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ANGULAR CONSTANTS OF MICROCRYSTALLINE PROFILES AND SILHOUETTES IN THE CONCLUSIVE IDENTIFICATION OF SUBSTANCES

Preliminary Paper

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Optical constants, always of vital importance in the conclusive identifications of substances, especially in forensic applications of microchemistry, assume an enhanced value in ordinary analytical procedure in dealing with poisons or violent explosives or where the commonly applied melting and boiling points are inapplicable as in cases of sublimation or decomposition of the substance under examination. Also, indices of refraction and angular measurements often are obtainable from mixtures which would have to be separated and purified before applying the ordinary tests for melting and boiling points. Microchemists, themselves, have singularly neglected micromeasurements on the angles of what may be termed the microcrystalline profile or silhouette, though these values may be accurately and quickly determined by the camparatively inexperienced operator equipped with relatively inexpensive apparatus, such as ordinary microscope fitted with a camera lucida. Often quite accurate measurements may be taken by protractor and straight edge from the

many available projections and microphotographs already recorded in the literature. Owing to the wide range of conditions and variety of reagents available to the microchemist, the production of microcrystals suitable for angular measurement is almost assured in any given case. It is true that angular measurements as known to the crystallographer, are made only with difficulty upon the minute individuals obtained on the microscopic slide. However, numerous forms may be produced having a tabular or analagous habit with maximum extensions in two directions and a minimum in the third, so that under the influence of gravity they will present a uniform facies for the examination of the profile or silhouette from which the constant angles may be consistently obtained. Since these angles must be some function of the actual interfacial angles, some law corrollary to that regarding the constancy of interfacial angles must apply to them with equal validity. That such corollaries have been tacitly accepted as axiomatic is evidenced by the published data, mostly on plant chemistry by such authorities as Molisch, Zimmerman et al, to be found in the literature. The constant citation of these meager results and the reproducibility of the published constants tends to support the idea that such values may be usefully applied to the conclusive identification of substances obtainable in a microcrystaline condition of a certain habit.

In support of this view, some data was experimentally obtained and the results compared with published constants in certain cases.

METHODS

The operations required in the production of the micro crystals is detailed in each individual case. The preparations were made on ordinary microscopic slides and then clamped to the rotating stage of a polarizing microscope. The angle to be measured was centered relative to the intersection of the cross hairs in the eyepiece of the microscope. First one side of the angle and then the other was brought in contact with a given cross hair and the angular rotation read by vernier from the graduated periphery of the rotating stage, in degrees.

POTASSIUM NITRATE

KNO_3 upon spontaneous evaporation from water solution or aqueous extracts of certain match heads, explosives, fertilizers, etc., separates in more or less perfect rhombic shaped crystals, especially around the margins of a drop placed upon the slide. Almost any random field here selected will yield at least one angle measureable under a low power of from 25-50 diameters. The writer obtained as averages of numerous satisfactorily agreeing results, the following values: Acute angle, 79.8°; Obtuse angle, 99.4°; Extinction angle, lying in the acute angle and measured to the nearest side, 38.7°. This compound is useful for identifying the potassium and nitrate ions, even in mixture. For example, the former may be separated as the acid tartrate from fairly concentrated solutions, especially from nitrites in alcohol. The acid tartrate is then gently ignited to the carbonate, on platinum wire, and the latter compound dissolved in a drop of dilute HNO_3 placed upon a slide where it is allowed to spontaneously evaporate.

SILVER DICHROMATE

$Ag_2Cr_2O_7$, may be precipitated from a hot dilute nitric acid solution of say, a silver assay bead on a slide, by a small crystal of chromic anhydride of ammonium bichromate. If the slide be supported on a small micro hot plate of metal and allowed to cool slowly upon the plate, it will yield almost perfect crystals. Any tendency to drying is combatted by adding a drop of hot water from time to time while cooling. When cool, excess

water may be removed by blotting followed by flushing with alcohol for final dehydration. The alcohol must be free from the more active reducing agents. The crystals may be then mounted in canada balsam in thick toluene solution, and examined. The writer obtained as means of numerous agreeing results the following values on rhombohedron shaped crystals: Acute angle, 44.5°; Obtuse angle, 136.3°; Extinction angle, almost in the diagonal connecting the acute angles of the rhomb, 22°.

MERCURIC IODIDE

The form of HgI_2 stable above 126°C is forensically important. This was obtained by dissolving the mixed mercury sublimate from two drops of a medicine in aqua regia repeatedly evaporating to a film on a microslide with excess HCl to remove HNO_3. The film $HgCl_2$ was heated to 126°C and a large drop of water containing a small drop of concentrated HI was led upon the film. Beautiful yellowish rhombs usually separate on cooling. The excess reagent is carefully blotted off and the crystals are allowed to air dry whereupon they are examined as soon as possible owing to the fact that they are unstable at lower temperatures. The writer found as a mean of closely duplicable measurements, an obtuse angle of 115.4°.

PARADICHLOROBENZENE

Paradichlorobenzene was sublimed from a commercial insecticide at as low a temperature as possible from a microcrucible set through a hole in a small strip of asbestos board on a microhotplate. The sublimate

FIG. 1

A. Gypsum. $CaSO_4 2H_2O$.(a)130°.(b),(c)53°.(d)104°.V.
B. Silver Dichromate, $Ag_2Cr_2O_7$.(a)44.5°.(b)136.3°.
C. Potassium Nitrate, KNO_3.(a)79.8°.(b)99.4°.
D. Asparagin.(a)50.7°.(b)129°188'.X.
E. Calcium Tartrate, $CaC_4H_4O_6.4\ H2O$.(a)57.3°.(b)122.7°.
F. Urea Nitrate.(a)49.8°.(b)130.2°.(c)81.8°.(d)98.2°.
F. Urea Nitrate.

was received upon a glass microslide cooled by a small metal cup of water set over the area receiving the deposit. The deposit is mounted in a very small drop of mucilage and covered with a slip. This must be accomplished as quickly as possible as the compound evaporates almost as quickly as the water at room temperature. Most fields contain crystals of no diagnostic value by this method as they exhibit rectangles and parallel extinction. Search, however, will generally reveal measurable angles and a few rhombohedral forms. The writer found the following: Acute angles of 59°; Obtuse angles of 121°; an Extinction angle of 26° lying in the obtuse angle measured to the nearest side. The melting point of the crystals closely approximated the theoretical (53°C).

HEMIN CRYSTALS OF TEICHMANN

Crystals were obtained by the usual methods of biochemical technique from dried human blood. The obtuse angle approximates 120°, and the acute angle is about 60°, as nearly as could be determined from the very small crystals which are also somewhat imperfect. The extinction angle

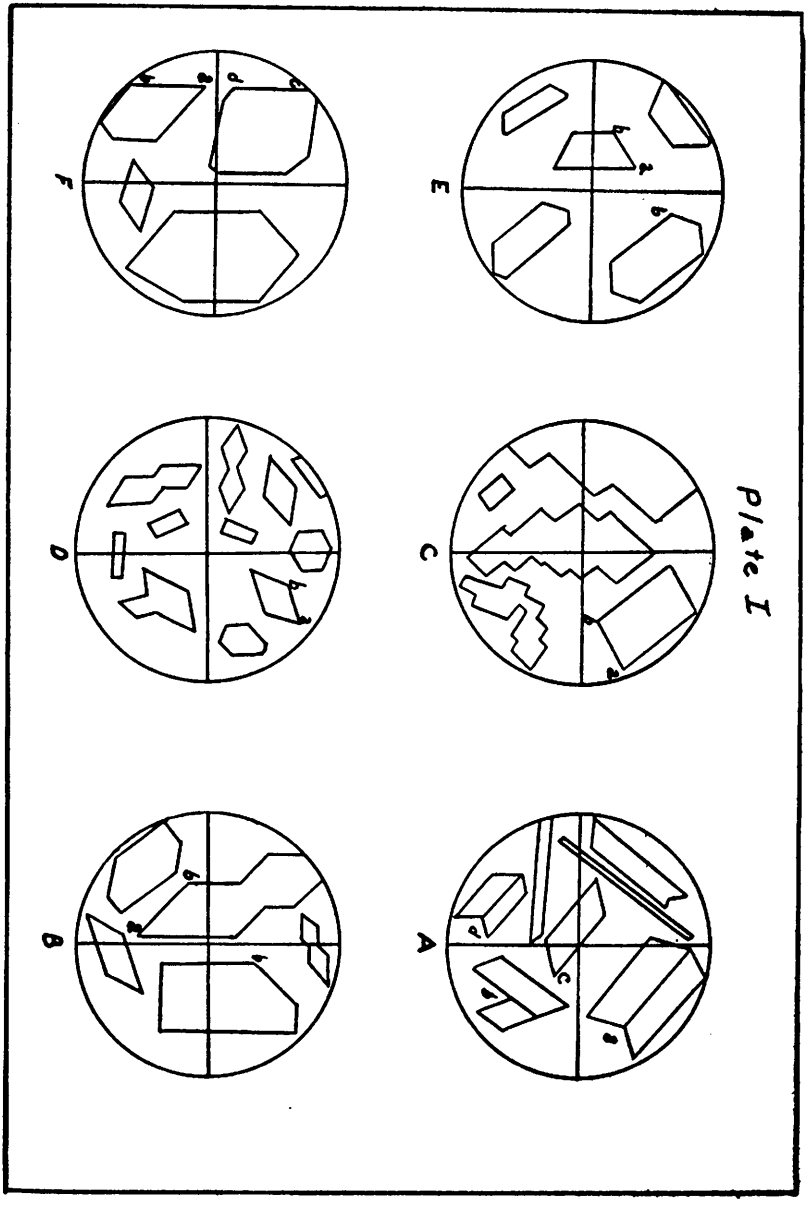

Plate I

TABLE

Profile and Extinction Angles of Crystals with Rhombohedral Habit

Substance	Preparational Method	Obtuse Angle	Acute Angle	Extinction Angle	Twinning Angles, etc.
Asparagin	Spon. Ev. fr. Alcohol	129°18′(X)		//to diagon.	65°(I) on 6 side xls
$Ba(SbO)_2(C_4H_4O_6)_2H_2O$	Tartar emetic+Ba^{++}	128°(IX)			
$BaC_2O_4H_2O$				28°(VI)	
$CdC_2O_43H_2O$	Oxalic Acid +Cd^{++}			24°(Ia)	
$CaC_2O_4H_2O$	Found in cell sap				141°31′(VII)
$CaSO_42H_2O$	Fr. 2% H_2SO_4	127°31′(V)	53	39°(V)	104, 130 Tw (V). 65° 36′ Hemipyramid(I)
$CaC_4H_4O_64H_2O$(VIII)	$Ca(C_2H_3O_2)_2$+$H_2C_4H_4O_6$ or its neut. salts		57°30′	//bisector acute angle	
P-Dichloro Benzene	Sublimation (low tem.)	121°	59°	26°	
Hemin				34.6°	
$HgC_2H_3O_2$	From Hot H_2O				Terminal ang. 100° on six sided xls(III)
HgI_2(+126°C)	Fr. Hot dilute HI	115.3°			
KNO_3	Spon. Evap. fr. H_2O	99.4°	79.8°	38.7°	
KNO_3	Spon. Evap. fr. H_2O	99°44′(X)			
$AgC_2H_3O_2$	From Hot H_2O				Terminal ang. 90° on 6 sided xls(III)
$Ag_2C_2O_4$	From Hot H_2O		58°(Ib)		
$Ag_2Cr_2O_7$	Fr. hot dil. HNO_3	136.3°	44.5°	22°	
$Ag_2Cr_2O_7$			43°(I)		
Na_2PtCl_6				22°(IV)	
Urea Nitrate	1 water soln		82°(IV)		
Urea Nitrate	urea or U-nitrate : 1 colorless conc. HNO_3	98.2	81.8		
Urea Nitrate		130.2	49.8		Term. angles 99.5 on hex. forms

with the elongation was found to average 34.6° as a mean of about 70 closely agreeing measurements. There is marked absorption of plane polarized light in the extinction direction.

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