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Determination and Correction of Analytical Biases and Study on Chemical Mechanisms in the Analysis of Cr(VI) in Soil Samples Using EPA Protocols

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EPA Methods 3060A (alkaline extraction) and 7196A (colorimetric measurement) currently constitute a pair of protocols for the measurement of Cr(VI) in environmental soil samples in EPA RCRA SW-846 Update III. To identify the sources of possible biases, we applied the newly developed Speciated Isotope Dilution Mass Spectrometry (SIDMS) as an alternative detection method to Method 7196A. SIDMS is capable of correcting for species transformation, while Method 7196A is not. In Method 3060A, soluble Cr(III) could be oxidized during extraction, resulting in positive errors of Cr(VI); Cr(VI) could be lost or reduced during neutralization, leading to negative errors of Cr(VI). When sand and soil extracts were analyzed, low recoveries were obtained with Method 7196A. However, SIDMS achieved approximately 100% recoveries. The influence of some soil matrix components on the detection of Cr(VI) using Method 7196A has been evaluated. As expected, reducing agents could cause low recoveries of Cr(VI). Surprisingly, we found that strong oxidizing agents could also result in low recoveries. We identify these method biases and discuss the mechanisms in this paper.

Introduction

Cr and its compounds have been extensively applied in industry as pigments, dyes, and refractory material and are used in leather tanning and electroplating processes (*1*, *2*). Cr exists in the environment in two dominant oxidation states: hexavalent and trivalent (*2*). The toxicity of Cr highly depends on its oxidation states. Hexavalent Cr is an inhaled carcinogen, poisonous to humans and other mammals (*2*−*4*). A trace level of trivalent Cr, however, is an essential nutrient as a mineral supplement (*5*). Thus, the accurate quantification of these two species of Cr, especially the toxic Cr(VI) in environmental samples, is an important issue for environmental protection and remediation (*4*, *6*, *7*).

Speciation analysis of Cr(VI) in environmental soil samples generally requires two major steps: extraction and detection. An optimal extraction procedure should completely extract Cr(VI) species without disturbing the species distribution (*6*, *7*). EPA RCRA SW-846 Method 3060A uses an alkaline solution (0.28 M Na_2CO_3/0.5 M NaOH) to extract Cr(VI) species from soil samples at 90−95 °C (*8*). This method effectively dissolves both water-soluble and water-insoluble Cr(VI) compounds and prevents the reduction of Cr(VI). However, it has also been observed that the same procedure can oxidize soluble Cr(III) although the oxidization is believed not to occur to insoluble Cr(III), which predominates Cr(III) in environmental soil samples (*7*, *9*).

Method 7196A (*10*), a spectrophotometric method based on Cr(VI)−diphenylcarbazide (DPC) reaction, is suggested as an appropriate detection method for Cr(VI) in Method 3060A. Compared with other detection methods, such as chromatography coupled with elemental detectors (*11*) and electrochemistry methods (*12*), Method 7196A provides a reasonable sensitivity, selectivity, and reproducibility with a lower cost. Cr(VI)-DPC based detection methods have been extensively used in the quantification of Cr(VI) in water samples and many other matrices by detecting the absorbance of the red-violet product, Cr(III)-diphenylcarbazone (DPCO), at 542 nm in a pH 2 solution (*13*, *14*). However, several problems have been documented when this method is applied to some types of samples with complex matrices (*15*, *16*). For example, large amounts of reducing agents coexisting in the sample may result in low recoveries. Our experiments indicate that Method 7196A may cause negative errors of Cr(VI) by different mechanisms.

We applied Speciated Isotope Dilution Mass Spectrometry (SIDMS) (*17*, *18*) as an alternative detection method to identify the steps that might alter species distribution in Method 3060A/7196A protocols. SIDMS is a new speciation analysis method that can mathematically correct for the interconversion between such species as Cr(VI) and Cr(III). The principle of SIDMS has been demonstrated in the patent and articles (*17*−*20*). Briefly, SIDMS uses the concept of spiking the sample with known amounts of enriched isotopes that have been chemically converted into the same forms of the species to be analyzed. The isotopic spike for each species has a unique isotope enrichment. For example, two isotopic spikes, ^{53}Cr(VI) enriched in ^{53}Cr and ^{50}Cr(III) enriched in ^{50}Cr, are prepared for the simultaneous determination of Cr(VI) and Cr(III). Water samples containing Cr species are spiked with both ^{53}Cr(VI) and ^{50}Cr(III). Any interconversions that occur after spiking are traceable and can be quantitatively corrected by monitoring isotopes in each species. Because SIDMS can measure species concentrations at the time of spiking, by spiking a sample before and after a treatment of the sample, SIDMS can be used as a diagnostic tool to identify the procedure that alters species in a multiple-step protocol (*18*). SIDMS was used in our experiments to identify the steps that cause biases of Cr(VI) in EPA Methods 3060A/7196A. In addition to SIDMS, we applied the MINTEQA2 software developed by the U.S. EPA (*21*) to quantitatively evaluate the species conversion and distribution. MINTEQA2 is a geochemical model capable of calculating equilibrium, aqueous speciation, and adsorption of metal, etc. in aqueous solutions.

Experimental Section

Instrument. A hot plate with stirring capability was used for the extraction of Cr(VI). A Cary UV−vis spectrophotometer (Varian) was used for detecting Cr(VI) with Method 7196A. A Cetac ANX 4605 Cr anion-exchange column (CETAC Corporation, Omaha, NE) was used to separate Cr(VI) and Cr(III) in SIDMS. A VG Elemental PlasmaQuad ICP-MS system (Winsford, U.K.) was used for isotope ratio measure-

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ments. Detailed description of the instrumentation in SIDMS can be found in ref *19*.

Reagents. Deionized water (18 MΩ cm^{-1}) prepared from a NANOpure Ultrapure Water System (Dubuque, IA) was used in the preparation of all solutions. The extraction solution (0.28 M Na_2CO_3/0.5 M NaOH) was prepared by dissolving 20 g of NaOH (98%, Fisher) and 30 g of anhydrous Na_2CO_3 (99.6%, Fisher) in 1 L of the deionized water. Cr(VI) and Cr(III) standard solutions were prepared from $K_2Cr_2O_7$ (NIST SRM1360e) and Cr metal (99.995%, Aldrich Chemical Co., Milwaukee, WI), respectively. The DPC solution was made by dissolving 0.5 g of DPC (Fisher) in 100 mL of acetone and stored in a light excluding bottle.

Two types of nitric acid, the regular colorless concentrated nitric acid (Fisher) and the sub-boiling distilled nitric acid were used. The latter was prepared from a quartz still (Milestone, Sorisole (BG), Italy). Unless specified, the regular nitric acid was used to neutralize the extracts in Method 3060A.

$PbCrO_4$ (Fisher) and $BaCrO_4$ (Aldrich) solids were used. All other chemicals were analytical reagents.

Extraction and Detection Procedures of Cr(VI) in Methods 3060A/7196A (*8*, *10*). Cr(VI) in solid samples was extracted with Method 3060A. The same procedure was applied when SIDMS was used for quantification. Fifty milliliters of the extraction solution and 2.5 g of soil sample were added into a beaker and heated to 90−95 °C on a hot plate. This temperature was maintained for 1 h. The cooled extract (pH > 12) was then filtered with a 0.45 μm membrane filter. This filtrate was neutralized to pH 7.5 with concentrated nitric acid and stored for detection. A proper amount of the neutralized filtrate and 1 mL of DPC solution was added to a 50 mL volumetric flask, and 10% sulfuric acid was used to adjust the solution to pH 2 for the formation of the red-violet Cr(III)−DPCO complex.

SIDMS Procedure. The extract was sampled at each step for SIDMS analysis to determine Cr species at that specific step (*18*). For example, after extraction and filtration, a portion of the filtrate (pH > 12) was transferred to a vial for SIDMS measurement, and the rest of the filtrate was neutralized to pH 7.5. Then, a portion of the neutralized solution was transferred to another vial for SIDMS measurement. Thus, the concentrations of Cr(VI) and Cr(III) before and after neutralization could be measured with SIDMS. By comparing the results obtained with pre- and post-neutralization spiking in soil extracts, reduction of Cr(VI) during neutralization was identified (*18*, *20*).

Results and Discussion

The distribution of Cr(VI) and Cr(III) species strongly depends on pH and potential (*2*, *4*). According to the pH-E diagram of Cr species, Cr(VI) is thermodynamically stable at relatively higher pH and E, while Cr(III) is stable at relatively lower pH and E (*2*). Kinetics also plays an important role in the interconversion between Cr(VI) and Cr(III). In environmental samples, the redox reaction between Cr(VI) and Cr(III) is controlled by several factors, including kinetics (*2*). It has been observed in the evaluation study of Method 3060A that soluble Cr(III) and freshly precipitated $Cr(OH)_3$ can be oxidized during extraction, but other forms of Cr(III) cannot be oxidized (*6*, *7*).

As described in the Experimental Section, the paired Methods 3060A/7196A consist of the extraction, neutralization, and colorimetric detection steps. Corresponding to the change of the pH, the formal reduction potential of Cr(VI)/Cr(III) changes from −0.04 V (pH 13) to 0.52 V (pH 7.4) then to 1.07 V (pH 2) (*22*). Based on these thermodynamic data, the oxidation of Cr(III) may occur during extraction; the reduction of Cr(VI) may occur during neutralization. Cr(VI) may react with coexisting reducing matrix rather than DPC in Method 7196A and consequently cause negative errors. In addition, some chromate compounds have a much lower solubility in the neutral solution than in the strong basic solution. Decreasing pH may cause the loss of Cr(VI). For example, $PbCrO_4$ has a solubility of 1.19 (wt %) in 0.41 M KOH at 15 °C, but the solubility is only 1.7×10^{-5} (wt %) in water at 20 °C (*23*). Briefly, biases may be present in the following steps in EPA Methods 3060A/7196A: extraction, neutralization, and detection.

Oxidation of Soluble Cr(III) During Extraction. Method 3060A effectively extracts Cr(VI) in the strong alkaline solution at the temperature of 90−95 °C (*6*, *7*). The strong basic solution prevents the reduction of Cr(VI). Cr(III) is thermodynamically unstable under such conditions. Despite this thermodynamic instability of Cr(III), only limited oxidation of soluble Cr(III) during extraction was previously observed (*6*). However, it has also been reported that the oxidation of Cr(III) highly depends on the chemical form of Cr(III): Cr_2O_3 and aged $Cr(OH)_3$ precipitate are resistant to oxidation; free Cr^{3+} and freshly precipitated $Cr(OH)_3$ are relatively easy to oxidize (*7*). Although the fresh $Cr(OH)_3$ precipitate is not a representative form of Cr in environmental samples, the possibility of biases caused by oxidizable Cr cannot be excluded. Because the free Cr^{3+} and freshly precipitated $Cr(OH)_3$ are the two most easily oxidizable Cr(III) species, the study of the oxidation of such Cr(III) species will help to estimate the possible biases introduced during extraction.

Cr(III) standard solution without matrix was used as a sample to study the oxidation of soluble Cr(III) during extraction. Method 7196A was used to quantify the produced Cr(VI). Because there was no other matrix component in the solution, Method 7196A should be accurate. (We will demonstrate later that Method 7196A suffers matrix effects when analyzing soil and sand extracts.)

Cr(VI) was detected after extraction, indicating that the soluble Cr(III) was oxidized to Cr(VI) during extraction. However, the total amount of the produced Cr(VI) was limited and independent of the amount of soluble Cr(III) added. For example, when 102 μg and 200 μg of soluble Cr(III) were extracted, the detected Cr(VI) were 12.2 ± 1.7 μg and 11.1 ± 1.2 μg, respectively. These results agree with the previous studies (*7*). Because there were no other oxidizing agents in these samples, the possible oxidant should be the dissolved oxygen in the extraction solution. Modeling with MINTEQA2 software shows that the oxygen is capable of oxidizing all soluble Cr(III) to Cr(VI) in the extraction solution if it is thermodynamically controlled. The kinetics model is being studied, however. Many studies reported that the oxidation of Cr(III) in soils requires the oxidized Mn as an electron linker between Cr(III) and O_2 (*2*). Unfortunately, no kinetic study of the oxidation of Cr(III) in the extraction solution has been reported. Overall, even without any matrix components, the extraction procedure can cause the oxidation of the soluble Cr(III) although the oxidation is limited. The oxidation of Cr(III) during extraction could vary with the sample matrix. As demonstrated in ref *4*, matrices can cause much more oxidation of Cr(III) during extraction. We are currently using SIDMS with the extraction procedure to monitor and correct for the oxidation of Cr(III) during the extraction procedure, and the results will be published in the future.

Loss of Cr(VI) During Neutralization. Among several methods for extracting Cr(VI) from soils, the alkaline extraction was regarded as the most appropriate (*6*). We used $K_2Cr_2O_7$, $BaCrO_4$, and $PbCrO_4$ solids in evaluating the effectiveness of this alkaline extraction method. $K_2Cr_2O_7$ is water-soluble; $BaCrO_4$ ($K_{sp} = 1.2 \times 10^{-10}$ at 25 °C (*24*)) and $PbCrO_4$ ($K_{sp} = 2.8 \times 10^{-13}$ at 25 °C (*24*)) are among the most water-insoluble Cr(VI) compounds. Both Method 7196A and

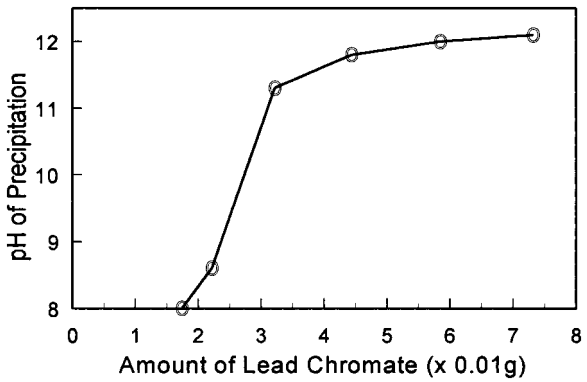

FIGURE 1. Relationship between the amount of $PbCrO_4$ extracted and the pH at which the precipitation starts to occur during neutralization.

SIDMS were used to detect Cr(VI). $K_2Cr_2O_7$ could be easily dissolved in the extraction solution as expected, and no reduction of Cr(VI) occurred during extraction. Based on our experiments, up to 24.4 mg of $BaCrO_4$, containing 5.01 mg of Cr(VI), could be completely extracted. After filtration, a small amount of white precipitate was observed on the filter paper. The filtrate remained clear during neutralization. The neutralized filtrate was analyzed. Approximately 100% recoveries of Cr(VI) were obtained with both detection methods, indicating that the precipitate produced during neutralization was not a Cr compound. On the other hand, when $PbCrO_4$ solid with a quantity larger than 17 mg, corresponding to 2.79 mg of Cr(VI), was extracted, white and yellow precipitates were observed during neutralization. In addition, the pH at which the precipitation started to occur depended on the amount of $PbCrO_4$ added. More $PbCrO_4$ caused the precipitation to occur earlier during neutralization (Figure 1). If no filtration was performed after neutralization, the precision of the determination with Method 7196A was poor. If the filtration was done, low recoveries of Cr(VI) were obtained with Method 7196A. However, 100% recoveries were achieved when the filtrate of $PbCrO_4$ (pH > 12) before neutralization was sampled and analyzed with SIDMS. In this case, we must evaluate the extraction and neutralization step separately. The 100% recoveries of Cr(VI) obtained with SIDMS indicate that the dissolution of $PbCrO_4$ was complete; low recoveries of Cr(VI) determined with Method 7196A were due to the reprecipitation of Cr compound(s) during neutralization.

We applied MINTEQA2 software to model the experiments. Based on the modeling, CO_3^{2-} in the extraction solution is essential in the dissolution of $BaCrO_4$, and the reaction can be expressed as $BaCrO_4(s) + CO_3^{2-}(aq) \rightarrow BaCO_3(s) + CrO_4^{2-}(aq)$. The results of the MINTEQA2 modeling indicate that CO_3^{2-} reacts with Ba^{2+} because of the high concentration of CO_3^{2-} (0.28 M), producing the $BaCO_3$ precipitate although the K_{sp} of $BaCO_3$ (5.1×10^{-9} at 25 °C (*24*)) is higher than that of $BaCrO_4$ ($K_{sp} = 1.2 \times 10^{-10}$ at 25 °C (*24*)). The precipitation of $BaCO_3$ greatly decreases the concentration of the free Ba^{2+} ions in solutions, driving the dissolution of $BaCrO_4$ and releasing CrO_4^{2-} as a free anion in solution. The precipitated $BaCO_3$ is removed at the filtration step. When neutralizing the solution from pH 12 to 7.5, CrO_4^{2-} cannot reprecipitate because nearly all Ba has been removed during filtration. Therefore, the alkaline extraction takes advantages of the formation of $BaCO_3$ to release CrO_4^{2-} from $BaCrO_4$ and the subsequent filtration to remove Ba to prevent the reprecipitation of $BaCrO_4$.

On the other hand, the dissolution of $PbCrO_4$ in the strong basic extraction solution does not require CO_3^{2-}. MINTEQA2 modeling indicates that the dissolution of $PbCrO_4$ involves the formation of $Pb(OH)_2$ ($K_{sp} = 1.2 \times 10^{-15}$ at 25 °C (*24*)) and $Pb(OH)_n^{2-n}$ ($1 \le n \le 4$, $K_1 = 1.5 \times 10^{-8}$, $K_2 = 1.4 \times 10^{-11}$, $K_3 = 2.6 \times 10^{-15}$ at 25 °C (*24*)). Although much of the Pb can be removed after extraction as $Pb(OH)_2$ by filtration, Pb still remains in the filtrate as complexes. According to MINTEQA2 modeling, the order of the conversion of Pb species during neutralization from pH 12 to pH 7.5 is $Pb(OH)_n^{2-n} \rightarrow Pb(OH)_2 \rightarrow PbCO_3$ ($K_{sp} = 7.4 \times 10^{-14}$ at 25 °C (*24*)) $\rightarrow PbCrO_4$ due to the continuously decreased concentrations of OH^- and CO_3^{2-}. Both K_{sp}, of each compound, and the concentrations of anions control the precipitation order. In some pH ranges, the precipitate is a mixture. For example, Pb precipitates as both $PbCO_3$ and $PbCrO_4$ at pH 7.5. Therefore, some of the dissolved $PbCrO_4$ reprecipitates during neutralization, resulting in the loss of the Cr(VI) from solution. The more $PbCrO_4$ solid is extracted, the more $Pb(OH)_n^{2-n}$ and CrO_4^{2-} could be present in the filtrate, and the earlier the precipitation occurs during neutralization (Figure 1).

Reduction of Cr(VI) During Neutralization. The neutralization could also cause the reduction of Cr(VI) depending on the matrix level. A soil extract was prepared using Method 3060A, and the filtrate was spiked with Cr(VI) standard solution. A portion of the pH 12 extract (before neutralization) and a portion of the pH 7.5 extract (after neutralization) were sampled for SIDMS analysis. In the pH 12 extracts, no Cr(III) was detected. In the pH 7.5 extracts, however, a small amount of Cr(III) was detected (Table 1). In addition, the recoveries of Cr(VI) obtained from the pH 7.5 extracts were 4.0%, 4.7%, and 2.6% lower than those obtained from the pH 12 extracts, while the recoveries of the blanks at both pHs were 100%. Mass balance study of these results suggests that the reduction of Cr(VI) accounts for the detected Cr(III) (*18*, *20*). The degree of the reduction was also related to the ratio of the matrix to Cr(VI). As expected, the more reducing matrix components, the more reduction of Cr(VI) occurred during neutralization.

Cr(VI) is easier to reduce in a pH 7.5 solution than in a pH 12 solution. According to Method 3060A, the extract of a sample can be stored after neutralization for future analysis because both Cr(VI) and Cr(III) are believed to be stable in the neutralized extracts. However, the reduction of Cr(VI) observed during neutralization suggests that Cr(VI) could be unstable under such conditions. This reduction may be kinetically slow, but extended storage time could cause significant loss of Cr(VI). Thus, we recommend prompt detection of Cr(VI) after neutralization in Methods 3060A/7196A.

Low Recoveries of Cr(VI) for Sand and Soil Samples with Method 7196A. Method 7196A could also cause analytical biases of Cr(VI). We evaluated the quantification of Cr(VI) using Method 7196A in three matrix types, including sand, soil, and chromite ore processing residue (COPR). Compared with SIDMS, Method 7196A obtained lower recoveries of Cr(VI) for sand and soil samples, while comparable results were obtained for COPR samples.

Review of the mechanism of Method 7196A prior to the discussion of the analytical biases in Method 7196A is appropriate. Different from many other color-development reactions, a redox reaction in addition to a complexation reaction is involved in DPC-based determination methods of Cr(VI) (*13*, *25*). Cr(VI) oxidizes DPC to produce DPCO at pH 2, and then the reduced Cr(III) combines with DPCO to form the detectable red-violet complex Cr(III)−DPCO. These redox and complexation reactions occur simultaneously *in situ* (*25*). Based on this mechanism, reagents that can react with either Cr(VI) or DPC could cause analytical biases: reducing agents may compete with DPC to reduce Cr(VI), and strong oxidizing agents may compete with Cr(VI) to oxidize DPC.

Sand and soil samples were extracted following Method 3060A. After filtration, the extracts (pH > 12) were spiked

TABLE 1. The Recoveries of Cr in Sand and Soil Extracts

sample	mass of sample (g)	Cr(VI) added (μg)	Method 7196A Cr(VI) (%)	SIDMS (pH > 12)[a] Cr(VI) (%)	SIDMS (pH 7.5)[b] Cr(VI) (%)	SIDMS (pH 7.5)[b] Cr(III) (%)
sand	2.50	1.024	86.9 ± 5.2[c]	100 ± 1.3	NA[d]	NA
soil 1	3.12	1.587	71.6 ± 6.2	99.5 ± 0.8	95.5 ± 1.6	2.7 ± 0.5
soil 2	3.06	2.993	81.9 ± 2.7	101 ± 0.8	96.3 ± 0.7	3.1 ± 1.9
soil 3	1.53	3.033	91.8 ± 4.2	100 ± 0.7	97.4 ± 1.0	2.0 ± 1.3
blank	0	2.997	101 ± 1.0	99.9 ± 0.6	100 ± 0.1	0

[a] SIDMS determination of Cr(VI) in the extracts (pH > 12) sampled prior to neutralization. No Cr(III) was detected. Cr was completely recovered as Cr(VI). [b] SIDMS determination of Cr(VI) and Cr(III) in the neutralized extracts (pH 7.5). Cr recovered as Cr(III) accounts for the lowered recoveries of Cr(VI), indicating the reduction of Cr(VI) during neutralization. [c] 95% confidence interval. [d] Not analyzed.

with different amounts of Cr(VI). These spiked solutions were used as sample solutions for further analysis by both Method 7196A and SIDMS. A portion of the spiked solution (pH > 12) before neutralization was sampled for SIDMS analysis, and the rest of the solution was neutralized to pH 7.5 with concentrated nitric acid and analyzed with Method 7196A.

Both Method 7196A and SIDMS achieved approximately 100% recoveries of Cr(VI) for the blank solutions. However, Method 7196A obtained lower recoveries for the sand and soil samples. On the other hand, SIDMS achieved approximately 100% recoveries of Cr(VI) for all samples as demonstrated in Table 1.

The analytical biases of Cr(VI) using Method 7196A depend on the matrix components. The ratios of soil matrix (g) to Cr(VI) (μg) were approximately 2:1, 1:1, 1:2, and 0 for soil samples 1, 2, 3, and the blank, respectively; the corresponding recoveries were 71.6%, 81.9%, 91.8%, and 101% using Method 7196A. As the disparity of recovery indicates, increasing the ratio of soil matrix to Cr(VI) resulted in lower recoveries of Cr(VI) in Method 7196A. The more concentrated the matrix, the lower the recovery of Cr(VI) using Method 7196A. The reducing matrix did reduce Cr(VI) in SIDMS samples, but SIDMS corrected for such species conversions and identified both the amount of Cr(VI) and Cr(III) in the final solutions and their origins. Although the species conversions influence the precision of the determination using SIDMS, they do not decrease the accuracy of SIDMS (*20*, *26*).

The detection limit of Method 7196A determined using a blank solution without matrix is 0.01 μg mL^{-1}. For real samples with reducing matrix, the detection limit could be higher because the reducing matrix may compete with DPC to react with Cr(VI) to produce an undetectable product. Moreover, Cr(VI) could be reduced by sample matrix with strong reducing capability during neutralization and measurement (at pH 2) even if they might exist in the strong alkaline extracts (pH > 12) before measurement. In such situations, Method 7196A will give severely biased results although the precision might be good.

Comparable Results for COPR Samples. COPR samples were extracted and analyzed. Unlike soil extracts, no reduction or precipitation of Cr(VI) was observed during neutralization (therefore, sampling before or after neutralization for detection does not make a difference). The neutralized extracts were sampled for the detection with both Method 7196A and SIDMS. As shown in Table 2, the Cr(VI) concentrations in these three COPR samples varied significantly. COPR 1 has the highest concentration (1410 μg g^{-1}); the concentrations of Cr(VI) in COPR 4 and COPR 3 were 408 μg g^{-1} Cr(VI) and 85.3 μg g^{-1}, respectively. Although the heterogeneity of these samples probably resulted in the decreased precision, these two detection methods were comparable for all three COPR samples, indicating that Method 7196A is an appropriate detection method for COPR samples.

TABLE 2. The Concentrations of Cr(VI) in COPR Samples Measured with Method 7196A and SIDMS

	Method 7196A		SIDMS	
sample	concn of Cr(VI) (μg g^{-1})	Cr(VI) (μg g^{-1}) (mean ± std)[a]	concn of Cr(VI) (μg g^{-1})	Cr(VI) (μg g^{-1}) (mean ± std)[a]
COPR 1	1330	1410 ± 85	1373	1445 ± 70
	1410		1449	
	1500		1512	
COPR 3	91.2	85.3 ± 5.2	93.9	88.8 ± 6.1
	81.5		82.1	
	83.1		90.4	
COPR 4	409	408 ± 7	420	418 ± 9
	414		426	
	400		408	

[a] Std: standard deviation, $n = 3$.

Generally, as we have seen, sample matrix components may affect Method 7196A, while SIDMS can correct for such interferences. Compared with the strongly reducing soil matrix, the less reducing capability of COPR matrices could be one of the reasons for the unbiased detection of Cr(VI) by Method 7196A. Another reason might be that the relative concentration level of matrix components to Cr(VI) in COPR extracts is much lower than that in the soil extracts tested. For example, the ratio of sample (g) to Cr(VI) (μg) in COPR 3 is approximately 1:85, which is much lower than the corresponding values of 2:1, 1:1, and 1:2, respectively, in soil extracts. Therefore, the matrix level in the detection solutions was so low that it did not cause interferences in Method 7196A. The quantification of Cr(VI) in sand, soil, and COPR extracts demonstrated that in the case where the sample contains strongly reducing matrix components and/or the Cr(VI) in the sample is low, Method 7196A might not be a proper detection method for Cr(VI). For such samples as COPR extracts, however, cost-efficient Method 7196A is an accurate detection method.

Sources of Biases in Method 7196A. Soils contain varying quantities of organic and inorganic compounds. Some of them were studied in this paper. Synthesized samples were used to evaluate the influence of various soil matrix components on the recovery of Cr(VI) by Method 7196A. Some selected results are shown in Figure 2.

The alkaline extraction solution used in Method 3060A can extract such organic acids as fulvic acids and humic acids from soil samples. At low pH, some of these organic compounds can reduce Cr(VI) to Cr(III) (*2*). Among a set of organic acids tested, we observed that phthalic acid (2.0 mM), tartaric acid (2.0 mM), and phenol (4.0 mM) decreased the Cr(VI) recoveries by 3.5%, 3.4%, and 2.6%, respectively. The number and the amount of organic compounds in soils vary with soil type and exposure to contaminants. The concentrations of organic compounds applied in these experiments

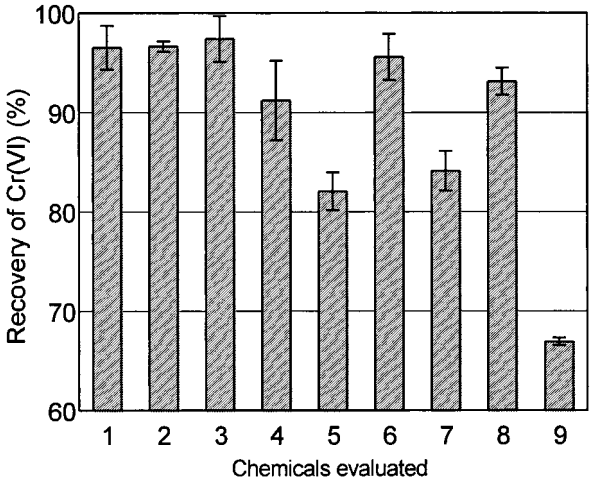

FIGURE 2. Effect of some soil components on the recoveries of Cr(VI) using Method 7196A. The concentration of Cr(VI) is 0.50 μg mL^{-1}. The concentration of each chemical is (1) 2.0 mM of phthalic acid; (2) 2.0 mM of tartaric acid; (3) 4.0 mM of phenol; (4) 67 μg mL^{-1} of Na_2S; (5) 131 μg mL^{-1} of Na_2S; (6) 0.4 μg mL^{-1} of Fe^{2+}; (7) 1.6 μg mL^{-1} of Fe^{2+}; (8) 2.0 μg mL^{-1} of Fe^{3+}; and (9) 8.0 μg mL^{-1} of Fe^{3+}. Error bars show standard deviations ($n = 3$).

were in the typical ranges of corresponding components in soil solution, which is defined as the aqueous liquid phase at field moisture contents (*27*). In the alkaline soil extracts, the concentrations of some organic compounds, especially water insoluble humic acids may be much higher than in the soil solution. Therefore, some other organic chemicals in soils may also have this effect. Even those which did not show an effect on Cr(VI) detection in our experiments may cause low recoveries of Cr(VI) when their concentrations are higher.

Experiments on reducing agents Fe^{2+} and sulfides (including H_2S) indicated that these agents significantly decreased the recoveries of Cr(VI) as expected. Surprisingly, we observed that Fe^{3+} also significantly decreased the recovery of Cr(VI) (Figure 2), contradictory to the statement in EPA Method 7196A that Fe^{3+} would cause a positive error due to the formation of a yellow complex (*10*).

Based on the mechanism of the color-development reaction that has been described earlier, we raise the hypothesis that the low recoveries caused by strong oxidants are due to the oxidation of DPC. We designed several experiments to verify this hypothesis. A blank extraction solution spiked with 0.5 μg g^{-1} Cr(VI) was used as a sample. In the first experiment, 1 mg of Fe^{3+} was added to the sample solution prior to acidification. The solution was then acidified to pH 2 following Method 7196A. During this pH adjustment, the solution turned yellow rather than red-violet. Adding more Cr(VI) did not change the color; adding more DPC, however, eventually turned the solution to red-violet, indicating that it was DPC that was changed by Fe^{3+}. As shown in Figure 3, the new peak at 335 nm demonstrates the reaction between DPC and Fe^{3+}. Except for the baseline elevation, no spectral interference at 542 nm was observed. We also tested $KMnO_4$ and the sub-boiling distilled nitric acid and obtained similar results. Because Fe^{3+}, $KMnO_4$, and sub-boiling distilled nitric acid are all strong oxidants, we believe that DPC was oxidized by these oxidants during these experiments rather than reacting with Cr(VI) to produce a measurable red-violet product. The oxidized DPC with the maximum absorbance at 335 nm did not show a spectral interference with Cr(VI) detection. Therefore, the effect of Fe^{3+} on Cr(VI) detection was dominated by the oxidation of DPC, not by the spectral overlap in our experiments.

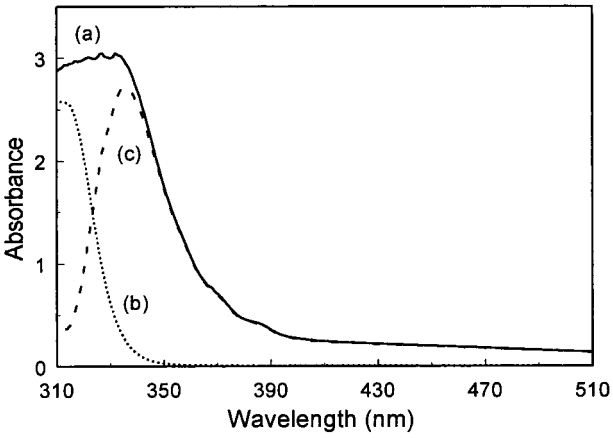

FIGURE 3. Effect of Fe^{3+} on DPC. (a) The spectrum of the yellow solution containing DPC, 10 μg mL^{-1} Fe^{3+}, and the blank extraction solution at pH 2. (b) The spectrum of the colorless solution containing DPC and the blank extraction solution at pH 2. (c) The difference spectrum of (a) and (b). Spectrum (c) indicates the conversion of DPC. Ten μg mL^{-1} Fe^{3+} has a very weak absorbance in this range. $KMnO_4$ and the sub-boiling distilled nitric acid have the same effects as Fe^{3+} on DPC.

The sub-boiling distilled nitric acid has a brown color and is prepared using infrared heating. Such tinged nitric acids contain high levels of NO_x due to the photoreduction reaction, enhancing the oxidization capability of the nitric acid. The authors of Method 3060A observed this difference between the "regular" nitric acid and the tinged nitric acid and stipulate that the nitric acid be discarded if it is observed to be tinged (*8*). However, the reason was not explained. We tested several types of acids in neutralization. Only when the tinged nitric acid was used, did we observe nonrecovery of Cr(VI). Using regular nitric acid, sulfuric acid, or hydrochloric acid in neutralization, however, a complete recovery was always obtained. These experiments, plus the observation on the effect of Fe^{3+} and $KMnO_4$ on the color development, indicate that the tinged sub-boiling distilled nitric acid oxidized DPC.

Summary

The extraction and neutralization steps in Method 3060A and detection Method 7196A could cause analytical biases of Cr(VI). Although the extraction procedure can completely extract Cr(VI), soluble Cr(III) could be oxidized to Cr(VI) during the same procedure. On the other hand, Cr(VI) that is already solublized during extraction could reprecipitate or be reduced during neutralization. Method 7196A obtained lower recoveries of Cr(VI) in sand and soil samples. These low recoveries of Cr(VI) could be due to the coexistence of such reducing matrix components as organic compounds or inorganic reducing agents. In addition, we found that Fe^{3+} could also cause negative errors, contradicting earlier reports. We evaluated the mechanism of the influence of oxidants on Method 7196A and provided the experimental evidences supporting the mechanism.

Unlike Method 7196A, the SIDMS technique can correct for the species transformations, including species' shift or loss. Currently, SIDMS has been successfully applied in the accurate determination of Cr(VI) in aqueous samples and soil extracts (*18*−*20*). Using SIDMS as a detection method with the alkaline extraction of Cr(VI) can eliminate the biases related to neutralization and detection with Method 7196A. We are now developing a new technique integrating SIDMS into the extraction procedure. The new method can additionally correct for errors occurring in the extraction step.

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