

## 34. Microanalysis by Means of an Electron-Probe Principle and Corrections

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The electron probe microanalyser developed in the Laboratories of the ONERA has already been described at the International Conference on Electron Microscopy, held in Paris in 1950. Its principle may be summarized as follows:

A selected spot on the surface of a sample, about one micron in diameter, is bombarded by an electron probe. The X-ray spectrum that is emitted by this spot contains the characteristic radiation of all the elements present at this spot. The operation consists of determining the chemical constitution of the very small volume of matter irradiated (about one cubic micron) by analysing the X-ray spectrum emitted from the sample.

Figure 34.1 represents a diagram of the apparatus. The probe is obtained by forming a reduced image of the cathode by means of two electrostatic lenses. The accelerating voltage is 30 kv. The electron beam current with a  $1\text{ }\mu$  probe is  $1.5 \times 10^{-8}$  amperes. Although the incident power on the sample is about  $600\text{ w/mm}^2$ , yet the local increase in temperature of the sample is only a few degrees since the bombarded area is very small; so that the analysis can be performed at room temperature.

The spectrometer includes a curved quartz crystal used in connection with a Geiger-Müller counter. The reflected intensity of the characteristic radiation of the main elements that constitute the sample usually measures several hundred pulses per second, whereas the continuum does not exceed one or two pulses per second. Consequently, an accurate analysis is possible. The purpose of this communication is to describe the experimental process of such an operation.

To start with, the various elements contained in the irradiated volume are easily detected by the presence of their characteristic radiation in the emitted spectrum. We will be concerned now with quantitative analysis.

Let  $I_A$  be the intensity of the characteristic radiation of the element A, emitted by the sample. Let  $I(A)$  be the intensity of the same radiation  $K\alpha_1$  emitted by a sample of pure A under the same conditions. An approximate calculation shows that the ratio of  $I_A/I(A)$  is equal, to the first order, to the mass concentration  $c_A$  of the element A in the analyzed volume. This has been experimentally verified for large samples. One can get a rough idea of this property by noticing that the different elements have approximately the same mass absorption coefficient for electrons of the same energy. Thus the mass of alloy irradiated by the electrons is approximately independent of its composition, and the number of atoms of A excited by the electrons

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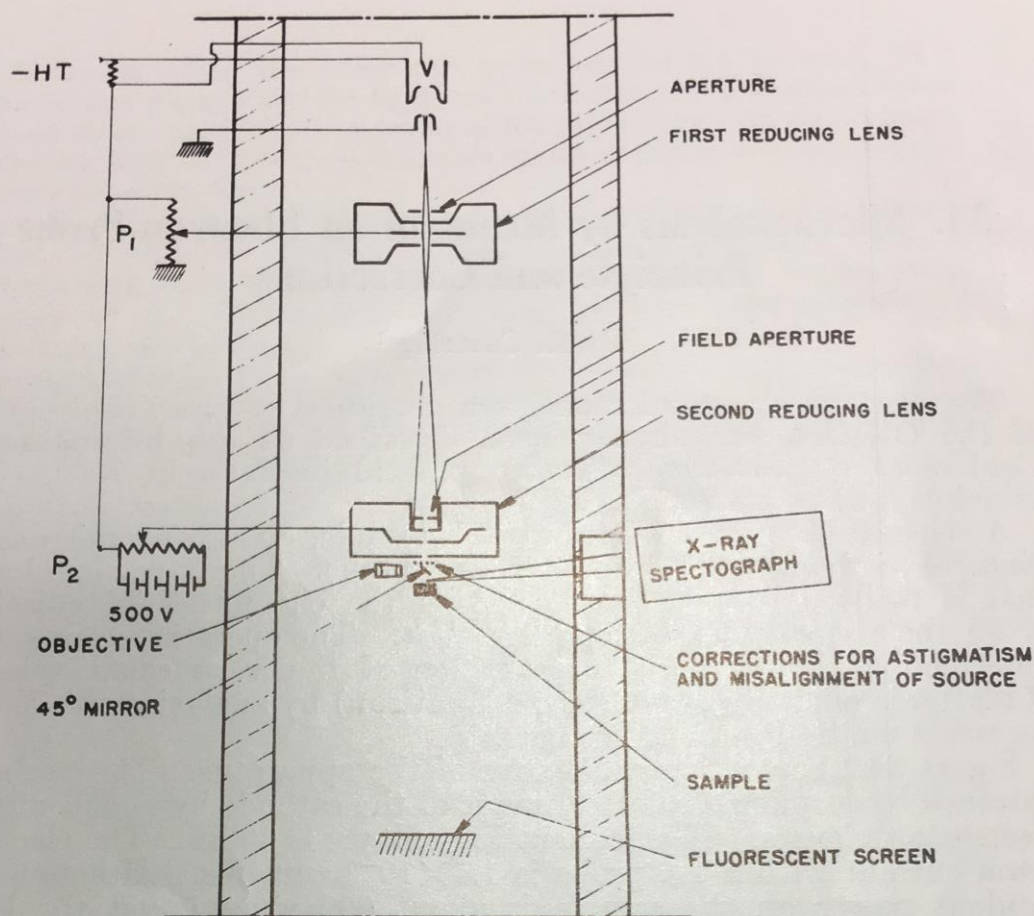


FIGURE 34.1.

is proportional to the mass concentration of the element A in the alloy. A better approximation is given by the relation

$$\frac{I_A}{I(A)} = \frac{\alpha_A c_A}{\sum_i \alpha_i c_i}$$

where  $\alpha_i$  is the electron mass absorption coefficient of the exponential Lenard law corresponding to each element. In fact, these coefficients are empirically determined once and for all by an analysis of an alloy of known composition.

Table 34.1 represents the results of four analyses performed on copper-aluminum alloys with copper concentrations 1, 4, 53, and 88 percent. It gives an idea of the accuracy of our approximations. The first approximation gives the copper concentration within a 2.6 percent maximum error. For the second approximation the results

TABLE 34.1.

Alloy	True concentration	First approximation	Second approximation
A <sub>1</sub>	0.01	0.0099	0.01075
A <sub>2</sub>	0.04	0.0373	0.0404
A <sub>3</sub>	0.53	0.504	0.525
A <sub>4</sub>	0.88	0.867	0.876

are still better, since the error can never exceed 0.5 percent. Yet aluminum and copper are far from each other in the periodical table. For closer elements the first approximation gives currently an accuracy of 1 percent, and we have seen that this approximation does not require any previous calibration.

The main advantage of this method is that the only emitted intensities that we have to compare to one another are always those of radiations that have the same wavelength, so that the variations in sensitivity of the counter and reflecting power of the crystals for various wavelengths do not have to be taken into account.

The problem is not always so simple, however, and some corrections are sometimes necessary. In the first place, when the absorption coefficient of the sample for the characteristic radiation that is being measured is large, the intensity that has been absorbed in the sample itself must be computed and this correction must be applied. Let us consider that radiation which is emitted from an elementary layer located at the depth  $z$  under the surface of the sample. The corresponding absorption is equal to  $e^{-\mu z \operatorname{cosec} \theta}$ , where  $\mu$  is the linear absorption coefficient of the alloy for this wavelength, and  $\theta$  the angle between the analyzed X-ray beam and the surface of the sample. It can be shown by a calculation, which will not be given here, that the ratio  $I(\theta)/I_0$  of the total intensity which is measured to the intensity which is actually emitted is a function of the form  $f\left(\frac{\mu}{\rho} \operatorname{cosec} \theta\right)$  where

$\frac{\mu}{\rho}$  is the mass absorption coefficient of the alloy for that wavelength, and  $f$  is, to the first order, a universal function, valid for any alloy, any characteristic radiation and any angle  $\theta$ . If we let the angle  $\theta$  vary, for a single given sample, we can determine the function  $f$ . Figure 34.2 shows the curve which represents  $\log f$  versus the quantity  $(\mu/\rho) \operatorname{cosec} \theta$ . Such a curve is valid only for a given accelerating voltage. In the present case, the voltage is 27.5 kv. Figure 34.3 shows the

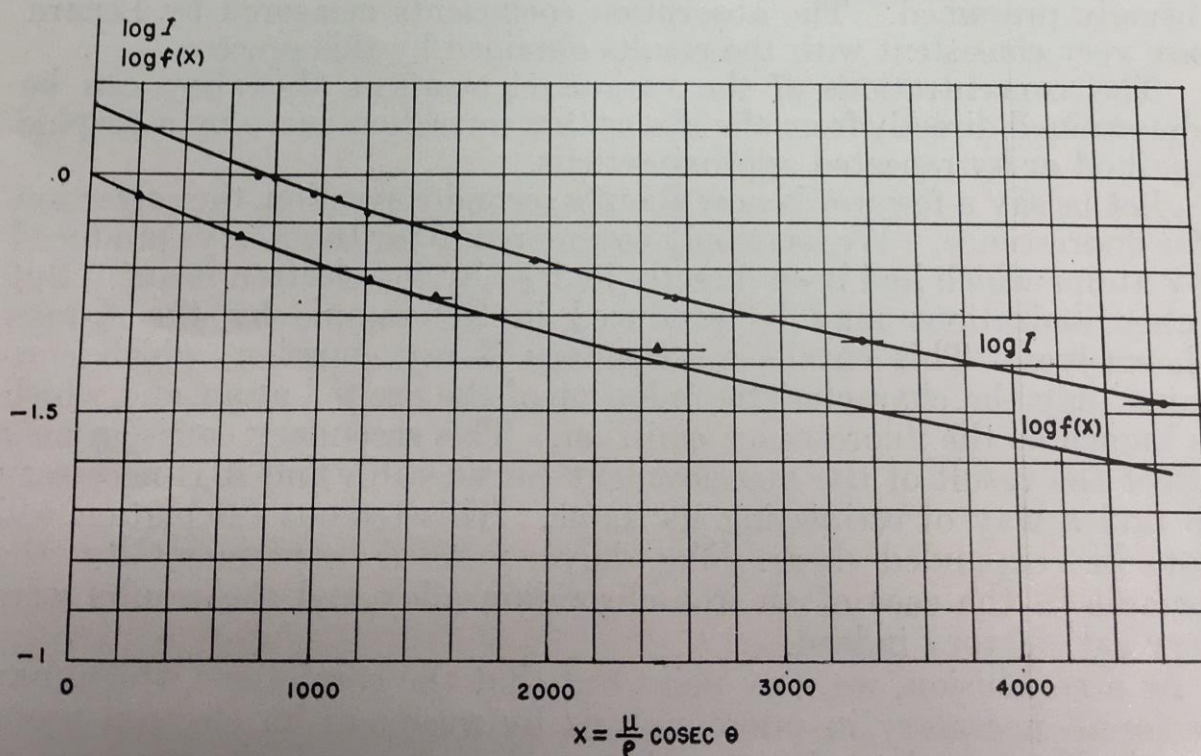


FIGURE 34.2.

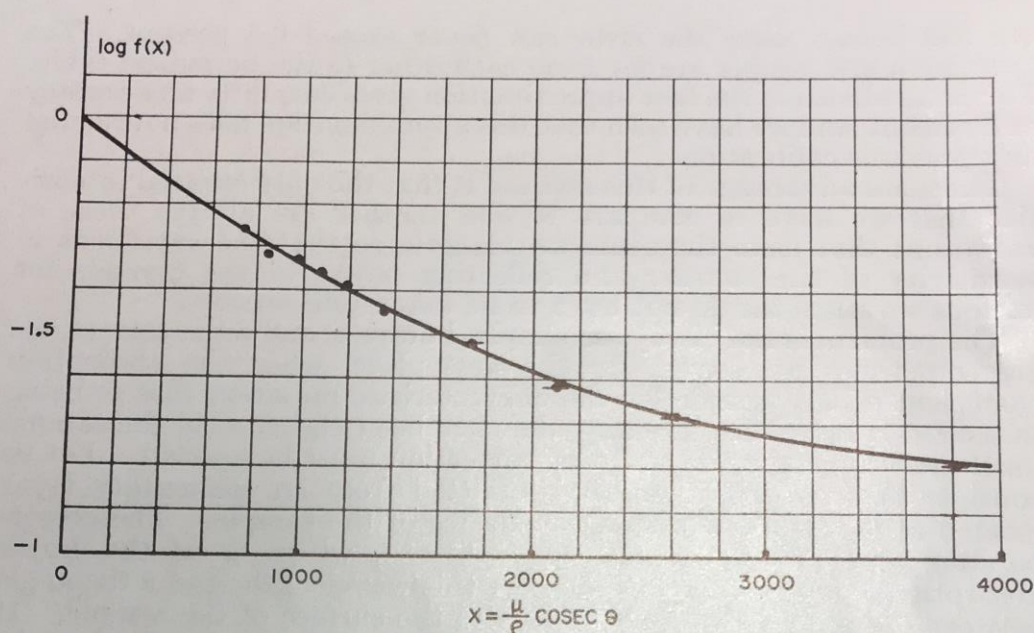


FIGURE 34.3.

correction curve for a 38 kv. The correction is larger for the same value of  $(\mu/\rho) \text{ cosec } \theta$  because the electrons go deeper into the sample and consequently the X-ray beam goes through a thicker mean layer of matter before emerging.

It so happens that the function  $f$  is the Laplace transform of the function that represents the decrease in intensity of the emitted X-rays versus the depth of emission in the anticathode. Thus, information about the law of decrease of this intensity may possibly be obtained by performing the transformation. It is found that the most important factor in the phenomenon is the exponential Lenard absorption, and not the slowing down of the electrons, as it was usually presumed. The absorption coefficients measured by Lenard are very consistent with the results obtained by this process.

The concentrations of the various elements in the alloy can be determined directly from the absorption correction curve by a graphic method or by repeated approximations.

Let us say a few words now about a second correction, the correction for fluorescence. We have only considered so far the X-rays produced by atoms which had been directly ionized by the electron beam. But other ionizations may be produced in the sample by the X-rays themselves. This entails a secondary X-ray emission, which contains only the characteristic radiation of the excited atom, and which is known as the fluorescence emission. This secondary emission may affect the result of the measurement considerably and it is necessary to find a way of estimating its value. This tedious calculation will not be expanded here. We have verified experimentally the formula in the case of an iron-chromium alloy and the results were very satisfactory indeed.

As a conclusion, we may point out that the corrections which may be found necessary in microanalysis by means of an electron probe are simple enough and leave the convenience and the accuracy of this method practically untouched.