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X-RAY IMAGE METHOD OF CHEMICAL ANALYSIS

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The earlier methods of x-ray spectroscopy have recently been supplemented by methods in which curved crystal surfaces are used to produce the spectra. Most of these methods (M. de Broglie and F. A. Lindemann; H. Johann;[1] Y. Cauchois[2]) give line spectra of the usual appearance. The advantage of these so called "focusing" spectrographs is the increased sensitivity.

As the author pointed out,[3] curved crystals can be used also for producing a new kind of x-ray spectrum consisting of a series of two dimensional images instead of the spectral lines. Each of these images is formed by x-rays of a definite wave length. They may, therefore, be called "spectral images." In the following the general features of x-ray image spectroscopy will be given.

I. THE PRODUCTION OF TRUE X-RAY IMAGES

For producing true images in ordinary optics either a lens or a mirror is needed. As the refraction of x-rays is very small, it is hardly possible to build a lens for x-rays. On the other hand, the diffraction of x-rays by crystals, which according to W. L. Bragg can be interpreted as reflection of these rays on crystal planes, permits the realization of an x-ray mirror producing true images.

If an x-radiation of wave length λ is incident on a crystal surface, a selective reflection takes place at the angle ϕ given by the Bragg formula:

$$n\lambda = 2d \cdot \sin\phi.$$

In this equation d means the grating constant belonging to the reflecting crystallographic plane and n is the order of reflection.

We can now compare in Fig. 1 the path of the rays reflected by a plane crystal surface with the path of rays reflected by a cylindrical concave crystal mirror.

In Fig. 1*a* the source O of the x-rays emits radiation of wave length λ. The plane crystal K reflects the rays with the glancing angle ϕ. The divergent reflected bundle of x-rays forms a part of a cone. Its intersec-

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[1] Johann, H., *Zeits. Phys.*, vol. **69**, p. 185, 1931.

[2] Cauchois, Y., *Jour. Phys. et Radium*, vol. **7**, III, p. 320, 1932.

[3] Hámos, L. v., *Nature*, vol. **134**, p. 181, 1934.

tion with the plane F, parallel to the crystal K and containing the point O, is a segment of a circle C.

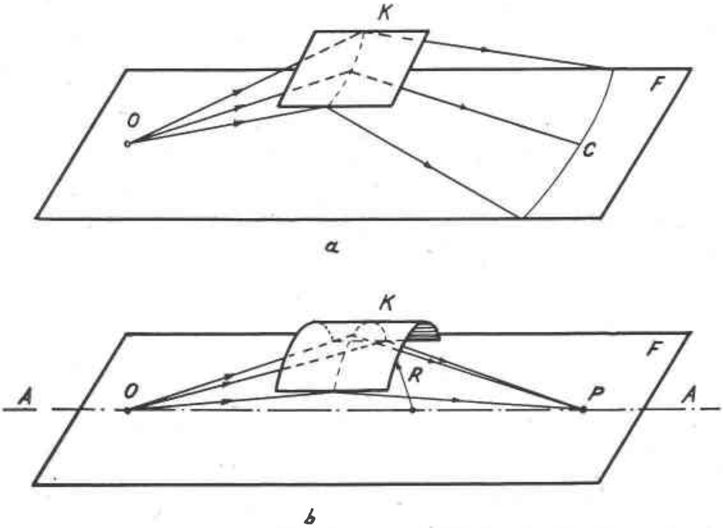

FIG. 1. Reflection of x-rays by (a) a plane, and (b) by a cylindrical crystal mirror.

In Fig. 1b the reflection takes place on a cylindrical crystal surface. The path of the reflected x-rays depends on the structure of the crystal. In order to get a convergent reflected bundle the structure of each surface element of the concave side of the crystal has to be orientated tangentially to the cylindrical surface. If this condition is satisfied, the rays having their origin in the point O (lying on the cylinder axis A–A) will meet again after reflection on the concave side of the cylindrical crystal K in the point P (lying also on the axis A–A). P is a true x-ray image of O.

It can easily be shown that even from points lying in the vicinity of the axis A–A true x-ray image-points will be formed. Figure 2 indicates the relative position of a two-dimensional x-ray source O, of a concave crystal mirror K, and of two different x-ray images B_1 and B_2 produced

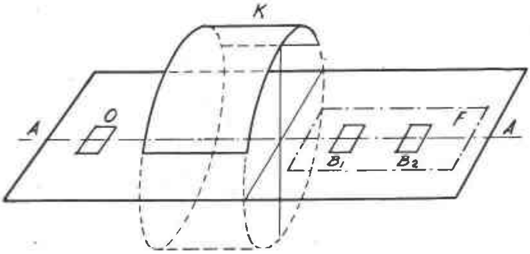

FIG. 2. Relative position of an x-ray source and its image spectrum.

by *K*. Each of these images corresponds to a definite wave length component of the radiation emitted by *O*.

If the source of *x*-rays is homogeneous, all parts of it emit radiation of identical spectral composition. The images of such a source will be of the same size as the source. In this special case there is consequently no essential difference between a line spectrum of the usual form and our image spectrum.

Let us now consider in Fig. 3 a schematical example of an *x*-ray source which is not homogeneous. We suppose that there are three different phases in the sample: *A*, *B* and $A+B$. The wave length emitted by *A* may be called λ_A, and the wave length emitted by *B*, λ_B The phase $A+B$ will emit both λ_A and λ_B. The image spectrum corresponding to the sample is also indicated in Fig. 3. In the spectral image corresponding to the wave length λ_A only the parts of the sample containing the element *A* appear. In the same manner the λ_B-image represents the parts of the sample containing the element *B*.

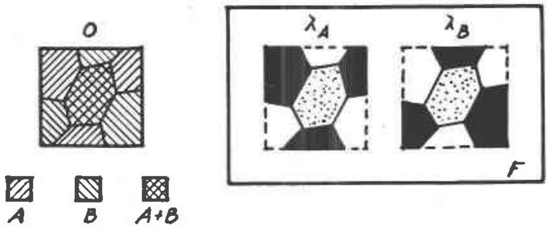

FIG. 3. Schematical example for an image spectrum.

We see from this simple example that *x*-ray images formed by a crystal mirror can be of different appearance, which is a new feature of *x*-ray image spectroscopy. We shall see later on that new possibilities of chemical analysis arise from this property of image spectra.

II. THE *X*-RAY IMAGE SPECTROGRAPH

An *x*-ray spectrograph operating with a cylindrical crystal mirror is schematically indicated in Fig. 4. *Q* is an *x*-ray tube producing the pri-

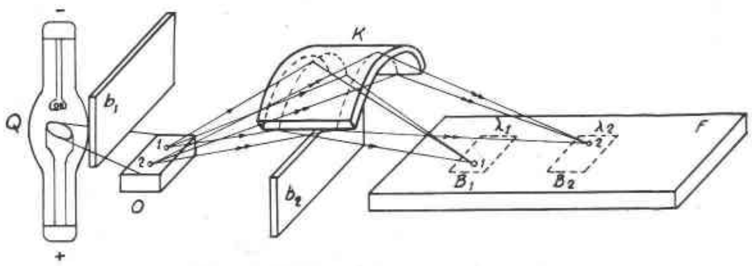

FIG. 4. The *x*-ray image spectrograph.

mary x-rays. O is the sample to be analyzed, having a plane surface. F is a photographic plate (or film) while b_1 and b_2 are diaphragms limiting the x-ray bundles.

The apparatus acts as follows: The *primary* x-rays from the x-ray tube Q reach the surface of the sample O and produce there *secondary* or characteristic x-radiation. As we shall see later on, the wave length of the secondary radiation is a function of the chemical composition of the emitting sample. The secondary x-rays emerging from the surface layer of the sample reach the concave side of the cylindrical crystal mirror. They are reflected according to their wave lengths and form a series of monochromatic x-ray images on the photographic layer F.

III. CALCULATION OF THE POSITIONS OF THE X-RAY IMAGES ALONG THE PHOTOGRAPHIC PLATE

Let us consider in Fig. 5 a cross section of the apparatus passing through the axis $A-A$ of the crystal cylinder. We shall calculate the distance $2X$ of a monochromatic x-ray image from the sample for a given wave length λ of the radiation. The direction X is coincident with the axis $A-A$. The distance $2X$ is calculated for corresponding points of sample and image. We get from the Fig. 5;

$$2X=2\cdot R\cdot\cot\phi$$

where R is the radius of the crystal cylinder. The glancing angle ϕ is given by the Bragg formula:

$$n\lambda=2d\cdot\sin\phi.$$

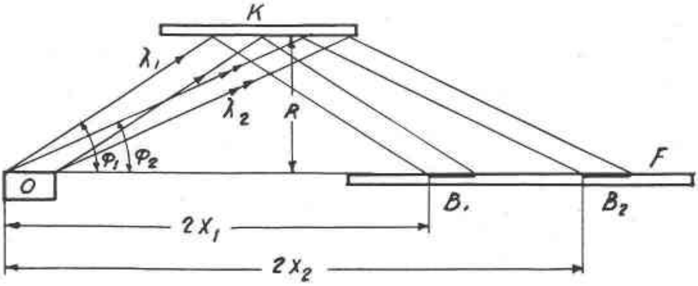

FIG. 5. Diagram of rays in the spectrograph.

By combining these formulae we get the fundamental equation of the image spectrograph:

$$2X=2R\sqrt{\left(\frac{(2d)}{n\lambda}\right)^2-1}.$$

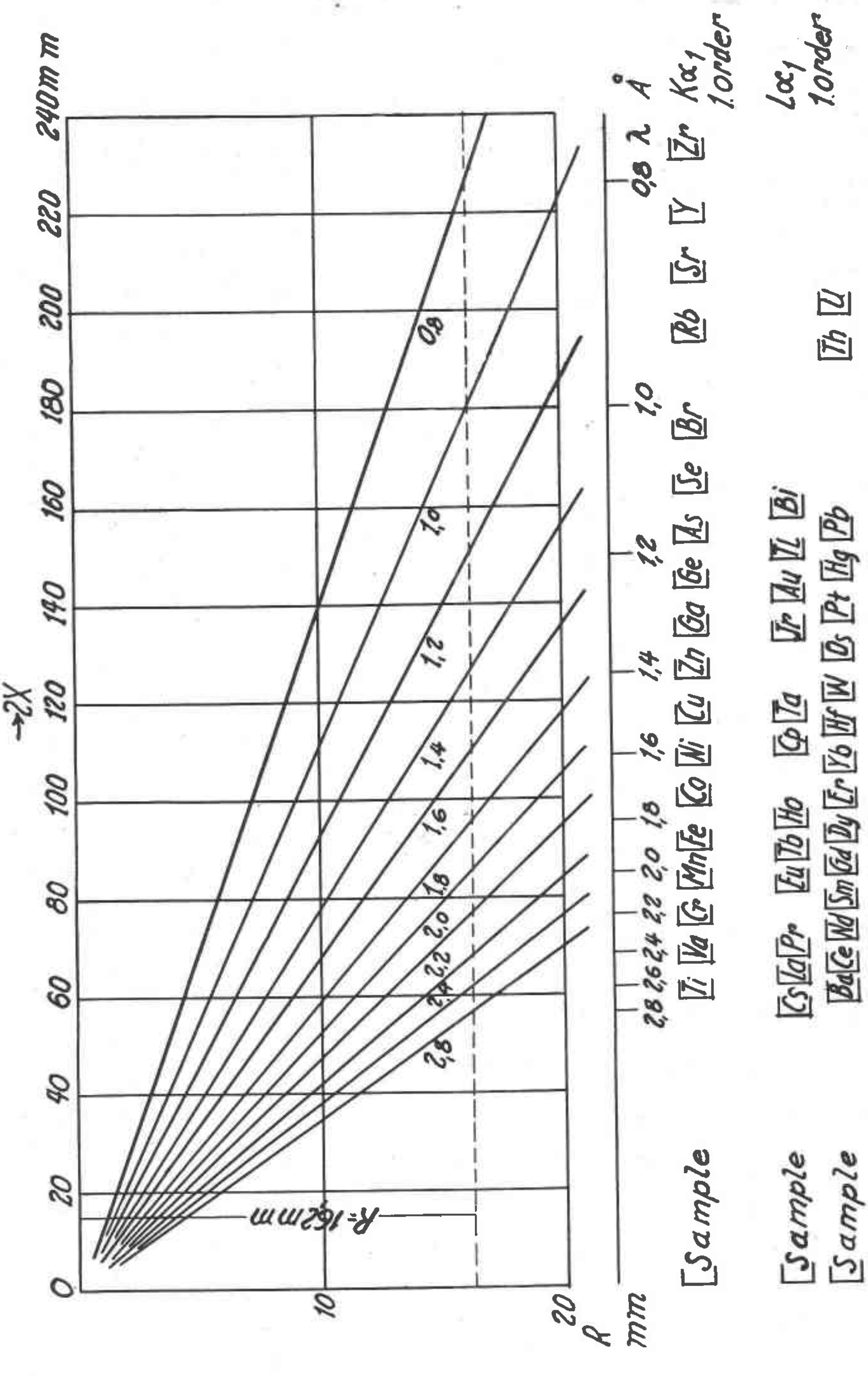

FIG. 6. Distance of the x-ray image from the sample as a function of the wave length of the x-rays given off by the sample, the cylindrical crystal mirror being NaCl. R is the radius of the cylindrical crystal mirror.

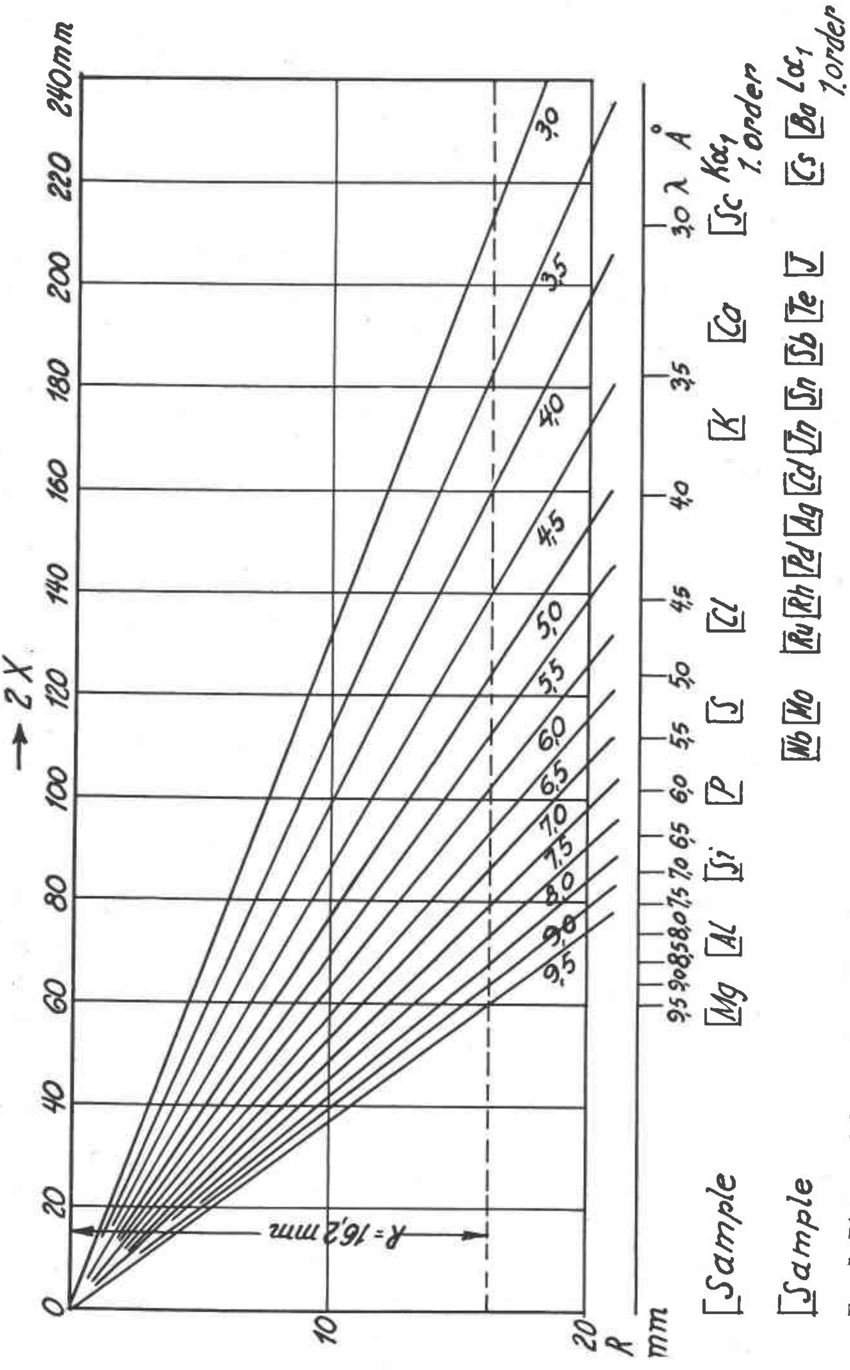

FIG. 7. Distance of the x-ray image from the sample as a function of the wave length of the x-rays given off by the sample, the cylindrical crystal mirror being muscovite. R is the radius of the cylindrical crystal mirror.

The nomograms in Figs. 6 and 7 illustrate this formula. Each of the nomograms is calculated for a definite value of the grating constant d belonging to the reflecting crystal surface. Figure 6 is based on the value $d=2.814$ Å (rocksalt), and Fig. 7 on the value $d=9.94$Å (muscovite). The distances between image and sample are plotted in the horizontal direction; the radius of the crystal in the vertical direction. The lines of constant wave length originate from the same point. The wave length scale for a definite radius can be constructed by drawing a line parallel to the X-axis at the distance of the actual crystal radius. The intersection points with the lines of constant wave length give the points of the wave length scale.

IV. LOCATION OF THE *X*-RAY IMAGES BELONGING TO THE DIFFERENT CHEMICAL ELEMENTS

It is known that every chemical element has a characteristic x-ray spectrum. The structure of these spectra is comparatively simple. The wave lengths of the x-ray lines can be found in the textbooks of x-ray spectroscopy. The above mentioned wave length scale gives in connection with the respective data of these tables the location of the different characteristic x-ray images.

To give an idea of the distribution of the x-ray images belonging to the different chemical elements we shall consider here only the most intense lines of the spectra. It is known that the characteristic x-ray lines of the chemical elements belong to different series, the so-called, K-, L-, . . . series. The most intense line of each series is denoted by α. In Figs. 6 and 7 the positions of the α images have been plotted beneath the wave length scale. To make the diagram clearer, the calculated positions have been located in different rows.

It may be seen that a NaCl crystal enables us to register the K-α images of the chemical elements between 22 Ti and 40 Zr, and the L-α images of the elements between 55 Cs and 92 U., the reflections being of the first order.

A range of longer wave lengths can be studied by a crystal with a larger grating constant, for instance muscovite. Such a crystal supplies the range of the K-spectra of the elements 12 Mg to 21 Sc, and the L-spectra between 41 Nb and 56 Ba, as illustrated by Fig. 7.

V. CHEMICAL ANALYSIS WITH IMAGE SPECTRA

Chemical analysis by the aid of an x-ray image spectrograph has much analogy with the ordinary methods of x-ray secondary spectroscopy. It would require too much space to give a complete description here of the methods of chemical analysis. We can consider only some characteristic features of the new method.

It is known that the characteristic x-radiation of a sample depends only on its elementary components. The molecular structure does not alter the wave length of the x-radiation emitted. The intensity of the secondary radiation is determined by the concentration of the chemical element in question. In ordinary x-ray spectroscopy the sample must be made homogeneous by chemical or mechanical processes. The analysis gives only the average content of each chemical element in the sample. A characteristic property of our new method is that the sample does not need to undergo any chemical or mechanical treatment. An essential condition is however, that its surface should be sufficiently plane. The spectroscopic process does not alter the sample, so it can be conserved and the result of the analysis can be controlled whenever necessary.

As we have seen above, a primary x-ray source is needed to excite the characteristic secondary radiation of the sample. The wave length of the primary x-rays must be somewhat shorter than the characteristic radiation of the sample in question. The same rules must be followed here as in ordinary secondary spectroscopy.

After a sufficient exposure several spectral images will appear on the photographic plate. These images have different structures according to the distribution of the chemical elements in the sample. In order to make an analysis with such image spectra, first the wave length of each image must be found and second the correlation between corresponding points of image and sample surface. A general rule for the solution of this problem cannot be given as there exists a great variety of different samples.

The interpretation of an x-ray image spectrum can be made easier by comparing it with the image spectrum of another sample of known composition. As the image method does not give simple spectral lines, but images of the same form as the sample in question, a sample for comparison can be placed beside the sample during the exposure. The spectrum of the sample of comparison gives then suitable wave length marks.

The method of comparing image spectra can even be applied to quantitative analysis of samples. There can be arranged a series of known samples of comparison with graduated chemical composition. These samples produce an intensity scale on the image spectrum. Quantitative estimation of the chemical content of a sample can be done by comparing the image intensity of the sample in question with the intensity scale given by the known samples.

There are two fields of chemical analysis, where the *x*-ray image method is particularly suitable: first, the investigation of chemical heterogeneities in a sample and second, the analysis of samples of very small size.

As we have seen in Fig. 3 each chemical heterogeneity will appear in the *x*-ray spectral images. There are many problems in mineralogy, metallography, and in other branches of inorganic chemistry where, besides the total elementary analysis, the distribution of elements in small parts of a sample also needs to be studied. The methods used hitherto had a more indirect character. By the *x*-ray image method chemical heterogeneities can be studied with great accuracy.

The *x*-ray image method enables us to make spectra of samples of very small dimensions. The intensity of an *x*-ray spectral image is to a very great extent independent of the volume of the emitting sample. The time of exposure needed for the production of an image spectrum is therefore nearly the same for a very small sample as for a larger one. The microscopic *x*-ray images can be enlarged and studied in the same way as the images of macroscopic objects. It is of very great interest that this method of spectroscopy does not destroy or alter the samples of microscopic dimensions under investigation.

VI. Examples of Image Spectra

We shall now illustrate the foregoing description of the new method with a few examples of image spectra. They have been taken by an arrangement according to the scheme outlined in Fig. 4. The primary *x*-ray tube was of the Coolidge type. It had a target of molybdenum and was operated at 60 kV and 5 mA. The distance between the target of the tube and the irradiated sample was about 15 mm. A cylindrical crystal mirror of rocksalt with a radius of 17.2 mm. was used.

Figure 8 shows a series of image spectra of different samples. They have been plane polished and covered with a tinfoil having a rectangular aperture according to Fig. 9. The aperture had the dimensions 4 mm.× 6 mm. On one side of the aperture a piece of brassfoil was fastened, giving suitable wave length marks (Cu- and Zn-radiation) along the spectra. The scale for the chemical elements was found by the diagram of Fig. 6. The image spectra in Fig. 8 correspond to following substances:

1. The brassfoil for comparison only (Cu and Zn).
2. Bornite (Cu K-α and K-β radiation).
3. Alloy of 12% Ni, 64% Cu and 24% Zn.
4. Alloy of 50% Co and 50% Ni.
5. Cobaltite.
6. Ore containing Fe and Zn.

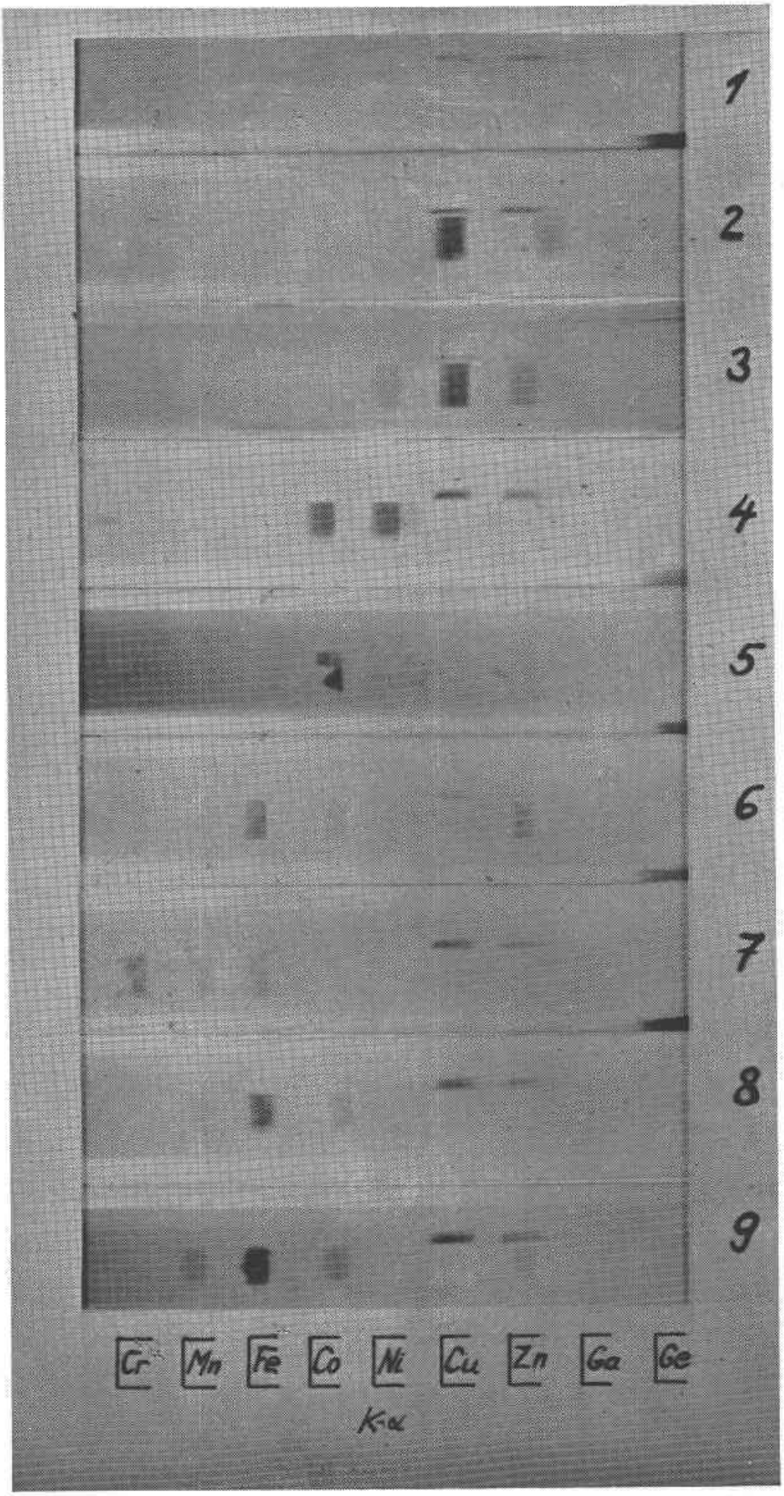

FIG. 8. Image spectra of different substances.

7. Chromite (containing Cr, Mn and Fe).
8. Ore (containing Mn and Fe).
9. Franklinite (containing Mn, Fe and Zn).

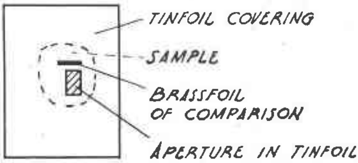

FIG. 9. Preparation of sample for spectroscopic analysis.

We see that in many cases even the K_β images appear in the spectra. In the case of homogeneous samples, as in 2, 3, 4 and 9 the spectral images have the size of the whole aperture of the tinfoil. In the other cases only the parts containing the chemical element in question will be blackened in the photograph.

Even microscopic heterogeneities in the chemical composition will appear in the spectral images. Figure 10 shows different enlarged spectral images of the same ore sample. They can be compared with the ordinary microphotograph of the same sample. The x-ray spectral images show the distribution of the elements Fe, Cu and Zn on the surface of the ore sample.

The method of x-ray image spectroscopy has been developed at the Riksmuseum of Natural History in Stockholm. The author would like to express his grateful thanks to Professor G. Aminoff, head of the Mineralogical Department, for giving him the opportunity to carry out this investigation.

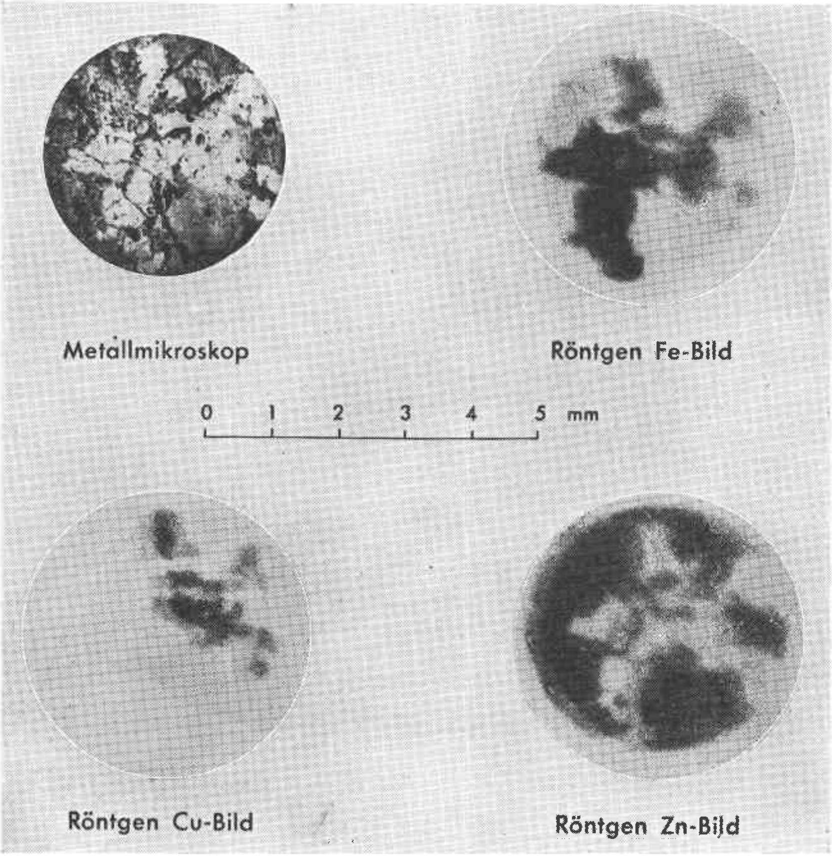

FIG. 10. Distribution of chemical elements in an ore-sample.