Detection Limits of a TXRF Analysis System in Double Reflection Mode

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Abstract. Total reflection X-ray fluorescence (TXRF) analysis system is described with regard to develop a new prototype in double reflection mode. We discuss the basic principles of the technique to design and set-up a new TXRF module, coupled to an old X-ray generator. Different geometries are analyzed and the system is calibrated with standard solutions of several elements and the detection limits are established in the range of \(4 \times 10^{-11}\) to \(13 \times 10^{-11}\) g. Finally, a certified standard sample is measured and the results are compared for all studied geometries. This research is focused on the analysis of micro traces, in scientific and technological applications.

1. Introduction

Total reflection X-Ray Fluorescence (TXRF) technique is a powerful analytical tool for micro and trace multi-elemental analysis and has the ability to simultaneously detect a wide range of elements (B-U) in a few minutes [1,2]. TXRF analysis is also of simple quantification, easy sample preparation and small sample amount is required, usually in the order of the micro liters. These characteristics make it a valuable tool in many fields of research, with varied applications to the environment and monitoring [3,4], mineralogy [5], oceanography [6], biology [7], forensic [8], industry and medicine. Liquid samples can be analyzed by TXRF directly. Soil, sediments, airborne particulate and solid samples in general, also can be analyzed after some pre-treatment like separation of suspended matters and acidic digestion. In another cases TXRF is highly suitable for nondestructive and micro analytical capabilities. In another cases TXRF is highly suitable for nondestructive micro analytical applications like as Biological tissue thin samples in medical and forensic applications [9, 10].

In this work we discuss the basic principles of the technique and the design and the development of a module in double reflection. An old Siemens Kristalloflex 710 / 710H X-ray generator is used, with Mo target and Zr filter, which is operated at 40kV / 20mA and the different TXRF geometries are coupled for comparatives measurements. The systems are calibrated with standard solutions of several elements and the limits of detection are established, comparing them with those obtained by the different TXRF geometries. Significant increase in signal-to-noise ratio is expected to establish detection limits in the order of picograms.

2. Basic principles

TXRF technique is a variation of energy dispersive X-ray fluorescence (EDXRF) technique because a significant difference in the excitation and detection geometry is observed. In the EDXRF technique (figure 1), the primary radiation excites the sample at an angle of about 45°, while TXRF is characterized by two fundamentally attractive factors: first, the primary beam interacts with the specimen at a critical angle less than to the critical angle at which the total reflection of the X-rays occurs (usually less than 0.1°) and second, the primary beam interacts on a plane with polished surface, e.g. quartz plate, containing the sample (figure 2).
Figure 1: Instrumental arrangement for conventional EDXRF.

The totally reflected beam having nearly the same intensity as the primary beam, is generated at the glancing angle smaller than the critical angle, when the primary beam is totally reflected due the grazing incidence.

Figure 2: Instrumental arrangement for a simple TXRF. 1: X-Ray Generator; 2: quartz plate; 3: detector; 4: X-Ray stopper and 5: Characteristics X-Ray Fluorescence from the sample.

The instruments that use the TRXRF phenomenon have been designed and operated based on the classical dispersion theory of light and the Fresnel equations [11-13].

Figure 3: Angular dependence of the Si, Ni and Pt surface reflectance under MoKα X-ray irradiation.
In this technique, the most important parameters studied are: the critical angle $\phi_c = \frac{99.1}{E} \sqrt{Z_p / \rho}$, the penetration depth $Z_p$, and the reflectivity $R$. The angular dependence of the reflectivity under MoKα X-ray irradiation, and the penetration depth of MoKα X-ray radiation versus incidence angle, for different reflectance surfaces are showing in figure 3 and figure 4, respectively [14].

Figure 4: Penetration depth of MoKα X-ray radiation for Si, Ni, and Pt versus incidence angle.

Penetration depth, for very small incidence angles, is independent of the energy of the primary beam. This gives an idea about the important role played by $Z_p$ in the superficial analysis, when the TXRF analysis technique is used. Table 1 shows the critical angles, penetration depths and reflectivity for different materials. Two energies for the X-ray beam are considered.

| Material      | $\rho$ g/cm$^3$ | $\phi_c$ (min) $E_i / E_z$ | $Z_p$ (nm) $\phi = 3\phi_c / E_i / E_z$ | $Z_p$ (nm) $\phi = \phi_c / 2$ $E_i / E_z$ | $Z_p$ (nm) $\phi = \phi_c$ $E_i / E_z$ | $\frac{R}{\phi = \phi_c / 2}$ $E_i / E_z$ |
|---------------|-----------------|-----------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| Plexiglass    | 1.20            | 9.9/4.6                     | 4.5/5.7                                | 4.9/4.9                                | 127.2/247                             | 0.997/0.999                            |
| Quartz        | 2.20            | 12.9/5.9                    | 3.4/3.8                                | 3.8/3.8                                | 40.1/84.3                             | 0.985/0.997                            |
| Silicon       | 2.32            | 13.2/6.1                    | 3.3/3.7                                | 3.7/3.7                                | 31.1/62.0                             | 0.973/0.994                            |
| Aluminum      | 2.69            | 14.0/6.4                    | 3.1/3.4                                | 3.5/3.5                                | 30.5/64.4                             | 0.978/0.995                            |
| Titanium      | 4.54            | 17.8/8.2                    | 2.4/2.6                                | 2.7/2.7                                | 11.6/26.2                             | 0.907/0.976                            |
| Germanium     | 5.31            | 18.9/8.7                    | 2.3/2.4                                | 2.6/2.6                                | 18.3/13.3                             | 0.966/0.937                            |
| Steel         | 7.80            | 23.5/10.8                   | 1.8/1.9                                | 2.1/2.1                                | 7.5/14.2                              | 0.875/0.963                            |
| Tantalum      | 16.60           | 31.9/14.6                   | 1.3/1.4                                | 1.5/1.5                                | 6.8/6.2                               | 0.915/0.900                            |
| Platinum      | 21.41           | 36.0/16.6                   | 1.2/1.2                                | 1.4/1.4                                | 5.4/4.9                               | 0.897/0.979                            |

2.1 Instrument design

In the design conditions of a TRXRF instrument, the energy levels that generate background noise must be minimized, but it is more important to maximize the intensity of the analyte signal. The operation of the X-ray tubes is limited to the loss of solid angle. This problem can be optimized or improved by reducing the distances between the tube anode and the position of the sample. Also the optical focus of the X-Ray can be improved.
2.1.1 TRXRF in Simple Reflection
The simplest arrangement used for surface analysis is shown in figure 5. It is noted that the equipment settings for performing a scanning displacement for large samples is simple.

Figure 5: Left side: Simple TRXRF Arrangement used for quartz crystal analysis. Right side: Spectrum of the quartz crystal; counting time 200 sec.

In this experiment, the quartz crystal is excited under its critical angle, with an energy of 40 KeV. Here in the spectrum one clearly observes the characteristic peak of the Mo tube, and the "backscattering Compton" produced by high energy photons. Naturally in this spectrum the background is very high and the limits of detection are drastically dependent on the signal-to-noise ratio. Here we can appreciate the characteristic peaks of the elements Si, Ar, Fe and Pb, corresponding to the quartz crystal.

2.1.2 TRXRF in Standard Reflection
A more general arrangement is shown in figure 6. This facility was acquired through the International Atomic Energy Agency [15] for trace element analytical applications. In this geometry the primary radiation attacks under the critical angle on a first reflecting crystal, with an energy of 40 KeV, which in turn reflects the X-rays towards de sample position (quartz crystal).

Figure 6: Left side: Standard TRXRF Arrangement used for quartz crystal analysis. Right side: Spectrum of the quartz crystal; counting time 200 sec.

Figure 6 shows a significant decrease in background noise. For the elements Si, Ar, Fe and Pb, the signal/noise ratio increases considerably, with respect to the arrangement in simple reflection. This geometry allows to reduce the elastic dispersion which is absorbed mainly in the first reflecting crystal, due the penetration depth of the primary beam.
The reflecting crystal interposed in the X-ray path serves as an effective filter, cutting all X-rays with energies greater than adjustable edge energy. On the other hand, the effect of filter on X-ray reflection allows the operation of the X-ray tube more effectively at maximum voltage, because the "Bremsstrahlung" normally present, is cut by the insertion of this lens ("cut-off").

2.2 TRXRF Module in Double Reflection

The new design described in this work, uses as an excitation system an old Siemens Kristalloflex 710 / 710H X-ray generator, with Mo target and Zr filter. The excitation system is operated at 40kV / 20mA. The X-ray beam passes through a lead collimator that has an aperture of 0.1 mm x 10 mm. Then two crystals of 100 mm long, 20 mm wide and 7 mm thick, are attached to the collimator and the crystals are separated from each other at a distance of 45 μm. These crystals have adequate optical characteristics that allow the production of the physical phenomenon of total reflection: perfectly flat, highly polished surfaces with an average surface roughness of 1 nm and optical quality (λ/20).

The expected effect is to produce the collimation of the primary beam, by using mechanical devices that allow an attack angle less than or equal to the critical angle (6.4 arc minutes for the Mo anode). Later, an Amptek detector, model XR-100CR, with Si-PIN X Ray Detection, active area of 7 mm², silicon thickness of 300 μm, with a beryllium window of 25 μm thickness, at a distance of 5 mm between the beryllium window and the glass surface is coupled to the double reflection module. Subsequently the system is connected to an associated electronics, for signal processing. More background information can be obtained directly from the corresponding author of this article.

Figure 7 shows the new prototype developed as an original contribution for the use of the TRXRF technique. This device allows a significant reduction of background noise with respect to the other systems described above. Figure 8 shows the comparative spectra of three TRXRF systems, corresponding to the surface analysis of a quartz crystal, measured in the same experimental conditions. Clearly, the new prototype exceeds the detection limits obtained by the other two TRXRF systems.

Figure 7: TRXRF Module in Double Reflection: 1: Siemens, Kristalloflex X-Ray generator. 2: Collimator and Zr filter. 3: Parallel quartz crystals. 4: X-Y geometry. 5: quartz simple holder. 6: System support. 7 Amptek Detector, model XR-100CR, Si-PIN X-Ray Detection.
2.2.1 Calibration of the TRXRF Module in Double Reflection

The total reflection module was calibrated to obtain the best geometric configuration, so that the excitation radiation illuminates on the sample holder under full reflection conditions. The critical angle $\phi_{\text{crit}}$ can be calculated by Eq. (7), where $E$ represents the energy of incident radiation (in keV), and $\rho, Z, A$, correspond to the density (g/cm$^3$), $Z$ at the electron number in an atom or molecule and $A$ is the atomic mass (g/mol) of the sample carrier, respectively.

$$\phi_{\text{crit}} = \frac{99}{E} \sqrt{\frac{\rho Z}{A}}$$

For the proposed system a quartz crystal (SiO$_2$) is used as the sample carrier. The parameters are: $\rho = 2.5$ g/cm$^3$; $Z = 30$ electrons/molecule, $A = 60,0863$ g/mol and an energy $E = 17.44$ keV of the $K\alpha$ X-ray from the incident radiation. Finally a critical angle of 6.4 min is obtained. This angle is adjusted using the micrometer screws of the reflector module.

The detection limit is obtained by:

$$L.D. = \frac{\text{Concentration}}{\text{Peak Area}} \cdot \frac{1}{3\sqrt{\text{Background}}}$$

2.2.2 Quantitative analysis

The results are obtained by evaluating the measured spectra of both samples and calibration standards using only the net intensity or area under the curve, according to the following expression:

$$I_i = G \varepsilon_i (E_i) K_i \rho_i \left(1 - e^{-X_i \rho_M / \rho_D} \right)$$

Where $S_i = G \varepsilon_i (E_i) K_i$ is called the sensitivity of the element $i$ and $\rho_i / \rho_M$ is the weight fraction of the element in the sample. In this way the sensitivity of each element is expressed as:
Here, $X_i$ is the absorption coefficient of the element $i$ in the sample and $D$ represents the thickness of the sample.

The used methodology, corresponds to the elemental sensitivities method applied to the multi-elemental analysis, considering the thin film approximation \[16\]. In order to establish the concentration of the elements present in the sample, these data are interpolated in the calibration curve (Figure 9 and Figure 10), considering the following expression:

$$S_i = a_0 + a_1 Z_i + a_2 Z_i^2 + ...$$  \hspace{1cm} (5)

Where $a_i$ are numerical factors and $Z_i$ corresponds to the atomic number of the analyte.

**Figure 9:** Experimental and fit Sensitivities of the $K\alpha$ lines (polynomial of order 6) as a function of atomic number of the elements.

**Figure 10:** Experimental and fit Sensitivities of the $L\alpha$ lines (polynomial of order 4) as a function of atomic number of the elements.
This calibration curve is constructed by measuring standard samples containing elements of high purity, with different and known concentrations. Later, using the AXIL software [17], the sensitivities of all the elements within that range of energies are calculated. Figure 11 shows the X-ray spectrum of two multielemental standards of 2x10^{-10} g and 10^{-9} g, respectively for each one of the elements.

![X-ray spectrum of two multielemental standards](image)

**Figure 11:** X-ray spectrum of two multielemental standards of 2x10^{-10} g and 10^{-9} g, respectively for each.

### 2.2.3 Sample preparation

Aliquots of 5 uL of each of standard solutions were prepared and were deposited on quartz supports. The Ga element was used as internal standard for all the samples. When the samples deposited on the quartz support are dried under IR light, a thin film is formed. The samples were excited for 300 s and the X-ray spectrum obtained for each one of them were adjusted by AXIL software. Finally the net areas of the characteristics X-ray peaks, for each element present in the sample were evaluated.

### 2.2.4 Results

For comparative purposes a sample carrier without the sample is measured under the same instrumental conditions, to establish the detection limits of each of the three TRFRX experimental arrangements, by means of the following expression:

\[
LD_i (ppm) = \frac{3\sqrt{BG_i}}{S_i} \tag{6}
\]

where \(BG_i\) are the counts at the position of the element \(i\) in the spectrum and the sensitivity of the \(i\) element is given by:

\[
S_i = \frac{Area}{Concentration} \tag{7}
\]

In table 2 and Figure 12, we report the detection limit obtained for the three TRXRF arrangement. Clearly the new TRXRF Module in Double Reflection exhibits the best results that allow to establish concentrations in the picograms order.
Table 2. Comparative detection limits of the three experimental TRXRF arrangements analyzed (A) Simple reflection, (B) Standard Reflection and (C) new TRXRF Module in Double Reflection (Results in grams x10^{-11})

| Z  | Elements | Energy (KeV) | (A) | (B) | (C) |
|----|----------|-------------|-----|-----|-----|
| 20 | Ca       | 3,690       | 600 | 65  | 13  |
| 23 | V        | 4,949       | 300 | 32  | --  |
| 24 | Cr       | 5,411       | --  | --  | 5   |
| 25 | Mn       | 5,894       | 160 | 18  | 4   |
| 26 | Fe       | 6,396       | --  | 16  | 4   |
| 27 | Co       | 6,920       | 160 | 16  | --  |
| 28 | Ni       | 7,471       | --  | --  | 4,5 |
| 28 | Cu       | 8,040       | --  | --  | 5,0 |
| 30 | Zn       | 8,838       | 150 | 15  | 4,5 |
| 34 | Se       | 11,207      | --  | 16  | 4,3 |
| 38 | Sr       | 14,100      | 150 | 16  | --  |
| 39 | Y        | 14,931      | 150 | 16  | 4,1 |

Figure 12: Comparative detection limits of the three experimental TRXRF arrangements analyzed (A) Simple reflection, (B) Standard Reflection and (C) new TRXRF Module in Double Reflection

Additionally to verify the applicability of the technique, from the precision and accuracy point of view, two certified rainwater samples were measured for a number of elements. The rain water samples from the Background Air Pollution Monitoring Network (BAPMoN 1, Austria) were measured by using de new TRXRF module in double reflection. Table 3 shows the analytical results.
Table 3. Analysis of certified rainwater simples from de BAPMON by using the new TRXRF Module in Double Reflection

| Elements | TRXRF (ppm) | BAPMON-1 (ppm) | TRXRF (ppm) | BAPMON-2 (ppm) |
|----------|-------------|----------------|-------------|----------------|
| Mn       | 40 ± 2      | 39             | 14 ± 2      | 14             |
| Ni       | 21 ± 1      | 24             | 13 ± 2      | 14             |
| Cu       | 74 ± 4      | 73             | 24 ± 2      | 22             |
| Pb       | 110 ± 5     | 109            | 33 ± 3      | 32             |
| Fe       | 70 ± 2      | 69             | 42 ± 2      | 41             |
| Zn       | 63 ± 2      | 64             | 10 ± 2      | 9              |

3. Conclusions

The detection limits obtained for the new prototype exceed 38 to 46 times those obtained by the system in simple reflection and between 4 and 5 times those shown by the TRXRF Standard system, for the energy range studied.

By decreasing the excitation-sample source distance, the intensity of the characteristic radiation increases while the measurement times are reduced.

The adjustment and calibration of the critical angle is considerably simpler than traditional reflection systems, furthermore exhibiting good reproducibility and stability.

The results obtained with this new device, project to this technique with applications to the simultaneous analysis of elements, in the order of $10^{-11}$ grams, for a variety of applications.

The costs involved in the construction of the new system are significantly lower than the conventional systems, because the number of precision mechanical parts is minimized. On the other hand an obsolete X-ray generator connected to a modern X-ray reflection and detection system is reused.

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