



	<b>Experiment title:</b> Calibration and quantification of Chromium (VI) and Chromium (III) in soils	<b>Experiment number:</b> EC 493
<b>Beamline:</b> BM08	<b>Date of experiment:</b> from: 11/02/2009 to: 16/02/2009	<b>Date of report:</b> 28/08/2009
<b>Shifts:</b> 15	<b>Local contact(s):</b> Chiara MAURIZIO	<i>Received at ESRF:</i>
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## Report:

### Introduction :

Contamination of soils with hexavalent chromium poses risk to human health as Cr(VI) is highly toxic. Thus, the quantification of the Cr(VI)/Cr total ratio is a key for a diagnostic of soil pollution and for the development of efficient remediation strategies. To run high quality quantitative analyses, certified reference materials (CRM)- where the Cr(VI) and Cr(III) contents and thus the Cr(VI)/Cr total ratio are accurately known- are required, and our laboratory is involved in the promotion of chromium reference soils in collaboration with the National Institute of Standards and Technology (NIST Gaithersburg, USA). In particular, we need to certify the total chromium concentrations, and the hexavalent chromium content of soil samples proposed as CRM. Such a work requires the intercomparison of results obtained with various analytical methods.

We have been studying chromium speciation by high-performance liquid chromatography (HPLC) combined to inductively coupled plasma mass spectrometry (ICP-MS), but the solid-liquid extraction protocol can disturb the chromium species distribution originally present in the sample. To verify that, we investigated the samples by Cr K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy. This is a tool of choice since it can be applied on non disturbed samples, thus avoiding the potential artifacts resulting from sample preparation, and the two oxidation states of chromium can be readily distinguished by the intensity of the pre-edge peak [1-3].

To quantify amounts of Cr(VI), and by difference, Cr(III) in soil samples, a calibration using standards with known Cr(VI)/Cr total ratios is necessary. The purpose of this experiment was to quantify the proportion of the two chromium species in standards artificially contaminated with various Cr(VI)/Cr(III) ratios, and to use this calibration to quantify the chromium speciation in three soils (an industrial soil, Nist soil, an organic sludge soil, Paint sludge soil, and an agricultural soil, Soil2).

## Materials and methods

Standards used for calibration were composed of silica acid washed spiked with total Cr concentration of 1% and Cr(VI)/Cr total ratio of 0%, 1%, 2%, 5%, 10%, 25%, 50%, 75% and 100%. Total Cr concentration in the three soils was 2% in Nist soil, 2.5% in Paint sludge soil, and 3000 mg/kg in Soil 2. The soils were digested in alkaline conditions to extract Cr(VI) while Cr(III) precipitated as in the analytical procedure. The residues were analyzed to evaluate the efficiency of extraction. Samples were manually grounded and prepared as pressed pellets. Cr K-edge XANES spectra were recorded using a Si(311) monochromator, and in fluorescence mode using a Germanium 13-element detector. Measurements were performed at 80°K with a liquid nitrogen cryostat.

## Results

Standards artificially contaminated show that Cr K-edge XANES is sensitive to the amount of the Cr(VI) ranging from 5 to 100% due to the pre-peak at 5993 eV increasing with increasing Cr(VI) (Fig. 1A). We are not able to distinguish 0, 1 and 2 % of Cr(VI) in samples while the spectrum for 5% Cr(VI) is clearly different (Fig. 1B). A calibration was established using the height of the pre-peak in standards (Fig. 2D). Using this calibration, the amount of Cr(VI) before and after Cr(VI) extraction is 9 % and 7 % in Nist soil, 80% and 6% in Paint sludge soil, and 43% and 22% in Soil2 (Fig. 2). The results are much higher than Cr (VI) contents obtained with analytical methods, and also the chemical extraction is not total. Consequently, these results question the validity of analytical results requiring chemical extraction steps. Isotopic dilution experiments are in progress to follow Cr(VI) and Cr(III) during the extraction process.

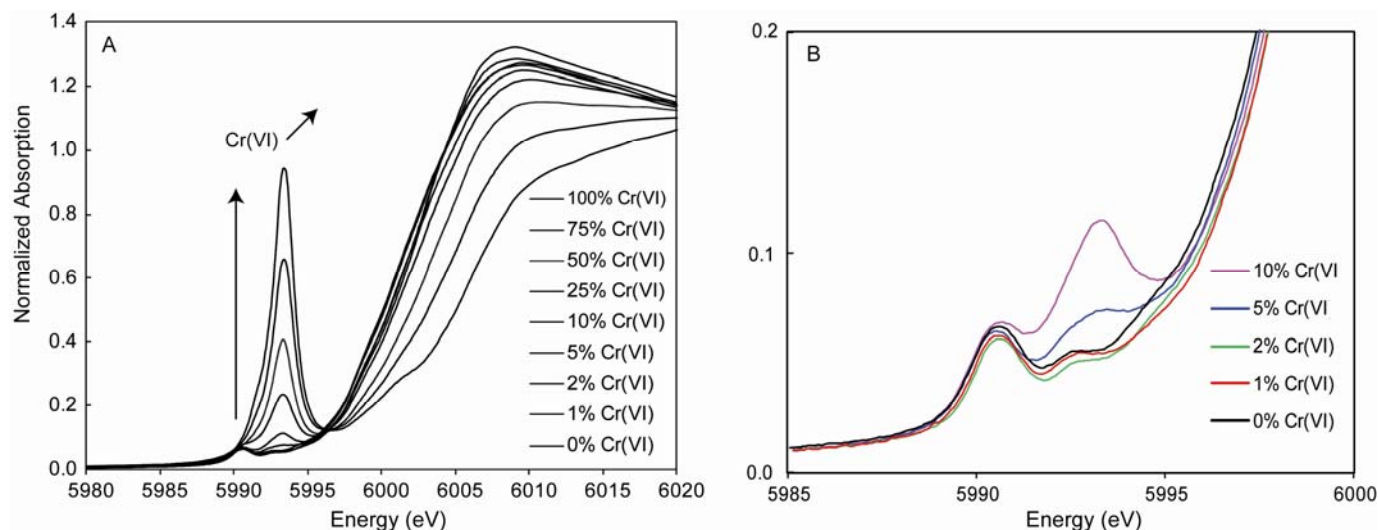
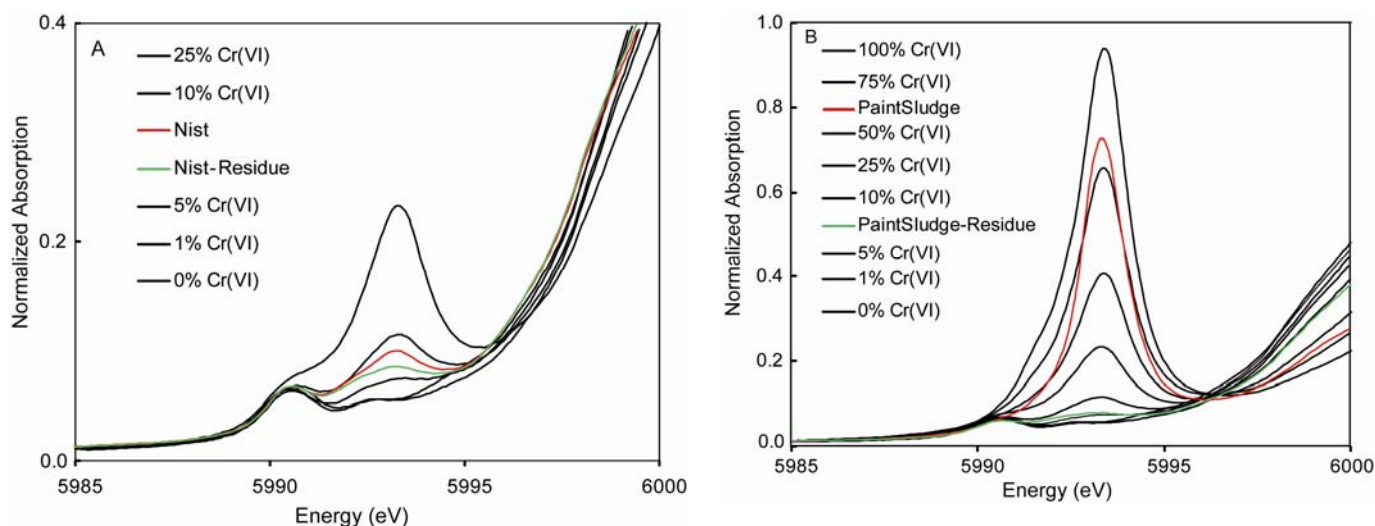


Fig. 1 : Cr K-edge XANES spectra for standards of silica contaminated with 0%, 1%, 2%, 5%, 10%, 25%, 50%, 75% and 100% of Cr(VI)/Cr total (A) and zoom enhancing the 0%, 1%, 2%, 5% and 10% spectra (B).



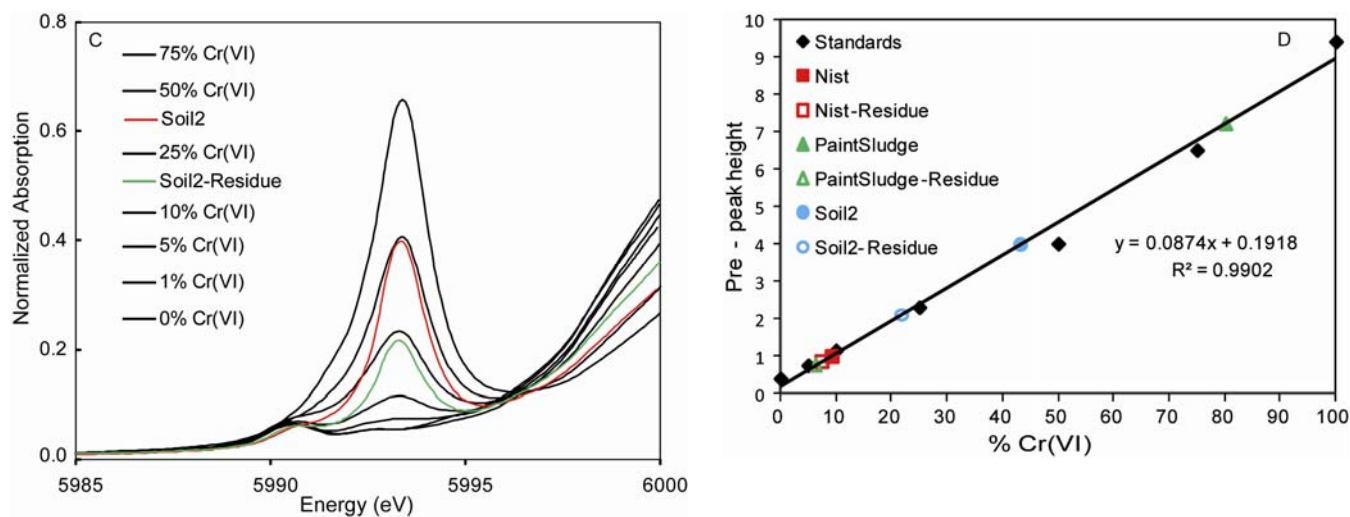


Fig. 2 : Cr K-edge XANES spectra of standards and soils before and after chemical extraction of Cr(VI) (A : Nist-soil and residue, B : Paint sludge soil and residue, C : Soil 2 and residue), and calibration (D).

## References

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