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Bradford Marvin

Joseph J. Garbarino

THE IDENTIFICATION OF BARBITURATES, NARCOTICS, AND PATENTED SPECIALTIES BY X-RAY DEFRACTION

Bradford Marvin and Joseph J. Garbarino

Bradford Marvin received a degree in Biochemical Sciences from Harvard College. During the preparation of this paper, he was serving as a chemist on the staff of the Provost Marshal General's Criminal Investigation Laboratory, Camp Gordon, Georgia. Mr. Marvin has recently returned to civilian life.

Prior to his separation from services, Joseph J. Garbarino was likewise a member of the Provost Marshal General's Criminal Investigation Laboratory. He is a graduate of Saint John's College and is now a member of the New York Police Department assigned to the Chemical Tests for Intoxication Program.—EDITOR.

The police chemist occupies a rather unique position in the field of analytical chemistry, for he is often called upon to analyze unknown materials that are present in only trace amounts, or at best, a pill or single capsule. He faces the additional problem of saving some of the unknown to be used at a later date in court, in accordance with the best evidence rule. This situation has forced the police chemist to adopt suitable micro-chemical techniques in performing his analysis, but even the most refined micro-technique consumes evidence. One of the solutions to this problem, which is quite simple and direct, is to analyze the unknown by means of x-ray diffraction. Unknowns can usually be identified as to the specific barbiturate, narcotic, or patented specialty by comparing the unknown diffraction pattern with the diffraction patterns of known barbiturates, narcotics, or patented specialties. The advantages of this method are twofold; first, and most important, the evidence is not consumed during the analysis, and second, the analysis can be performed in a relatively short time, giving a permanent record of the analysis.

X-ray diffraction analysis is not a new technique. It was described as early as 1919 by Hull (1), who was one of the first to apply x-rays to chemical analysis. Hull stated the basis of the method as follows:

> "Every crystalline material gives a pattern; the same substance always gives the same pattern; in a mixture of substances, each substance will produce its own pattern independently of the other, so that the photograph obtained will be the superimposed sum of the photographs that will be obtained by exposing each of the components separately for the same length of time. This law applies quantitatively to the intensities of the lines (provided the absorption is negligible for each of the components) as well as to their positions, so that the method is capable of development as a quantitative analysis."

Such diffraction patterns are a "fingerprint" of the particular crystalline substance. However, as in fingerprints, there must be a known standard to compare with the unknown before the pattern can be of value.

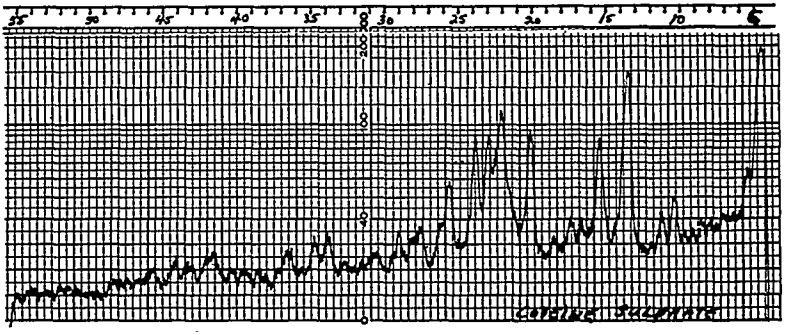

Figure 1

Typical X-Ray Diffraction Pattern of Codeine Sulfate. (All illustrations made with Copper radiation, wavelength 1.54050 A°.)

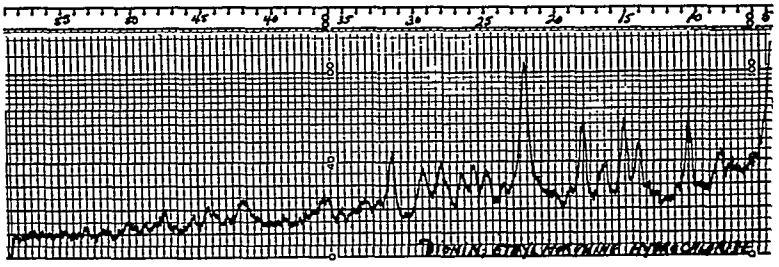

Figure 2

Typical X-Ray Diffraction Pattern of Dionin, Ethyl Morphine.

The diffraction patterns may be recorded by two different methods; first, and most widely used, is the method of recording the diffractions photographically, and reading the pattern from the resulting negative, while the second, and newer method is that of recording the diffractions by means of a modified Geiger-Muller tube mounted on a goniometer. The Geiger tube picks up the diffracted x-rays, which are then transformed electronically into mechanical motion of a pen on a standard recorder. The result using this method is a continuous graph with series of peaks and valleys, the peaks corresponding to the intense lines on the film, and the valleys corresponding with the background on the film. (See figures 1 through 4.) The advantage of this method over the photographic method is quite obvious, for there is no concern about the vagaries in processing film; shrinkage of the film emulsion; misreading the line intensities, for the peaks are recorded on semi-logarithmic paper, and an almost direct reading of the intensities can be made. Both charts and films are quite easily stored, but it is easier to superimpose the charts upon one another than it is to superimpose films when comparing unknowns with knowns.

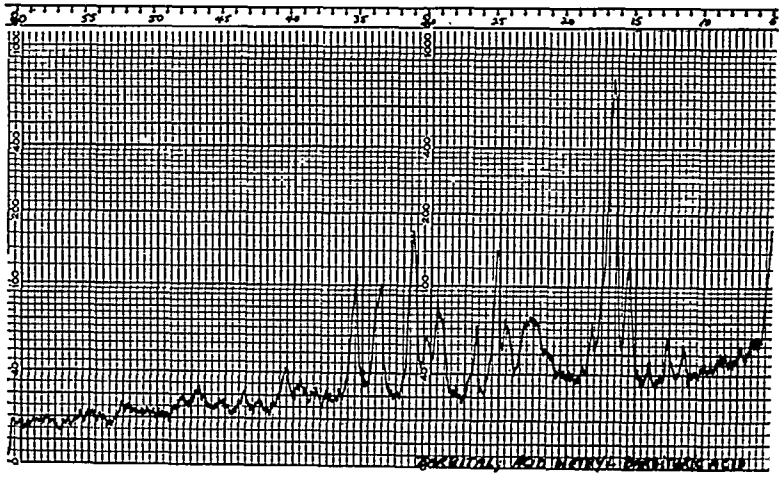

Figure 3

Typical X-Ray Diffraction Pattern of Barbital, Diethyl Barbituric Acid.

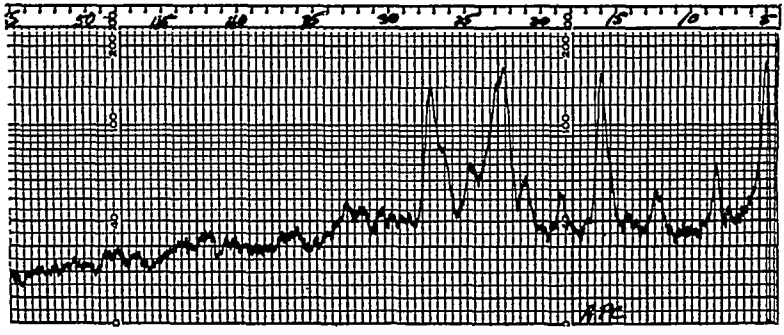

Figure 4

Typical X-Ray Diffraction Pattern of APC Tablet, Acetophenetidin, Acetylsalicylic Acid, and Caffeine.

At the Provost Marshal General's Criminal Investigation Laboratory at Camp Gordon, Georgia, unknown capsules, powders, and tablets are often received for analysis. Many times the sample submitted for analysis is too small for a complete chemical analysis, and it is here that x-ray diffraction plays an important and valuable role in assisting in the identification of the unknown. The method employed is as follows: The unknown substance is ground in a mortar to a fineness which will permit the sample to pass through a 200 mesh sieve. (This is to insure uniform particle size, and also to insure complete randomness of sample. Variations in particle size and incomplete randomness of sample will result in fluctuations of pattern, and it is important to employ standard methods of sample preparation so that unknown patterns will correspond

to known patterns.) The unknown substance is then mounted on a plastic sample holder by means of a spatula, and the sample holder is placed on the machine. While the x-rays are bombarding the sample, it will be rotated through eighty degrees of rotation to the beam of the x-ray, and the diffraction pattern will be recorded on the graph. It has been our experience that eighty degrees of rotation is sufficient for most of the organic compounds, while the inorganic compounds make it necessary to rotate them through over one hundred degrees.

The method of identifying the pattern is that described by Hanawalt (2). This entails measuring and recording the angular displacement of the three most intense diffractions, in order of their decreasing intensities. The angular measure is then converted mathematically into the corresponding "d" value or interplaner spacing. These "d" values will then serve to locate the unknown in the file of known patterns. Once a standard has been found with the corresponding "d" values, it is removed from the file and checked for all the other peaks. A positive comparison is easily obtained by superimposing one graph upon the other and checking for the appearance of all the peaks. If all the peaks of the unknown are found to correspond with the known, not only as to angular displacement, but also as to relative height, it can be said that a positive identification has been made. A pattern file is maintained at the Criminal Investigation Laboratory of most of the known barbiturates, narcotics, and patented specialties.

In the case of "home-made" mixtures, as are commonly encountered in narcotic investigations, the process of identification is somewhat lengthened. Any component in a mixture can be identified with the same degree of certainty as an isolated substance; however, it will be necessary to measure more than the first three intense peaks, since the strongest peaks may include certain peaks of each constituent. At times a narcotic or barbiturate will be bound with lactose, quinine, starch, or some other type of material, and the binder will mask the diffraction pattern of the narcotic or barbiturate. The solution in situations like these is to separate the component parts of the mixture chemically, and run each part separately. Once the unknown has been identified by x-ray diffraction, it must be corroborated by special chemical tests for the substance in question, so that any future court appearance will have greater weight. This corroboration by the classical chemical tests is necessary because of the unfamiliarity of the courts with x-ray diffraction analysis at the present time. Should an unknown be encountered for which there is no pattern in the file, it is our practice to secure a known sample of the material after it has been identified chemi-

cally, and then check the patterns of the unknown against the known. In this manner we keep our file of standards up to date.

Our experience at the Criminal Investigation Laboratory in the application of x-ray diffraction to police chemistry shows that it is a practical and effective method of analysis.

The method increases in effectiveness as we increase our library of standards. Briefly, its advantages are as follows:

a. A characteristic and specific pattern is obtained for any given crystalline substance. (Only approximately five percent of solid inorganic substances are amorphous and will not yield a sharp diffraction pattern.)
b. Only a small amount of sample is needed. (Quantities are low as .0007 mg. have been detected and identified by means of x-ray diffraction.)
c. A permanent record of analysis is obtained.
d. The sample does not need to be pure (only a small percentage of the material is necessary in the absence of heavy absorbing inorganic salts).
e. The material is studied in its "as received" state (provided it is actually in a crystalline state).
f. The sample is not consumed in analysis.
g. The substances present show their true crystal state, hence their true chemical state may be determined.
h. Quantitative estimations are possible with a small change in the procedure described above.

However, it must be recognized that there are some inherent disadvantages to x-ray diffraction which are as follows:

a. Special training and experience is necessary to use this method of identification in the police laboratory.
b. The initial high cost of diffraction equipment.
c. The necessity of having standard patterns for comparison before the diffraction pattern of the unknown can be meaningful.
d. The weak diffraction peaks of some substances.
e. The presence of colloidal mixtures which may give unsatisfactory diffraction patterns.

Despite these disadvantages, the use of x-ray diffraction analysis is of great value to the police chemist because he can identify unknowns as to what they specifically are, whether they are barbiturates, narcotics,

or patented specialties, quickly and simply, getting a permanent record of his analysis, and finishing his analysis with the same amount of sample as he had at the beginning of his analysis. It is with x-ray diffraction analysis that the police chemist can solve the dilemma that he is constantly facing, that of saving part of his unknown for court appearance, while at the same time conducting a complete analysis on the unknown.

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