

DIRECT DETECTION AND IDENTIFICATION OF URANIUM(VI)-BEARING SOLIDS BY TRLFS AND CHEMOMETRICS ANALYSIS

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Uranium can be naturally found in the environment in the form of minerals, precipitates, and/or associated to other compounds like iron (hydr)oxides or clay rocks. Identification of the nature of the uranium compounds is of major importance for geological survey, mining exploration, and management of the environmental impact of industrial sites. Many studies have been conducted to characterize uranium-bearing solids with low uranium content from ppm to hundreds of ppm. This requires a careful search of uranium-rich zones in the sample, and the use of characterization methods such as SEM, XRD, and total elemental analysis. Such a methodology is rather long and difficult, and limits the survey to a small number of samples.

Time-resolved laser induced fluorescence spectroscopy (TRLFS) is a classical technique that enables the detection of U(VI) at low level, and has been largely used for quantitative and speciation analyses, in solution [1] and in minerals [2]. The rapidity of the analysis is particularly interesting to investigate a large number of samples with no or limited preparation steps, to detect traces of U(VI) and to obtain spectroscopic information that can be related to the nature of the uranium(VI)-bearing phases such as phosphates. In this study, about twenty U(VI) fluorescence spectra have been recorded on a large set of samples from several environmental sites. The fluorescence intensity is however highly variable regarding the phases due to enhancing and quenching effects on the fluorescence. Interpretation of these measurements is not straightforward. Measurements on cooled or cryogenized samples can considerably increase the fluorescence intensity and the resolution of the spectra, and help identifying the chemical family of the phases [3]. However the resulting spectral analysis is often ambiguous for phase identification and improved data treatment methods need to be developed.

Chemometrics provide useful multivariate methods for spectral and classification analysis, but is seldom used in TRLFS data analysis. We have applied multivariate methods to a set of U(VI) minerals and synthetic phases (phosphates, vanadates, arsenates, silicates) as reference materials. Independent Components Analysis (ICA) has been used to determine pure independent signals contributing to the fluorescence spectra. The resulting spectral signatures have been interpreted regarding the nature of the phases, and may evidence mixtures of compounds or U(VI) chemical sites in natural minerals. Using ICA, the spectral data sets have been categorized into classes that were successfully described using Principal Components Analysis (PCA). Iterative PCA has proved a good efficiency to discriminate most of the samples in our reference data set (Figure 1). Several classes cannot be easily distinguished, and exhibit a significant variability, which may suggest less pure compounds.

The use of predictive methods with a dedicated spectral data base is under development in order to identify U(VI) phases in unknown samples. This combined TRLFS and chemometrics approaches has already demonstrated its great performance for U(VI) phases identification, and perspectives will be presented.

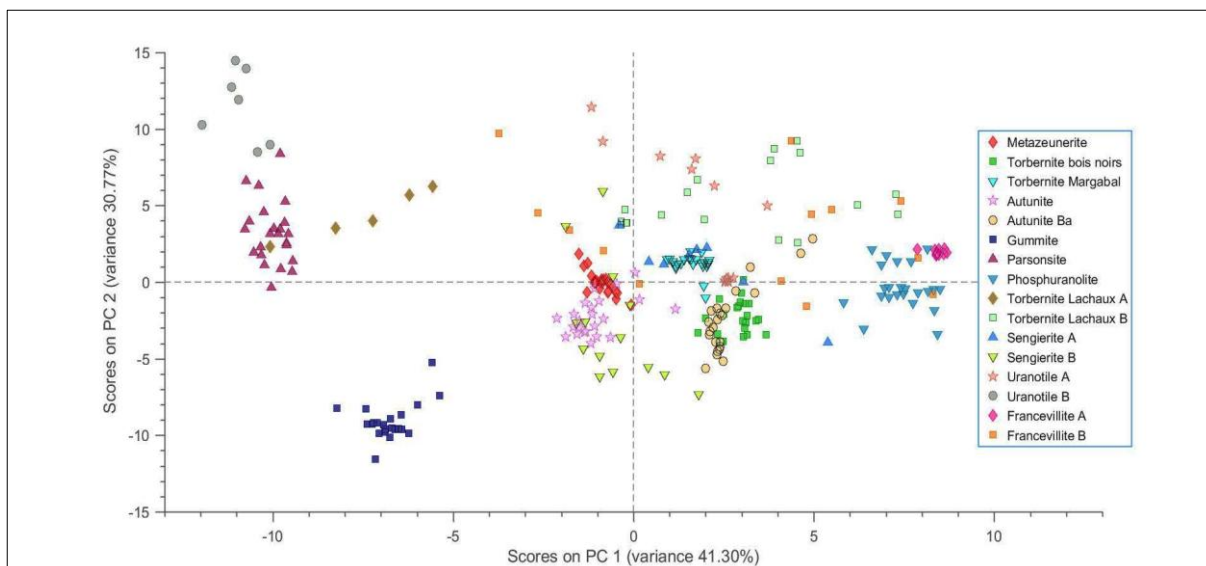


Figure1. PCA representation using the first two components, showing a partial discrimination of classes of U(VI) minerals

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