

Laser Raman Spectroscopic Technique: A Tool for the Characterization of Acid Mine Drainage

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INTRODUCTION

Sulfate minerals are found in the Earth and can be associated with volcanism, hydrothermalism, evaporation, or mining. The natural process of acid rock drainage (ARD) is often intensified by such activities. For instance, as a result of mining, large amounts of sulfides are exposed to water, air, and often microbes that catalyze the oxidation. As a consequence, waters currently draining oxidized sulfide deposits and mine-waste sites have particularly high concentrations of dissolved sulfate and metals. Contamination of natural waters by acid mine drainage (AMD) has a negative impact in the surrounding environments.

We believe that a characterization of the hydrogeochemistry of sulfate-rich sites is crucial in order to describe all of the different processes and settings of iron and sulfate deposition, serving to describe the environmental impact of AMD, predicting the potential/evolution of AMD sites, and shaping AMD remediation strategies. Rio Tinto (SW Spain) environment is a sound example of AMD environments, and is accepted by some as a geo/bio/mineralogical setting where technologies related to AMD remediation can be defined and tested.

Raman spectroscopy (Fig. 1) is regarded as a powerful characterization technique for the sulfate systems due to its intrinsic features: it requires little or no sample preparation prior to spectra collection, and allows real-time identification of species in acidic waters and associated precipitates and very rapid quantification of their abundance, among others. Furthermore, recent advances in optics, lasers and detector systems allow for the development of compact

field Raman instruments for in-situ analyses. This fact, together with the capabilities of the Raman spectroscopy for the unambiguous characterization of mineral phases make the Raman technique an outstanding tool for the exploration of sulfate-rich areas.

In this work we show the fundamentals of the laser Raman spectroscopy and a practical application of this technique to the characterization of Rio Tinto's streams waters. Particularly, Raman spectroscopy is a noninvasive and nondestructive technique and aqueous samples can be readily analyzed without any preparation. The relative abundance of sulfate and bisulfate ions and water, predominant species in acid mine groundwaters, has been derived from the Raman spectra of aqueous samples.

THE TECHNIQUE

Raman spectroscopy is a technique that has experienced a tremendous revival due to technological advances in lasers, detectors and spectroscopic optical systems. The inelastic scattering of light was first demonstrated by Sir Chandrasekhara Venkata Raman.¹ When light strikes a sample, a small fraction of the incident photons (10^{-5} to 10^{-9}) interacts with vibrations in the sample and is scattered at higher or lower energy (Raman scattered). Raman spectroscopy involves the measurement of the difference in energy between the incident light and the Raman scattered photons, which corresponds to the energy of the vibrational transitions.

From a classical point of view, the interaction can be regarded as a perturbation of the molecule's electric field. The

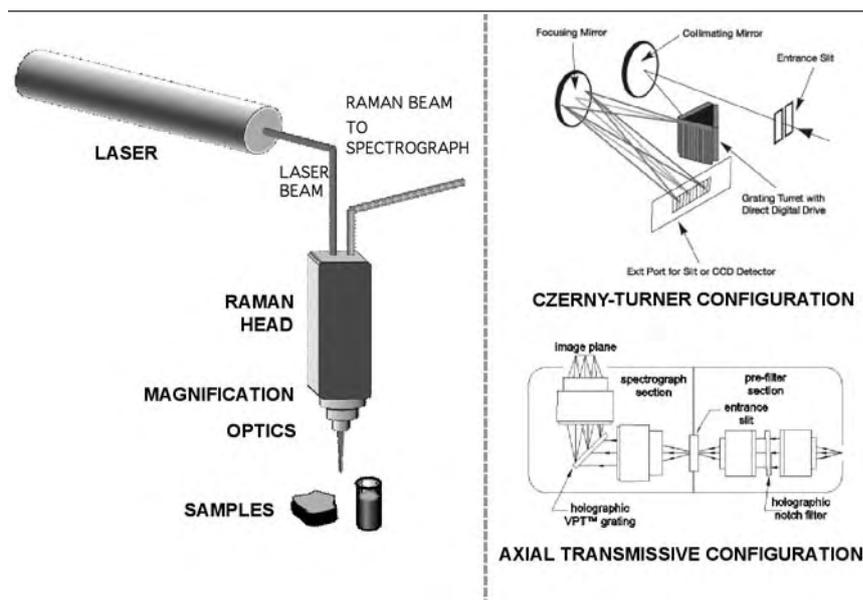


Fig. 1. Typical configuration of a Raman experiment (left) and the two classical spectrograph configurations

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quantum mechanics approach describes the scattering as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The scattering event occurs in the order of 10-14 seconds. A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of wavenumbers, cm^{-1}). This difference is called the Raman shift. Note that, because it is a difference value, the Raman shift is independent of the frequency of the incident radiation.

A typical Raman spectrometer is made up of three basic parts (Fig. 1): the laser, the collection device, and the spectrograph: (1) Laser: A laser is used to excite Raman spectra because it gives a coherent beam of monochromatic light. This gives sufficient intensity to produce a useful amount of Raman scattered light and allows for clean spectra, free of extraneous bands. Lasers used for Raman spectroscopy must exhibit good wavelength stability and low background emission; (2) Probe: The probe is a collection device that collects the scattered photons, filters out the Rayleigh scatter and any background signal from the fiber optic cables, and sends the Raman scattered light into the spectrograph. Many probes also focus and deliver the incident laser beam; (3) Spectrograph: When Raman scattered photons enter the spectrograph, they are passed through a diffraction grating to separate them by wavelength and passed to a detector (PMT, CCD, ICCD, etc) which records the intensity of the Raman signal at each wavelength.

RAMAN SPECTROSCOPY OF RIO TINTO WATERS

Surface and stream water samples from acid mine effluents were collected from several spots in Rio Tinto area. Raman spectra of the aqueous samples were collected at a constant temperature of 20 °C with a confocal Raman microscope (WiTec alpha300 R in the spectral range 75-3900 cm^{-1}). The spectral resolution was 1 cm^{-1} . The 532.4 nm line of a frequency doubled Nd:YAG laser was used as the excitation source. The Raman spectra of five selected aqueous samples in the region 800-1900 cm^{-1} are displayed in Fig. 2. This wavenumbers region is of particular interest for the study of sulfates in aqueous solutions since both sulfate/bisulfate and water vibrational

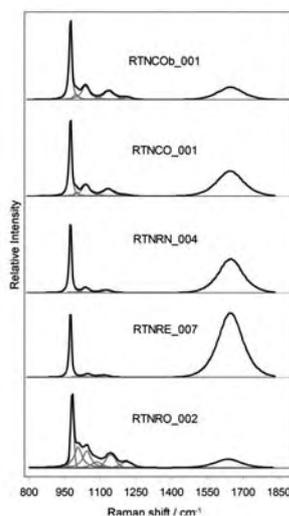


Fig. 2. Raman spectra of samples RTNRO_002, RTNRE_007, RTNRN_004, RTNCO_001 and RTNCOB_001 in the region 800-1900 cm^{-1} .

modes are observed simultaneously. Bands at 981 and 1105 cm^{-1} are ascribed to ν_1 and ν_3 symmetric stretching of sulfate, respectively. The bands around 1250 and 1140 cm^{-1} are related to the sulfate and bisulfate asymmetric stretching modes, respectively. The intensity of a band in the Raman spectrum is a function of the concentration of its associated species. The relative intensities of sulfate, bisulfate and water are reported in Table 1.

Sample	Band relative intensity		
	982 cm^{-1}	1044 cm^{-1}	1640 cm^{-1}
RTNCOB	1.00	0.18	0.16
RTNCO	1.00	0.15	0.34
RTNRN	1.00	0.08	0.49
RTNRE	0.97	0.05	1.00
RTNRO	1.00	0.27	0.09

Tabla 1. . Relative intensities of sulfate, bisulfate and water bands measured from the Raman spectra of the stream waters from Rio Tinto.

CONCLUSION

Spectral fingerprints of sulfate, bisulfate and water molecules have been detected in the Raman spectra of the stream water samples from Rio Tinto, and the relative abundance of these species has been derived from the Raman spectra of the natural aqueous samples. Mine tailings such as the site under study contain large amounts of sulfur-rich mineral and are characterized by highly acidic waters. Characterization of the chemical constituents of stream water in acid mine drainage-contaminated sites is exceedingly important because it is extensively used to design treatment strategies. Further, an early detection of the ionic species associated with acid sulfate waters may help predicting the potential for acid mine drainage. For this purpose we have performed ex-situ Raman spectroscopy as

a means of characterizing the hydrogeochemistry of Rio Tinto area. However, the possibility of using a portable Raman spectrometer for in-situ analysis of Rio Tinto stream waters and mineralogy is currently being explored and preliminary Raman spectra obtained in-situ² justify the importance of Raman spectroscopy as a potential tool for the characterization of Rio Tinto hydrochemistry, and hence of any environment containing AMD.

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