Spectrochimica Acta Part B 140 (2018) 76–83

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Effect of modulation of the particle size distributions in the direct solid analysis by total-reflection X-ray fluorescence

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ARTICLE INFO

Article history:
Received 3 August 2017
Received in revised form 5 December 2017
Accepted 13 December 2017
Available online 14 December 2017

Keywords:
TXRF
Direct solid analysis
DSA
DSA-TXRF
Particle size distribution (PSD)
PSD modulation
Laser diffraction (LD)
Mechanical grinding
Accuracy
Uncertainty
Detection limit
Analytical parameters

ABSTRACT

The main goal of this work was to investigate, in a systematic way, the influence of the controlled modulation of the particle size distribution of a representative solid sample with respect to the more relevant analytical parameters of the Direct Solid Analysis (DSA) by Total-reflection X-Ray Fluorescence (TXRF) quantitative method. In particular, accuracy, uncertainty, linearity and detection limits were correlated with the main parameters of their size distributions for the following elements; Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Rb, Sr, Ba and Pb. In all cases strong correlations were finded. The main conclusion of this work can be resumed as follows; the modulation of particles shape to lower average sizes next to a minimization of the width of particle size distributions, produce a strong increment of accuracy, minimization of uncertainties and limit of detections for DSA-TXRF methodology. These achievements allow the future use of the DSA-TXRF analytical methodology for development of ISO norms and standardized protocols for the direct analysis of solids by mean of TXRF.

1. Introduction

Total-reflection X-Ray Fluorescence (TXRF) spectrometry is a well-know analytical technique that it is every time more applied to different scientific fields to solve routine and more complicated analytical questions in an every time higher number of different materials [1]. TXRF spectrometry has several and very diverse analytical capabilities but one of the more interesting features is its ability for the direct quantitative analysis of solids without sample chemical distortion i.e. acid leaching or digestion processes. Up to now, this way of analysis by TXRF has been applied to very diverse kind of solid matrixes, i.e. soils [2], algae [3], ceramics [4] or sediments [5] are only some of them. In this way, "slurry", "suspension" or "solid dispersion" concepts have been extensively used in the TXRF literature [6,7,8]. In this paper we propose a new denomination for these kinds of sample preparation with the aim of unification and normalization of the methodology. In all the cases the analytical procedures can be defined as a Direct Solid Analysis (DSA) of samples quantified by Total-reflection X-Ray Fluorescence (TXRF). So, the proposed acronym is DSA-TXRF method. Common characteristics of the DSA-TXRF methodology are as follows; first, this method requires a minimum sample preparation effort based mainly in a small quantity of necessary sample (micro-analytical method) an adequate grinding, suspension and internal standardization of the sample. Moreover, results are obtained in an analytical and quantitative way, where the matrix effects, mainly absorption and second and third interactions, can be avoided. This is because deposited solid is excited with an X-ray source with an angle down to the critical angle of the sample-support material. As consequence, an X-ray Standing Wave (XSW) field is generated due to the constructive interaction between the incident and reflected monochromatic X-ray beam. Taking in consideration the physic of the XSW for solid particles deposited over the surface of the TXRF sample-support (reflectors), the sizes and the distribution of the deposited particles play an important role in the analytical quality of the TXRF measurements [9]. Nevertheless, the more relevant sample preparation parameters of the DSA-TXRF method have not been yet investigated in a controlled way. Some initial tries of optimization were carried out by Fernández-Ruiz et al., related with solid matrixes of different kind of nanoparticle systems [10,11,12] or by Amberger et al. [13] evaluating the surfactant composition and pH effects in a DSA-TXRF analysis of traces in boron nitride powder. The basis and first principles to apply the DSA-TXRF procedure were given by

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https://doi.org/10.1016/j.sab.2017.12.007
0584-8547/© 2017 Published by Elsevier B.V.

Klockenkämper and Von Bohlen in the pioneer work [14] and more recently by Hellin et al. [15] and Fernández-Ruiz [16]. Therefore, the main objective of present work was to investigate, in a systematic way, the influence of the modulation of the particles size distribution (PSD) of a generic solid with respect to some of the more relevant analytical parameters of the DSA-TXRF method. In particular, a soil of sedimentary rock sample named JSd-2 [17] was used as reference in this research. Several parallel goals were investigated, in particular, the main mechanical parameters of the micro-grinding system, i.e. grinding time and grinding frequency, were optimized during the research of the size modulation of the JSd-2 material. As result, four suspensions with defined sample concentration, named DS0, DS1, DS2 and DS3, were modulated varying adequately grinding parameters and characterized by Laser Diffraction (LD) for evaluating their particle size distributions (PSD's). The behaviors of following analytical parameters of the DSA-TXRF method were evaluated in each one of the JSd-2 suspensions; accuracy, as recovery, precision, as expanded uncertainty, and limits of detection. Additionally, the lineal correlations between DSA-TXRF results and JSd-2 certified results were evaluated with the goal of validate previous results by mean of an independent statistical evaluation. The main results achieved are presented in this work.

2. Materials and methods

2.1. Instrumentation

Qualitative and quantitative TXRF analysis were performed with a benchtop S2 PicoFox TXRF spectrometer from Bruker Nano (Germany), equipped with a Mo X-ray source working at 50 kV and 600 μA, a multilayer monochromator with 80% of reflectivity at 17.5 keV (Mo K_α), a XFlash SDD detector with an effective area of 30 mm^2 and an energy resolution better than 150 eV for 5.9 keV (Mn K_α).

The modulation of the particle size distributions were performed with a MM-400 mechanical micro-grinding system from Retsch™ (Germany). The particle size distributions (PSD's) were determined with a MasterSizer-2000 Laser Diffraction (LD) system from Malvern Instruments Ltd. (England).

Linear correlations study, modeling and fitting of several analytical parameters behaviors and paper figures were performed by using OriginPro 8.0 software package form OriginLab Corporation (USA).

2.2. Modulation of the JSd-2 particle size distribution

JSd-2 material is a certified geochemical reference material of sedimentary rocks from the Japanese National Institute of Advanced Industrial Science and Technology (AIST) as part of the geological survey of Japan. Sampled rocks were roughly crushed with a jaw-crusher, and powdered in a ball-mill. The powder was screened with a 250 μm sieve, homogenized, and approximately 100 g of the powder were put in each glass bottle. So, the upper particle size limit waited for the JSd-2 material was lower than 250 μm. Each one of the solid suspensions was made with 50 mg of JSd-2 material in powder which were introduced in a grinding jar of agate with one agate ball for a MM-400 grinding instrument. After the first tries of grinding in a solid way very strong adherences and even sintering effects in the material were observed. So, a first study and optimization of the main grinding parameters were carried out with the aim of optimize the correct solid suspension of the JSd-2 analyzed sample. These parameters were first the volume of water added to the grinding jar and second and third, frequency and time of the grinding process respectively.

2.2.1. Influence of water added

The first parameter was the water added during grinding process. The purpose to add water to the jar of the grinding system was to minimize the adherences of the solid microparticles to the jar walls and ball, to avoid sintering effects and additionally, to reduce the temperature of the grinding process due to friction. In this way, three samples were prepared; without water, with 0.5 mL and with 1 mL of milli-Q water respectively. The grinding time and frequency were fixed to 1 h and 30 Hz respectively. The particle size distributions associated to the obtained solid suspensions were measured by laser diffraction spectroscopy (LD). Fig. 1 shows that the addition and increase of water in the grinding process produces a damping effect of the energy transferred by the ball to the particles of the sample during grinding. As consequence, the high size fractions are more populated for 1.0 mL that 0.5 mL. In fact, the Dv50 values for both distributions, which define their median values, were 3.06 μm and 2.04 μm respectively. The sample without water added presents a shape distribution different. In this case, the higher sizes are more populated with Dv50 sizes of 14.9 μm. Additionally, the Dv90 values, which define higher sizes with 90% of probability, were 9.59, 6.83 and 32.6 μm for 1 mL, 0.5 mL and 0 mL of water added respectively.

These results confirm that the use of 0.5 mL of water in the grinding process is optima because eliminate the adherences and possible sintering process, observed for the sampled grinded without water. Additionally, this volume of water minimize the high sizes fractions and increase the nanometric sizes population compared with samples grinded with 1.0 mL of water. In the case of the sample grinded without water the nanometric population is higher than for samples grinded with water. This fact can be explained because the damping effect is not present without water and then the energy transferred from the ball to the particles is maxima allowing, as consequence, a more efficient grinding process for lower size particles. Nevertheless and simultaneously, this increment of the energy can induce sintering process which explains the increase of the high sizes population.

2.2.2. Influence of the grinding frequency

The second parameter evaluated was the influence of the grinding frequency in the modulation of the particle size distribution of the JSd-2 material. A series of solid suspensions obtained with following grinding frequencies were prepared: 0 (without grinding), 10, 15, 20, 25 and 30 Hz. In all the cases the grinding time was fixed to 1 h and the volume of water added was 0.5 mL. Fig. 2 shows the particle size distributions obtained by LD, for each one of the JSd-2 material suspensions. LD results show that JSd-2 particle size distributions were clearly modulated to lower sizes when the applied frequencies increase. In a first approximation, an increment of the grinding frequencies implies a modulation of the distributions to lower particles sizes. In a more analytical approximation, the experimental size distributions showed in Fig. 2, named $I(\delta)'$s, are multimodal and complexes. So, the

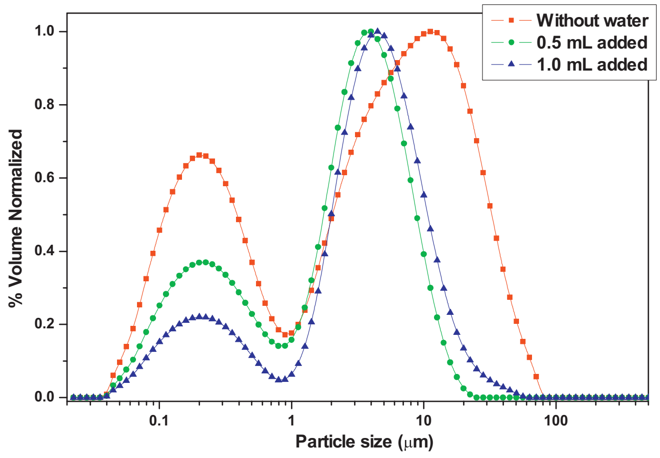

Fig. 1. Modification of particle size distributions (PSD's) of JSd-2 soil versus volume of water added to the grinding jar.