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Computer-aided optical characterization and sensing applications: from minerals to waste

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Abstract. Optical based characterization techniques and related analytical methodologies, originally utilized in the mineral sector, can be profitably applied to solid waste streams products as resulting from different recycling processes. This approach, when supported by digital tools allows to perform a full characterization of compositional and textural attributes of the different particulate solids constituting the waste flow streams. To reach this goal specific physical-chemical attributes must be collected, analyzed and processed in order to define, according to market requirements, specific classes of quality to assume as reference to define optimal processing strategies. Computer-assisted optical characterization, coupled with hyperspectral sensing devices and embedding recognition/classification logics, can contribute to reach these goals, dramatically reducing analytical time and costs. In this work an example of this "transfer approach", from minerals to waste, is presented, analyzed and discussed, with reference to a porphyry copper ore sample and a WEEE product.

Keywords: Computer assisted microscopy, Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF) analysis, Near Infrared (NIR) HyperSpectral Imaging (HSI) Spectroscopy, porphyry copper, WEEE.

1 Introduction

In the last decades, we have assisted to a large knowledge transfer from mining to secondary raw materials sector, especially with reference to material processing and resulting products control [1, 2]. The main challenge to economically and environmentally develop and improve sustainable recycling processes relies on a good and reliable characterization of the specific product waste. In this scenario, computer-assisted optical characterization, and the related sensing applications, represents a powerful tool, especially for particulate solids waste handling, control, selection and when certification actions must be carried out. Applied mineralogy usually investigates the identities of major, minor and trace elements, the compositions of minerals – metals, the quantities of minerals - metals, particle and grain size distributions and textures of the explored material, mineral - metal liberations and the surface coatings on minerals – gangue material [3]. The same detection logic can be applied to waste, that is: the exploration of elemental identities, material – metals and/or alloy composition, particle and grain morphological, morphometrical, textural analysis and materials liberation. In this paper, a comparison, in terms of applied methodologies and obtained results, is presence with reference to a primary (i.e. copper ore) and secondary (i.e. waste electrical and electronic equipment recovered products) raw materials.

2 Materials and methods

2.1 Materials

Two samples have been utilized to perform the study. The 1st one consisting of milled product (-1100 + 600 µm) as resulting from the mechanical processing of a porphyry copper ore (Figure 1a) from Rio Blanco - Los Bronces in the Central Chile Metallogenic Segment (Late Miocene Porphyry Copper Deposits), on the west side of the Andes [4], constituted by monzonite quartz, tourmalinic breccia, andesite and chalcopyrite (CuFeS2). The 2nd one a WEEE sample coming from a Waste Electrical & Electronic Equipment (WEEE) processing plant which utilizes an innovative separation technology, the MDS (Magnetic Density Separator). The investigated product belongs to the MDS output fraction below 10 mm and characterized by a density ranging between 1300 and 2200 kg/m^3. As can be seen in Figure 1b, the product is mainly constituted by PCBs, polymers and ceramics. A small amount of metals, mainly copper, still occurs in this output. Ideally, in this density range metals should not occur. Their presence is mainly due to finer fractions resulting from milling, PCBs and wires [5].

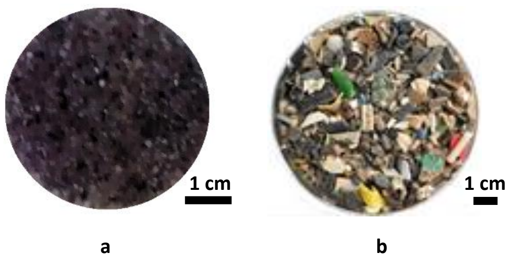

Fig. 1. Polished section of a milled product (-1100 +600) µm as resulting from the mechanical processing of a porphyry copper ore (**a**) and +10 mm bulk WEEE products fed to Magnetic Density Separation (MDS) (**b**).

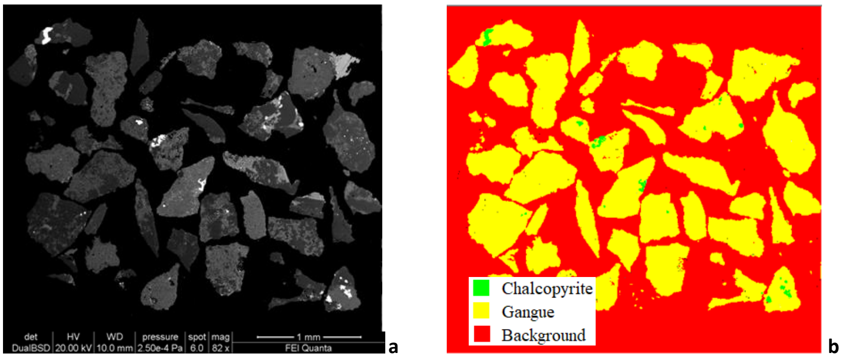

Fig. 2. SEM–BSE image acquired at 82 x for -1100 + 600 µm polished sample of particles containing chalcopyrite (**a**) and RGB image, segmented by thresholding, processed in Image-Pro® Plus (**a**). SEM analyses have been carried out using a Hitachi S2500 SEM equipped with a EDS-Kevex 8000 microanalysis unit with a Si(Li) detector.

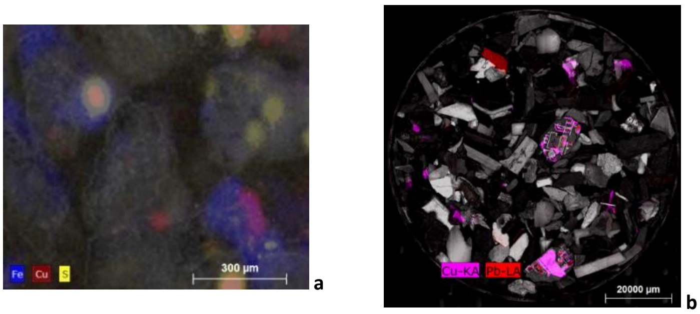

Fig. 3. XRF elemental maps of a polished section ROI (Region of Interest) identifying Cu and S of chalcopyrite grains (**a**) and metallic elements mainly occurring in Printed Circuit Boards (PCBs) (**b**) of +10 mm bulk WEEE products fed to MDS. µ-XRF analyses were performed using a benchtop XRF spectrometer (M4 Tornado, Bruker®). Elemental maps are the results of a XRF peak deconvolution of the sum spectra collected pixel by pixel.

2.2 Analytical techniques

Scanning Electron Microscopy (SEM) and X-Ray Fluorescence (XRF). The Scanning Electron Microscope (SEM) and the X-Ray Fluorescence (XRF) can be considered among the most versatile and widely used electron beam based analytical instruments for material characterization [6]. Examples of the potentialities offered by these approaches are shown in Figures 2 and 3, where SEM analysis, combined with image processing, allow to assess minerals distribution inside the porphyry copper ore grains (Figure 2) and the elemental maps (i.e. element determination referred to samples surface), determined by XRF analysis (Figure 3), of chalcopyrite ore milled product and WEEE products gives a clear picture of presence and distribution of the different elements inside the grains.

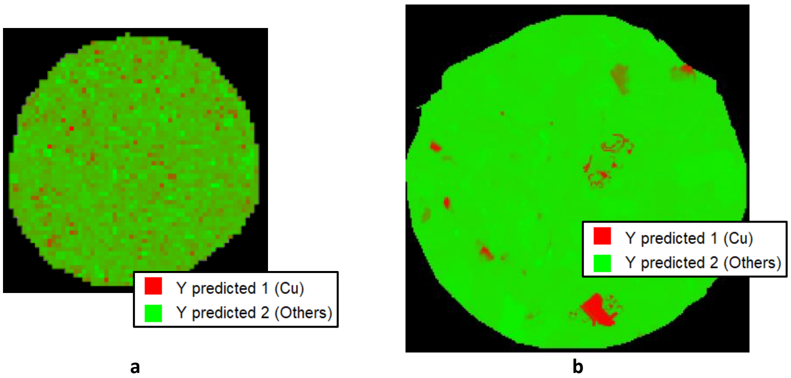

Fig. 4. a: PLS-DA copper prediction maps as resulting from the XRF mapping of -1100 + 600 µm polished sample of particles containing and gangue minerals (**a**) and of the +10 mm bulk WEEE products fed to MDS (**b**).

In recent years, SEM and XRF technologies started to be more and more utilized to characterize wastes and in particular electronic waste [7], where the problems related to materials recovery, inside a flow stream constituted by particles of different composition and textural characteristics, are very similar to those to face in mineral processing. Among these two techniques the most promising is XRF thanks to its capability to operate non-destructive chemical analyses working on wavelength-dispersive spectroscopic principles [8]. XRF is profitably applied when bulk chemical analyses of major elements (i.e. Ca, Na, K, P, Si, Al, Fe, Mg, etc.) and trace elements analyses (i.e. for quantities greater than 1 ppm: Ba, Ce, V, Y, Zr, etc.) have to be carried out in raw materials [9]. A limit of this technique is that the most available instruments cannot accurately measure the abundances of elements with an atomic number lower than 11 [10]. Furthermore, the utilization of XRF also allows to perform a "domain classification" (i.e. grain area characterized by the presence of specific element/s) over the acquired hypermap [11]. To reach this goal chemometric tools, such as the Partial Least Square - Discriminant Analysis (PLS-DA) can be applied [12]. An example of the potentialities of this approach in respect of the two reference samples (i.e. chalcopyrite and gangue minerals and WEEE product) considered in this paper are reported in Figure 4.

Computer-aided optical-spectroscopy and H*yper*S*pectral* I*maging* (HSI). Today, thanks to the development of innovative spectroscopic sensing units and the utilization of advanced chemometric tools, computer-aided optical spectroscopy, coupling "classical" optical magnification devices (i.e. macro- and micro-optical devices) and spectrometers (i.e. VIS, NIR, SWIR, Raman, etc. detection units) are more and more utilized to perform identification, recognition and classification of materials. In this framework Near Infrared Spectroscopy (NIRS) can play an important rule for its not invasive and not destructive characteristics and allowing to the determination of molecular composition of the surfaces or a quantitative analysis of compounds within a mix of materials [13].

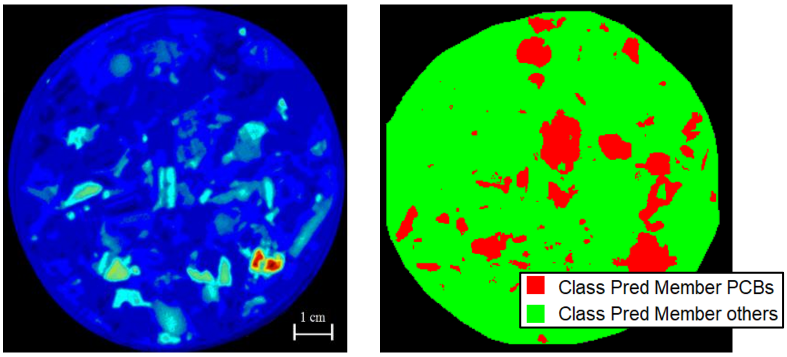

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Fig. 5. Mean reflectance hyperspectral image (1000 – 2500) nm of the +10 mm bulk WEEE products fed to MDS (**a**) and the related PLS-DA prediction map identifying the PCBs (**b**). Analyses have been carried out utilizing a SISUChema XLTM Chemical Imaging Workstation (Specim, Finland), equipped with an ImSpector™ N25E imaging spectrograph working in the 1000-2500 nm wavelength range.

Infrared (IR) detection units use an active source to irradiate and analyze the material. The spectrometer detects the reflected radiation including the absorption bands, generating a specific spectrum (i.e. "spectral signature" or "fingerprint") of the material [14]. A big step forward in the utilization of this technique, is represented by the introduction on the market of H*yper*S*pectra*l I*maging* (HSI) detection devices, allowing the implementation of innovative detection/inspection logics to utilize to solve a variety of industrial tasks such as automatic material sorting and/or quality control applications [15,16]. The utilization of Short-Wave Infrared (SWIR) – HSI units was addressed not only to mineral phases, or rocks (e.g. gangue) recognition [17] but also to materials of different origins and characteristics. With reference to secondary raw materials and more specifically considered WEEE derived products [18] in Figure 5a is shown an example of a hyperspectral image, acquired in the SWIR region: 1000 nm to 2500 nm and referred to the + 10 mm mixed WEEE milled product fed to MDS.

3 Conclusions and future perspective

Optical-digital sensing techniques, originally developed for the minerals sector, can be also profitably applied for the classification of secondary raw materials. For their characteristics, the utilization of this techniques can be addressed not only at a laboratory scale but also at plant scale, thanks to their not invasive and not destructive properties. More specifically XRF and HSI based techniques could dramatically contribute to improve the quality of solid waste derived products, allowing the possibility to implement both easy to apply laboratory controls and on-line quality control strategies for a continuous recovered products monitoring.

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