

# Non-destructive Analytical Methodologies for the Mineralogical Characterization of Mine Materials

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## INTRODUCTION

Determination of the actual chemical composition and crystalline structure of a mineral is difficult without the proper analytical equipment (Dyar and Gunter, 2009). Whilst most of the traditional analytical methodologies are useful in establishing the identification of relatively common minerals, including their chemical composition, they are not very helpful for species which are complex or when they are polymorphs.

In an outline of the main identification methods developed during the last fifty years in an ongoing effort to make minerals show some of their secrets, several hyphenated analytical techniques have been developed. Furthermore, in a period in which analysis based on non-destructive and direct techniques for their further application in many fields (art, environment, etc.) are in vogue, science is asking also not only for in situ measurements, but also for the application of a green chemical approaches (i.e., without the use of chemicals or minimizing their volume). Therefore, the present work bets on non-destructive techniques, such as Raman Spectroscopy (RS), Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and the Energy Dispersive X-Ray Fluorescence (ED-XRF) for the mineralogical characterization of mine-polluted areas.

## MATERIALS AND METHODS

The results here explained were obtained in 2 abandoned mining areas: a Zn-Pb mine located in Western Biscay (north of Spain) and a Cu-Fe mine placed at Eastern Biscay.

The identification of minerals generally starts in the field by visual examination. Based on properties such as colour,

hardness, etc., often in combination with detailed knowledge of the regional geological history, a first identification of many rock-forming minerals is possible.

It becomes more difficult to identify the more rare minerals mostly present in only minor amounts and often as small crystals.

As an attempt to better characterize the mineralogy of the impacted area several kind of samples were collected:

- Rolling stones (outside and inside the mines).
- Rocks of the galleries walls (inside).
- Soils (outside and inside).
- Efflorescences, newly formed powder-type re-precipitations (inside).
- Particulate matter deposited on vegetation (in the run-off, outside).

## Analytical Equipment

**Raman Spectroscopy:** for the molecular characterization.

An interesting non-destructive complementary alternative to the X-Ray diffraction is the Raman microscopy. Extensive and growing databases of reference spectra give RS the potential to become a widely used tool for routine mineral identification (Gasharova, 2008). Despite its potential advantages (e.g. little or no sample preparation, multi-micron-scale single grain analysis, molecular analysis, in-situ analysis) it has not yet been widely employed by the geosciences community (Hope G. A. et al., 2001).

- A portable dispersive Raman microprobe Renishaw RA100 spectrometer (Renishaw, Gloucestershire, UK) with a 785 nm excitation diode.

- InVia Raman confocal microscope by Renishaw (Renishaw, Gloucestershire, UK) equipped with excitation lasers of 785 nm, 514 nm and 325 nm.
- A portable InnoRam™ Raman spectrometer (B&WTEK INC., Newark, EEUU) provided with a 785 nm excitation laser.

**Portable Micro-Energy Dispersive X-Ray Fluorescence Spectroscopy ( $\mu$ -ED-XRF):** for the identification of elemental composition. The portable ArtTax  $\mu$ -XRF (Röntec, currently Bruker AXS, Berlin, Germany) was employed in laboratory analysis.

**Handheld Energy Dispersive X-Ray Fluorescence Spectrometer (ED-XRF):** for the identification of elemental composition. A portable analyzer X-MET5100 (Oxford Instruments, UK) allowed in situ elemental analysis.

**Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDS):** for elemental characterization and sample imaging. An EVO@40 Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany) provides the electron image acquisitions. An X-Max Energy Dispersive X-Ray Spectrometer (Oxford Instruments, Abingdon, Oxfordshire, UK) is connected to the SEM to perform the determination of the elemental composition.

## RESULTS AND DISCUSSION

We have studied a number of spectra of various minerals (Table 1 summarizes some), all with crystals not larger than a few millimeters. This will demonstrate the strength of the RS technique as it shows that each spectrum is unique and can be used as a sort of fingerprint for the identification of the mineral when a large enough database of mineral spectra is available.

**palabras clave:** Espectroscopia Raman, Muestras medioambientales, No destructivo, Análisis in situ.

**key words:** Raman Spectroscopy, Environmental samples, Non-destructive, In situ analysis.

ELEMENT	MINERALS
Lead	Litharge, massicot, plattnerite, minium, galena, cerussite, anglesite
Zinc	Zincite, sphalerite, rosasite, smithsonite, leiteite, hemimorphite
Iron	Hematite, goethite, lepidochrochite, pyrite, siderite, sarcopside
Copper	Tenorite, villamaninite, delafossite, libethenite, tsumebite, olivenite

Table 1. Some minerals identified by means of RS.

As shown in Fig. 1, some spectra obtained can be found to be a mixture (i.e., two or more minerals present in the same spot), which is not a problem for RS which can gather spectra on individual grains.

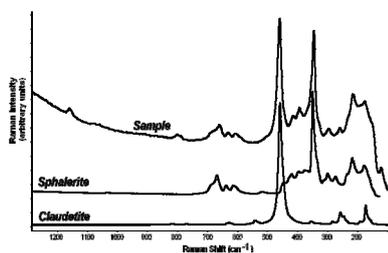


fig 1. A mineral mixture identified by RS.

Once having assigned the RS to a concrete mineral, its elemental composition may be analyzed more in depth. For instance, the molecular formula of the minerals itself do also give a clue of the oxidation state of the elements that constitutes it. It is worldwide know that the redox state of the elements is directly linked to both the environmental and the human health risk of such components. Thus, the risk associated can be deduced, and consequently the needed control actions taken.

With regard to the mineral structure, the possibilities are different. In some cases, as seen in Fig. 2, the camera of the RS microscope at 50X or 100X can give a good image of the studied grains.



fig 2. Prismatic structures of a sieved ( $\phi<250\ \mu\text{m}</math>) soil sample seen in a RS camera.$

For a more in depth textural analysis, however, SEM turns to be a more suitable tool, due to the fact that the magnifications are higher. At this point, further study of the results obtained may provide other kind of helpful

information. For instance, the particle size given by SEM (Fig. 3) provides better knowledge of the health risk assessment associated to the abandoned mine studied, as far as the atmospheric particulate matter (PM) below  $10\ \mu\text{m}$  is considered to be harmful (i.e., cancer). Furthermore, the elemental composition of such PM (mainly derived from the erosion of the tailing wastes) do also inform about the possible risks associated to the metals present (i.e., Pb, Zn, S) in each type of particle size.

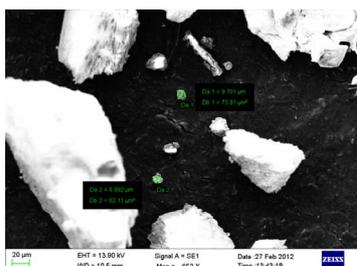


fig 3. A SEM image of a re-precipitated sample after run-off phenomena.

Since a huge amount of minerals may present impurities, an advanced elemental analysis of the samples is required. To achieve this goal, several analytical techniques such as  $\mu$ -ED-XRF, ED-XRF or EDS may be applied. For instance, Fig. 4 shows the elemental composition of a solid sample studied by EDS.

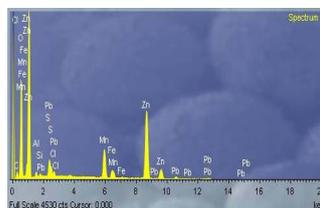


fig 4. An EDS spectrum with the identification of several elements present in a efflorescence sample.

**CONCLUSIONS**

This work explains the application of non-destructive in situ techniques for the identification of minerals. In the present research, RS has been successfully used for the identification of minerals (Goienaga et al., 2011) and

it has also been suitable for single crystals as small as a few hundred micrometers.

At the molecular level, the information provided for the above mentioned techniques seemed to be also helpful not only for the identification of the presence of impurities, but also for a semi-quantitative analysis of the environmental samples studied. Since occasionally better results are needed, the sample collection may be required for their lab analysis (i.e., by  $\mu$ -ED-XRF, InVia Raman or RA100). The results obtained thereof may be clearer and more detailed. Anyway, frequently the field measurements are good enough for a good characterization of the minerals present in environmental samples.

Even if these analytical tools are suitable for the research linked to the geological field, the best identification of any mineral, however, will be that in which converge the results of all the available techniques, XRD, RS, XRF, EDS, etc.

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