X-ray Fluorescence Analysis of Powdered As$_x$Se$_{100-x}$ Samples

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Abstract—A procedure was developed for the X-ray fluorescence determination of components in powdered samples of As$_x$Se$_{100-x}$, and its performance characteristics were determined. The relative standard deviation was 0.15% for the major components. The results of X-ray fluorescence analysis were in good agreement with data of atomic absorption spectroscopy.

Previously, procedures were reported for the X-ray fluorescence (XRF) analysis of two-component powdered samples of As$_x$S$_{100-x}$ chalcogenides [1] and As–Se films 1 to 11 μm thick on glass supports [2]. No data are available on the X-ray fluorescence analysis of mixtures of As$_x$Se$_{100-x}$ powders, although these mixtures can be used for fabricating chalcogenide glasses [3] and thin films.

The aim of this work was to develop a procedure for determining components of powdered chalcogenide samples using a VRA-20R X-ray fluorescence spectrometer (Carl Zeiss, Jena, Germany).

EXPERIMENTAL

Thoroughly homogenized mixtures of high-purity arsenic (OSCh-21-5) and selenium (OSCh-19-5) [4, 5] were used as reference samples (RSs). The composition of seven reference samples varied from As$_{15}$Se$_{85}$ (RS 1) to As$_{50}$Se$_{50}$ (RS 7) and covered the analytical range of the powdered samples to be analyzed. The amounts of arsenic and selenium were calculated for 10-g sample portions. The reference and test samples were pressed as pellets 24 mm in diameter under a pressure of 2·10$^7$ Pa (200 atm).

A cadmium collimator with a 20-mm aperture was used to collect X-ray fluorescence. The optimal working conditions for the VRA-20R spectrometer are listed in Table 1.

Table 1. Optimal working conditions for a VRA-20R X-ray fluorescence spectrometer (W anode: 30 kV/10 mA, LiF (200), scintillation counter)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength $\lambda$ (nm)</th>
<th>Angle $2\theta$ (deg)</th>
<th>Collimator (deg)</th>
<th>Exposition time $t_{exp}$, (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{\alpha}$</td>
<td>$K_{\beta_{1-3}}$</td>
<td>$K_{\beta}$</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.117588</td>
<td>0.105730</td>
<td>0.104500</td>
<td>33.97</td>
</tr>
<tr>
<td>Se</td>
<td>0.110477</td>
<td>0.099218</td>
<td>0.097974</td>
<td>31.85</td>
</tr>
</tbody>
</table>

The counting intervals ($t_{exp}$) were selected in accordance with the pulse rate $I = \frac{N}{t_{exp}}$ [6]:

$$\frac{t_1}{t_2} = \sqrt{\frac{I_2}{I_1}}.$$ (1)

The arsenic and selenium $K_{\alpha}$ lines were taken as the analytical lines. Their relative intensities were calculated for samples with the maximum concentration of the corresponding element (As$_{50}$Se$_{50}$ for arsenic and As$_{15}$Se$_{85}$ for selenium).

RESULTS AND DISCUSSION

Determination of the composition of As$_x$Se$_{100-x}$

The relative fluorescence intensities of the arsenic and selenium $K_{\alpha}$ lines as functions of the element concentrations were studied using As$_x$Se$_{100-x}$ reference samples (Figs. 1, 2).

The calibration equations for the relative intensities of the $K_{\alpha}$ lines of analytes and their concentrations in reference samples are as follows:

$$c_{As} = \frac{51.574 (I_1/I_7)_{As} - 1.567}{R},$$ (2)

$$R = 0.9963; \quad \overline{SD} = 1.13; \quad N = 7; \quad RSD = 3.3 \times 10^{-2};$$

$$c_{Se} = \frac{101.678 (I_1/I_7)_{Se} - 16.571}{R},$$ (3)

$$R = 0.9994; \quad \overline{SD} = 0.46; \quad N = 7; \quad RSD = 0.7 \times 10^{-2},$$

where $c_{As}$ and $c_{Se}$ denote the concentrations of As and Se in the $i$th reference sample, respectively, and $I_1$ is the fluorescence intensity of the analyte line minus the background intensity.
Arsenic and selenium are neighbors in the periodic table; therefore, the background intensity was determined using a special background sample [5].

For the $\text{As}_{30}\text{Se}_{70}$ sample (RS 3), the following relative fluorescence intensities were obtained for arsenic and selenium $\lambda_k$ lines:

\[
\frac{I_{30}}{I_{70}} = 0.6207 \pm 0.0004;
\frac{I_{33}}{I_{14}} = 0.7553 \pm 0.0011; \quad n = 20, \quad \alpha = 0.95.
\]

The line-to-background intensity ratios $I_l/I_b$ were 33.1 and 24.2 for arsenic and selenium, respectively.

The validity of the polynomial was assessed by the dispersion of the regression equation:

\[
\sum_{k=1}^{n} \left(c_{ik}^{\text{RS}} - c_{ik}^{\text{XRF}}\right)^2 \quad \frac{n}{n-m},
\]

where $c_{ik}^{\text{RS}}$ is the concentration of the $i$th element in the $k$th reference sample, $c_{ik}^{\text{XRF}}$ is the concentration of the $i$th element in the $k$th reference sample as calculated using the selected polynomial, $n$ is the number of reference samples used, and $m$ is the number of coefficients in the regression equation.

The residual standard deviation (the percentage ratio between the standard deviation and the mean concentration of an element for all reference samples) was 3.3% for arsenic and 0.7% for selenium ($\overline{c}_{\text{As}} = 34.29$ wt %; $\overline{c}_{\text{Se}} = 65.71$ wt %). The value RSD = 0.7% found for selenium is acceptable for its concentrations found using the reference samples and the calibration equation. The wide spread of the experimental points and the unacceptably high value RSD = 3.3% found for arsenic can be explained by the mutual interference of elements (the matrix effect). The analysis of the wavelengths of the base lines and absorption edges of elements present in the $\text{As}_{x}\text{Se}_{100-x}$ system (see below) points to the selective absorption of primary and fluorescence radiation and the selective excitation of elements present in the sample (Table 1).

Selective absorption at characteristic analyte wavelengths. It is known [5] that the selective absorption at the $i$th analytical wavelength of element $A$ is due to the presence of element $B$, for which the wavelength of the absorption edge $\lambda^B_q$ is only slightly longer than the wavelength of the analytical line: $\lambda^A_i < \lambda^B_q$. The larger the difference between $\lambda^A_i$ and $\lambda^B_q$, the weaker the absorption effect.

This effect was not observed for the $\text{As}_{x}\text{Se}_{100-x}$ system, because the wavelength of the $K_{\text{As}}^{\text{As}33}$ line is slightly longer than the wavelength of the $K_{\text{Se}}^{\text{Se}34}$ absorption edge: $\lambda^{\text{As}33}_{K_{\text{As}}} = 0.110477$ nm and $\lambda^{\text{Se}34}_{K_{\text{Se}}} = 0.104500$ nm.

Selective excitation at characteristic analyte wavelengths. This effect was observed in the system under