogen, and 50 c.c. of hydrochloric acid containing 0·25 grm. of hydroquinone added through a tap-funnel. The nitrogen (3 litres) is passed through the apparatus for an hour, and the hydrogen sulphide liberated carried over into a mixture of 130 c.c. of 1 per cent. zinc acetate and 5 c.c. of 10 per cent. sodium hydroxide solutions. The blue colour is then produced by addition to this mixture of 25 c.c. of a 0·1 per cent. solution of *p*-aminodimethylaniline sulphate in 50 per cent. hydrochloric acid, and 5 c.c. of 0·02 *M* ferric chloride solution in 4 per cent. acid, and may be matched after 2 hours against that produced by a standard solution of sodium sulphide or allylthiourea in the presence of the same reagents. If the standards are equivalent to about 0·1 mgrm. of hydrogen sulphide they are stable for some weeks and may be prepared in advance. Total sulphur may be determined by heating the sample in a current of hydrogen and absorbing the hydrogen sulphide as before. The relation of the results to "labile to lead" sulphur and to cystine sulphur is discussed (*cf.* Maxwell, Bischoff and Blatherwick, *J. Biol. Chem.*, 1927, **72**, 51). J. G.

Determination of the Liquefying Power of Malt Diastase. S. Józsa and H. C. Gore. (*J. Ind. Eng. Chem.* (*Anal. Edition*), 1930, **2**, 26–28.)—The method depends on the decrease in viscosity produced in specially prepared starch paste under the action of the liquefying, as distinct from the saccharifying, enzymes of malt. Pure potato starch containing 84·22 grms. of dry matter is suspended in 200 c.c. of water at 50° C. and added to 1800 c.c. of boiling water in a tared enamel pan. The thick mass is stirred with a high-speed mixer for 3 minutes, cooled to 25° C., 50 c.c. of a Walpole buffer solution (*p*H 4·6) added, and the total weight made up to 2 kilos. with water. The paste is then filtered through a 100-mesh sieve; it retains its viscosity for several hours. Six 150 grm. portions of paste are stirred for 1 minute at 20·5° C. with 15 c.c. of water, mixed together, and added in varying proportions to fully liquefied starch prepared by the action of 90 c.c. of a 10 per cent. diastatic malt infusion on 900 grms. of original starch

paste at 65° C. for 1 hour. The fully-liquefied starch should be boiled, cooled, and water added to make 990 grms. The times of outflow of these mixtures from a jacketed 100 c.c. pipette at 21° C. are determined, and the curve obtained by plotting the percentage decrease in viscosity against the weight of dry starch liquefied is the reference curve of the apparatus. The malt sample is then made into a 2 per cent. infusion, filtered clear after 1 hour at 20° C., 50 c.c. diluted to 1 litre, and 15 c.c. stirred with the high-speed mixer for 1 minute with 150 grms. of starch paste at 20·5° C. The outflow time is measured after 1 hour at 21° C., the decrease in viscosity being obtained from the initial outflow time, as measured under the same conditions with 15 c.c. of water in place of malt infusion. The reference curve then gives the corresponding weight of dry starch liquefied. Duplicate experiments should agree to within 5 seconds. J. G.

Moisture and Combined Water in Coal. S. Iki. (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 371B.)—The results of some experiments on the exposure of dried coal in atmospheres of varying relative humidity are summarised. The amount of moisture absorbed at a certain humidity cannot be driven off by drying, *i.e.* wetting and drying are not reversible. The lower the caking power, the larger the moisture absorption. The four constituents of coal (α, β, γ and ulmine) absorb moisture in the order γ, β, α and ulmine. Moisture is regarded as the loss of weight at 100–200° C., and combined water as the loss at 200–900° C. The ratio of moisture to combined water decreases by weathering. R. F. I.

Inorganic Analysis

Isohydric Indicators and Pure Water for Accurate Measurement of Hydrogen Ion Concentrations and Salt Errors. S. F. Acree and E. H. Fawcett. (*J. Ind. Eng. Chem.* (*Anal. Edition*), 1930, **2**, 78–85.)—It is shown that for accurate *p*H measurements in dilute or weakly-buffered solutions it is preferable to use the isohydric indicator method, *i.e.* to measure the *p*H in terms of that of an indicator solution adjusted so that its colour is unchanged on addition to the sample. The stock indicator solution (usually 0·001 *M*) is divided into 100 c.c. portions, which are titrated with 0·05 *N* alkali until a 0·2 c.c. portion exactly matches in colour another 0·2 c.c. portion, plus 0·2 c.c. of a 0·001 *M* buffer solution of a particular *p*H. Similar colour standards are prepared for other *p*H values, the slight dilution of the indicator being compensated, if necessary, by the use of an increased volume. If the indicators are stored in Pyrex bottles with ground hollow stoppers they are stable for a year to within 0·1 *p*H, and the effect of atmospheric carbon dioxide may be eliminated by thorough aeration. The standards should be sterilised and sealed in Pyrex tubes. Studies with this method showed that for the sulphonephthalein indicators, apart from salt errors, correct *p*H values are obtained if the indicators are adjusted (1) at their mid-point *p*H for the usual buffers and for media up to 50-fold dilutions; (2) at their lowest, mid-point and highest useful *p*H values for 50 to 100-fold dilutions; and (3) in 0·2 steps of *p*H for very dilute solutions

(0·0001 *M*) and for water. Water of *p*H 7·0 may be prepared from ordinary distilled water by distillation from a flask, with a Pyrex still-head filled with tin, through a block-tin condenser. Air passed through moist soda-lime and filtered in a Chamberland filter is bubbled through the boiling water, and then passes through the condenser to the distillate, which is stored in Pyrex glass reservoirs in an atmosphere of the carbon dioxide-free air, and is transferred by siphon tubes or pipettes filled with such air. Data are provided showing the relation of dilution to salt and protein errors, as determined by means of the new technique, such errors now being defined as the difference between the isohydric colorimetric and the standard electrometric *p*H values. J. G.

Determination of Silver in Photographic Emulsions. J. P. Lawrie. (*J. Soc. Chem. Ind.*, 1930, **49**, 28.)—The following modified cyanometric method (Eggert and Zipfel, ANALYST, 1919, **44**, 358) is rapid and sufficiently accurate for routine purposes. Baines's method (*J. Chem. Soc.*, 1929, 2037) has a difficult end-point, and may give high results, whilst Volhard's method is slow. The strip (20 sq. ins.) is immersed in 100 c.c. of water, 8 per cent. of ammonia (d. 0·880) added, and the solution back-titrated at 20° C. to incipient turbidity with 0·2 *N* silver nitrate solution after addition of 10 c.c. of 0·2 *N* potassium cyanide and 5 c.c. of 5 per cent. potassium iodide (indicator) solutions. J. G.

Colorimetric Determination of Arsenic. A. Polijakow and N. Kolokolow. (*Biochem. Z.*, 1929, **213**, 375–379.)—The Feigl colorimetric reaction is used. To 5 c.c. of the test solution 2–5 drops of a freshly prepared cold saturated solution of ammonium molybdate are added, followed by a solution of stannous chloride in hydrochloric acid, until the blue cloudy liquid becomes greyish. It is then boiled until clear, and (for very small amounts of arsenic) the colour is brownish green. After cooling, 3 c.c. of amyl alcohol are added to extract the blue coloured compound, the colour of which is masked. After being shaken and allowed to stand, the blue amyl alcohol solution settles above the aqueous solution. A standard solution of arsenic acid (As_2O_5) is similarly treated, and the colours compared. In test experiments the following results were obtained: Arsenic found, 0·05 mgrm.; present, 0·046 mgrm.; found, 0·025 mgrm.; present, 0·029 mgrm.

In blood and serum, etc., after ashing with *aqua regia*, oxides of nitrogen, and possibly phosphates, influence the reaction. The arsenic can therefore be separated from the aqueous solution of the ash by precipitation with sodium hypophosphite (1 part in 10 parts of 25 per cent. hydrochloric acid), filtered, and dissolved after oxidation with hydrogen peroxide (perhydrol), and the solution diluted with water for the colorimetric test. J. W. B.

Delicate Test for Mercury in Systematic Qualitative Analysis. A. W. Scott. (*J. Amer. Chem. Soc.*, 1929, **51**, 3351–3352.)—The mercurous chloride precipitate obtained in Group 1 is dissolved in *aqua regia*, or the mercuric sulphide from Group 2, in hydrochloric acid and sodium chlorate. The resulting solution is evaporated to 1 c.c., and diluted in a test tube with 5 c.c.

of water. It is treated with 4 to 8 drops of a freshly-prepared alcoholic solution of diphenylcarbazide, and gradually with a large excess of solid sodium carbonate. In presence of mercury, the foam resulting from the neutralisation will be tinged blue; when the carbonate is in excess the whole solution will turn blue. If no mercury is present, an orange to pink colour should be obtained; a colourless solution indicates that the reagent has deteriorated. The alcoholic solution alters on standing. If the test solution has been prepared by means of *aqua regia*, the test should be completed without delay after addition of the reagent, otherwise the treatment with sodium carbonate will not produce the blue colour.*

W. R. S.

* The author ignores Kolthoff's statement that copper also gives the coloration, and Feigl's statement that copper must be separated. It has been shown that the liquid may be orange-pink in the presence of mercury.—EDITOR.

Volumetric Determination of Thallium with Ceric Sulphate. H. H. Willard and P. Young. (*J. Amer. Chem. Soc.*, 1930, **52**, 36–42.)—Thallous sulphate in hydrochloric acid solution reacts stoichiometrically with ceric sulphate. The end-point can be ascertained electrometrically, or visually, if the solution to be titrated is colourless, as 0·05 c.c. of 0·1 *N* ceric sulphate solution produces a pale yellow colour at or above 80° C. in 200 c.c. of solution containing 20 c.c. of strong hydrochloric acid. The ceric solution is made to contain 5 per cent. by weight of sulphuric acid, and is standardised against sodium oxalate (ANALYST, 1928, **53**, 404). The results obtained were in close agreement with Zintl and Rienäcker's bromate method (*Z. anorg. allgem. Chem.*, 1926, **153**, 276). Cupric, ferric, stannic, mercuric, or antimonic salts do not interfere, nor do selenites, tellurites, or arsenates; trivalent antimony and arsenic are oxidised. Nitric acid should not be present.

W. R. S.

Gravimetric Determination of Thallium in Rat Poison. W. Lepper. (*Z. anal. Chem.*, 1930, **79**, 321–324.)—The following process was found to be more rapid and convenient than Mach and Lepper's chromate method (ANALYST, 1926, **51**, 367). The paste or ground wheat (5 grms.) is heated with 100 c.c. of nitric and 10 of sulphuric acid in a Kjeldahl flask until the nitric acid is expelled; sodium nitrate is added in small portions until the acid is colourless or pale yellow. Water (60 to 70 c.c.) is added, and the solution boiled; any thallic sulphate formed is reduced with 25 c.c. of 6 per cent. sulphurous acid, and the sulphur dioxide boiled off. The liquid is neutralised with ammonia against rosolic acid. The contents of the Kjeldahl flask are transferred to a 200 c.c. flask, 5 c.c. of glacial acetic acid being added; after adjustment of volume, 100 c.c. of filtrate are heated to 90° C., and the thallium precipitated with 25 c.c. of 4 per cent. potassium iodide solution. After cooling, the precipitate is collected in a porous crucible, washed with a solution containing one per cent. each of potassium iodide and acetic acid, then with a little 80 per cent. acetone, dried for half an hour at 120 to 130° C., and weighed. Tl factor, 0·6170.

W. R. S.

Analytical Chemistry of Gallium (Part III). A. Brukl. (*Monatsh. Chem.*, 1929, **52**, 253–259.) (Part I: ANALYST, 1929, **54**, 64; Part II: *id.*, 367.)—The paper describes separations of gallium from titanium, zirconium, thorium, vanadium, molybdenum, tungsten, and rare earths. A. *From titanium, zirconium, thorium by cupferron.* Free mineral acid is neutralised with ammonia and an excess of ammonium oxalate added, then sufficient oxalic acid to produce a *N* solution. The quadrivalent metals are precipitated by cupferron, the precipitate filtered under slight suction after 15 minutes, washed with *N* oxalic acid, and ignited. The filtrate is treated with hydrogen peroxide and a measured quantity of strong sulphuric acid, and evaporated till the acid fumes. The cold mass is diluted to 1·5 *N* acidity, the solution tested for absence of hydrogen peroxide with a drop of permanganate solution and decolorised with a little sulphurous acid, and the gallium precipitated with cupferron (Part II). B. *From zirconium.* The hot solution, containing the sulphates in 2 *N* sulphuric acid, is precipitated with phenylarsonic acid (ANALYST, 1926, **51**, 318) and filtered hot; the precipitate is washed with warm dilute sulphuric acid, ignited—finally under hydrogen—and weighed as ZrO_2. The cold filtrate is treated with cupferron, gallium being precipitated arsenic-free. C. *From thorium.* Large amounts of thorium are precipitated as oxalate from hydrochloric solution, the precipitation being complete in absence of sulphates. Gallium is precipitated with cupferron after destruction of the oxalic acid as before. D. *From vanadium by o-hydroxyquinoline.* The solution containing vanadate and gallium salt is made ammoniacal (5 per cent. by volume in strong ammonia), gallium hydroxide re-dissolving; ammoniacal hydroxyquinoline solution is added until the gallium precipitate ceases to be formed. After 15 minutes on the water-bath, the solution is filtered and the precipitate washed with one per cent. ammonia. The filtrate is exactly neutralised with acetic acid, treated with 1 c.c. of saturated ammonium carbonate solution, boiled till neutral to litmus, cooled, and left for 2 to 3 hours; the balance of the gallium is thus precipitated, generally more or less contaminated with vanadium; the precipitate is, therefore, dissolved in a little hot dilute sulphuric acid and the precipitation by hydroxyquinoline repeated. The two gallium precipitates are dissolved in warm 2 *N* sulphuric acid, and the solution cooled and precipitated as before with cupferron. E. *From molybdenum and tungsten.* The separation is carried out as for vanadium. F. *From scandium and rare earths.* The cold, 1·5 *N* sulphuric acid solution is precipitated with cupferron, the ignited precipitate fused with bisulphate, the melt dissolved in 1·5 *N* sulphuric acid, and the precipitation repeated. The filtrates containing the rare earths are heated with hydrogen peroxide and evaporated until fumes of sulphuric acid appear, diluted, and precipitated with ammonia. Good results were obtained with yttrium, erbium, and scandium. W. R. S.

Analytical Chemistry of Indium (Part I). L. Moser and F. Siegmann. (*Monatsh. Chem.*, 1930, **55**, 14–24.)—Indium may be weighed as pale yellow sesquioxide or sesquisulphide. *As oxide*: Contrary to earlier statements, the

oxide was found not to be volatile at blast burner temperatures; it is not hygroscopic after strong ignition. It is obtained by ignition of the hydroxide, precipitated by ammonia from chloride, nitrate, or sulphate solution; ammonium salt need not be present, and excess of ammonia is immaterial, as the hydroxide is insoluble therein. The solution is boiled till the precipitate becomes dense; it is filtered hot and the precipitate washed with hot water, very thoroughly if chlorides are present, as indium chloride is volatile. Precipitate and paper are dried in a tared porcelain crucible, ignited gradually, then for 15 minutes over a blast burner. Indium is not completely precipitated as basic acetate. An important new precipitation method is as follows: The cold, feebly acid solution (200 to 400 c.c.; ammonium salts immaterial) is treated with methyl orange and enough 10 per cent. potassium cyanate solution to produce a yellow coloration. On boiling, dense indium hydroxide is precipitated; it is washed free from chlorides and ignited to oxide as before. *As sulphide*: Indium is known to be quantitatively precipitated by hydrogen sulphide from solutions containing acetic acid and ammonium acetate. The yellow precipitate is washed with weak ammonium acetate solution, heated to 350° C., cooled in a current of hydrogen sulphide, and weighed as In_2S_3. The authors find that the sulphide is precipitated quantitatively from 0·03 to 0·05 *N* hydrochloric acid solution. Indium oxide may be quantitatively converted into sulphide when heated in hydrogen sulphide as described.

Separations.—Those from the common metals of the ammonia and ammonium sulphide group are described. A. *From zinc*: Separation of indium as basic sulphite is known to be inaccurate; the cyanate method gave good results. The feebly acid solution is treated with six times as much ammonium chloride as there is zinc present, methyl orange, and potassium cyanate solution (*v. supra*), and gradually heated to boiling. If more than a tenfold excess of zinc over indium is present, the collected precipitate is dissolved in dilute hydrochloric acid and the operation repeated. B. *From nickel*: The cyanate method, as described under zinc, is effective. No unnecessary excess of cyanate should be used, as otherwise nickel may be co-precipitated. C. *From cobalt*: The cyanate procedure must be modified as follows: The solution is treated with sodium carbonate to neutrality, enough potassium cyanide to cause re-solution of the precipitate, and a few c.c. of cyanate solution. After some minutes' boiling, the precipitate is filtered off. Precipitation is repeated if a tenfold excess of cobalt is present. The precipitate, being contaminated with alkali, must in all cases be dissolved in acid and re-precipitated with ammonia. D. *From manganese*: Indium must be precipitated as sulphide from acetate solution (30 c.c. of 2 *N* acetic acid and 10 of 2 *N* ammonia in 100 c.c., being the maximum permissible bulk per 0·01 grm. of In_2O_3; mineral acid is first neutralised with ammonia.) A single precipitation is adequate. E. *From aluminium*: The solution (bulk as under manganese) is treated with sulphosalicylic acid, neutralised to methyl orange with ammonium carbonate, acidified with a little acetic acid and, after being heated, precipitated with hydrogen sulphide. The indium sulphide is collected, dissolved, and converted into hydroxide, which is ignited. F. *From iron*: The following procedure was found to be superior to all the

others: the solution is treated with ammonia, drop by drop, to the appearance of a precipitate, which is just re-dissolved in 0·1 *N* hydrochloric acid. The acidity should not exceed 0·05 normality. Hydrogen sulphide is passed for two hours at 70° C.; the precipitate is washed with hydrogen sulphide solution barely acidified with hydrochloric acid. Large quantities of ferric iron are first reduced with hydrogen sulphide in acid solution; the solution is then boiled, with a current of carbon dioxide passing through it, for the removal of hydrogen sulphide, cooled, neutralised, etc. G. *From chromium*: Indium is precipitated from the feebly acid solution, containing chromate, by the cyanate procedure. W. R. S.

Determination of Available Alkalinity in Commercial Lime. C. M. Jovellanos. (*Phillipine J. Sci.*, 1929, **41**, 71–74.)—The indefinite end-point in the titration of calcium carbonate with standard acid, with phenolphthalein as indicator, is due to the presence of impurities such as calcium silicates, ferrites and aluminates, whose retarding effects on the end-point follow the order named. The A.S.T.M. method, modified to minimise absorption of carbon dioxide, gave reliable results, 1 to 1·5 grms. of powdered (100 mesh) sample being boiled for 5 minutes in a litre flask with a long narrow neck with 400 c.c. of freshly-boiled distilled water, cooled, and titrated slowly with 0·5 *N* hydrochloric acid in the presence of phenolphthalein. When the solution is almost decolorised, any small lumps are broken up, the flask tightly stoppered for 30 minutes, and the titration continued till the solution remains colourless for 1 minute. J. G.

Determination of Small Amounts of Hydrogen Peroxide and of Ozone. N. Allen. (*J. Ind. Eng. Chem.* (*Anal. Edition*), 1930, **2**, 55–56.)—A number of qualitative colour tests for hydrogen peroxide and ozone have been examined as to their suitability for colorimetric methods of determination. For hydrogen peroxide the best method is to add the sample to a slight excess of a dilute acid potassium permanganate solution in the presence of a little magnesium sulphate as catalyst, the tint of the partly decolorised solution being matched against that produced in the same quantity of reagent by known amounts of peroxide. The method will detect 1 part in 10 million. The reaction with titanium sulphate may also be used, and is accurate to 1 part per million. Ozone may be absorbed in dilute alkaline potassium iodide solution, an aliquot portion of the solution acidified, and the colour produced on addition of starch solution matched against that from a standard solution of iodine in potassium iodide. The ozone content is calculated from the equation: $4O_3+10HI \rightarrow H_2O_2+5I_2+4H_2O+3O_2$, and the method may be used for 10^{-6} grm. J. G.

Quantitative Determination of Osmium by means of Strychnine Sulphate (Micro Method). S. C. Ogburn, junr., and L. F. Miller. (See p. 222.)

Microchemical.

Quantitative Determination of the Composition of Potato Starch according to Size of Granule. G. Bredemann and O. Nerling. (*Chem. Ztg.*, 1930, **54**, 87–88.)—One-quarter, cut lengthwise, is taken from each of 50–80

tubers, representing the different sizes present in the bulk in their respective proportions. Each of these pieces is ground and the starch separated by washing and settling, the latter process occupying 10–12 hours in a cool room. The water is then poured off, and the starch air-dried in a thin layer at 20–30° C., and passed through a 1·0–1·5 mm. sieve. An average sample of 50–100 grms. is rubbed through a 0·1–0·2 mm. gauze or brass sieve by means of a pestle covered with a rubber cap. After three or four sievings, the sample may be diminished to about 40 grms., this being again sieved several times to mix it. About 5–10 grms. are then dried at 100–110° C. until constant in weight, and cooled in a desiccator. A small quantity (0·01–0·02 grm.) is distributed with a lancet needle in a few drops of olive oil on a microscope slide, no cover-glass being used. Two or more such preparations should be examined.

The slide is examined under a microscope fitted with a movable stage, use being made of a drawing apparatus and of a scale drawn on millimetre squared paper. Adjustment of the magnification is made so that 1 mm. on the scale corresponds exactly with 1 micromillimetre of the stage micrometer. In measuring the dimensions of the granules, about 1000 of which are measured in each preparation, the longest diameter and the longest diameter perpendicular to this are added, and the sum divided by two. According to the values of the mean diameter thus obtained, the granules are classified as: 3 to 5, 6–10, 11–15, etc., up to 96–100 micromillimetres. In calculating the weight of the proportion of the total granules in any group, use is made of the weight-normal numbers, which represent the weights in mgrms. of one million granules for the different sizes, and were determined experimentally. In this way the percentages of the total weight represented by granules of each mean diameter are determined. In order to characterise any starch by a single number, termed the characteristic diameter, the percentage by weight of granules of each size is multiplied by the corresponding mean diameter, all the products thus obtained being added together, and the sum divided by one hundred. The result is a single figure, by means of which different starches may be directly compared. T. H. P.

Quantitative Determination of Shell in Cocoa and Cocoa Preparations. M. Wagenaar. (*Pharm. Weekblad*, 1929, **66**, 1185–1202.)—A summary of microscopic methods for the determination of the shell content is given. The new method is founded on the amount of sclerenchyma (woody cells with honeycomb structure) in 1 grm. of de-fatted dry cocoa powder. The cells are recognised in polarised light, being doubly refracting. The de-fatted shell powder, cocoa, or cocoa preparation, is finely powdered and sieved through silk gauze (sieve B40), and 0·5 grm. is heated in a covered beaker for 10 minutes over a boiling water-bath with 20 c.c. of 5 per cent. potassium chlorate and 10 c.c. of 4 *N* hydrochloric acid. Then 25 c.c. of 4 *N* sodium hydroxide are added and heating continued for 10 minutes, when the destroyed cell fragments are transferred to a 100 c.c. measuring cylinder, allowed to settle for several hours, and the supernatant liquid siphoned off. The sediment is washed and again allowed to settle. The volume of cell

fragments is usually about 10 c.c. The whole, or an aliquot part, is centrifuged in a conical tube, the residue mixed with glycerin and stirred with a rod. The weight of the rod and glycerin are known. From 1 to 6 drops of the mixture are transferred to as many microscope slides and used for duplicate determinations. The glycerin suspension and stirring rod are re-weighed to give the weight of drops removed, for the final calculation. Each drop is covered with a calibrated covering glass (2·8 × 2·3 cm. and 0·5 mm. thick), etched in square mm., with a magnification 50–60 times, about 1 mm.^{2} being in the field. By using a micrometer eyepiece scale, etched in squares, of which 49 (7 × 7) correspond to 1 mm.^{2} in the microscopic field, the size of the schlerenchyma groups, visible as transparent fragments of cell tissue in polarised light, can be measured. The author used as unit a cell grouping 100μ square (0·1 mm. × 0·1 mm.). From determinations on different varieties of cocoa he fixed the standard factor as 2100 mm.^{2} in 1 grm. of fat-free shell powder. By using this factor good results were obtained with mixtures in which the quantity of shell was known. J. W. B.

Quantitative Determination of Osmium by means of Strychnine Sulphate. S. C. Ogburn, jr., and L. F. Miller. (*J. Amer. Chem. Soc.*, 1930, **52**, 42–48.)—Osmium may be quantitatively removed from solutions of its salts with a saturated solution of strychnine sulphate (prepared at room temperature, and containing 3·2 per cent. of the salt). The composition of the compound was found to be $(C_{21}H_{22}O_2N_2)_3OS$, a co-ordinated salt in which osmium has a co-ordination number of 6. Using a gravimetric factor of 0·1758, the percentage content of osmium may be obtained from the weight of the canary yellow precipitate which has been washed with distilled water and dried at 105° C. The solubility of the precipitate in water up to its boiling point is negligible.

Separation of Osmium from Ruthenium.—A solution containing 1·4 mgrms. of osmium and 1·6 mgrms. of ruthenium in soluble form was treated with a slight excess of a saturated solution of quinine sulphate. Immediate precipitation followed. An equal volume of 95 per cent. ethyl alcohol was added, and the mixture was boiled until the precipitates dissolved. On cooling, the osmium came down (the ruthenium remained in solution for several days). After 1½ hours the mixture was filtered. The filtrate gave no reaction for osmium with β-naphthalamine hydrochloride. The weights of precipitates found were 7·6 and 7·8 mgrms. (theoretical 8·0 mgrms.); osmium found, 1·4, 1·4 mgrms.; theoretical, 1·4 mgrms. J. W. B.

Microchemistry of Berberine. M. Wagenaar. (*Pharm. Weekblad*, 1930, **67**, 77–79.)—The hydrated salt, $C_{20}H_{17}NO_4 + 6H_2O$ (neutral reaction), loses 4 aq. at 100° C. It melts at 140° C., and has refractive indices (α and β) 1·50 and 1·74. It is soluble in 500 parts of cold water, and in 1250 parts of cold alcohol, is easily soluble in boiling water and alcohol, but dissolves with difficulty in benzene, and is insoluble in ether. Under ordinary pressure it sublimes without crystallising, but gives crystals when sublimed under reduced pressure (10 minutes at 90° C.,

3 cm. Hg.). The sensitiveness of its reactions (observed under the microscope) were as follows:—

	Limit. of conc. in which reaction takes place.	Smallest amount detectable. μ grm.
Precipitation with salts	1:2000	0·5
Reaction with potassium bismuth-iodide	1:1000	1
,, ,, iodine in potassium iodide	1:1000	0·1
,, ,, bromine in potassium bromide ..	1:1000	1

J. W. B.

Microchemistry of Brucine. M. Wagenaar. (*Pharm. Weekblad*, 1929, **66**, 1170–1176.)—The free alkaloid $C_{23}H_{26}N_2O_4+4H_2O$, is a strong base, crystallising in rhombic prisms, refractive indices, α and β, 1·48 and 1·66. On heating to 100° C. above sulphuric acid it loses its water of crystallisation. When crystalline it melts at about 100° C.; when anhydrous at 178° C. Its solubility in water is 1: 320 parts (cold), 1: 150 parts (boiling). It is readily soluble in alcohol and chloroform, but with difficulty in ether. Its aqueous solution is laevo-rotatory. It sublimes without decomposition, and under reduced pressure at about 160° C.

The sensitiveness of the reactions (observed under the microscope) were as follows:—

	Limit of conc. in which reaction takes place.	Smallest amount detectable. μ grms.
Precipitation (usually with sodium carbonate)	1:1000	2
Reaction with potassium chromate	1:500	5
,, ,, potassium dichromate	1:1000	2
,, ,, mercuric chloride	1:1000	2
,, ,, mercuric bromide	1:1000	1
,, ,, mercuric iodide	1:1000	0·5
,, ,, cadmium chloride	1:1000	2
,, ,, cadmium bromide	1:1000	1
,, ,, cadmium iodide	1:1000	0·5
,, ,, zinc chloride	1:1000	2
,, ,, zinc bromide	1:1000	1
,, ,, zinc iodide	1:1000	0·5
,, ,, picric acid	1:200	10
,, ,, picrolic acid	1:500	5
,, ,, sodium nitroprusside	1:200	10
,, ,, ammonium cyanide	1:100	10
,, ,, iodine in potassium iodide	1:1000	2
,, ,, bromine in potassium bromide ..	1:500	5
,, ,, potassium ferrocyanide	1:1000	1
,, ,, potassium ferricyanide	1:500	5
,, ,, soluble iodides	1:100	10
,, ,, cobalt cyanide .. .. (cobalt acetate + ammonium cyanide)	1:100	10

J. W. B.

Physical Methods, Apparatus, etc.

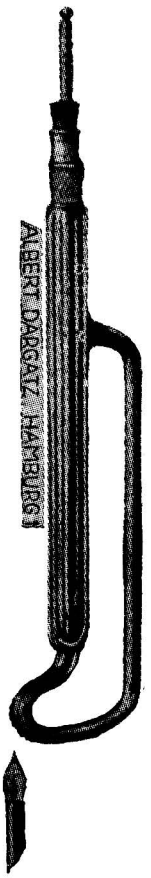
Examination of Coal and Coke by X-Rays. C. N. Kemp. (*J. Roy. Soc. Arts*, 1929, **78**, 114–136.)—The examination of coal by means of an *X*-ray apparatus, such as the "Carboscope," is described. The radiographs obtained show clearly the way in which the coal is traversed by numerous thin veins of

mineral matter having a general direction perpendicular to the bedding planes of the coal. Before jigging, the coal shows a more or less uniform mixture of all the pieces present of whatever composition. If, however, the sample is placed in a small jig and subjected to the action of intermittent water pressure in the same way as in a large-scale washing box, the radiograph renders evident the existence of two distinct layers if any heavy shaly matter remains in the coal; the depths of the two layers are proportional to the quantities of the two categories, the clean coal above and the shale below. In spite of the very high proportion of ash in the shale (often 80 per cent.), it is now possible to clean small coal continuously and consistently down to within less than 1 per cent. of the intrinsic or inherent ash. Examination of a number of coal samples shows that, with more efficient cleaning, the ash content of coal supplied as a washed product could often be diminished by 50 per cent. In coal boring, information regarding the seams pierced may be obtained by preparing a radiographic record of the cores obtained. T. H. P.

Analysis of Pharmaceutical Drugs by means of Ultra-violet Rays. P. Ernst and J. Jentschitsch. (*Pharm. Monatsh.*, 1929, **10**, 67–73; *Ann. Chim. anal.*, 1930, **12**, 18.)—To 1 grm. of the drug are added 100 c.c. of water, and an extract is prepared according to the Austrian Codex. The clear liquid is decanted, divided into three portions of 25 c.c. each, and 5 c.c. of water added to the first, 5 c.c. of *N* ammonia to the second, and 5 c.c. of *N* acetic acid to the third, and a band 30 cm. by 2·5 cm. of Schleicher paper put in each for 1 hour. The bands are then dried and examined by ultra-violet light. The substances in the infusions have constant capillarities, and they are drawn to varying heights in the papers, and successive zones of fluorescence are seen. The characteristic fluorescences in neutral and alkaline extracts are recorded for the drugs in the Austrian Pharmacopoeia. D. G. H.

Photography by means of Heat Rays by Plotnikov's Method. L. Šplait. (*Arhiv za Hemiju*, 1929, **3**, 169–177.)—This method makes use of infra-red and heat rays, and is carried out with Eastman-Kodak and Agfa plates, sensitised for such rays. Since these plates permit of photography through fog, Plotnikov suggested their use with substances of higher densities. The experiments described show that different substances allow these rays to pass through them in different ways, and that the permeability to the rays changes considerably with the wave-length. It appears that these rays of high wave-length may give rise to phenomena analogous to those observed by von Laue with *X*-rays. Different organs of the animal or human body exhibit different powers of absorbing them, and the blood of a rabbit varies in its absorption with the nature of the nutriment taken by the animal. Pathological and physiological changes may also be detected with the plates. Reproductions are given of photographs, taken in this way, of a British treasury note showing the marking on the reverse side, of the writing of a letter photographed through the envelope, etc. T. H. P.

Benzenometer. W. Vaubel. (*Chem. Ztg.*, 1929, **53**, 859–860.)—The apparatus consists of a vessel of 1050 c.c. capacity in which are placed 100 c.c. of benzole or similar motor fuel. It is then closed by means of a rubber stopper carrying an inverted 50 c.c. eudiometer tube, 70 cm. long, adjusted so that its open end almost reaches the bottom. The vessel, which should not be shaken, is maintained at a constant temperature (*e.g.* 18·5° C.) in a thermostat or by means of cotton-wool or other insulating material, the height of the liquid read after 1 and 2 hours, and, for accurate work, suitable corrections applied. Comparative values of the partial pressures of a number of pure volatile solvents (*e.g.* ether, alcohol, acetone, benzene, methyl ethyl ketone and carbon tetrachloride) were thus obtained, and the effects of addition of these in varying proportions to pure benzene was investigated. Thus, for example, the reading for benzole mixtures is higher than for pure benzene, whilst in the presence of 0·1 per cent. of water it is depressed; iron pentacarbonyl raises the value to an extent which depends on the amount present. Normally, a maximum reading is obtained for a particular value of the composition of the mixture of benzene and other solvent. J. G.



New Apparatus for the Determination of Corrected Melting Points. C. Junge. (*Chem. Ztg.*, 1929, **53**, 996.)—This apparatus consists of two parts. The outer tube contains sulphuric acid, which is heated and circulated by a flame at C. The inner co-axial tube contains a small amount of a second liquid, in which the thermometer bulb with the melting point tube is immersed. By this arrangement the whole of the mercury of the thermometer is surrounded by the heating liquid, the corrected melting point being thus obtained. The heating is facilitated if the tube in which the sulphuric acid descends is lagged with asbestos string. T. H. P.

References to Scientific Articles not Abstracted.

THE MEASUREMENT OF THE COLOUR OF TEXTILE FABRICS AND SOME APPLICATIONS TO PROBLEMS OF FADING. By P. W. CUNLIFFE. *J. Soc. Dyers & Col.*, 1929, **45**, 305 (Nov.).

Introductory—The Guild Trichromate Colorimeter—The Spectrophotometer—The Lovibond Tintometer—Comparative Results with different Colorimeters.

LOSS OF ULTRA-VIOLET TRANSPARENCY IN GLASSES. By S. ENGLISH. *Nature*, 1930, **125**, 85 (Jan. 18).

Comparison of natural and artificial ageing of glass—Spectra—Experiments do not support the view that natural solarisation is complete in a few days—Greatest loss of transparency occurs during the first few weeks, but deterioration not usually complete in less than six months.

Reviews.

THE PARACHOR AND VALENCY. By S. SUGDEN, D.Sc., A.R.C.S. Pp. vii+224. London: Geo. Routledge & Sons, Ltd. 1930. Price 12s. 6d.

This book will be heartily welcomed by advanced students of chemistry, as it supplies the first connected account of the author's recent advances in our knowledge of the significance of surface tension. To the majority of older chemists, however, it is probable that the term "parachor" will have little meaning, and a word of explanation may therefore not be out of place. Very soon after the introduction by McLéod, in 1923, of the empirical formula connecting the difference between the densities of a liquid and its vapour with the surface tension at the same temperature, Sugden arrived at the conclusion that the formula could be used to calculate values for different liquids which would be characteristic of the liquids themselves, and also would be proportional to their specific volumes at constant surface tension. By choosing unity as the constant surface tension, and multiplying these values by the respective molecular weights of the liquids, the values or "parachors" so obtained are considered to bear a simple relationship to the molecular volumes.

A perusal of the book suffices to show what remarkable use Sugden has made of McLeod's simple formula in regard to molecular constitution. He has been able, by a process of elimination, to calculate the atomic parachors, the values to be attributed to the different linkages, and, moreover, to show their additive and constitutive properties. On the whole, his figures and conclusions concerning simple organic compounds are convincing, although certain people may be dissatisfied with regard to the parachors deduced for some of the more complicated groupings.

Two chapters are devoted to "Atoms and Spectra" and "Polar and Non-Polar Linkages." Unless a student has read physics to a fairly advanced stage, it is to be feared that he will find the treatment accorded to these important subjects beyond his reach. This is a disadvantage. One feels that the value of the work would have been considerably enhanced if more attention had been given to the practical basis of the subject.

More complicated molecular structures, involving higher valencies and the various types of electron linkages, are discussed by correlation with the parachor. The last three chapters deal with "Associated Liquids," the "'Quantum Theory' of shared Electrons," and the "Experimental Methods of Determining Densities and Surface Tensions."

With regard to the application of electronic formulae to more complicated chemical compounds, the book seems to suffer, in common with many other recent publications, from an excess of speculation.

HUBERT T. S. BRITTON.

OUTLINES OF BIOCHEMISTRY. By ROSS AIKEN GORTNER. Pp. 793+xv. New York: John Wiley & Sons, Inc.; London: Chapman & Hall. 30s.

Professor Gortner has brought within the compass of 700 pages most of the essential knowledge of the sub-division of natural science classified as biochemistry. His book deals with the colloidal state of matter, the chemistry of proteins, carbohydrates and allied compounds, tannins, plant pigments and fats, lipides and essential oils. A section on the biocatalysts (vitamins and enzymes) brings the whole to a successful conclusion. In spite of the mass of material dealt with, the book is essentially readable, and the lucidity with which all the varying sections are handled cannot fail to evoke the admiration of any laboratory worker who has essayed also to be a writer. The section of the book devoted to the colloid state is a model for the treatment of a complex subject, and, though Professor Gortner modestly suggests that the biochemical beginner should make a preliminary study of one of the standard books on colloid chemistry before starting on "Outlines of Biochemistry," the present reviewer feels that the order of study should be reversed, and that any beginner in colloid chemistry would be well advised to read Part I of Professor Gortner's book before proceeding to tackle any of the standard works on the subject.

Professor Gortner's range is so wide that he can pass from the principles governing the precipitation and analytical determination of a salt, such as silver bromide, to the commercial possibilities in the catalytic hydrogenation of fats, and then to the genetic distribution of plant oxidases and their association with the colours of flowers, without once halting in his narrative. All the recognised analytical tests for proteins, fats and carbohydrates (including the use of bacteria for the diagnosis of the less common sugars) are given in detail, as well as numerous references to quantitative methods of determination.

Where so much has been accomplished, it seems ungracious to ask for more; but, although throughout the book Professor Gortner keeps the biological aspect of his subject before his readers, the amount of space devoted to the enzymes seems hardly adequate to their importance. Is it too much to ask that in the second edition, which one may anticipate will shortly be appearing, this section may be considerably extended, and that a chapter on biological oxidations and reductions should be added? An extended account of modern work on haemoglobin would certainly be an advantage, and, in a work of this character, cytochrome should at least receive mention. An account of the organism as a working machine and of the energy relations between an organism and its environment would be welcomed from the pen of a writer who has proved himself such a master of lucid exposition.

The reviewer is going to indulge in one small grumble in the matter of the English equivalents used as translation of German scientific terms. "Dispersionsmedium" would be better translated as "dispersion medium"—"dispersions medium" certainly is at variance with all recognised rules of English grammar—"proteïnspaltproduct" reproduces its meaning best in English as "protein degradation product," and, surely, the expression "press juice" has sufficient

standing to make it unnecessary to drag the awkward word "presssaft," with its trinity of sibillants, over into another language.

The book has been produced by the publishers in pleasing form, and the price is reasonable. DOROTHY JORDAN LLOYD.

STANDARD METHODS FOR TESTING TAR AND ITS PRODUCTS. Published by the Standardization of Tar Products Tests Committee, 166, Piccadilly, London, W.1. Pp. xxiii+246, with illustrations and graphs. Price 7s. 6d.

This volume, produced under the auspices of the Joint Fuel Committee, makes a welcome appearance. The Standardisation of Tar Products Tests General Committee, of which the first chairman was Mr. W. J. U. Woolcock, followed by Mr. H. W. James, was fully representative of the coal tar industry. Its seven panels have worked since the resolution that called it into existence was passed, and after a paper read by Mr. W. G. Adam to the Tar Conference, early in 1926. A large amount of laboratory work has been done, and most valuable assistance has been rendered by the National Physical Laboratory.

The book begins with "Definitions and Descriptions" of the substances to be dealt with, and this is followed by recommendations regarding sampling. Under "General Principles" is a valuable disquisition on specific gravity and on distillation. The tests begin with crude tar, which is divided into general tests, a sorting test, and commercial analysis. Then follow the tests for refined tar, including road tar. Here contact is made with the Ministry of Transport and the British Engineering Standards Association, in that the standards tests have been adopted in connection with the road tar specifications, but with one exception. The Standardisation of Tar Products Tests Committee, after long and very careful discussion, replaced the Hutchinson tar tester by the tar viscometer. The borough and other surveyors, however, insisted on a similarity of figures to be given them from the two methods. This was not yet completely possible, so that the Hutchinson instrument was temporarily retained for No. 2 tar.

Low-boiling fractions are dealt with along well-known lines, except that the determinations of paraffins, including naphthenes, and of total sulphur, are made with improved apparatus. Something like a triumph has been attained by establishing a method of numerical description of the colour obtained by acid washing, by means of the Lovibond tintometer, (The use of this instrument is one of the rare exceptions to the Committee's rule of avoiding the standardisation of patented articles.)

Then follow tar acids, including Graesser's modification of Lowe's test, and naphthalene. The methods for examining tar bases are "methods of procedure," as standardisation was thought to be undesirable at this stage. Creosote oil and crude naphthalene also proceed along conventional lines.

The softening point of pitch follows a modification of a modification of Krämer and Sarnow's method, the ball and ring method being considered to be unsuitable. The fusing point test has been improved and the twisting point is obtained mechanically.

The volume continues with Appendix I—Apparatus Schedules, including a valuable collection of thermometers. The adoption of Crow receivers will simplify the collection of distillates.

Appendix II gives Constants and Equivalents. In Appendix III are collected together all the graphs required by the methods of analysis; copies of these for laboratory use are to be obtained at a low cost from the Committee's office. Finally, means are provided for including such further tests as may be determined upon. For this purpose, partly, the Committee remains in being.

The general "get up" of the book is excellent, the illustrations are good, and the matter most carefully arranged.

P. E. SPIELMANN.

THE EXTRA PHARMACOPOEIA. By MARTINDALE and WESTCOTT. Revised by W. H. MARTINDALE. Nineteenth Edition. Vol. II. Pp. xxxviii+759. London: H. K. Lewis & Co. 1929. Price 22s. 6d. net.

This publication, of which the previous edition was reviewed in the ANALYST (**1925, 50, 585**), requires no introduction to the majority of readers, since former issues have for long occupied a well-deserved place in the literary armamentaria of medical men, pharmacists, analysts and other workers in science.

The present volume is far more than an appendix to Vol. I (ANALYST, **1928, 53, 513**), and provides information on a great variety of subjects, much of which is the result of recent investigations, published as late as the latter months of **1929**. The reviser, in common with most of us, is unfortunately experiencing the difficulties of keeping abreast of the ever-increasing mass of scientific literature, and has been compelled, to some extent, to sacrifice his former thoroughness; but when any matter of importance is omitted, adequate references are provided both to the original sources and to previous editions of this work.

Among the subjects of chief interest to the analyst which appear for the first time are the following: The detection of aldehydes and peroxides in ether, reactions of the various organic arsenical compounds, the occurrence and methods of estimation of iodine in water and foodstuffs, the chemical "improvement" of flour, and lead poisoning in general and in connection with the use of lead tetraethyl in motor fuel. In addition, the information on the analysis of water, urine, stomach contents, milk, butter, etc., on antiseptic power, bacteriological methods, and modern indicators, together with a comprehensive scheme for the classification of therapeutic substances and corroborative tests for their identification will ensure frequent reference to the volume.

The above items represent but a portion of the material enclosed between the covers of this book, and the remainder contains, in addition to summaries of legal regulations and Acts of Parliament relating to foods, drugs, preservatives, colouring matters and proprietary medicines, a diversity of knowledge difficult to find elsewhere when required at short notice. It would be by no means easy to overemphasise the value of this production, for the soundness and precision of the statements and opinions expressed render it an invaluable reference book.

The general style of the type and binding corresponds with that of former editions, and the text is remarkably free from errors, only three, and those of quite minor importance, being detected throughout the volume. The index, which is complete and of a high degree of accuracy, contains references to both volumes of this edition, these being readily distinguished by the use of different numerical type.

It would be difficult to find another work covering such extensive ground so successfully, and the reviser and publishers are to be congratulated on the production of yet another volume which will be eagerly welcomed by workers in many branches of scientific activity.

T. J. WARD.

THE CHEMISTRY OF LEATHER MANUFACTURE. By JOHN ARTHUR WILSON, D.Sc. Second Edition. Vol. II. Pp. 682. New York: The Chemical Catalog Co., Inc. Price 50s.

Dr. J. A. Wilson has gathered together an immense amount of information into a couple of volumes. His second volume deals with tanning by means of vegetable tannins, chrome salts, iron, oils, aldehydes, quinone and sulphonic acids. It also includes an account of the finishing processes in leather manufacture and the properties of different leathers. In a book ranging over so wide a field it is difficult not to lose sight of the wood in cataloguing the trees. This difficulty has not been altogether avoided in the present volume. Even in the more chemical, as distinct from the more technological, chapters, a conscientious account of the details of an experiment frequently obscures the thread of the theoretical narrative. The volume, however, gathers together much work that is only at present available in scattered papers. If a somewhat undue emphasis is given to the experimental work of the author and his American colleagues, this can hardly be regarded as an unforgivable offence; the various theories of tanning at present competing for supporting evidence all receive due mention.

Meunier's theory, that vegetable tanning involves the oxidation of the basic groups of the collagen, with subsequent combination of quinone at these oxidised groups, is concisely summarised, and Freudenberg's theory, that tanning consists essentially of the combination of a weak organic base (collagen) with a phenol (tannin), is also given briefly and lucidly. Strangely enough, Mr. Wilson only becomes obscure in the account of the Procter–Wilson theory of tanning. In this theory, a positive charge on the collagen fibres is held to arise from the unequal distribution of the hydrogen ions in an acid solution on either side of the semi-permeable surface of the colloidal fibril, the collagen acting as a weak base; "each tannin particle is negatively charged" and the tannins may, therefore, be regarded as organic acids with colloidal anions. Unfortunately there is no consideration of the possibility that diffusible or non-diffusible organic acids may have very different effects on the potential of the collagen fibril. It is also assumed that there is an unequal distribution of diffusible ions between the bulk of the liquid and a surface film of liquid localised round the tannin particle. Moreover, "it makes no difference to the theory whether the tannin particle is solid, like a gold particle, or a jelly

particle capable of absorbing solution." The assumption, that generalisations derived from a study of two liquid phases separated by a membrane can be applied to the case of a liquid phase and a surface film, might have passed muster in 1916, when the theory was first promulgated, but can hardly be expected to do so in 1930, since the ten years that have just passed have shown that the laws of matter in bulk cannot be applied, without modification, to matter condensed in films. In spite of its mathematical form, the Procter–Wilson theory of tanning has not shown any signs of developing in the fourteen years that have passed since it was enunciated. A reconsideration of this interesting theory from first principles, but made in the light of modern knowledge, would be welcomed from its part author.

Dr. Wilson gives a summary of recent work on the chemistry of chromium, a very lucid account of Werner's theory of the constitution of the salts of chromium and of the applications of this theory to the chemistry of chrome-tanning. The chemistry involved in other types of tannage is dealt with as far as possible, in view of the scanty supply of experimental data.

A chapter on the chemical composition of leather is included, with detailed instructions for carrying out all the analytical operations required to obtain a full analysis of either vegetable or chrome leather. In the account of the method for analysing for glucose, the inclusion of Munson and Walker's table for converting the mgrms. of copper oxide obtained into their equivalent weights of dextrose, will be of great value to analytical workers. A table of analytical results for eighteen typical samples of shoe leather is also a valuable addition to the volume.

The book is published by the American Catalog Co., and the clearness of the type and of the printing of the numerous photo-micrographs calls for considerable praise. The price charged, however, will strike English readers as high; it would appear to be about double that at which a volume of the same size and standard of production would be listed by the publishing houses in this country.

DOROTHY JORDAN LLOYD.

A CHEMICAL DICTIONARY. By J. W. D. HACKH. Pp. viii+790. London: J. & A. Churchill. 1930. Price 42s.

This dictionary has been designed to bridge the gap between the large library chemical and technological dictionaries and the smaller semi-popular dictionaries, and it serves its purpose well. The amount of information which has been compressed into the space of 790 pages is surprising, and it is not confined solely to chemistry, but includes also the cognate sciences. For instance, an excellent outline is given of Ehrlich's side-chain theory, illustrated with diagrams, and there are concise definitions of the most recent biochemical terms. Similarly, the theories of physical chemistry are briefly outlined, and such conceptions as the Pauling structure, Rydberg's formula, and Langmuir's theory are dealt with at sufficient length to make them clear.

A point of particular value to the analyst is that the proportions of the constituents of many of the recognised reagents are given, such as, for instance, the composition of Pavy's solution, Mayer's reagent, etc.

Dr. Hackh acknowledges in his preface his indebtedness to Dr. Julius Grant, who has revised the more strictly chemical items in the dictionary, and who may be congratulated upon his success in giving the work something of an international character.

An interesting feature of the dictionary is the full series of the portraits of those whose names are familiar to chemists all over the world, but whose features (except in a few outstanding instances) are but little known outside the country of their work.

The few points that are open to criticism sink into insignificance when contrasted with the immense amount of excellent work, and the dictionary, as a whole, may be thoroughly recommended as a production which will be of the greatest use to everyone whose work is directly or indirectly associated with chemistry.

EDITOR.

Publications Received.

ATMOSPHERIC CORROSION OF METALS. THIRD EXPERIMENTAL REPORT TO THE ATMOSPHERIC CORROSION RESEARCH COMMITTEE. A Discussion held by the Faraday Society, 1929. Price 5s. 6d.

THE PRACTICE OF SPECTRUM ANALYSIS WITH HILGER INSTRUMENTS. Fourth Edition. Pp. 38. Adam Hilger, Ltd. 1929. Price 1s. 6d.

THE DETECTION AND INVESTIGATION OF POISONS BY SPECTROSCOPY. Pp. 18. Adam Hilger, Ltd.

ALPHABETICAL INDEX AND NUMERICAL LIST OF FEDERAL SPECIFICATIONS PROMULGATED BY THE FEDERAL SPECIFICATIONS BOARD (Complete to Nov. 1, 1929). Circular No. 378. Bureau of Standards, U.S.A.

TANNING MATERIALS OF THE BRITISH EMPIRE. London: The Imperial Institute; published by John Murray. 1929. Price 2s.

HELLIGE-DUBOSCQ COLORIMETERS AND NEPHELOMETERS. (Apparatus and Description of Methods.)

A TEXTBOOK OF BIOCHEMISTRY. By A. T. CAMERON. Second Edition. Pp. xi+482. London: Churchill. Price 15s.

A COURSE IN PRACTICAL BIOCHEMISTRY. By A. T. CAMERON and F. T. WHITE. London: Churchill. Price 8s. 6d.

THE SCIENTIFIC EXAMINATION OF PICTURES. By A. M. DE WILD. London: G. Bell & Sons. Price 15s. net.

Historical and Scientific Investigation—Blue Pigments—White Pigments—Yellow and Brown Pigments—Red Pigments—Green Pigments—The Restoration and Preservation of Paintings—*X*-Ray Photography of Pictures—Examination by means of Ultra-violet Rays.