Physical Methods, Apparatus, etc.

Particle Size by Spectral Transmission.
E. D. Bailey (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**,
365–370)—A method is described for determining
two-parameter size distributions from transmission
measurements on suspensions in the visible and
near infra-red, based on an empirical relationship
between scattering, particle size, refractive index,
and wavelength.

Suspensions are prepared by means of a pestle
and mortar, and the concentration is adjusted to
give about 20 per cent. transmission with blue light.
Transmissions are measured at 14 points over a
wavelength range of 0.4–$2.0\,\mu$, a monochromator
and photo-cell or vacuum thermopile being used.
The results are plotted and compared with a stan-
dard family of curves computed from the distribu-
tion law of Lansing and Kraemer (*J. Amer. Chem.
Soc.*, 1935, **57**, 1369). The experimental curves

are evaluated in terms of r_0, the radius value of the maximum of the distribution, B, the non-uniformity coefficient which defines the spread of the curve, and a percentage expressing the extent to which the selected distribution law is obeyed. The method of analysis is rapid, requiring only 2 hours, but is limited to non-absorbing materials and to particle sizes for which optimum scattering occurs in the wavelength ranged used ($r_0 <$ about $1\,\mu$.).

The results are in fairly good agreement with those obtained with the ultracentrifuge.

Comparisons of particle-size distributions in samples of anatase, bentonite, rutile, and zinc oxide are given.   B. A. S.

Internal Standard Method of Spectrographic Analysis as applied to the Determination of Lead in High-Purity Zinc.   L. Griffith and J. N. Kirkbride (*J. Soc. Chem. Ind.*, 1946, **65**, 39–48)—

An investigation has been made into the fundamental features of the internal standard method of spectrographic analysis, the controlled direct current arc-method for the determination of lead in high-purity zinc with bismuth as the internal standard being used as the example. The working conditions for this investigation were standardised, and, using the average deviation as a criterion, a precision of 2 per cent. over the lead range 0·025– 0·003 per cent. was reached.

The principal error arises from the failure of the Eastman " 33 " plates used to obey the reciprocity law. Reduction of this error can only be achieved by using plates having little reciprocity failure, since the use of the direct-current graphite-arc precludes utilisation of a relative intensity calibration. Allied to this, is the error due to the intermittency effect, which can be reduced by speeding up the stepped sector.

The second error is the Eberhard effect, which occurs when there is a large range of density over a small distance of plate; this gives rise to local differences in concentration of the developer, and produces an erroneous density - intensity curve. The best solution to this problem seems to be increased agitation of the plate during development.

Bismuth is not an ideal internal standard since the lead line 2833·07 A and the bismuth line 2897·98 A are not a perfectly homologous pair. Although this constitutes the third source of error, it is doubtful whether any improvement is possible.

The error involved by the use of the direct current arc is certainly less than the errors already enumerated.   D. A. P.

Comparison of Optical and Electron Microscopy of Pigments.   D. L. Tilleard and N. D. P. Smith (*J. Soc. Chem. Ind.*, 1946, **65**, 261–264)—

The high resolving power of the electron microscope enables problems relating particle size and shape to pigment colour, wetting, and other characteristics to be investigated. The small numerical aperture (0·001 radian) employed and the resultant depth of focus (10 μ. as opposed to about 0·4 μ. with N.A. 1·25) enables useful stereoscopic micrographs to be obtained.

Most pigments can be dispersed in a mixture of linseed stand oil and white spirit by grinding on a glass plate with a spatula. A drop of this dispersion is placed on a supporting film prepared by allowing a drop of a 2 per cent. solution of nitrocellulose (high nitrogen content; medium viscosity) in amyl acetate to fall on the surface of clean water. When the spirit has evaporated, selected portions of the film are attached to supporting screens and the excess oily matter is removed with white spirit. *Comparison of optical and electron micrographs*— The electron micrographs of various pigments frequently show particles whose size is below optical resolution. The detail of the shape of many particles in the region of uncertain optical resolution (between 0·5 and 0·25 μ.) is disclosed. In the electron micrograph some particles of red earth pigment appear grey, indicating that they are extremely thin; others suggest a hexagonal shape similar to that observed in micrographs of clay. The micrograph of "ferrite" yellow shows rod-shaped particles, 0·03 to 0·1 μ. wide and about 0·5 μ. long, whereas another synthetic iron oxide pigment, Turkey Red, shows rounded particles less than 0·1 μ. diameter. The varying sizes and shapes of zinc oxide pigments to be seen in the electron micrographs reproduced may be related to methods of manufacture; the electron microscope reveals the regular crystalline shape of the particles of all the zinc oxides examined. Differences in samples of lead chrome pigments are also seen, and may be related to the lead sulphate content of the pigment, although the tendency to change from monoclinic towards orthorhombic habit with an increase in lead sulphate content cannot be deduced from the micrographs. When interpreting electron micrographs it is necessary to remember that the particles seen may be only the smallest in the pigment; particles commensurate with the size of the whole field of the microscope may be neglected; and that the quantity of material in the whole field is very small and, except in special circumstances, quantitative conclusions are not justified. G. A. B.

Oxide Films Formed on Alloys at Moderate Temperatures.   Electron Diffraction and Electron Microscope Study.   E. A. Gulbranson, R. T. Phelps, and J. W. Hickman (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 640–652)—

This paper describes the study of oxide films by reflection and transmission methods of electron diffraction, in addition to electron microscope studies. The alloys studied were those consisting principally of iron, cobalt, nickel, and chromium, and are typical commercial protective, refractory, magnetic, and sealing

alloys. A miscellaneous group of experimental alloys has also been included.

Electron diffraction results—(1) Iron and chromium ions diffused more readily to the surface of the oxide film than the other metal ions. (2) Stratification of oxides occurred even for films 100 to 300 A thick. (3) Chromium sesquioxide was always observed in the oxide films on the protective or refractory alloys examined; where stratification occurred, chromium sesquioxide appeared to be in contact with the substrate. (4) Nickel monoxide was never observed on the surface of the film, but sometimes occurred in the body of the film; this may indicate a low diffusion rate for the nickel ion. (5) Solid solution of two simple oxides to give the spinel-type structure may occur. (6) Except for iron and chromium, metals constituting not more than 5 per cent. of the alloy did not occur as simple oxides on the outer surface, but appeared to form spinels in the body of the film. (7) Simple oxides of cobalt, manganese, silicon, vanadium, and tungsten were not observed.

Electron microscope results—(1) The thin oxide films consisted of a continuous film of oxide crystals 100 to 1600 A in size. (2) The oxide films were not of uniform density and the crystals had irregular shapes. (3) Longer oxidation time increased average crystal size. (4) Crystals on non-protective alloys such as mild steel, at 250° C., were of the same size as those found on protective and refractory alloys at 600° C. (5) At a given temperature, a correlation may exist between crystal-size of the oxide and the protective quality of film. (6) Thickness of boundary zone between crystals in the mosaic structure was of the order of 50 A.

Electron diffraction data, and numerous electron micrographs of oxide films on stainless steels, nichrome, cobalt-iron, chrome-iron, silicon-iron, manganese-iron, Iconel, and mild steel are reproduced. E. G. S.

Determination of Extinction Corrections in Infra-red Analysis of Gaseous Hydrocarbon Mixtures. J. H. Lee (*Ind. Eng. Chem., Anal. Ed.*, 1946, 18, 659–661)

—The usual procedure in the infra-red analysis of gaseous hydrocarbon mixtures involves the calculation of various corrections to be applied to the observed extinction coefficients of the mixtures. The sources of error for which corrections must be applied are, energy scattered within the instrument, the structure of the absorption band, and inter-molecular action. By use of the relation, $E_c = E_o(1 + \alpha E_o)$, where E_c and E_o are, respectively, the corrected and the observed values of log. I_o/I, and α is a constant for the particular instrument, gas, and absorption band concerned, one method of correction, allowing for the errors caused by the several factors, can be applied. When molecular interaction has an appreciable effect on absorption, addition of a diluting agent such as air is desirable if the proposed method of correction is to be used. Details of the method for calculating corrections to be applied directly to observed extinctions are given. B. A.

Preparation of Powdered Materials for Electron Microscopy. M. C. Schuster and E. F. Fullam (*Ind. Eng. Chem. Anal. Ed.*, 1946, 18, 653–657)

—The aggregates in powdered materials must be adequately dispersed to furnish electron micrographs suitable for statistical particle-size distribution analysis. Specimens are mounted on thin (10 to 30 mμ.), electron-transparent, resin films which are in turn supported on 0·3-cm. diameter metal screens having perforations of 20 to 100 μ. Deflocculation may often be brought about by choice of a mounting medium with suitable wetting properties. A common method of film formation is to drop a small amount of resin solution on water and allowing it to spread and dry. Screens may be placed on it and picked up from beneath with an annular tool. The thickness of the film is determined by the concentration and spreading coefficient of the solution and the volatility of the solvent. A purified nitrocellulose dissolved in amyl acetate is in general use. Mercury is, theoretically, an excellent substrate, but the manipulative difficulties are considerable. Tougher films are formed by Formvar 15/95, Grade E, a polyvinyl formal polymer. A solution (0·2 to 0·4 per cent. by weight) in ethylene dichloride, which should be stored in a brown bottle, is spread evenly on to a microscope slide and held vertically in an atmosphere of the solvent to dry. The film is scored round the edge with a needle and floated on water by inserting the slide obliquely. Breathing on the dry slide and application of additional coats of solution round the edge facilitate stripping. Films showing interference colours are too thick.

Powders that can be dispersed in a volatile liquid may be mounted by placing a drop of suspension on a filmed screen and allowing it to dry. An adaptation of the turpentine dispersion method in optical microscopy has been devised. The pigment in a drop of turpentine is rubbed out with a glass rod on a microscope slide until dry. The dispersion is flooded with resin solution and floated on to water. Screens are placed on areas selected under an optical microscope. This method is most suitable for uniform powders 0·5 μ. and greater. Many excellent dispersions may be prepared by working a pigment suspended in a viscous resin solution on a plate glass table with a stiff, stainless steel spatula. The proportion of specimen to resin for a suitable concentration of particles in the field depends on particle size and can only be found by experience. Substances too soft to rub out mechanically may be made brittle by freezing with solid carbon dioxide.

Dispersion by supersonic and other vibratory methods has not been entirely satisfactory. A small pile of dry powder placed on a filmed slide may often be dispersed by passing a spark from a Tesla coil across the under side of the slide. Mechanical mills for dispersion have the disadvantage of requiring a large sample. The resin containing a dispersed material is made into a thin film by methods similar to those already described for clear films. Alternatively, the suspension may be evaporated to the consistency of thick cream and drawn down on a slide with a spatula by a series of short strokes. Samples prepared in this way exhibit fewer holes in the film. Large-size powders (1 to 10 μ.) may be mounted, using dibutyl phthalate or a high-boiling hydrocarbon as suspending medium and drawing down as before on a film-covered slide.

Electron micrographs of different types of mounts showing the particle size and shape of iron oxide, antimony oxide, chromium oxide, zinc oxide, calcium carbonate, and ultramarine are reproduced.

TABLE I. RESINS AND SOLVENTS

Resin	For dispersion[a]	Recommended solvents		
		For mounts cast on glass[b]	For mounts spread on water[c]	For mounts drawn down on glass[c]
Nitrocellulose (Parlodion)	Cellosolve acetate	Methyl acetate Ethyl acetate	Methyl acetate Ethyl acetate Amyl acetate Cellosolve acetate Octyl acetate	Ethyl acetate Amyl acetate
Formvar 15/95	Dioxan plus a few drops of dimethyl dioxan Nitroethane	Ethylene dichloride Nitroethane	Dichloroethylene Propylene dichloride Ethylene dichloride plus 0·1 per cent. of oleic acid Nitroethane 1:1 Dichloro-2-nitroethane	Dioxan Nitroethane
Polystyrene	Xylene	Ethylene dichloride Toluene	Benzene Toluene Xylene	Benzene Toluene
Methyl methacrylate or cellulose acetate	Methyl amyl ketone Methyl ethyl ketone plus 10 per cent. of *iso*phorone	Acetone	Methyl ethyl ketone Methyl amyl ketone *Iso*phorone	Methyl ethyl ketone

[a] 10 to 20 per cent. solutions, approximately.   [b] 0·1 to 0·5 per cent. solutions, approximately.   [c] No fixed concentration; suspension allowed to dry to suitable consistency.

G. A. B.