



# Development of Total Reflection X-ray fluorescence spectrometry quantitative methodologies for elemental characterization of building materials and their degradation products☆

Cristina García-Florentino<sup>a,\*</sup>, Maite Maguregui<sup>b</sup>, Eva Marguá<sup>c</sup>, Laura Torrent<sup>c</sup>, Ignasi Queralt<sup>d</sup>, Juan Manuel Madariaga<sup>a</sup>

<sup>a</sup> Department of Analytical Chemistry, Faculty of Science and Technology, University of Basque Country UPV/EHU, P.O. Box 644, 48080 Bilbao, Basque Country, Spain

<sup>b</sup> Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, P.O. Box 450, 01080 Vitoria-Gasteiz, Basque Country, Spain

<sup>c</sup> Department of Chemistry, University of Girona, Faculty of Sciences, C/M. Aurèlia Campmany, 69, Girona, Spain

<sup>d</sup> Institute of Environmental Assessment and Water Research, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain

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## ABSTRACT

In this work, a Total Reflection X-ray fluorescence (TXRF) spectrometry based quantitative methodology for elemental characterization of liquid extracts and solids belonging to old building materials and their degradation products from a building of the beginning of 20th century with a high historic cultural value in Getxo, (Basque Country, North of Spain) is proposed. This quantification strategy can be considered a faster methodology comparing to traditional Energy or Wavelength Dispersive X-ray fluorescence (ED-XRF and WD-XRF) spectrometry based methodologies or other techniques such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In particular, two kinds of liquid extracts were analysed: (i) water soluble extracts from different mortars and (ii) acid extracts from mortars, black crusts, and calcium carbonate formations. In order to try to avoid the acid extraction step of the materials and their degradation products, it was also studied the TXRF direct measurement of the powdered solid suspensions in water. With this aim, different parameters such as the deposition volume and the measuring time were studied for each kind of samples. Depending on the quantified element, the limits of detection achieved with the TXRF quantitative methodologies for liquid extracts and solids were set around 0.01–1.2 and 2–200 mg/L respectively. The quantification of K, Ca, Ti, Mn, Fe, Zn, Rb, Sr, Sn and Pb in the liquid extracts was proved to be a faster alternative to other more classic quantification techniques (i.e. ICP-MS), accurate enough to obtain information about the composition of the acidic soluble part of the materials and their degradation products. Regarding the solid samples measured as suspensions, it was quite difficult to obtain stable and repetitive suspensions affecting in this way the accuracy of the results. To cope with this problem, correction factors based on the quantitative results obtained using ED-XRF were calculated to improve the accuracy of the TXRF results.

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## 1. Introduction

Total Reflection X-ray fluorescence (TXRF) spectrometry is an analytical technique that is increasingly being used for multi-elemental characterization in many different types of matrices, especially in liquids, powders or solid micro-samples [1,2]. At the end of the 80s and beginning of the 90s, there was a boom in TXRF research for trace metal determination in water samples [3,4] and in other kind of liquids such

as wines or coffee [5] and tea [6] or environmental aerosol particles [7] and also for layer analysis [8,9]. The use of TXRF was replaced somehow due to the strong competitiveness of other spectroscopic techniques such as Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP). However, the recent development and commercialization of benchtop TXRF instrumentation, which does not require water cooling systems and liquid nitrogen cooled detectors, as they needed the large-scaled instruments with high power X-ray tubes, has increased again the use of TXRF [10–13]. In fact, TXRF presents some advantages such as the small amount of liquid sample required, the simplicity of sample preparation (both reducing the amount of chemical residues from analyses) and the simplicity of the experimental set up, and the lower investment and running costs of the instrumental systems [14]. There are also recent studies in which certain elements are

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\* Corresponding author.

E-mail address: [cristina.garciaf@ehu.eus](mailto:cristina.garciaf@ehu.eus) (C. García-Florentino).

preconcentrated or isolated from different matrices and then, the quantification is performed using TXRF [15,16].

Despite these recent studies especially focused on environmental or food sciences, TXRF is still very little used in art, archaeology and in general in Cultural Heritage investigation field. Only few papers exist related to Cultural Heritage applications and they are dedicated to pigments characterization [17–19]. The authors of this work developed two different ED-XRF based quantitative methodologies to analyse aqueous and acid extracts from building materials (mortars) and their degradation products coming from a building from the early 20th century with a high historic and cultural value located in Getxo (Basque Country, North of Spain) [20]. Considering that these kind of methodologies require the preparation of empirical calibration procedures, which can be time consuming, in this work, we propose the application of TXRF for the elemental characterization of the same liquid extracts, as a faster and sustainable quantification methodology. In particular, two kinds of liquid extracts were analysed: a) water soluble extracts from different mortars which their composition can provide an idea of the degradation reactions that are suffering the materials; and b) acid extracts from mortars, black crusts, and calcium carbonate formations (stalactite shape) for the elemental quantification of the acidic soluble part. In order to try to avoid the acid extraction step of the materials and their degradation products, the TXRF direct measurement of the powdered solid suspension of the materials was also studied. This suspension was then deposited as a thin layer on the reflector surface trying to minimize the matrix effect present in ED-XRF analysis of solid materials (powders and pressed powders) such as mortars, cements and concretes. The obtained results were compared to the ones provided by ion chromatography and ICP-MS in the case of liquid extracts and by ED-XRF for solid suspensions.

## 2. Experimental

### 2.1. Reagents and solutions

The TXRF quantification was performed using a 1000 mg/L stock solution of Rh (III) in HCl 3 M from Romil Pure Chemistry (Cambridge, UK) as internal standard. For the deposition of the samples in the quartz glass disc reflectors, a silicone solution in isopropanol (Serva electrophoresis GmbH & Co, Heidelberg, Germany) was deposited in order to obtain a hydrophobic film before sample depositions.

Two reference materials, BCR-032 (Trace elements in Moroccan phosphate rock, Institute for Reference Materials and Measurements, Belgium) and NIST-634a Portland Cement (National Institute of Standards and Technology, Gaithersburg, Maryland, USA) were measured in order to validate the TXRF quantification methodology in the case of the solid suspensions analyses.

### 2.2. Sample description

The analysed samples in this work are building materials and their degradation products from a 1918 building called Punta Begoña Galleries located in front of the sea in Getxo (Basque Country, North of Spain). The galleries are divided into two levels. Samples from the Upper Gallery (North orientation) are labelled as UG and samples from the Lower Gallery (South orientation) are labelled as LG. According to this nomenclature, mortars from the Upper Gallery are referred as MUG and mortars from the Lower Gallery are referred as MLG. When the mortar sample is placed over the reinforced concrete, it is labelled as CLG-L with a number at the end indicating the position of the layer (1 external, 2 intermediate, 3 internal one). Finally, the mortar coming from an external railing over the Lower Gallery is labelled as MER or as BCER for the black crust growing over it. As it was mentioned above, two main types of degradation products were analysed. On the one hand, black crusts (BCLG, BCUG or BCER), gypsum crusts formed due to the interaction between the original material ( $\text{CaCO}_3$ ) and the

$\text{SO}_2$  present in the atmosphere that can trap carbon and metallic particles. On the other hand, calcium carbonate stalactite-like formations (FLG or FUG) originated from dissolution/reprecipitation processes of the  $\text{CaCO}_3$  present in mortars.

The aqueous extracts of the mortars and their degradation products were obtained by water extraction assisted by ultrasonic energy [21] while the acid extracts were obtained by microwave acid digestion following the EPA 3051A method [22]. The aqueous extracts were supposed to contain salts composed mainly by elements with low Z value such as K, Na, Ca and Mg. However, in the case of the acidic extracts of the building materials and the calcium carbonate formations, heavier elements such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Pb and Ba were expected.

### 2.3. Sample preparation

In the case of the analyses of the liquids extracts, the TXRF measurements were performed by depositing and weighting 1 mL of each sample in an Eppendorf tube together with 50  $\mu\text{L}$  of a 100 mg/L Rh solution. In this way, a final Rh concentration of 5000  $\mu\text{g/L}$  concentration was achieved using a negligible volume of internal standard in comparison to the sample volume. All kinds of samples were measured using quartz glass disc reflectors. For the liquid samples (aqueous and acid extracts) 10  $\mu\text{L}$  of silicone in each reflector were firstly deposited and dried under an Infrared (IR) lamp. Once the silicone was dried, the standardized sample was stirred in a vortex and 10  $\mu\text{L}$  of the mixture was deposited over the silicone and then dried under the IR lamp.

For TXRF measurements of the solid samples, as TXRF is design for the analysis of micro-samples, big fragments of each mortar were grinded and homogenised in a ball mill. Then 50 mg of the obtained solid powder were weighted together with 1 mL of Milli-Q water and 100  $\mu\text{L}$  of 100 mg/L of Rh solution in order to achieve a 10,000  $\mu\text{g/L}$  concentration of the internal standard in the samples. The prepared solid suspensions were also stirred with a vortex and were also deposited over 10  $\mu\text{L}$  of silicone previously dried. In the case of the suspensions, the volume deposition used in all the cases was 5  $\mu\text{L}$ .

Determination of loss of Ignition (LOI) in solid samples was conducted at 975 °C during 4 h and using 1 g of each powdered sample in order to obtain the  $\text{CO}_2\%$ . Then, this value was used to take into consideration the absorption effect for the calculations of the semi-quantitative ED-XRF analyses by Fundamental Parameters in the solids and thus, to obtain more accurate results. Afterwards, these values were used to compare them with the TXRF results.

### 2.4. Instrumentation

The Total Reflection X-ray fluorescence analyses were performed using a benchtop instrument S2 PICOFOX™ (Bruker Nano Analytics GmbH, Berlin, Germany) equipped with an air-cooled tungsten target X-ray tube (max. power 50 W), a multilayer monochromator (35.0 keV) and a Peltier cooled Silicon Drift Detector with a resolution <160 eV at Mn- $K_{\alpha}$ . The equipment is provided with a cassette changer for 25 samples that allows the programming of different measurement sequences. The evaluation of the spectra and the calculation of the elements concentrations were performed using the Spectra-Picofox 6.2.0.0 (Bruker Nano Analytics GmbH, Berlin, Germany) software. The measurements were performed at 50 kV and 1 mA in air conditions in all cases. It must be highlighted that S2 PICOFOX™ does not allowed to work under vacuum conditions and thus the determination of elements with low Z value is more restricted being the limits of detection too high comparing with ED-XRF or WD-XRF spectrometers that can work under vacuum.

For comparison purposes, a commercial benchtop Energy Dispersive X-ray fluorescence instrument (S2 RANGER, Bruker AXS, GmbH, Germany) was used to analyse the solids materials. The S2 RANGER ED-XRF system is equipped with a Pd X-ray tube (max. power 50 W)

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