Micro-X Ray Fluorescence (micro-XRF) Usefulness in Waste Analysis

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Abstract

Micro-XRF is capable of detecting elements directly in waste samples without need of digestion. Its reliability is well-established, making it a trusted method for elemental analysis. Micro-XRF also allows detecting elements with spatial resolution generating concentration maps and thus allowing a homogeneity-heterogeneity control for the sample. This can be important in complex matrices like wastes that show often great variability and great heterogeneity.

Introduction

Waste characterization often requires carrying out analyses on very complex matrices. The composition of a waste may include very different materials (i.e. stones, bricks, wood, paper, cloths, plastics etc.) solid and/or liquid mixed together so that the first step when starting a characterization - sample homogenization - may result very difficult. In the case of a solid waste the grinding phase, necessary for adequate homogenization of the sample, may not be adequate for all types of materials here present, if carried out with only one type of mill. The plastic particles can melt if the sample is overheated during this second grinding phase, limiting the reduction in particle size and compromising the homogeneity of the sample. Furthermore, if there are fibrous materials (mineral, synthetic or vegetable), the fibrous part, even reduced to small dimensions, is very difficult to mix and homogenize with the non-fibrous powdery part.

Despite the grinding and homogenization phase, waste samples and more complex materials, may still exhibit some "residual microheterogeneities" which can impact the repeatability and uncertainty of the result. Such residual microheterogeneity can also be critical in the case of analysis results that show indicative values towards the hazardous nature of the waste. To highlight any evidence on sample microheterogeneity we analyzed some waste samples both with the ICP-OES technique -after mineralization- and with the micro-XRF technique. Micro X-Ray Fluorescence (micro-XRF) is a technique now consolidated in various research fields (e.g. geology, limnology, archaeology, forensic and environmental sciences) [1-8] and offers the great advantage of a rapid, direct and non-destructive elemental analysis of the various materials investigated. Furthermore, it is capable of achieving high spatial resolution, producing elemental maps of a sample with a resolution of the order microns. Its ability to provide an elemental fingerprint of the sample can allow us also to check the sample homogeneity or otherwise it can show particles or areas with different concentrations for a given element thus highlighting micro-heterogeneity problems in the sample itself. When working on homogenized samples the XRF offers undoubted capability to produce data well aligned with those results obtainable with Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). The only limitation for ICP-OES is the digestion step: mineralization procedures do not always successfully dissolve all metals, especially those bound in certain crystalline phases. In some cases the use of strong acid mixtures, including hydrofluoric acid, is required, which significantly increases the safety risks for operators. In our laboratory solid waste samples usually are prepared at sizes <4 mm by crushing in a Retsch BB 250 jaw crusher and/or Retsch RM100 cutting mill. Following this initial crushing, the samples are further ground to sizes smaller than 1 mm using a Retsch ZM200 centrifugal mill. Samples for metal analyses are further ground to 0.1 mm (where applicable, depending on the materials in the matrix) by means of a Retsch MM500 Nano mixer mill. In this case, abatement powders are often already in fine forms so that only the two last steps were needed. Samples were then analyzed with a M4 Tornado Plus micro-XRF spectrometer. For ICP-OES analyses the sample were digested in a CEM Mars-X microwave system and finally analyzed with an Agilent 5800 ICP-OES spectrometer. The samples were also previously analyzed for crystalline phases screening with a Siemens D5000 Kristalloflex X-ray diffractometer (XRD). The present work reports examples on three samples (Sample A, Sample B and Sample C) of waste abatement dust characterization.

Conclusion

The three XRD spectra in Figure 1a-1c show the results of a qualitative screening for crystalline phases for Sample A, Sample B and Sample C respectively from left to right.
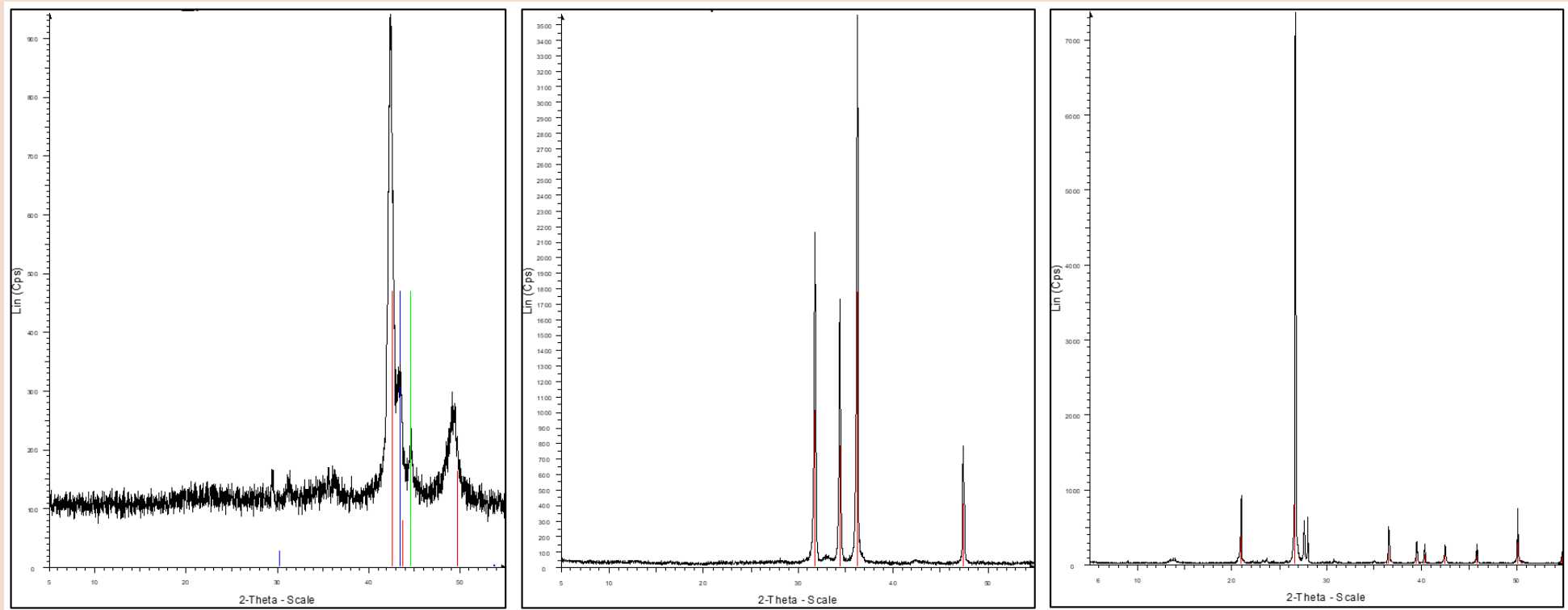

Figure 1a (left): X-ray Diffraction (XRD) trace of Sample A; 1b) (center): XRD trace of Sample B; 1c) (right): XRD trace of Sample C. 2θ scale from 5° to 55°.

The main diffraction lines in Sample A (red marks, 2θ = 42.5° and 49.7°) correspond to Brass while the line at 2θ = 44.7° (light green mark) corresponds to Iron. In Sample B the four lines (red marks, 2θ = 31.8°, 34.4°, 36.1° and 47.5°) are indicative for Zinc oxide. The diffraction lines in Sample C (red marks, 2θ = 20.9°, 36.4°, 39.5°, 40.4°, 42.5°, 45.8° and 50.1°) are characteristic of Quartz.

Table 1 lists the data of the main metals in the sample using both ICP-OES and micro-XRF techniques in parallel. In general, a strong agreement can be observed between the two sets of data obtained with ICP-OES and micro-XRF, except for those elements present in lower amounts (i.e. < 3%). In Sample A the relative amounts of Cu and Zn are respectively in accord with the composition of alpha-Brass[9].

Oxygen is detected by micro-XRF but as for other elements with a low atomic number, the determination only allows for an approximate quantity. The detection however, in amounts comparable or compatible (considering the other elements presents) with the stoichiometry of ZnO for Sample B and of Quartz for Sample C, confirms the findings by X-Ray Diffraction.

Sample	Element	Results by ICP-OES	Results by micro-XRF
A	Cu	28%	25%
	Zn	13%	13%
	Fe	2.7%	2.0%
	Al	0.6%	1.0%
B	Zn	40%	40%
	O[1]	nd	15% [1]
C	Si	nd	28%
	Al	0.3	1.0%
	O[1]	nd	40% [1]

Table 1: Metals and element analysis for the three samples A, B and C with the techniques ICP-OES and micro-XRF in parallel. "nd" = not determined; (1) indicative data, in the XRF analysis of low-Z elements.

Figure 2a-2c display micro-XRF images showing the sample area analyzed for each of the three samples in the main box (upper section), all detected elements are displayed together, in the lower boxes, each element is shown individually, offering a detailed, element-by-element visualization.
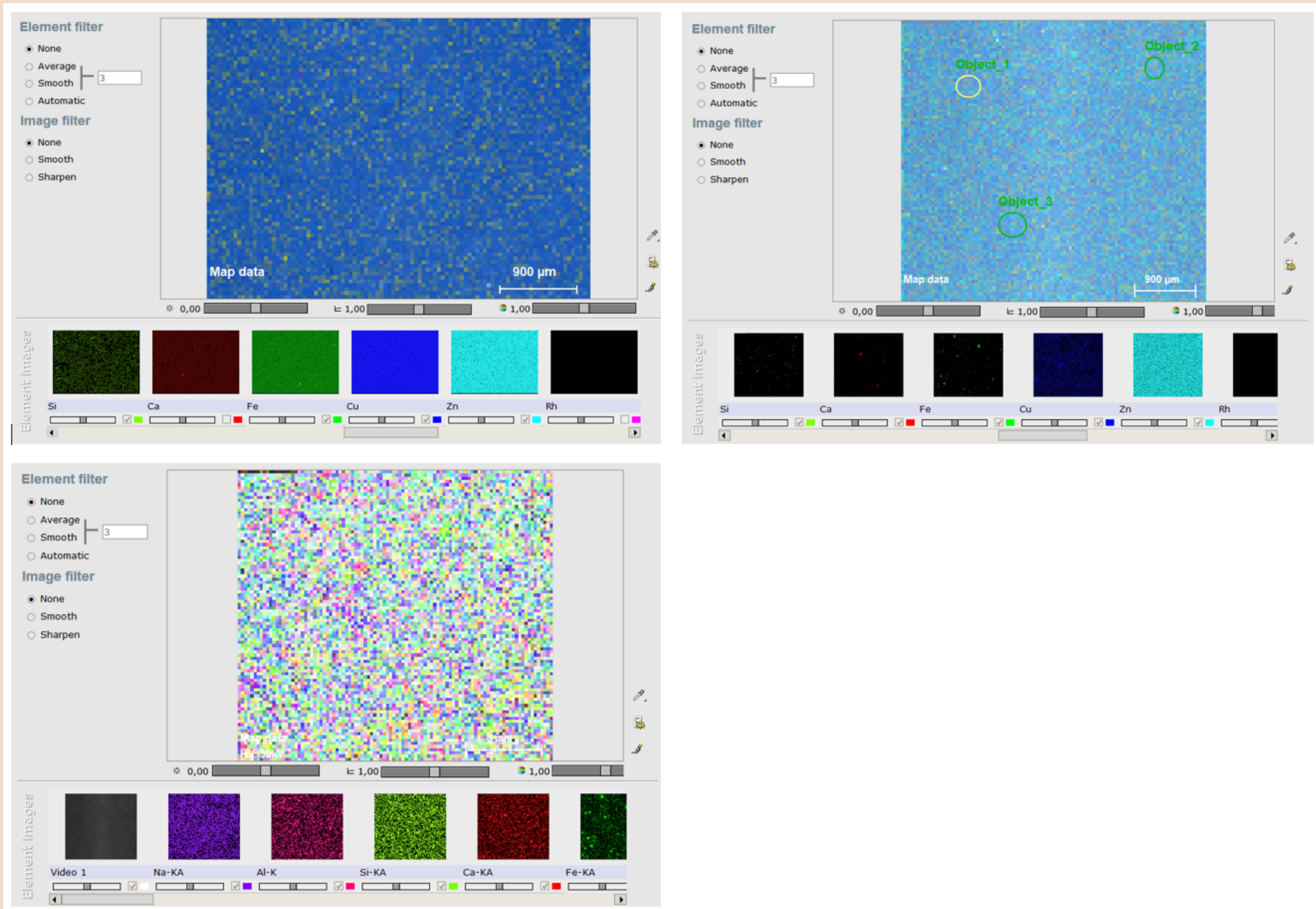
Figure 2a (upper left, Sample A), 2-b (upper right, Sample B) and 2-c (lower, Sample C): appearance with different colors and different scaled intensities of the elements detected, with spatial resolution indicating the homogeneity or peculiar non-homogeneities in the investigated sample.

Micro-XRF can offer great advantages in waste analysis not only by detecting metals and elements in an easier and quicker way with respect to ICP-OES but also by highlighting spatial distribution of the particles containing a given metal or element thus giving some control about sample homogeneity or heterogeneity after the preparative steps (grinding, sieving etc.). This could be of great importance with potentially strong heterogeneous materials like unknown waste from abandoned production sites or landfills and when analytical findings reveal probable hazardousness like the cases of Sample B and C.

Sample A and Sample B show good homogeneity. Sample A shows prevalence of Cu an Zn whereas some areas indicate Fe prevalence distributed with less homogeneity. The strong prevalence of Zn with respect to other metals in Sample B is also confirmed from this graph. Sample C exhibits a clear presence of Si but mixed with all the other elements detectable, shows up in lower amounts. The main box and the element boxes indicate a good distribution of the particles in a homogeneous sample. The last box on the right (lower row) indicates an uneven distribution for some rare Iron particles only.

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