ANGULAR CONSTANTS OF MICROCRYSTALLINE PROFILES AND SILHOUETTES IN THE CONCLUSIVE IDENTIFICATION OF SUBSTANCES, II. MICROSUBLIMATION, MICROPRECIPITATION, TRIBROMOPHENOL BROMIDE, PICRIC ACID, MORPHINE, MERCURIC IODIDE, TRICHITES*

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A preliminary paper** cites the advantages of the micropreparation of derivatives having measurable profile angles for the conclusive identification of substances. This thesis has been recently corroborated by Hartshorne.*** Some further data is now offered along the same lines.

Crystals are produced directly on the slide or in some kind of tube by sublimination, by precipitation, by evaporation, by the cooling of a melt, or by various combinations of such methods. Among these individual forms, those are selected which are the simplest geometrically and the outlines of which are the sharpest, especially under high magnification. A high degree of symmetry is also indicative of material suitable for angular measurements. Parallelograms and hexagons with the simplicity of line drawings are often to be found.

Microsublimation, recently ably discussed by Hoffman ****, when properly carried out often yields crystals suitable for profile angle measurments. Conditions *on the condensing surface* seem to be the critical factors involved. A maximum temperature compatible with condensation in the solid condition affords optimum results. A maximum time for reworking and enlarging the sublimed crystals is also conducive to perfection of form. A minimum of material sublimed favors suitably spaced individuals rather than useless continuous films. The optimum temperature *on the condensing surface* may be obtained experimentally by placing thereon grains of substances having known melting points, or, more roughly, by means of a thermometer. The proper *condensing temperature* is probably identical with the *sublimation temperature* as obtained in the apparatus described by Hoffman****. A list of optimum temperatures for the condensation of numerous substances is to be found in the paper just cited. Twelve hours—overnight—is a convenient "digestion" period for the sublimate at the optimum temperature. A tenth of one milligram is a convenient quantity for sublimation.

An excellent cell, consisting of a brass ring 1 mm high and about 1 cm in diameter, conveniently cut from the barrel of an old Bunsen burner, closed below by metal foil or a glass slide and above by a glass slide, has proven satisfactory for atmospheric sublimations in this laboratory. The cell rests upon a circular hot plate bored diametrically to provide a thermometer well. The metallic ring forming the slides of the cell prevent sublimation upon the cell wall and acts in a lens-like manner to

*Contribution from the chemical laboratories of the University of Oklahoma.

**A. C. Shead, "Angular Constants of Microcrystalline Profiles and Silhouettes in the Conclusive Identification of Substances," I. Okla. Acad. Sci. 15, 86 (1935).

***N. H. Hartshorne, "Identification of Some Aromatic Nitro Compounds by Optical Crystallographic Methods," J. Chem. Soc. 1830 (1934).

****H. Hoffman, Jr. and W. C. Johnson, "Analytical Sublimation with Special Reference to the Field of Micro sublimation." J. Assoc. Off. Ag. Chem., 13, 367 (1930)

concentrate a small sublimate in a restricted area on the condensing surface, which is conducive to sensitivity.

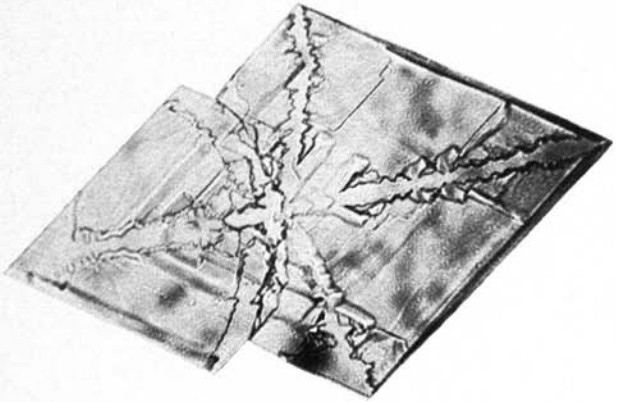
Microprecipitation must be carried out in a special manner to provide crystals suitable for profile angle measurements. The precipitation is carried out at maximum temperatures compatible with the melting point and volatility of the substance under examination. The *clear hot saturated solution* is obtained by decantation or filtration and then evaporated until the solute begins to separate at the maximum temperatures permitting the appearance in the solid phase. As soon as the precipitate begins to appear under these conditions, the solution is set aside to cool slowly. As micro-amounts of solution have low heat capacity, they are best treated in a small tube held in the mouth of an erlenmeyer flask by a cork segmented to permit the escape of steam. The comparatively large body of hot water in exterior contact with the solution under treatment through the walls of the containing tube permits the requisite slow cooling when the system is set aside. The preliminary evaporation of the hot solution is conducive to the formation of well-shaped nuclei, by digestion. These serve to "seed" the solution and to determine the perfection of the larger crystals that grow upon them as a basis by reason of the subsequent slow cooling. The precipitate, filtered from the hot saturated solution, will be found to be unsuitable for micromeasurement, but if sublimable, may be dried and submitted to that operation.

Tribromophenol bromide may be precipitated as just described at a temperature not exceeding its melting point (92-96°C) by hot saturated bromine water from a hot dilute solution of phenol, carbolic acid, or an allied compound such as salol, salicylic acid, benzenesulfonic acid, etc. The precipitate, best collected on a porous glass or biscuitware filter, is dried at low temperatures and sublimed in the cell, previously described at a hot plate temperature of 110°C (uncorr.) and condensed on a glass slide heated to 70°C by the unshielded hot plate, 1 mm distant. The filtrate was treated at waterbath temperature (ca. 70°C) as described under "microprecipitation." The common form of separating by both methods is the simple parallelogram with an acute angle of 69.6° (sublimed) or 69.9° (precipitated) and an obtuse angle of 110.4° (sublimed) or 110.2° (precipitated). The hexagonal form is rare but when it occurs has two apicial angles closely approximating and probably identical with the obtuse angle of the paralellogram (111.0° observed). Each of the four other angles of the hexagon averages 124.5°. Plate 1, Fig. 1, shows sublimed tribromophenol bromide and Fig. 2, the precipitated compound (Magnification, ca. 225X).

Picric acid, formed by nitration in the usual way of phenol and allied compounds as mentioned above, mono nitro-, dinitrophenol, etc., was submitted to microsublimation and microprecipitation by the general methods as described. Since picric acid tends to condense in a liquid condition from the vapor phase it had to be sublimed at a temperature much below its melting point (122.5°C); namely, at a hot plate temperature of app.105°C and a temperature on the condensing slide of about 65°C. Likewise superheating of an aqueous solution in the precipitation method must be avoided as molten picric acid solidifies as trichites rather than in the desired crystalline form. The presence of an acid salt of sulfuric acid and an alkali metal facilitates the crystallization of picric acid, but does not affect its crystal form. Spontaneous evaporation of aqueous solutions of picric acid also often yields good crystal forms. There are at least two sets of related parallelograms and hexagons. The commonly met parallelogram has an acute angle of 87.3° (sublimed), 86.5° (precipitated) and an obtuse angle of 92.7° calc. (sublimed) and 93.5°

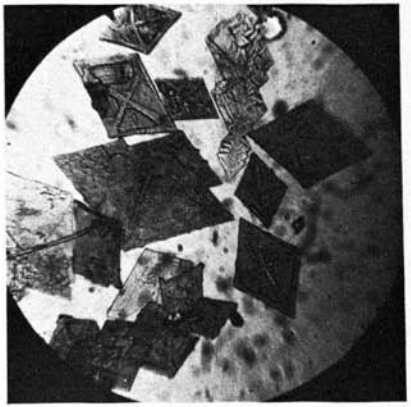
PLATE I.

Fig. 1



Tribromophenol Bromide Sublimed 225 X

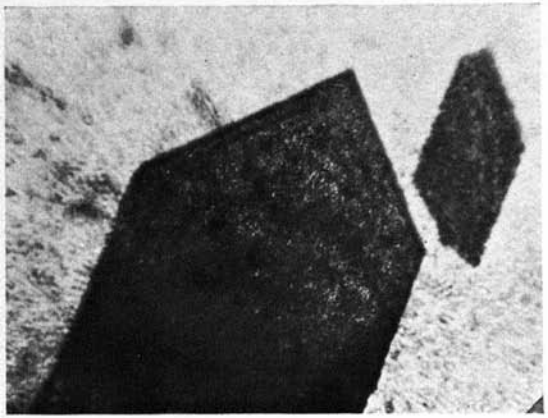
Fig. 2



Tribromophenol Bromide Precipitated
110 X

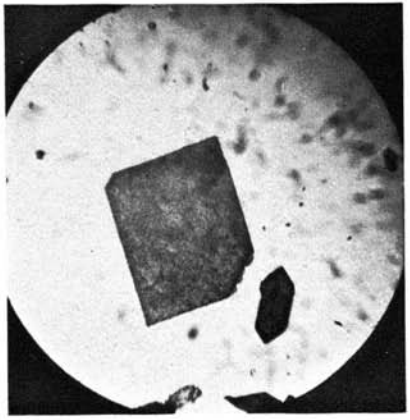
PLATE II.

Fig. 1



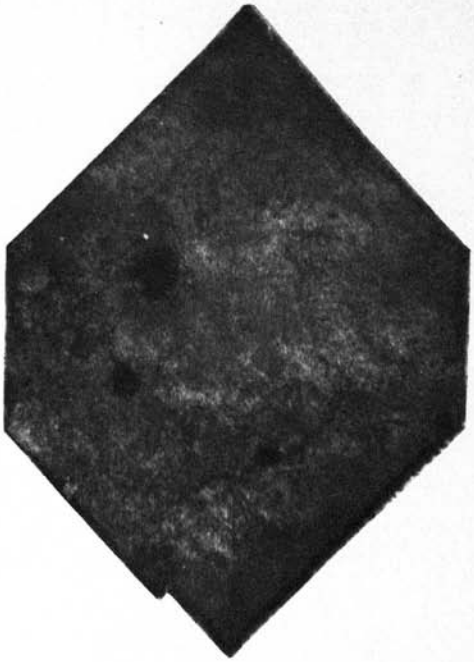
Picric Acid Sublimed 225 X

Fig. 3



110 X

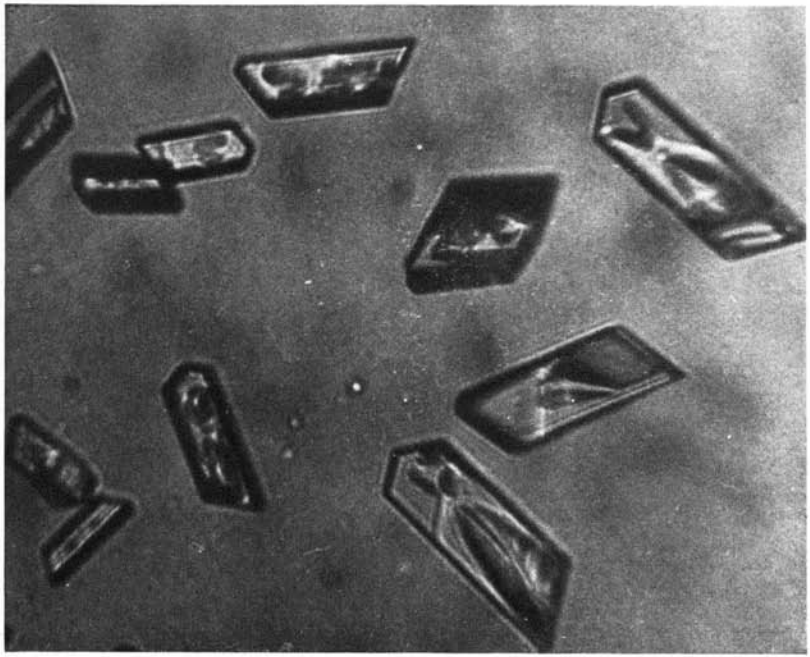
Fig. 2



Picric Acid Precipitated 225 X

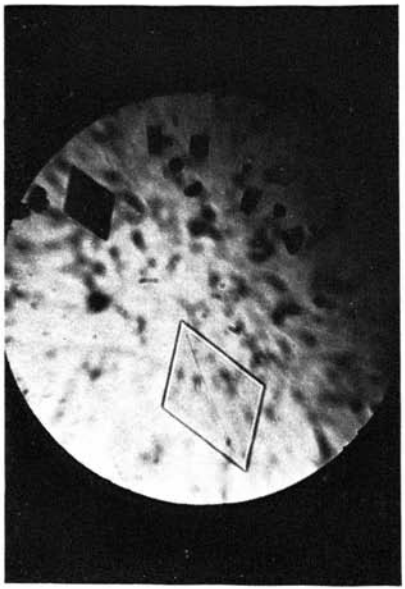
PLATE III.

Fig. 1



Morphine Sublimed 900 X

Fig. 2



Mercurie Iodide Sublimed 110 X

(precipitated). The two apicial angles of the corresponding hexagon, each measure 87.3° (sublimed), 86.5° (precipitated) and each of the four other angles measure 136.6° (sublimed), 136.7° (precipitated). The rarer parallelogram has an acute angle of 71.5° and an obtuse angle of 108.5° while the two apicial angles of the corresponding hexagon each are 108.5° and the four others each measure 126.3°. Plate II shows sublimed hexagonal picric acid in its commoner form (Fig. 1) and the same, precipitated (Fig. 2). The common parallelogram (precipitated) is shown in Fig 3 (Magnification 225X).

Morphine was sublimed at a hot plate temperature of 205°C. The acute angle of one parallelogram measured 59.1° with an obtuse angle of 120.9°. The two apicial angles of the hexagon each measured 118.2° while the four other angles each measured 120.9.° Plate III, Fig. 1, shows morphine crystals magnified about 900X.

Mercuric Iodide was sublimed at a hot plate temperature of 100°C, corresponding to a condensation temperature on the receiving slide of 60-65°C. The acute angle of the parallelogram measures 64.6° and its obtuse angle 115.4°. A drop of hot solution of $HgCl_2$ on a slide will yield an excellent crop of the same kind of parallelograms on addition of a droplet of conc. HI from the sharp point of a *splinter of glass*. Plate III, Fig. 2, shows parallelograms of sublimed mercuric iodide.

Trichites, or curly hair-like crystallites are formed by sudden cooling of molten substances, especially when the latter is in emulsion dispersed through an immiscible liquid. These non-diagnostic forms are often figured as microtests for different substances and were often noted while working with tribromophenol bromide and with picric acid suspended in water.

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