# X-Rays as an Analytical Chemical Tool

**Symposium on X-Rays as an Analytical Chemical Tool, presented before the Division of Analytical Chemistry at the 122nd Meeting, AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J., 1952**

# Introduction to the Symposium

G. L. CLARK

*Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill.*

WHEN the officers of the Division of Analytical Chemistry of the AMERICAN CHEMICAL SOCIETY decided to feature an x-ray symposium at the Atlantic City meeting in September 1952, it was an immediate recognition of an important area in the entire field of instrumental techniques.

X-ray science is nearly 58 years old. This is young in comparison with the field of classical chemical analysis, but perhaps old in comparison with nuclear chemistry and the numerous modern applications of electronics. X-ray research people are scattered through many university and industrial departments and divisions, although there is a surprising number of x-ray laboratories directly connected with analytical chemical divisions. Perhaps most of the x-ray laboratories are to be found connected with physics, engineering, metallurgy, and other specific fields of applied science. The people who do x-ray testing and research seem to gravitate together as a natural consequence of specialization and become very well acquainted with each other through associations such as the American Crystallographic Association, where the common interest is in the development of techniques and interpretations rather than extensions to the solution of the specific problems such as chemical analysis.

When this great opportunity presented itself, therefore, invitations to x-ray people working in a wide diversity of fields were most enthusiastically accepted. Though x-ray methods need no defense because they are relatively well known and widely accepted, yet the symposium itself was characterized by zeal of almost missionary intensity and a sense of enjoyment felt by all of those who participated, which was communicated to the audience. Here was the chance to aim all of the guns in one single direction. The result was a series of papers over a period of one and one half days that served as a well-balanced cross section of progress in the analytical applications of x-rays. Through the generous and enthusiastic cooperation of the editor of ANALYTICAL CHEMISTRY it is thus possible to bring most of the papers presented at Atlantic City together in this single issue of ANALYTICAL CHEMISTRY. This series constitutes a clear account of the present status of this application and in a sense a valuable 1953 textbook of the subject. Fourteen of the papers actually presented at Atlantic City are included in this symposium, together with two additional papers given earlier at the Pittsburgh Conference. These two papers fit so well into the scheme of this symposium that it has been a great pleasure to add them as valuable contributions.

Attention should be directed especially upon the number of different analytical techniques which employ x-rays. This diversity and versatility always surprise people who are not familiar with x-ray methods. These techniques involve: absorption, the very first property of x-rays discovered by Roentgen in 1895 and now adapted to one of the most powerful methods of automatic chemical analysis (Liebhafsky); fluorescent spectral analysis (Birks *et al.*); photoelectron spectra for surface analysis (Steinhardt and Serfass); direct emission spectroscopy of micro specimens (Castaing and Guinier); low-angle scattering analysis of particle size (Yudowitch); the powerful method of powder analysis which is most familiar to analytical chemists, represented by papers illustrating the most quantitative procedures leading to measurements of highest precision (Straumanis, Klug); a new method of analysis combining absorption and diffraction (Leroux *et al.*) and a practical example of routine examinations of ore minerals which is an outstanding industrial development (Black); new techniques which assist in the evaluation and recording of diffraction data, such as electronic visualization of x-ray patterns (Bertin), and the use of punched card and computing machine techniques (Hudgens and Ross, Merritt, Black); the application of low temperature techniques opening up a field for a vast body of materials which heretofore could not be investigated (Post and Fankuchen); single-crystal techniques applied specifically to problems of analytical chemical interest such as the structure of nickel dimethylglyoxime (Merritt) and of mercury compounds with ammonia, so long familiar in the first group of the qualitative system (Lipscomb); and finally, specific applications illustrated by the studies of clay minerals (Bradley) and pharmaceuticals (Kern) as well as the routine examinations of ores already mentioned.

The presiding officer of the symposium finds it difficult to express adequately the deeply felt appreciation of the enthusiastic teamwork by all the contributors; but it is safe to say that the response by the members of the Division of Analytical Chemistry who listened to the symposium was a spontaneous indication of interest and appreciation to these contributors from so many fields, which was far beyond any expectations.

It is, of course, to be regretted that every single paper given in the symposium could not be included in this published series. Special mention must be made of the contribution by Peter Debye in his modest and whimsical reminiscences of his long association with x-ray research and his pioneer development of the powder diffraction technique and so many other valuable additions to the science of x-rays as we know it today. No one will ever forget this historic occasion and the richly deserved tribute given to Debye by the audience which overflowed the meeting room.

Similarly, the privilege of hearing P. P. Ewald, another one of the great pioneers and present editor of *Acta Crystallographica*, and A. Guinier, of Paris, as special guests, will long remain in the memory of the listeners.

The greatest proof of the value of a symposium of this kind is clearly indicated by the awakened and renewed interest in this young-old science since the Atlantic City meeting. Now it is hoped that the permanent record represented by the publication together of these papers will serve as an added impetus to people who may have interest in this ever-growing area of instrumental analysis. If and when the Division of Analytical Chemistry of the AMERICAN CHEMICAL SOCIETY desires to have another symposium to report further progress, it will find a most willing and enthusiastic group of contributors.

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SYMPOSIUM ON X-RAYS AS ANALYTICAL CHEMICAL TOOL

# Point-by-Point Chemical Analysis by X-Ray Spectroscopy

## *Electronic Microanalyzer*

RAYMOND CASTAING, *University of Toulouse, Toulouse, France,* AND
ANDRÉ GUINIER, *University of Paris, Paris, France*

THE control of the quality of alloys and the development of new ones are obviously based on the knowledge, as complete as possible, of the ultimate structure of the solid. The metallographic microscope shows that most of the usual metals are not homogeneous but are formed by the aggregation of constituents of varying nature: They are differentiated from each other by their aspect in photomicrographs in such a way that it is possible to determine the size, the shape, and the distribution of the grains of the various phases; but the microscope does not give any direct information about a fundamental point, the chemical composition of the metals at each point. The usual methods of analytical chemistry give only the average composition of domains which contain various phases, even if the attempt is made to cut very small specimens, because the individual grains are often so minute that there are no practicable means of isolating them from the bulk of the metal.

To solve, at least partially, this major problem in metallography—point-by-point chemical analysis—the electronic microanalyzer has been very recently built in France. The complete description of this apparatus has been now published (*1*) and this paper gives only a brief account of the possibilities offered by the microanalyzer to the chemical analyst.

The electronic microanalyzer is able to perform a quantitative chemical analysis of a volume of about 1 cubic micron—i.e., a mass of $10^{-11}$ gram. The analysis, which can be made in a few minutes, does not alter the sample, and there are no special difficulties involved in measurements at elevated temperatures.

The microanalyzer is a combination of three different pieces of apparatus: a metallographic optical microscope, an electronic microscope, and an x-ray spectrograph. The electron microscope is not a conventional one; its purpose is to give an extremely narrow electron beam which is focused on the surface of the specimen within an area of only 1 or 2 square microns.

The specimen is a small piece of metal of any form which must have a surface plane and is polished by ordinary metallographic techniques. This surface is viewed by means of the optical microscope. The specimen can be moved from the outside of the apparatus very accurately in such a way that any point of its surface can be reached by the electrons; these movements are con-

**An electronic microanalyzer is described which consists of three parts: a metallographic optical microscope, an electron microscope, and an x-ray spectrograph. The first is for the purpose of delineating surface structure such as the grains in metals and alloys; the second is for collimating an extremely fine beam of electrons to impinge upon areas as small as 1 micron square; the third is to analyze the characteristic x-rays emitted in these small dimensions. The result is a point-by-point chemical analysis, both qualitative and quantitative, for a heterogeneous fine-grained specimen. Several examples especially for metallic systems are cited.**

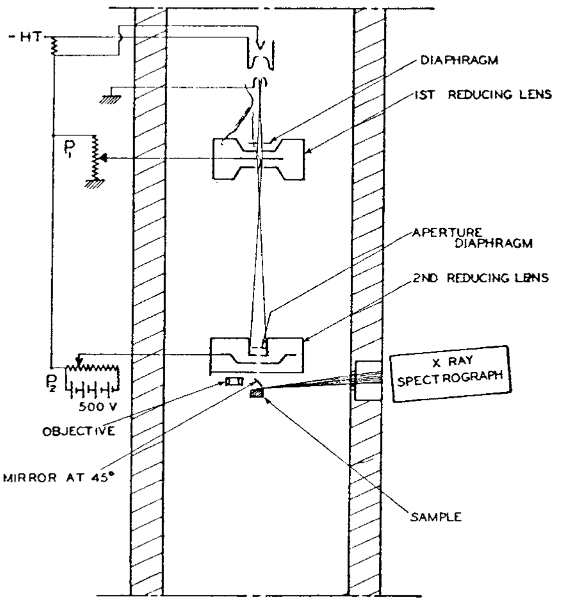

**Figure 1. Diagram of Microanalyzer**

## APPLICATIONS

Although the microanalyzer itself is somewhat complicated, its use is simple, so that it can be regarded as an instrument for routine work. The sample, after polishing, is put in the apparatus and the analysis can begin after a few minutes, just as when an object is examined in an ordinary electron microscope. The measurement itself requires only a few minutes. The sample is not at all deteriorated by the impact of the electrons, because the power of the beam is extremely weak. This means that the

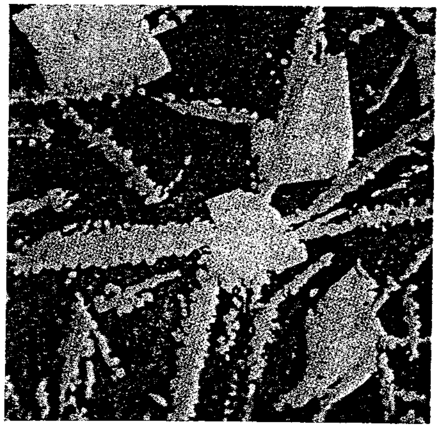

**Figure 2. Microphotograph of Copper-Tin-Antimony Alloy Showing Three Phases (×250)**

trolled visually with the optical microscope until the point of particular interest is submitted to the action of the electrons.

When electrons bombard a metallic surface, x-rays are emitted. In fact, the apparatus works simply as an x-ray tube, but with a focus 1,000,000th that of an ordinary tube used for crystallographic work. As the electrons are very rapidly stopped in the metal, the active part of the specimen, which emits x-rays, has a volume of the order of only 1 cubic micron.

The wave lengths of the x-rays depend on the nature of the elements bombarded by the electrons; to each element correspond a small number of characteristic wave lengths. So the analysis of the spectrum of the x-ray beam with a spectrograph (the third part of the microanalyzer) permits the determination of the elements present in the volume of matter touched by the electrons. In this manner, point-by-point chemical analysis of the specimen is effected. The analysis can be made quantitative if the intensity of one characteristic wave length of a given element is measured and if this intensity is compared with the intensity emitted under the same electronic conditions by a sample of the pure element.

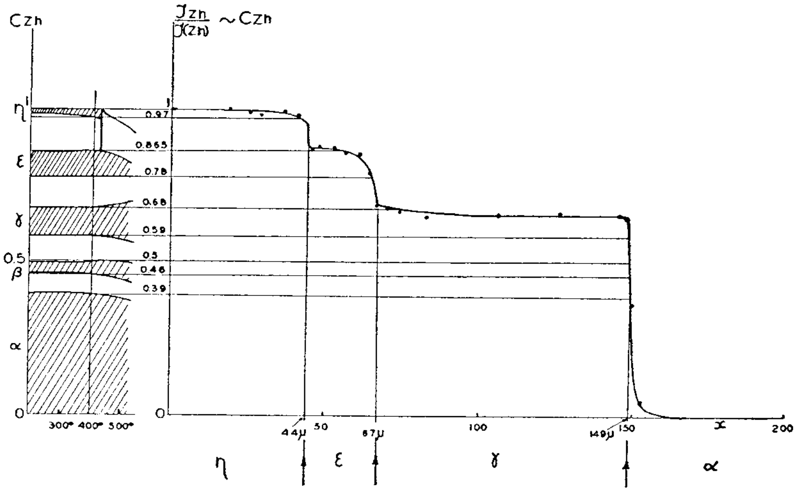

**Figure 3. Variation of Composition of Copper-Zinc-Alloy in Region of Diffusion**

Zn content

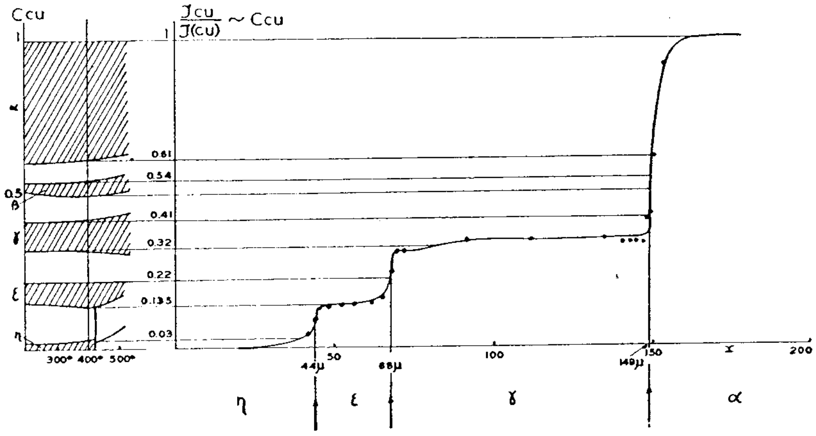

**Figure 4. Variation of Composition of Copper-Zinc-Alloy in Region of Diffusion**

**Cu content**

sample after being analyzed can be used for other measurements or that new analyses can be done at the same place after various treatments.

While the first apparatus, which is now in operation, is able to detect a limited number of elements only (zinc to titanium), it is easy to increase this number by a modification of the x-ray spectrograph. But it is difficult to deal with the elements of low atomic number. The wave lengths of the characteristic radiations increase and these long wave lengths are still difficult to detect. New researches are now in progress and it is hoped that the microanalyzer will be able to deal with all elements following aluminum in the periodic table.

Up to now the case of metals has been chiefly considered, but it seems possible to analyze nonmetallic solids as well. Examples of application of the microanalyzer include the determination of local variations of the composition of an alloy, and the analysis of precipitates or inclusions of an unknown or incompletely known nature. The possibility cannot be dismissed that for specimens involving nonconducting precipitate particles or inclusions in a conducting metallic matrix, the electron beam will be deflected from nonconducting to conducting phases, thus resulting in erroneous spectral line intensities. This can be avoided, as proved in experiments just completed, by coating the specimen with an exceedingly thin transparent layer of aluminum (of the order of 40 A. thickness).

Figure 2 represents a micrograph of a copper-tin-antimony alloy which, in addition to blocks of antimony about 0.1 mm. wide, contains needles with a dark central area and a brighter rim. The problem was to determine the composition of these needles. A qualitative analysis shows immediately that they contain some copper; quantitatively the conclusion is reached that the central part has the composition $Cu_3Sn$, whereas the bright rim corresponds to the formula $Cu_5Sn_4$.

The resolving power of the instrument is of the order of 2 microns. This was checked with an aluminum-copper alloy containing grains of the phase $Al_2Cu$, the dimensions of which ranged from 1 to 15 microns. If the probe is moved on particles of decreasing sizes, the intensity emitted in the characteristic radiation of copper remains constant as long as the diameter of the particle is larger than 2 or 3 microns. For smaller sizes, there is a loss of intensity which is due to the diffusion of electrons outside the grain of the precipitate.

The analysis of the various phases of complicated ternary or quaternary alloy is a difficult problem with the ordinary methods of metallography, and it is very likely that the electronic microanalyzer will be a useful tool in this field.

Another of the first applications of the apparatus was the study of the intermetallic diffusion. A sample formed by a plating of copper and zinc was heated at 400° C. for 1 hour. The whole diffusion area, as revealed by the microscope, was 0.1 mm. wide. The electronic probe was moved across the diffusion area and the copper-zinc diffusion curve was obtained in two different ways. First, with the spectrometer adjusted to register the radiation of zinc (ZnKα), the measured intensity represents the variation of the zinc concentration in the sample between 100% (pure zinc) and 0% (pure copper). The abrupt variations correspond to the change from one intermediate phase to the next, but there are also steady variations inside a given phase. The data of the equilibrium diagram of the two metals are shown also in Figures 3 and 4. Phase β does not appear in the analysis; in fact, further measurements showed that this phase is present, but its thickness is less than 1 micron. The agreement between the experimental measurements and the predictions drawn from the diagram is generally good.

The analysis can also be performed in measuring the concentration of copper across the diffusion area; this is done by changing the adjustment of the x-ray spectrograph to receive the copper radiation instead of the zinc radiation. Figure 4 gives the results of this second measurement. It is easy to check that the sum of the ordinates of the two independent curves is at any point equal to 100%, within maximum variations of 1%. This is a good test of the basic relations used for the calculation of the concentration from the observed intensities of the characteristic radiations.

## LITERATURE CITED

(1) Castaing, R., "Application des sondes electroniques à une méthode d'analyse ponctuelle," Office National d'Etudes et Recherches Aeronautiques, Paris, France, 1952.

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