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Evaluation of Hexavalent Chromium Extraction Method EPA Method 3060A for Soils Using XANES Spectroscopy

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S Supporting Information

ABSTRACT: Hexavalent chromium (Cr(VI)) occurrence in soils is generally determined using an extraction step to transfer it to the liquid phase where it is more easily detected and quantified. In this work, the performance of the most common extraction procedure (EPA Method 3060A) using NaOH–Na₂CO₃ solutions is evaluated using X-ray absorption near edge structure spectroscopy (XANES), which enables the quantification of Cr(VI) directly in the solid state. Results obtained with both methods were compared for three solid samples with different matrices: a soil containing chromite ore processing residue (COPR), a loamy soil, and a paint sludge. Results showed that Cr(VI) contents determined by the two methods differ significantly, and that the EPA Method 3060A procedure underestimated the Cr(VI) content in all studied samples. The underestimation is particularly pronounced for COPR. Low extraction yield for EPA Method 3060A was found to be the main reason. The Cr(VI) present in COPR was found to be more concentrated in magnetic phases. This work provides new XANES analyses of SRM 2701 and its extraction residues for the purpose of benchmarking EPA 3060A performance.



INTRODUCTION

For solid samples, few analytical techniques enable direct determination of Cr speciation without converting samples to the liquid state. X-ray absorption near edge structure spectroscopy (XANES) is a technique of choice for environmental samples because it allows quantification of the Cr(VI)/Cr(III) ratio with good sensitivity. For example, a limit of detection around 10 mg/kg has been reported for Cr(VI).¹ This technique relies on the presence of electronic transitions sensitive to the valence, geometry, and distortion of molecules. In the case of Cr, pre-edge features are much more pronounced for Cr(VI) compounds, which have a tetrahedral coordination, than for Cr(III) compounds, which mostly have a centrosymmetric octahedral coordination.^{2,3} However, this technique is only available in synchrotron facilities, and thus, most speciation studies are performed using wet chemistry methods, which are more sensitive, but require

an extraction step to dissolve Cr(VI). Extraction is challenging because ideally it should be complete, and interconversion of Cr species (e.g., reduction of Cr(VI) to Cr(III)) must be prevented to avoid under- or overestimation of the Cr(VI) content.

Different extracting solutions have been used to perform the extraction of Cr(VI).^{4,5} In these studies, the yield of extraction, the possible interconversion of Cr species, and their recoveries were evaluated by spiking soils with exogenous Cr(III) and Cr(VI). The method yielding the best results was obtained using a combination of Na₂CO₃ and NaOH with continuous swirling and heating at 95 °C. The pH of the Na₂CO₃/NaOH mixture

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should be >12, above which Cr(VI) is stable in solution. This method was promoted in 1996 by the U.S. Environmental Protection Agency (US-EPA) with the reference EPA Method 3060A (hereafter called 3060A in this paper).⁶ Once the Cr(VI) is extracted, different quantification methods are available. The latest and most accurate one is performed using high-performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS)⁷ and involves isotopic spiking of the sample to enable the correction of species inter conversion taking place during preparation and analysis steps.^{8,9} However, even if the precision of the quantification step is an important parameter, a complete extraction step is still necessary to obtain accurate results.

Using XANES, Szulczewski et al.¹⁰ recently showed that the phosphate buffer extraction procedure proposed by James et al.⁴ (50 mL K₂HPO₄/KH₂PO₄ 5 mM + 30 min shaking) as a possible method for determining Cr(VI) was ineffective with 0.5–10% recovery of the total Cr(VI) in contaminated soils. Dermatas et al.¹¹ and later Wazne et al.¹² and Jagupilla et al.¹³ found discrepancies in Cr(VI) content of chromite ore processing residue (COPR) between 3060A extracted soils and XANES. They pointed out that the presence of reducing compounds resulted in artificially low Cr(VI) concentrations in the extraction solution. However, another explanation has recently been proposed by Chrysochoou et al.,¹⁴ who demonstrated that the Cr(VI) found in COPR was sometimes entrapped in nodules or bound to phases that are stable over a wide pH range, making it difficult to extract Cr(VI) quantitatively. These studies suggest that it is difficult to determine whether observed differences are due to interconversion of chromium species in the extracts or to a low extraction yield of EPA3060A or to both of these possibilities.

To our knowledge, no in-depth studies have evaluated the actual extraction yield of Method 3060A on different matrices. The aim of this study was to compare the amount of hexavalent Cr found using XANES to Method 3060A combined with state-of-the-art detection methods such as EPA Method 6800 (hereafter called 6800). Three solid samples with different matrices were investigated by wet chemistry following the 3060A procedure. The raw samples and their extraction residues were also analyzed using XANES for comparison. Among the studied samples is a new standard reference material (SRM)¹⁵ recently developed for extractable Cr(VI) content in soil using method 3060A.

MATERIALS AND METHODS

Samples. Three Cr-containing samples with distinctive matrices and compositions were selected for this study (Table 1): SRM 2701 hexavalent chromium in contaminated soil (high level)¹⁵ is a soil composed largely of COPR originating from New Jersey, a loamy soil from Belgium,¹⁶ and a paint sludge from Italy.¹⁶ The samples were used as received; i.e., no additional treatments were performed as indicated on the 3060A extraction procedure. However, for SRM2701 the effect of pregrinding prior extraction was tested (using XANES on extraction residues) but was not found to have a significant effect.

The total Cr content in these samples (Table 1) was determined using Instrumental Neutron Activation Analysis (INAA) (total Cr for SRM 2701 was certified using three independent methods as described in the Certificate of Analysis), a solid state technique, because it has been shown that some samples could be

Table 1. Sample Descriptions and Compositions^a

SRM 2701	paint sludge	loamy soil
Mineralogy Identified by XRD		
(++) chromite	(++) calcite	(++) quartz
(++) maghemite/magnetite	(++) maghemite	(+) calcite
(++) calcite	(++) chromite	(+) brucite
(+) quartz	(+) quartz	(+) biotite
(t) hydrocalumite	(t) larnite	(t) hydrocalumite
(t) hydrogarnet	(t) felspar	(t) alumina
(t) periclase	(t) biotite	(t) maghemite
(t) brownmillerite	(t) periclase	(t) chromite
		(t) hydrogarnet
Matrix Composition (mass %)		
Fe = 22.9	Ca = 11	Si = 15
Ca = 7.4	Fe = 5.8	Ca = 9.3
Mg = 7.4	C = 2.7	Fe = 6.5
C = 4.9	Si = 2.6	Al = 2.5
Si = 4.2		
Total Cr (mg/kg)		
42 600 ± 1200 ^b	17 150 ± 640	12 160 ± 450
Cr(VI) by EPA3060A (mg/kg)		
551 ± 35	11 400 ± 1300	2070 ± 250

^a (++) Major phase. (+) Minor phase. (t) Trace. Uncertainties are discussed in the text. ^b Certified value.

difficult to totally digest using conventional liquid methods due to the presence of refractory phases.¹⁷ The Cr(VI) content in these samples was certified¹⁵ or determined by means of interlaboratory comparisons,¹⁶ using 3060A as an extraction procedure.

EPA Method for Cr(VI) Extraction from Solid Samples and Speciation Analyses. The determination of Cr(VI) content in soils involves four steps: extraction, separation, detection, and quantification. The extraction step was performed following Method 3060A,⁶ which is the most widely used protocol. Briefly, approximately 0.1 g of a sample was weighed and placed into a microwave vessel. Then, 2 mL of the digestion solution consisting of 0.5 M NaOH and 0.28 M Na₂CO₃ was added into the vessel along with 16 mg of MgCl₂ and 0.02 mL of a 1.0 M K₂HPO₄/KH₂PO₄ buffer. This combination of MgCl₂ and buffer has been shown to reduce the oxidation of Cr(III) to Cr(VI). A modified Method 3060A was used for heating by using microwave-assisted extraction (CEM Discover, Matthews, NC, set to 95 °C for 30 min with continuous stirring) instead of a hot plate. This modified method has been shown to give comparable results to those obtained with a hot plate.^{8,18} Extraction residues were separated by centrifugation, washed three times with deionized water, and prepared for XANES and X-ray diffraction (XRD) analyses as described in those sections.

The different Cr species present in the extracts were separated using HPLC with an anion exchange guard column (IONPAC AG 11, Dionex, Sunnyvale, CA), and detected using ICP-MS (Elan 6100 DRC, PerkinElmer, Waltham, MA) equipped with a Meinhard nebulizer fitted to a cyclonic spray chamber.

Methods Used for Cr(VI) Quantification after Extraction. Several methods exist to quantify Cr species¹⁹ following chemical extraction. To compare them in terms of precision and accuracy,

four of these methods were used on the loamy soil and paint sludge: external calibration using HPLC-ICP-MS, standard additions using ICP-MS, isotope dilution mass spectrometry (IDMS), and Method 6800. Such a study¹⁵ has already been carried out on SRM 2701 in which determinative bias as high as 30% was observed, depending on the method used. Briefly, external calibration relies on the preparation of standards of known Cr(VI) concentrations in water,²⁰ the standard addition method requires the addition of known quantities of the Cr(VI) to the sample,²⁰ IDMS requires the addition of a known amount of isotopically enriched ⁵⁰Cr(VI) to the sample (in our case this addition was performed before and after extraction),²¹ and Method 6800 requires the addition of known amounts of two isotopically enriched species ⁵⁰Cr(VI) and ⁵³Cr(III).⁶ Although exogenous spikes will not behave exactly as the analyte present within the matrix, EPA6800 is widely perceived as the most accurate quantification method because it can correct for conversions of Cr(VI) to Cr(III) and of Cr(III) to Cr(VI) during preparation and analysis of samples.²² External calibration and standard addition methods were carried out using Cr(VI) and Cr(III) stock solutions (Sigma-Aldrich, St. Louis, MO). Isotope dilution and Method 6800 methods were carried out using isotopically enriched Cr(VI) and Cr(III) synthesized from solid, ⁵⁰Cr-enriched Cr₂O₃ and ⁵³Cr-enriched Cr₂O₃. For each detection method, the entire extraction–detection suite was repeated on three replicate specimens.

X-ray Diffraction. XRD measurements were performed on raw soil samples before and after 3060A extraction. Residue from SRM 2701 was also magnetically separated, and both fractions were analyzed by XRD. XRD data were collected using a Bruker AXS D8 Advance unit using a θ – θ configuration with the source and a two-dimensional detector scanned with a 0.016° 2 θ step size for a total scan time of 35 min. The Cu X-ray tube was operated at 35 kV and 45 mA with a Ni filter to remove K-M ($K\beta$) radiation leaving just the K-L_{2,3} ($K\alpha_{1,2}$) radiation (λ = 0.154 nm).

XANES. *Standards for XANES Calibration.* Mixtures of Cr(VI) and Cr(III) were prepared to calibrate XANES. In the environment, Cr(VI) and Cr(III) are the most abundant forms of Cr because the other oxidation states (+II, +IV, +V) are less stable. Two sets of Cr-doped silica standards were prepared to contain 1% and 0.5% total Cr (by mass) and each set having Cr(VI)/Cr_{total} ratios of 0%, 1%, 2%, 5%, 10%, 25%, 50%, 75%, and 100%. For silica standards containing 1% total Cr, aqueous Cr(III) or Cr(VI) was prepared by dissolving CrCl₃·6H₂O or K₂Cr₂O₇ in purified water. For standards containing 0.5% total Cr, SRM 3112a Chromium (Cr) Standard Solution and SRM 2109 Chromium(VI) Speciation Standard Solution were used as sources of Cr(III) and Cr(VI), respectively. Aqueous Cr(III) or Cr(VI) solutions were added to pure solid silica in a solid/liquid mass ratio of 1:3 in 50 mL flasks which were closed and stirred on a rotating table for 24 h, after which the solids were freeze-dried. The dried Cr(III)- and Cr(VI)-doped silica were manually ground. The final calibrants were prepared by mixing weighed amounts of these dried, Cr-doped silicas to the required Cr(VI)/Cr_{total} ratios. Pure silica was analyzed by synchrotron X-ray fluorescence, and no Cr was detected.

Additional standard samples consisted of commercial powders of Cr₂O₃ (Baker) and K₂CrO₄ (Aldrich), and a chromite mineral containing FeCr^{III}₂O₄ provided by the mineral collection from Paul Sabatier University (Toulouse, France). Another reference sample was made by mixing pure powders of K₂CrO₄ and

Table 2. Comparison of Cr(VI) Mass Fractions Obtained for the Loamy Soil and the Paint Sludge with Different Quantification Methods^a

	paint sludge (mg/kg)	loamy soil (mg/kg)
literature value	11 400 ± 1300	2070 ± 250
HPLC-ICPMS external calibration	10 652 ± 349	1985 ± 95
HPLC-ICPMS standard addition	9460 ± 113	not determined
IDMS, spiked before extraction	10 628 ± 44	1986 ± 40
IDMS, spiked after extraction	10 796 ± 411	1936 ± 35
EPA 6800, double spike IDMS	10 700 ± 38	1920 ± 31

^aUncertainties are discussed in the text.

CrK(SO₄)₂·12H₂O (Fisher Scientific) to a Cr(VI)/Cr_{total} ratio of 5.3%.

The standard additions method (detailed in ref 23) was applied to samples of SRM 2701 by spiking, grinding, and mixing sample aliquots with increasing amounts of solid K₂Cr₂O₇.

Instrumentation and Data Treatment. XANES measurements were performed on beamline BM08 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, using a Si(311) monochromator. Solid samples, solid residues from EPA extraction procedures, and calibration standards with 1% total Cr were prepared as pressed pellets and measured using a cryostat operating at 80 K to minimize potential speciation change of Cr under beam exposure. Cr K edge XANES spectra were collected in fluorescence mode using a 13-element Ge detector and an energy step size of 0.1 eV in the vicinity of the edge. Energy calibration was performed by measuring Cr foil between samples and defining the maximum of the first derivative of the absorption spectrum as 5989.0 eV.

Additional measurements were performed at NIST beamline X23A2 at the National Synchrotron Light Source (NSLS) in Upton, NY, using a Si(311) monochromator. Unknown samples and silica standards with 0.5% total Cr were enclosed between two 2.5 μ m polyester sheets (Somar International, Reno, NV) in a polyethylene holder. Samples were rotated during measurements to average out effects of heterogeneity by passing a greater area of the specimen through the small primary X-ray beam (10 mm × 0.5 mm). XANES spectra were recorded in fluorescence mode using a four-element Si drift detector (Vortex-EX, SII Nanotechnology, Northridge, CA). Again, Cr foil was employed for energy calibration. For each specimen, collected spectra were pre-edge background subtracted using a linear fit, postedge normalized using a quadratic polynomial and averaged in the Athena software.²⁴

RESULTS AND DISCUSSION

Comparison of the Cr(VI) Quantification Strategies after 3060A Extraction. Results for both the loamy soil and the paint sludge show that the amount of Cr(VI) obtained with four out of five methods is within the uncertainty range determined by the interlaboratory study¹⁶ (Table 2). Only the standard additions method using ICP-MS gave a slightly underestimated result, which is difficult to explain as the Cr(VI) added to the sample should be stable at the pH condition (pH > 12). The IDMS method with single spiking of ⁵⁰Cr-enriched Cr(VI) gave almost the same result whether the isotopic spike was added before or after 3060A extraction, meaning that the spike does not react

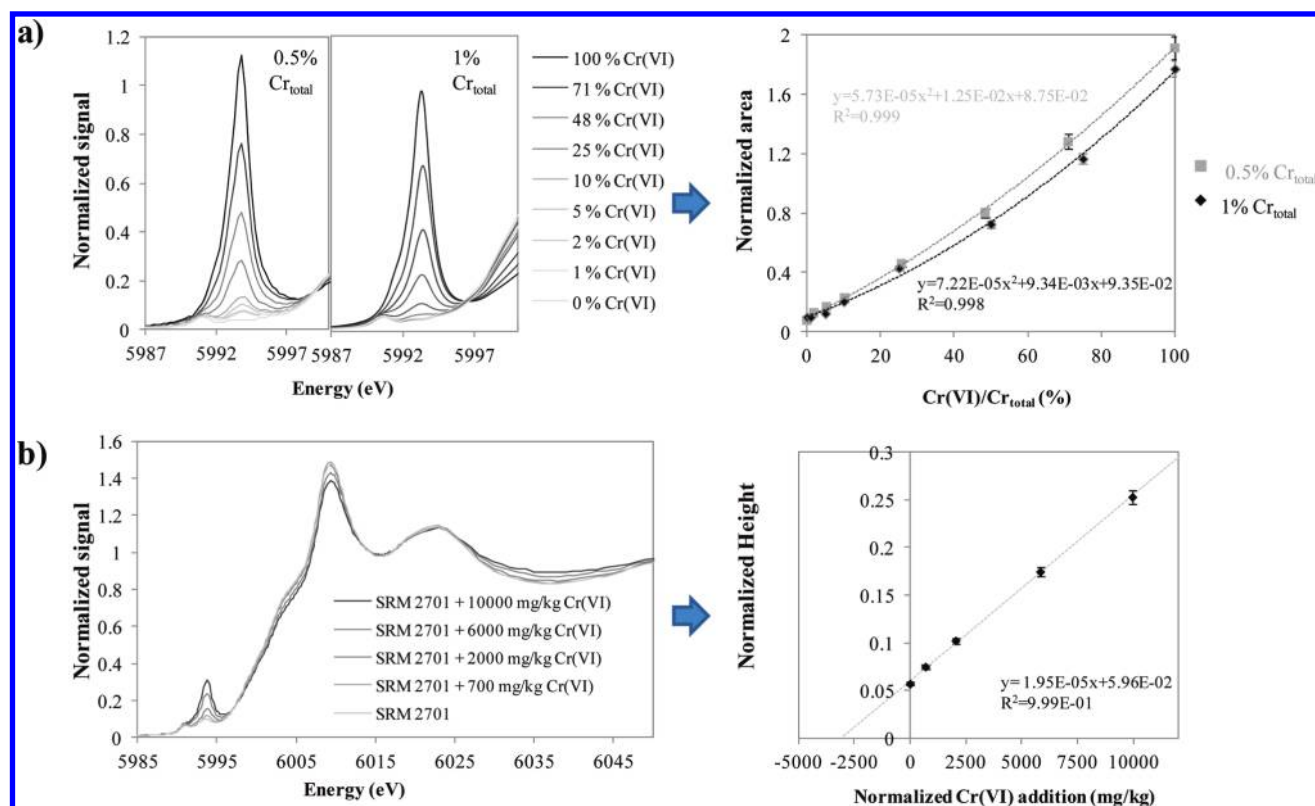


Figure 1. (a) Correlation between the area of pre-edge peak areas and the mass fraction of Cr(VI) for doped-silica mixtures of 0.5% and 1% total Cr. (b) Calibration curve obtained using the height of pre-edge peaks when mixing SRM 2701 with increasing amount of K₂Cr₂O₇ for the method of standard additions. The relative standard deviation of replicate area and height determinations was <3%.

much with the solid matrices of the two samples. Method 6800 appears to give the best repeatability although IDMS is similar when spiked before extraction. Also, Method 6800 yields almost the same accuracy as the other detection methods used for the two soils analyzed. In a previous study¹⁵ on SRM 2701, Method 6800 gave 30% higher Cr(VI) mass fractions than the other methods. This could be due to the presence of reducing agents (such as Fe(II) or organic matter⁸) in SRM2701 matrix that can have an impact on the conversion of Cr species during extraction, and Method 6800 can correct for interconversion of Cr species.

Because the results for paint sludge and loamy soil agree well for a single extraction procedure followed by different quantification methods, there is no evidence of species interconversions or other phenomena resulting from chemical extraction and procedures in the quantitative methods. In contrast, prior results for SRM 2701¹⁵ lead one to question whether the cause is related to the material and its behavior under extraction conditions. XANES results obtained on the original materials and XRD determinations of mineralogy are discussed below for the purpose of comparing the results of nondestructive analysis of the materials to results involving the extraction procedure.

XANES Analysis of Samples and Their 3060A Residues.

Pre-Edge Peak Calibration. The pre-edge and superimposed X-ray lines were fitted using an error function and Gaussian components, respectively, as previously described by Szulczewski et al.¹⁰ The distinctive peaks for the doped-silica standard end-members (0% and 100% Cr(VI)) were characterized in terms of position and width, and these data were applied to fit spectra from mixtures (see Supporting Information Figure S1). The two peaks surrounding the 1s3d transition of Cr(VI) result from moiety

distortion²⁵ present in K₂CrO₄, which was the source of Cr(VI) in the Cr(VI)-doped silica standards. The area of the 1s3d peak corresponding to the Cr in tetrahedral configuration was determined and plotted versus the fraction of Cr(VI) in the calibrants with a high degree of correlation as shown in Figure 1a.

The two calibrations performed at two separate beamlines compare well. For all spectra, the relative standard deviation of replicate ($n = 3$) area determinations was <3%. Limits of detection were not estimated in the normal, rigorous manner. Rough estimates were made by comparing the peak areas from low Cr(VI) calibrants. For the calibration performed with 1% total Cr, the 5% Cr(VI)–silica could be unambiguously distinguished from the lower Cr concentrations, but it was not possible to differentiate the 0%, 1%, and 2% Cr(VI)–silica standards. For the calibration performed with 0.5% total Cr, it was possible to distinguish 0% from 1% and 2% Cr(VI)–silica but not 1% from 2%. The limit of detection for Cr(VI) must therefore be in the range 0–2% total Cr which represents 100 mg/kg of Cr(VI) in absolute value. The small difference between the slopes of these calibration curves performed in different synchrotron facilities is likely due to differences in reference compounds and total chromium concentrations of the two calibration sets.

Table 3 shows the mass fraction of Cr(VI) obtained by multiplying the ratio of Cr(VI)/Cr_{total} from XANES analyses and the total Cr. Uncertainty estimates were calculated by combining contributions from INAA and XANES. The uncertainties for INAA contribute approximately 2% relative standard uncertainty. The main source of uncertainty for XANES is related to differences observed among Cr K edge spectra of the model compounds used in the calibration and the spectra of the actual

Table 3. Quantification Results Using XANES

sample	Cr(VI) XANES (mg/kg) ^a	total Cr (mg/kg)	extraction yield (%) ^e	mass balance error (%) ^e
SRM 2701	3390 ± 373 ^b 3312 ± 364 ^c 3055 ± 137 ^d	42 600 ± 1200	32.2	15.3
3060A extraction residue	2330 ± 256 ^b 2078 ± 229 ^c	35 270 ± 190		
3060A extraction residue, nonmagnetic part	270 ± 30 ^b	10 380 ± 238		
3060A extraction residue, magnetic part	3592 ± 395 ^b	48 820 ± 1120		
paint sludge	12 177 ± 1339 ^b 11 821 ± 1300 ^c	17 150 ± 640	94.9	−0.1
3060A extraction residue	567 ± 62 ^b 662 ± 73 ^c	10 560 ± 190		
loamy soil	4796 ± 528 ^b 4591 ± 505 ^c	12 160 ± 450	57.1	13.0
3060A extraction residue	2101 ± 231 ^b 1922 ± 211 ^c	9460 ± 350		

^a Estimated uncertainties, see text for details. ^b Using 1% Cr_{total} calibration. ^c Using 0.5% Cr_{total} calibration. ^d Using standard addition. ^e See text for details.

Cr compounds in the samples. It has been shown that, depending on the Cr(VI) compound used in the calibration, the K edge spectrum may present noticeable differences, particularly in the 1s3d region of Cr(VI).²⁵ The samples being likely composed of more than two Cr species and their natures being for most cases unknown, it is difficult to evaluate this uncertainty. However, its order of magnitude can be deduced in two ways. The first one involves comparison of the calibration end-members' (0% and 100% Cr(VI)) pre-edge peak heights to those of pure reference compounds such as Cr₂O₃, chromite, and K₂CrO₄ (see Supporting Information, Figure S2). The difference in height between K₂CrO₄ and silica doped with 100% Cr(VI) added to the difference in height between chromite and the silica doped with 100% Cr(III) represents a relative difference of approximately 6% in Cr(VI) content. The second way to evaluate the uncertainty is to analyze a reference material. This was done utilizing compounds having different Cr atom environments than those used for the calibrations in a mixture having 5.3% Cr(VI). Quantification of this reference sample using external calibration gave a value of 4.4% Cr(VI), which represents a relative error of 16%. About the same error (17%) was encountered when using a linear combination of the two pure compounds (K₂CrO₄ and CrK(SO₄)₂·12H₂O) used to make the mixture with 5.3% Cr(VI) as done by Parsons et al.²⁶ Similar errors were reported by Fandeur et al.³ The two different methods used to evaluate uncertainties indicate that the true relative error must be between 6% and 16%. The intermediate value of 11% was therefore taken to calculate the relative error of external calibrations. Two recommendations can be made to minimize these uncertainties:

- (1) Cr₂O₃ or eskolaite should be avoided as a Cr(III) reference compound, if it is not present in the sample, because Cr in Cr₂O₃ is located in a distorted octahedral site. Its transition energy is close to the energy of the tetrahedral Cr(VI) feature and represents a spectral interference.^{3,25} If present here, its abundance is minor because it was not detected by XRD analyses (Table 1).
- (2) Cr(VI) compounds should be carefully chosen because the intensity and the peak width of the 1s3d transition of chromates is not unique and will be affected by CrO₄²⁻

moiety distortion; e.g., there will be differences between monochromate and dichromate.²⁵ Choices can be made by comparing peak widths of sample and reference compounds.²⁷

The method of standard additions applied to XANES, which to our knowledge has not been tested to date, proved to be suitable for Cr(VI) determination in SRM 2701 (Figure 1b). This approach allows easier spectrum fitting because just one compound is added, and the compound can be chosen using data from published studies^{2,25,28} to have the approximate same peak width as the Cr(VI) found in the sample. No Cr(III) model compound is required; therefore, the uncertainty linked to the choice of compound used to model Cr(III) is eliminated. Figure 1b illustrates the advantages offered by the standard addition approach for SRM2701. Because the Cr(III) chromite dominates the Cr speciation in the initial and spiked samples, the postedge portion of the spectrum remains similar among the original and spiked samples, facilitating normalization and deconvolution because all parameters, except the 1s3d peak height, can remain the same for treating all spectra. A relatively strong linear correlation was found between the height of the 1s3d peak and the amount of added Cr(VI). This approach gave a result of 3055 mg/kg which is about 10% lower than the external calibration, likely due to a difference in the Cr(VI) compound used. Standard addition depends on a good linear correlation between count rate and amount of analyte added. No X-ray fluorescence calibration is truly linear because self-absorption²⁹ causes a decrease in the ratio of counts per amount of analyte as the amount of analyte increases. In our case, spike samples containing up to 18 000 mg/kg of Cr were tested, and deviation from linearity was apparent at the highest amount of total Cr. Non-linearity of this nature causes overestimation of the amount of Cr(VI). A second limitation of standard additions is the ability to completely mix the spike with the original sample. The implicit assumption is that perfect mixing has occurred and that X-rays will not be affected by differential absorption between particles of soil and particles of spike compound, in this case, K₂Cr₂O₇ powder. The assumption can be tested by observing the goodness of fit of the unspiked sample to the calibration line. In our case, a test showed a potential bias of approximately +4% relative

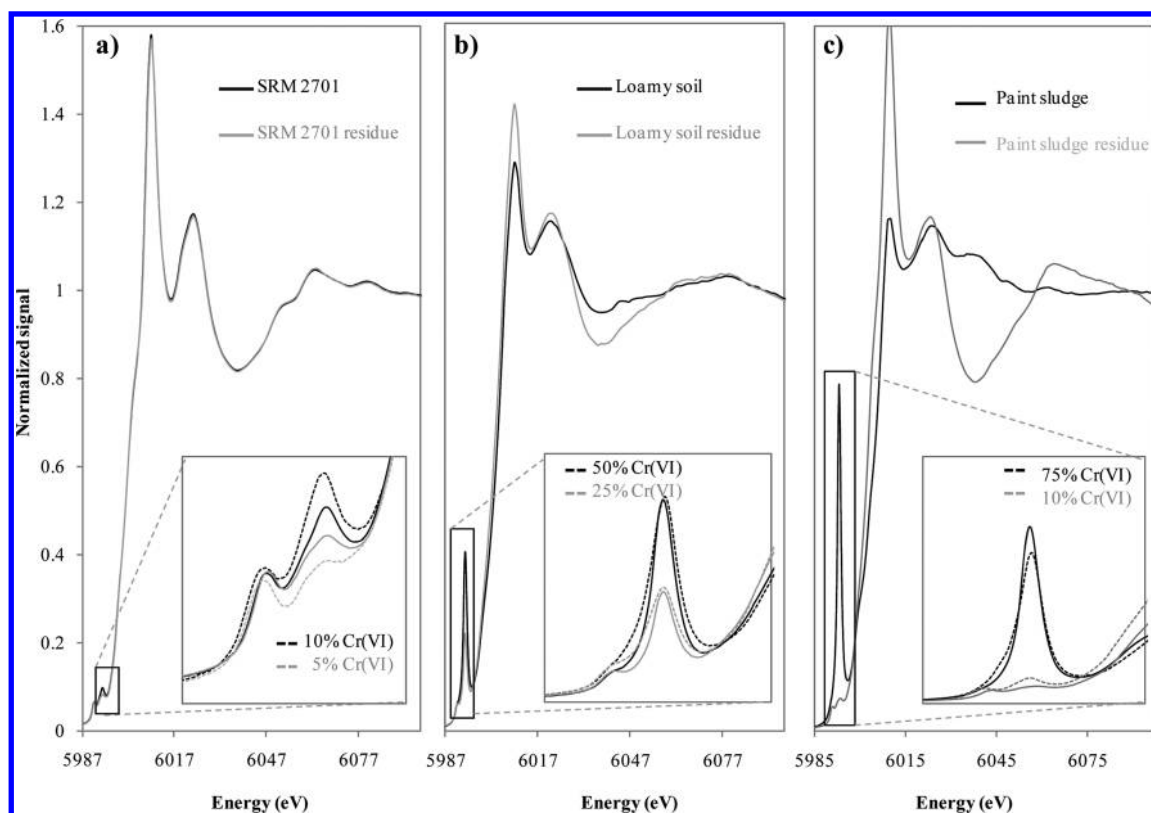


Figure 2. Superimposed Cr K edge spectra of doped-silica standards and (a) SRM 2701, (b) loamy soil, and (c) paint sludge. The pre-edge region used for quantification purpose is featured in the zoom box.

between results from lines with and without the original sample. A standard additions calibration must be carefully designed to minimize the influence of self-absorption and limitations of mixing of spike and sample. Overall, the estimated uncertainty in this instance is a factor of 2 lower than for external calibration because just the errors linked to Cr(VI) addition must be included. As no reference material for total Cr(VI) in solids exists, further studies are needed to determine which method is the most accurate.

Samples. Table 3 shows that the chemical extractions and XANES quantifications are reproducible because the results using the two sets of extractions are similar within the uncertainty intervals. Depending on the sample, the determined Cr(VI) mass fraction can vary significantly between XANES and EPA-based methods. The worst case is SRM 2701 where 3060A underestimates the mass fraction of Cr(VI) by a factor of 6 (see comparison with Table 1). The XANES analyses performed on the extraction residues show that an incomplete extraction step is responsible for Cr(VI) underestimation by 3060A because non-negligible amounts of Cr(VI) were present in the residues (Figure 2). The masses of extraction residues were compared to the initial sample masses, and no significant differences were observed. Extraction yield Y was calculated as follows

$$Y(\%) = \frac{\text{Cr(VI)}_{\text{sample}} - \text{Cr(VI)}_{\text{residue}}}{\text{Cr(VI)}_{\text{sample}}} \times 100 \quad (1)$$

where $\text{Cr(VI)}_{\text{sample}}$ and $\text{Cr(VI)}_{\text{residue}}$ are the means of the XANES Cr(VI) values obtained using both calibrations.

The extraction yields differ significantly among samples, indicating a possible influence of the sample matrix. The postedge part of the spectrum in Figure 2 shows that the SRM 2701 Cr-binding phases

have not been disturbed significantly after extraction in contrast to the two other soils for which the extraction was more efficient. As said earlier, this observation is most likely due to the fact that the postedge is dominated by the chromite phases, which are much more abundant than Cr(VI)-bearing phases. The INAA result for the paint sludge residue is likely overestimated, mainly due to the combined effects of the small sample amount available and sample heterogeneity; however, it is not expected to have a significant impact on extraction yield, which is already 95%.

Other factors than a low-yield extraction could explain the underestimation of Cr(VI) by the 3060A method, for example, interconversion of chromium species during the detection step. To clarify that point, and considering that the amount of Cr(VI) determined by XANES in raw samples should be equal to the amount of Cr(VI) extracted by 3060A plus the amount of Cr(VI) left in the extraction residues, the mass balance error, ∂_{MB} , was calculated as follows

$$\partial_{\text{MB}}(\%) = \frac{\text{Cr(VI)}_{\text{sample}}^{\text{XANES}} - (\text{Cr(VI)}_{\text{residue}}^{\text{XANES}} + \text{Cr(VI)}_{\text{extract}}^{\text{EPA}})}{\text{Cr(VI)}_{\text{sample}}^{\text{XANES}}} \times 100 \quad (2)$$

where $\text{Cr(VI)}_{\text{sample}}^{\text{XANES}}$ and $\text{Cr(VI)}_{\text{residue}}^{\text{XANES}}$ are the averages of the XANES Cr(VI) values obtained using both calibrations. The relative errors in mass balance range from -0.1% to 15.3% , which is reasonably good considering the uncertainties associated with the results of each method. Therefore, it can be concluded that extraction yield is the main reason for underestimation of Cr(VI).

Effect of 3060A Extraction on the Mineralogy of SRM 2701. The mineralogy of SRM 2701 (Figure 3) includes

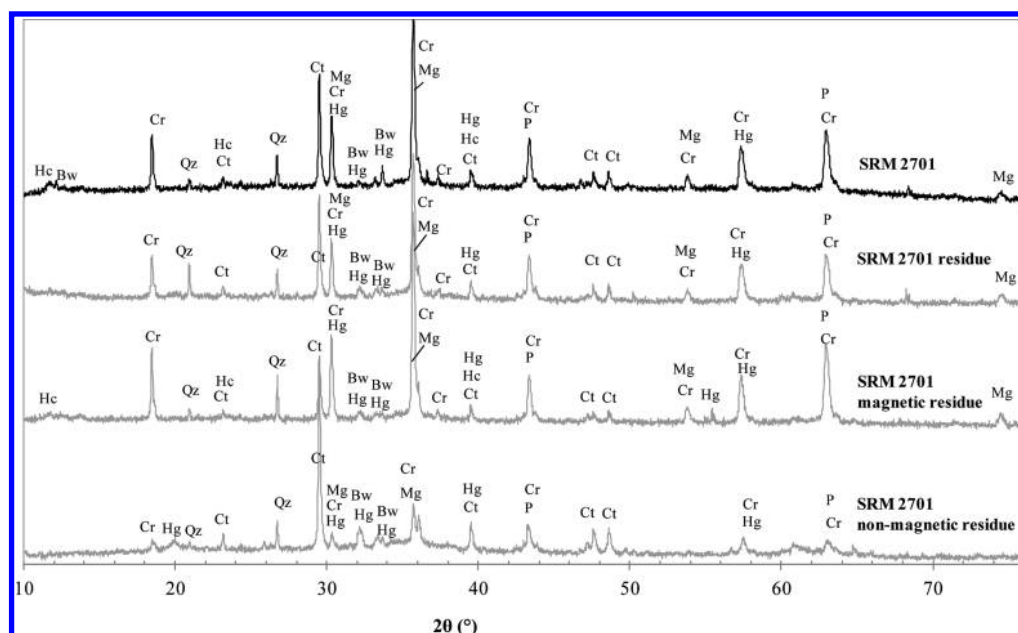


Figure 3. XRD patterns from SRM 2701 and its extraction residue before and after magnetic separations: Ct, calcite CaCO_3 ; Cr, chromite FeCr_2O_4 ; Hc, hydrocalumite $\text{Ca}_2(\text{Al,Fe})(\text{OH})_7 \cdot 3\text{H}_2\text{O}$; P, periclase MgO ; Hg, hydrogarnet $\text{Ca}_3(\text{Al,Fe})_2(\text{OH})_{12}$; Mg, maghemite/magnetite $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$; Qz, quartz SiO_2 ; Bw, brownmillerite $\text{Ca}_2(\text{Fe,Al})_2\text{O}_5$.

chromite, magnetite, maghemite, brownmillerite, calcite, and periclase and is characteristic of such samples.^{30–32} The mineralogy of COPR can be influenced by the composition of initial chromite-bearing minerals, the processes used to extract chromium, and conditions to which the material is subjected. XRD analyses (Figure 3) performed on SRM 2701 subjected to different treatments showed that chromite, the main chromium(III)-bearing mineral, was still present in the residue of extraction as expected. In addition, maghemite and magnetite were still present, but due to the high pH of the medium these iron-oxides are unlikely to sorb Cr(VI) as observed for some iron-oxyhydroxides in relatively acidic lateritic soils.^{3,33,34} Lesser amounts of calcium-containing minerals, namely calcite (CaCO_3), hydrogarnet ($\text{Ca}_3(\text{Al,Fe})_2(\text{OH})_{12}$), and hydrocalumite ($\text{Ca}_2(\text{Al,Fe})(\text{OH})_7 \cdot 3\text{H}_2\text{O}$) were identified in the raw sample and in the residue. Common in COPR, hydrogarnet and hydrocalumite were found to incorporate hexavalent Cr in their structure,^{31,35} and above pH 11, Cr(VI) solubility would be controlled by Cr(VI)-substituted hydrogarnet and Cr(VI)-hydrocalumite.³² In Cr(VI)-hydrocalumite, Cr(VI) is present in the interstitial spaces of the layered double-hydroxide, and should be easily extractable. In Cr(VI)-bearing hydrogarnet, Cr(VI) is included in the structure, which suggests it is more stable. The incorporation of CrO_4^{2-} in the structure of calcite was also reported by Tang et al.³⁶ and suggested by Hua et al.³⁷ Brownmillerite is also present in SRM 2701 and in the residue, and the incorporation of chromate in its structure in COPR has been reported by Gibbs³⁸ and more recently Chrysochou.³⁰ Furthermore, it is present as resistant nodules where Cr(VI) is not easily extractable.³⁰ Thus, it can be hypothesized that hydrogarnet, hydrocalumite, calcite, and/or brownmillerite can trap chromate and make it unavailable for chemical extraction, but further studies are needed to confirm these mechanisms. The INAA and XANES analyses (Table 3) on these fractions showed that the magnetic fraction is highly enriched in both total Cr and Cr(VI) compared to the

nonmagnetic fraction. The XRD analysis clearly shows that the magnetic fraction is enriched in the chromite/maghemite/magnetite phases and the nonmagnetic fraction is enriched in calcite; thus, it can be inferred that the main part of Cr(VI) is not trapped in calcite only, but it is difficult to estimate the enrichment or not in hydrogarnet, hydrocalumite, and brownmillerite. XRD analyses appear to show that the major part of the nonextracted Cr(VI) is associated with phases present in the magnetic fraction of the residue, but their nature remains difficult to determine due to the relative similarity between the XRD spectra of the magnetic and nonmagnetic fractions. Further research is needed to fully understand the mechanism involved in the retention of Cr(VI) and so improve its extraction.

The difference in extraction yield between paint sludge (94.9%) and SRM 2701 (32.2%) can be explained by a different repartition of Cr(VI) within mineral phases. Calcite, chromite, and maghemite were the main crystallized phases identified in the raw paint sludge and were still in the residue while calcite was the major phase removed by the chemical extraction. It can be hypothesized that Cr(VI) was removed with calcite because CrO_4^{2-} is possibly sequestered in its structure.^{36,37} It can also be mentioned that the XANES spectra of raw paint sludge and its residue are markedly different, especially in the postedge region, indicating that the main initial Cr(VI) bearing phase(s), which represents the dominant part of Cr, was removed.

For the loamy soil, 57.1% of Cr(VI) was extracted. Quartz, calcite, biotite, feldspars, brucite, and a small amount of chromite were identified as the main crystalline phases in the raw and residue samples. Calcite was the dominant mineral extracted by 3060A. It can be hypothesized that Cr(VI) is associated with calcite and/or brucite ($\text{Mg}(\text{OH})_2$) as hypothesized by Chrysochou.³⁰ Also, the binding of Cr(VI) in $\text{Ca}(\text{OH})_2$ at high pH was reported by Ginder-Vogel.³⁹

XANES as a Tool To Improve Measurement of Cr(VI) in Soils Using Chemical Extractions. This study on three different

soils showed that 3060A does not completely solubilize all forms of hexavalent chromium, depending on soil matrix. In particular, the soil composed of COPR was found to contain Cr(VI) which was not extracted chemically. This work also showed that the use of spiked soils for extraction studies is not an ideal approach for studying alkaline extraction methods as this does not necessarily reflect the complexities of real soils. XANES represents a powerful tool, but unfortunately synchrotron facilities are difficult to access and generally not conducive to high throughput analytical methods at this time. It is conceivable that XANES spectroscopy can serve as a benchmark for improvements or modifications to alkaline extraction methods, which might consist of sequential extraction approaches or different extraction conditions, tailored to the type of matrix being studied. This future work would be of particular importance in the case of environmental studies dealing with the toxicity of Cr(VI), which may concern easily extractable Cr(VI) but also more insoluble phases.^{40,41}

■ ASSOCIATED CONTENT

S Supporting Information. Figures S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ DISCLOSURE

Certain commercial equipment, instruments, and materials are identified in this work to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.

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