

Total Reflection X-ray Fluorescence Analysis.

Section 3

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3. Quantification

TXRF is a reference method; standards are required for both, calibration procedure and to assess the quality of the quantitative results. The standards are measured, intensities obtained, and certain calibration (intensities vs. concentration) is established. In XRF practice the analytical signal that is proportional to the concentration of the element of interest W_i is the count rate I_i (s^{-1}) of its characteristic emission radiation. The proportionality ratio is commonly described using the Sherman expression:

$$I_i = G \varepsilon(E_i) \int_{E_0 > E_{ab}}^{E_{\max}} K_i W_i \frac{[1 - \exp(-\chi_i \rho_s d)]}{\chi_i} I_0(E_0) dE_0$$

$I_0(E_0)$ is the probability distribution by energies of the excitation flux (s^{-1} , srad^{-1} , mA^{-1}), $\varepsilon(E_i)$ is the detector intrinsic efficiency for energy E_i , $\rho_s d$ is the sample aerial density (g/cm^2).

$$\chi_i(E_i, E_0) = \mu_s(E_i) / \sin \theta_2 + \mu_s(E_0) / \sin \theta_1$$

is the effective mass attenuation coefficient (g^{-1}cm^2).

$$K_i = f_K \times \omega_K \times \left(1 - \frac{1}{J_K}\right) \times \tau_i(E_0)$$

is the x-ray production rate.

$$G = \frac{\Omega_{Det}}{4\pi} \frac{\Omega_{Source}}{\sin \Theta_1}$$

is a proportionality factor that accounts for effective solid angles of excitation and detection.

3.1- Quantification model in TXRF

The relationship between the characteristic emission intensity of an element and its concentration is a linear dependence if the sample aerial density (g/cm^2) is relatively small, as it is the case of a small specimen deposited on an appropriate carrier. In such case, a simplification to the Shermann expression can be made:

$$\begin{aligned} \chi_i \rho_S d &\rightarrow 0 \\ \Rightarrow \frac{[1 - \exp(-\chi_i \rho_S d)]}{\chi_i} &\rightarrow \rho_S d \\ \Rightarrow I_i = G \varepsilon(E_i) \int_{E_0 > E_{ab}}^{E_{\max}} K_i w_i \frac{[1 - \exp(-\chi_i \rho_S d)]}{\chi_i} I_0(E_0) dE_0 &\rightarrow \\ \rightarrow I_i = G \varepsilon(E_i) w_i \rho_S d \int_{E_0 > E_{ab}}^{E_{\max}} K_i I_0(E_0) dE_0 = G \cdot w_i \cdot S_i [I_0(E_0)] \cdot \rho_S d & \end{aligned}$$

The more advantageous feature in this simplification is the fact that the attenuation of the radiation in the sample does not depend on the sample matrix. The instrumental sensitivity S_i ($\text{s}^{-1}\text{g}^{-1}\text{cm}^2$) depends on the type of excitation that has been used (cut-off or monochromatic), the selected value of high voltage for x-ray tube operation, and on a fixed geometry arrangement of the sample in regard to the excitation and the detection effective solid angles.

Nevertheless, this expression is not commonly used in TXRF practice, since it is unfeasible to assess the aerial density of the TXRF samples (the dry residue from a few microliters of a solution deposited on a flat carrier).

3.2- TXRF spectra

The analytical signal is the count rate of the characteristic emission. To determine the count rate, the net area of the characteristic emission peak has to be determined in the measured spectrum. This evaluation is done by fitting the spectra using proper application software, such as the QXAS package developed by the IAEA.

The QXAS package installation is available as a free download from the IAEA XRF Laboratory website:

<http://www.iaea.org/OurWork/ST/NA/NAAL/pci/ins/xrf/downloads/qxassetup.zip>

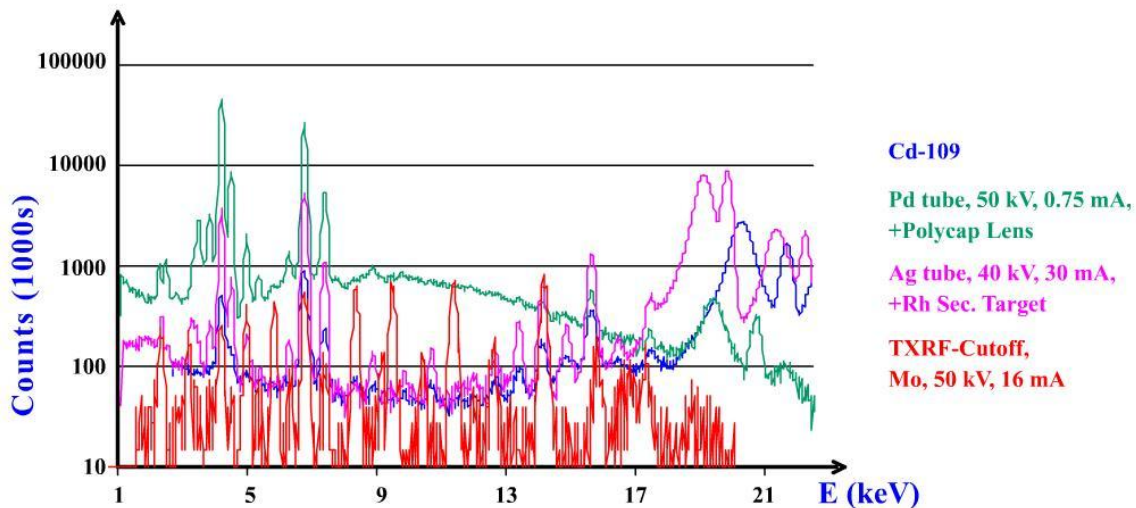
The User Manual is included in the installation, but can also be separately downloaded from:

http://www.iaea.org/OurWork/ST/NA/NAAL/pci/ins/xrf/downloads/QXAS_Manual.pdf

The QXAS includes different quantification procedures, and one of them is dedicated to TXRF calibration and quantification.

The main feature of TXRF spectra is a drastically reduced background under the characteristic emission peaks. In the case of using a Cut-off reflector as modifier, there is still some contribution to the background due to the scatter of the continuum from the excitation spectrum in the sample residue. When using monochromator devices, the background under the peaks is minimal.

TXRF spectra



3.3- Internal standard

As it was mentioned before, in TXRF the sample specimen is rather small; and is unfeasible to assess its aerial density. Moreover, it is difficult to ensure that the position of the dry residue in the sample carrier or the position of the sample carrier itself will be reproducible.

Therefore absolute sensitivities are seldom used in TXRF, instead relative sensitivities are preferred for calibration (sensitivities relative to the sensitivity of a particular element). This element is referred thus as 'internal' standard. For the determination of the relative sensitivities different standard solutions (either multi-elemental or single element standards) are spiked with some known amount of the internal standard and measured. For internal standard addition, some element that would not commonly be found in the sample is selected, such as Ga, Y or some Rare Earth Element.

Quantification model is favored by the use of internal standardization:

$$I_i = G \varepsilon(E_i) w_i \rho_s d \int_{E_o > E_{ab}}^{E_{\max}} K_i I_0(E_0) dE_0 = G \cdot w_i \cdot S_i [I_0(E_0)] \cdot \rho_s d$$

As this expression is valid for both, the element of interest and for the internal standard, the ratio I_i/I_{ISt} does not depend on sample aerial density, the geometry factor, the measurement time or even on the excitation flux intensity:

$$\frac{I_i}{I_{ISt}} = \frac{N_i}{N_{ISt}} = \frac{\varepsilon(E_i) w_i \int_{E_o > E_{ab}}^{E_{\max}} K_i dE_0}{\varepsilon(E_{ISt}) w_{ISt} \int_{E_o > E_{ab}}^{E_{\max}} K_{ISt} dE_0} = \frac{w_i S_i}{w_{ISt} S_{ISt}}$$

$$\Rightarrow w_i = \frac{N_i}{N_{ISt}} \frac{1}{S_i / S_{ISt}} w_{ISt}$$

3.4- Calibration

The plot of the measured peak area ratio vs. the ratio of the concentrations

$\left(\frac{N_i}{N_{ISt}} = \frac{w_i S_i}{w_{ISt} S_{ISt}} \right)$ gives a calibration straight line. Its slope is called relative (to

the internal standard) sensitivity. The relative sensitivities $\frac{S_i}{w_{ISt} S_{ISt}}$ are

established for a group of elements by performing calibration measurements. The sensitivity calibration can be extended for non-measured elements which characteristic energies are within the limits given by the characteristic energies of the measured elements.

