THE INFLUENCE OF SPECIMEN SIZE AND BEAM DIVERGENCE ON QUANTITATIVE XRF BY FUNDAMENTAL PARAMETER METHODS

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ABSTRACT

In most spectrometers with x-ray tubes the source is positioned as close as possible to the specimen in order to gain high intensities; consequently the specimen is irradiated by a rather divergent primary beam. Intensity as well as spectral distribution of the primary beam varies with each irradiated spot, and (slightly) different relative fluorescent intensities must be expected for each line. In order to study this effect and its implication for quantitative analysis, we used a set of masks with holes at different distances from the center that were placed in front of the sample and rotated with a stepper motor. Thereby a sequence of small sample areas at controlled positions was exhibited to the primary beam. The measurements and computations show that intensities and count rate ratios vary with position and that the effect is higher for lighter elements.

INTRODUCTION

The fundamental parameter method has matured over the years to a point where most major and many minor effects can be accounted for by modern, sophisticated software. There are, however, still a few approximations that are accepted by many models: e.g. the assumption of a well-defined pair of angles of the incident and observed radiation, and a smooth, flat surface of the specimen.

Most computer programs are based on primary and secondary excitation for bulk materials and thin films, while more advanced programs account for Koster-Kronig transitions and specify fluorescent yields for each sub-shell. But generally the divergence of the primary beam, the varying spectral distribution and intensity of the primary beam as well as the effect of several geometrical factors are (to our knowledge) not included. The observed relative intensity is then in principle a weighted average over the specimen surface. It depends therefore (in a crystal spectrometer) on the specimen size (in relation to collimator- and crystal sizes and 2Θ-angle) and other geometrical factors.

Fortunately the effect is rather small, but as the analytical accuracy of XRF improves steadily, we found it reasonable to discuss the accuracy-limits implied by such simplifications. We have made a number of radiographs (using films) to show the basic effects and used a set of masks, which allowed us to observe the fluorescent intensities from individual spots of the specimen.

A Siemens SRS303AS spectrometer with a Rh-target end-window x-ray tube has been used. The measured samples where C, Al, Cu, Mo and In as pure elements with a diameter of < 40 mm (<34 mm irradiated in the sample holder). A general scheme of the instrument geometry is shown in fig.1.
SELECTION OF INDIVIDUAL SAMPLE SPOTS

In order to select fluorescent radiation from a specific area of the specimen, a set of masks (Ag) has been made with holes of 5 mm diameter at different positions (centered and out of center), as shown below. The masks are placed directly atop of the specimen.

In order to set the exact position, a stepper motor is used to rotate the sample and thereby the mask. The selected area of the sample is defined by the size of the hole, the distance of the hole from the center, $R$, and the rotation angle, $\varphi$. Angular positioning of the mask was possible in steps of $\Delta \varphi = 7.2^\circ$ (50 steps per revolution). The direction of the primary beam projects to the line from $57^\circ$ to $252^\circ$ (see fig.3.) With these four masks and the stepper motor most of the irradiated area of the sample can be covered.
RADIOGRAPHS

Films positioned at sample tray. In order to verify the varying irradiation of the sample by the primary beam, the film was placed at the position of the sample surface. As expected the intensity was higher at that sample side which is closer to the x-ray tube as shown in Fig. 4. The direction of the primary beam is indicated by an arrow and the most intensely irradiated area by a white line. The unexposed triangle at the bottom corresponds to the zero-point position of Fig. 3 and the direction of the arrow is from $57^\circ$ to $252^\circ$.

Figure 4: Radiograph at specimen position

Figure 5: Radiographs taken at $2\theta=45.02^\circ$ (left) and at $2\theta=148^\circ$ (right). The blades of the collimator are visible within the irradiated area.

Figure 6: Radiograph taken at a rotation angle $\phi=80^\circ$ (top) and at $\phi=260^\circ$ (bottom). Diameter of the mask: 5 mm.
Films positioned at crystal holder. To show where the fluorescent radiation from the various specimen positions hits the analyzer crystal, films were mounted at the crystal holder and exposed to fluorescent radiation from selected spots of the specimen. The radiographs shown in fig.5 are from a copper specimen without mask (i.e. the fluorescent radiation from the full specimen area) and in fig.6 from a copper specimen with a mask. The exposure times were about 40 minutes (20 kV/20 mA) for the radiographs without mask and 1 hour with masks. The unexposed half circle at the right top is of a lead mask used to indicate the orientation.

RESULTS

Intensities as a function of spot-position. The intensities of Cu-Kα, In-Lα, Al-Kα, and Mo-Lα were measured with all four masks; results are shown in fig.7.

For mask 0 there is naturally no dependence on φ and fluctuations are statistical. A minimum at φ=250° is found in the measurements with mask 1 and 2. This corresponds to the maximum distance of the irradiated sample spot from the tube; fluorescent radiation from this spot hits the analyzer crystal at maximum deviation from its center of rotation. These two facts reduce the intensity; the first is responsible for a slightly flatter minimum than that of the second. The measurement with mask 3 shows the most pronounced variation of intensity. The deviation of the collimated fluorescent beam from that in the center of rotation has two maxima at φ=57° and φ=250°, where the irradiated sample spot is nearest and farthest, respectively, to the tube.

Peak widths and peak positions. In addition to only counting the 2θ set to the peak maximum, the peak was also scanned over its full width. The idea was to see, if there are any displacements of the maximum and changes in the peak profile. For these measurements mask 3 was used, where the dependence of the intensity by φ is most pronounced. As an example for the peak

Figure 7: Intensity distribution of Cu, Al, Mo and In, depending on the rotation angle φ
measurements fig.8 shows some selected peak shapes of carbon and aluminum at different rotation angles and fig.9 shows a selection for copper.

![Figure 8: Peak shapes of C Kα (left) and Al Kα (right)](image)

![Figure 9: Peak shapes of Cu Kα](image)

![Figure 10: Peak position 2θ of Cu Kα](image)

As expected, the Kα-peak profiles show a shift of the peak position and a varying maximum intensity. The differences between the extreme values during a φ-rotation decrease with atomic number. The aberrations of the peak position (as shown in fig.10) are due to the flat crystal diffraction geometry.

Intensity ratios to pure elements as a function of position (computations). Fundamental parameter models were used to simulate the experiment and to compute the count ratios, R, for Cu-Kα, Al-Kα, Ni-Kα and Fe-Kα from Al-bronze (Cu 80%, Al 12%, Ni 4%, Fe 4%). The spectral distribution of the primary beam was modified according to the varying path lengths through the Be-window for the different beams in the divergent bundle. The results as a function of incident angle of primary radiation are shown in fig.11. “Filter” indicates the curves for which the varying absorption by the Be-window has been accounted for. It should be noted that the effect is in fact higher because of the additional angle-dependent absorption within the tube-target.
CONCLUSION

It has been demonstrated that the absolute and relative intensities vary with the spot of origin at the specimen surface, in some cases significantly (fig.11). Reasons are the divergence of the primary beam and the diffraction geometry with the analyzer crystal. The analytical error was estimated by integrating the intensities over all incident angles (and taking the varying absorption of tube radiation by the tube window into account), and comparing the resulting relative intensities with the values from a single incident angle. The differences are in the order of 1% for medium atomic numbers and slightly higher for light elements. Using standards with similar composition as the unknown decreases the error significantly.

Figure 11: Computed count rates, \( n \), (left) and ratios, \( R \), (right), for Al, Ni, Fe, Cu in Al-bronze