C. PHYSICAL SCIENCES

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

R. C. SHANK, M. D. GRIMES, and A. C. SHEAD
University of Oklahoma

The theory of two dimensional crystallography has been discussed in previous papers. (3,4,5,6) The purpose of advancing this new theory might best be shown by pointing out some of the uses to which it can be adapted. It is a constant of the molecule as a whole and should be used in the same manner as the boiling point, freezing point, or index of refraction constants. It may be used to distinguish between homologs in a given series having the same or no functional groups or between metamers in organic compounds. It can be used to differentiate between different hydrates which have the same elementary or ionic composition. In the case of explosive or unstable compounds it will prove its value, as other constants may not be available. And of course it will supplement other constants where they overlap.

The angular constants can also be used to furnish general derivatives. For example tribromophenol bromide has been characterised which is a derivative of phenol. Phenol could be derived from aniline by the diazo reaction or from salicylic acid and certain derivatives of salicylic acid. It could also be used to identify derivatives of several bromophenols. From this short sketch possibilities for the use of angular constants can readily be seen.

In anticipation of the time when the angles of different crystals come within the limits of error, which is 0.2° (2), further classification of the crystals will be necessary. First they may be classified as to the elements or ions present. Next the compounds can be classified as to the solvents and reagents used to make the crystals. A third method of distinction, that has already proved very useful, is the color of the crystals. So far these three methods of classification have been sufficient to characterize any crystals that have been studied.

The crystals presented in this paper belong to the simple symmetrical type. (5) As more crystals are studied it will probably be discovered that the methods of preparation will fall into several different set types along with some special cases. One of these types will be crystallization from a hot acid solution by spontaneous cooling and violent agitation. The crystals are poured upon the microscope slide and the mother liquor poured off at a low pouring angle, the remaining liquid being gently blotted off with filter paper. Six of the crystals in this paper fall under this general type with the concentration of acid being the only variation in their method of preparation.

PREPARATIONS

Lead Chloride **is prepared in the above manner using concentrated hydrochloric acid.**

Lead Sulfate is prepared similarily from concentrated sulfuric acid. These crystals may be washed with alcohol to aid in removing the sulfuric acid which is difficult to blot off with filter paper.

Barium Chloride is prepared from a solution of 1 or 2 parts water to 5 parts hydrochloric acid. Barium chloride is too insoluble in concentrated hydrochloric acid to make suitable crystals.

Meconic Acid is prepared from a solution of 5 parts hydrochloric acid to 7 parts water. Meconic acid is peculiar to opium and therefore can be used to identify it. The best method found for its extraction is given by Annett and Bose. (1)

Helianthine (Methyl Orange) is prepared as given above from a saturated solution containing sufficient acetic acid to transpose the salt.

Benzidine Hydrochloride is prepared from a solution of 1 part water to 5 parts hydrochloric acid by adding a small amount of benzidine. Benzidine is an important dye intermediate.

Benzidine Sulfate is prepared from a very dilute solution of benzidine hydrochloride. Its dilution should be of the order of 1 gm. of benzidine to 1000 c.c. of water to 5 c.c. of hydrochloric acid. To this solution is added sulfuric acid or sodium hydrogen sulfate, diluted 1 to 50, in the ratio of 1 part sulfate to 20 parts benzidine hydrochloride. This may be done in the cold. This procedure will yield mostly hexagons.

If concentrated sulfuric acid is added to a hot solution of benzidine hydrochloride in the ratio of 1 part acid to 5 parts benzidine, parallelograms are formed.

Benzidine itself may be crystallized from hot water with many good angles but few complete crystals. Benzidine is too soluble in hot water to make this a good test and of the three preceding tests the hydrochloride is recommended.

Cupric Ammonia Picrate is crystallized by adding about 4 drops of a saturated solution of picric acid to 1 c.c. of hot cupric ammonia hyroxide. The cupric ammonia hydroxide may be made by precipitating cupric hydroxide, washing, and dissolving in sufficient ammonium hydroxide to make a saturated solution.

Cupric Ammonia Cuprocyanide makes an excellent test for small amounts of cyanide. HCN is distilled by heating a small amount of a cyanide with $NaHSO_4$ or other acid, into 2 c.c. of cuprous ammonia hydroxide until the solution becomes colorless. The solution is boiled until the odor of ammonia is faint and then more cuprous ammonia hydroxide is added until the blue color just remains. Heat to boiling and add 0.5 c.c. of boiling cupric ammonia hydroxide. On cooling and with agitation crystals will form. Allow crystals to subside, decant, wash with distilled water and recrystallize from 10 drops of water and 2 drops of ammonia hydroxide. These crystals are green but on continued digestion they may be converted into large lavender crystals with different angles, which indicate they are probably dimorphous. It is even possible to have this color transformation without the angles changing. This may be explained on the basis of the lavender form being a pseudomorph after the green variety.

The data of the foregoing crystals are given in the following table. Any other desired angles may be calculated by methods already described. (5,6)

BIBLIOGRAPHY

(1) Annett, H. E., and Bose, M. N., Analyst, *47*, 387-91 (1922)
(2) Reichert, E. T., and Brown, A. P., Pub. *116*, 145, Carnegie Institute of Washington (1909)
(3) Shead, A. C., Proc. Oklahoma Acad. Sci., *15*, 86 (1935)
(4) Shead, A. C., Proc. Oklahoma Acad. Sci., *16*, 87 (1936)
(5) Shead, A. C., Ind. Eng. Chem., Anal. Ed., *9*, 496 (1937)
(6) Shead, A. C., Ind. Eng. Chem., Anal. Ed., *10*, 662 (1938)

TABLE

Substance	Preparational Method	Color	Usual Shape	Shoulder or obtuse angle
Lead Chloride	From hot conc. HCl	Colorless	Parallelogram	118.5°
Lead Sulfate	From hot conc. H_2SO_4	Colorless	Parallelogram	104.8°
Barium Chloride	From hot $1H_2O$:5HCl Sol.	Colorless	Parallelogram	92.9°
Meconic Acid	From hot $7H_2O$:5HCl Sol.	Colorless	Hexagon	140.6°
Helianthine (Methyl Orange)	From hot dil. $HC_2H_3O_2$ Sol.	Red	Parallelogram	92.9°
Benzidine Hydrochloride	From hot $1H_2O$:5HCl Sol.	Colorless	Parallelogram	100.4°
Benzidine Sulfate	Special	Colorless	Hexagon	130.4°
Benzidine	From hot H_2O	Colorless	Hexagon	125.2°
Cupric Ammonia Picrate	From hot $Cu(NH_3)_4(OH)_2$	Lt. Yellow	Hexagon	133.0°
Cupric Ammonia	Special	Green	Hexagon	133.7°
Cuprocyanide		Lavender	Hexagon	122.8°