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 the application and 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 1885 and now adapted to one of the most powerful methods of automatic chemical analysis (Liebelfsky); fluorescent spectral analysis (Birk and others); photodensity spectra for surface analysis (Steinhardt and Serfoss); 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 (Berin), and the use of punched card and computing machine techniques (Hudgens and others, Black); the application of low temperature techniques opening up a field for a vast body of materials which heretofore could not be investigated (Paul and Funkhausen); 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 of these contributions 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.
Point-by-Point Chemical Analysis by X-Ray Spectroscopy

Electronic Microanalyzer

RAYMOND CASTAING, University of Toulouse, Toulouse, France, AND ANDRE 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 site, 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 $10^{-15}$ 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 to 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 electron; 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.

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

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 electron conditions by a sample of the pure element.

Figure 1. Diagram of Microanalyzer

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

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

Zn content
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 θ 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 spectrophotometer 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


Received for review November 19, 1952. Accepted January 9, 1953. Work done in the laboratories of the Office National d'Etudes et Recherches Aérospatiales, Paris, France.