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Field Method for the Determination of Hexavalent Chromium by Ultrasonication and Strong Anion-Exchange Solid-Phase Extraction

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A simple, fast, sensitive, and economical field method was developed and evaluated for the determination of hexavalent chromium (Cr^{VI}) in environmental and workplace air samples. By means of ultrasonic extraction in combination with a strong anion-exchange solid-phase extraction (SAE-SPE) technique, the filtration, isolation, and determination of Cr^{VI} in the presence of trivalent chromium (Cr^{III}) and potential interferents was achieved. The method entails (1) ultrasonication in basic ammonium buffer solution to extract Cr^{VI} from environmental matrixes; (2) SAE-SPE to separate Cr^{VI} from Cr^{III} and interferences; (3) elution/acidification of the eluate; (4) complexation of chromium with 1,5-diphenylcarbazide; and (5) spectrophotometric determination of the colored chromium−diphenylcarbazone complex. Several critical parameters were optimized in order to effect the extraction of both soluble (K_2CrO_4) and insoluble ($PbCrO_4$) forms of Cr^{VI} without inducing Cr^{III} oxidation or Cr^{VI} reduction. The method allowed for the dissolution and purification of Cr^{VI} from environmental and workplace air sample matrixes for up to 24 samples simultaneously in less than 90 min (including ultrasonication). The results demonstrated that the method was simple, fast, quantitative, and sufficiently sensitive for the determination of occupational exposures of Cr^{VI}. The method is applicable for on-site monitoring of Cr^{VI} in environmental and industrial hygiene samples.

Environmental chromium exists primarily in two valence states, trivalent (Cr^{III}) and hexavalent (Cr^{VI}). The trivalent state is relatively nontoxic and is an essential trace nutrient in the human diet.[1] On the other hand, Cr^{VI} has been shown to be a human respiratory carcinogen in epidemological studies of workplace exposures[1,2] and has been classified by the U.S. Environmental Protection Agency (EPA) as a Group A inhalation carcinogen.[3] Hence, analytical methods are desired which can be used to speciate chromium so that human exposures to Cr^{VI} can be monitored.

Workplace exposure to Cr^{VI} has been associated with a number of industrial sources, such as metal plating, spray painting, welding, tanning, and abrasive blasting operations.[4,5] Environmental sources of Cr^{VI} include deteriorated or disturbed chromate-containing paint, combustion sources such as automobiles and incinerators, and fugitive dusts from contaminated soils.[6,7] Because of the desire to accurately measure Cr^{VI} at low levels, the development of analytical methods for the determination of Cr^{VI} has been a subject of significant interest in occupational and environmental health.[4,8−12]

Several challenges have been encountered in efforts to determine hexavalent chromium in environmental and industrial hygiene samples. These include the instability of Cr^{VI} on filter media used for sampling of airborne particulates in workplace atmospheres[13−15] and the instability of chromium species (both trivalent and hexavalent) during sample preparation procedures, especially extraction.[4,15,16] The availability of a field-portable method for the determination of hexavalent chromium would help to alleviate problems with sample instability on sample collection

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media, since analyses could be conducted on-site in the field before sample degradation could take place. Also, the sample preparation method should not only isolate and stabilize the chromium species of interest, but it should also be user-friendly. In this work, we have endeavored to develop and evaluate a field-portable method for the determination of Cr^{VI} which satisfies the above criteria.

In this work, solid-phase extraction (SPE) was used to isolate Cr^{VI} from Cr^{III} and other metal cations. The use of SPE for the separation and preconcentration of trace polar or nonpolar target analytes has been widely investigated,[11,12,17] and the advantages of such a technique over a conventional liquid−liquid extraction, coprecipitation, electrochemical deposition, and evaporation have been well documented.[18−20] By using either off-line or on-line methodologies, SPE has been employed for the isolation and preconcentration of a variety of analytes.[21,22]

Despite these advances, there have been few applications of SPE to inorganics, including heavy metals.[23] Previously, no detailed studies on the use of a strong anion-exchange (SAE) solid-phase extraction for the isolation of Cr^{VI} have been reported. To our knowledge, this work is the first application of SAE-SPE as part of a quantitative field method for the isolation and determination of Cr^{VI} in environmental samples and workplace air. In a previous paper, we described the use of strong anion-exchange for the isolation and preconcentration of Cr^{VI} for flow injection analysis.[24] The method described herein was developed based on the use of SPE of Cr^{VI} with prepacked SAE sorbent loaded in cartridges.

Ultrasonic extraction (UE) for the purpose of dissolving target metal analytes in environmental samples is a technique that has not been used extensively, although it offers great promise.[25,26] UE has been demonstrated to perform well for the quantitative dissolution of several metals in a variety of environmental matrixes,[27−29] including Cr^{VI}.[15,24,30] UE in basic extraction solution (ammonium buffer) is used in this work in order to extract Cr^{VI} from environmental and workplace samples. The use of UE instead of more traditional extraction methods, such as hot plate digestion,[31,32] allows for the possibility of simplifying the extraction procedure. Also, UE can help to stabilize chromium species of interest by preventing oxidation of trivalent and/or reduction of hexavalent chromium.

In this work, experiments were performed in order to demonstrate the utility of UE for chromium extraction and speciation. After extraction and separation by strong anion-exchange solid-phase extraction, Cr^{VI} was determined using the 1,5-diphenylcarbazide (DPC) method.[30,33−35]

EXPERIMENTAL SECTION

Instrumentation and Reagents. Ultrasonic extraction was performed using a Sonicor 115V, 60-Hz laboratory sonicator. The solid-phase extractor was obtained from Supelco, Inc., and was attached to a small vacuum pump via a pressure metering valve. The strong anion-exchange cartridge used in the solid-phase extraction contained 500 mg of quaternary amine-bonded silica sorbent with Cl^- as counterion for strong anion-exchange (capacity 0.2 mequiv/g); the tube size was 3 mL. A portable cataloging spectrophotometer (HACH DR/2010) was used for spectrophotometric measurement. The sample path length was 1 cm.

Hexavalent and trivalent chromium standards, ammonium sulfate, ammonium hydroxide, 1,5-diphenylcarbazide (DPC), chromium oxide (Cr_2O_3), potassium chromate (K_2CrO_4), and hydrochloric, sulfuric, and nitric acids were all reagent grade and were purchased from Aldrich. Tris-HCl [tris(hydroxymethyl)-aminomethane hydrochloride] was obtained from Sigma. Lead chromate ($PbCrO_4$) was purchased from Fisher Scientific. Chromium-containing reference materials were used as supplied (paint chips, U.S. EPA Certified Reference Material [CRM] 013-050; coal fly ash, National Institute of Standards and Technology [NIST] Standard Reference Material [SRM] 1633a). A new reference material for hexavalent chromium in welding dust loaded on glass fiber filters, Institute for Reference Materials and Measurements (IRMM; formerly BCR) CRM 545, was obtained from the European Commission. Preloaded filter cassettes containing mixed cellulose ester membrane (MCE) filters (0.8-μm pore size, 37-mm diameter) were obtained from SKC.

Solid-Phase Extraction Procedures. Solid-phase extraction (SPE) was performed with the aid of an extractor and strong anion-exchange (SAE) cartridges. The SAE cartridges contained a silica sorbent to which a quaternary amine was bound; chloride ion functioned as the counterion. Cartridges were conditioned with 3 mL of deionized water, which activated the functional groups on the sorbent, allowing for binding of Cr^{VI} onto the SAE sorbent. Subsequently, a 3-mL aliquot of sample solution was loaded on the SAE cartridge. After sample loading, the cartridge was rinsed with 3 mL of deionized water. Then, elution of the Cr^{VI} concentrated on the SAE cartridge was performed with 9 mL of 0.5 M ammonium sulfate buffer solution in three 3-mL fractions.

Breakthrough and Elution Studies. Breakthrough was determined using spiked Cr^{VI} solutions (spiked mass ranged from 2 to 40 μmol) produced by dissolving K_2CrO_4 in 0.02−0.3 M ammonium sulfate/ammonium hydroxide buffer solutions (pH 8). The breakthrough of Cr^{VI} was determined by analyzing the

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collected eluate (after complexation with DPC) for different aliquots (0.1−10 mL) of the spiked solutions that were loaded onto the SAE cartridges.

For elution studies, ammonium sulfate/ammonium hydroxide buffer was chosen as an elution buffer solution. To determine the elution volume necessary to obtain optimum recoveries, spiked Cr^{VI} solutions of varying concentrations were eluted in several fractions with 0.5 M ammonium sulfate/ammonium hydroxide buffer solution (pH 8).

Air Sample Collection. Workplace air samples were collected during aircraft painting operations at U.S. Air Force bases using MCE filters.[31] Air samples were collected using Gil Air 3 air sampling pumps calibrated to an air flow rate of 2.0 ± 0.1 L/min. Samples were obtained from different work practices including priming, sanding, alodining (metal pretreatment), cutting, and grinding. The samples were transported to the laboratory immediately after collection and stored in a refrigerator at 4 °C until prepared for analysis.

Preparation of Environmental and Workplace Air Samples. Samples were placed into 15-mL plastic centrifuge tubes. Sample preparation consisted of adding 10 mL of 0.05 M $(NH_4)_2SO_4$/0.05 M NH_4OH (pH 8) buffer solution to the sample, followed by sonication in an ultrasonic bath for 30 min at ambient temperature (<40 °C). After sonication, a 3-mL aliquot of the supernatant was loaded onto a strong anion-exchange cartridge. After washing with 3 mL of water, the Cr^{VI} was eluted with 9 mL of 0.5 M $(NH_4)_2SO_4$/0.1 M NH_4OH (pH 8) buffer solution in three 3-mL fractions at a flow rate of 2 mL/min. After isolation, the eluate was acidified with 100 μL of 37% HCl solution. This was followed by mixing with 2 mL of 20 mM DPC complexing reagent. The reaction of DPC with Cr^{VI} is completed in a few seconds, and the color of the complex is stable for at least 8 h.

Analysis. Quantification of Cr^{VI} was done by external standard or standard addition methods with the spectrophotometer set at 540 nm. Blank filters and quality control/quality assurance samples (standard solutions of known Cr^{VI} concentration) were analyzed at a minimum frequency of 1 per 20 samples.

RESULTS AND DISCUSSION

Analytical Methodology. In the development of the methodology, the significant differences in the behavior of Cr^{VI} and Cr^{III} in aqueous media, and the stability of the chromium valences as a function of pH, must be considered. The standard reduction potential for the Cr^{VI}/Cr^{III} redox couple at high pH is negative [$CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_2^+ + 6OH^-$ ($E° = -0.13$ V, pH = 14)],[36] which indicates that alkaline medium favors stabilization of Cr^{VI}. In acidic media, the standard reduction potential for the Cr^{VI}/Cr^{III} redox couple is positive [$HCrO_4^- + 7H^+ + 3e^- = Cr^{3+} + 4H_2O$ ($E° = +1.21$ V, pH 1)],[37] which favors Cr^{III} stabilization. When pH < 10, Cr^{VI} predominates as anionic species (CrO_2^{2-}, $HCrO_4^-$), whereas Cr^{III} exists as cations (Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^+$).[37] Thus, pH is an extremely important factor in the relative stability of Cr^{VI} and Cr^{III} species in aqueous systems. Previous work on chromium speciation has indicated that the use of a slightly basic ammonium buffer solution may help stabilization of chromium species in aqueous systems.[38,39]

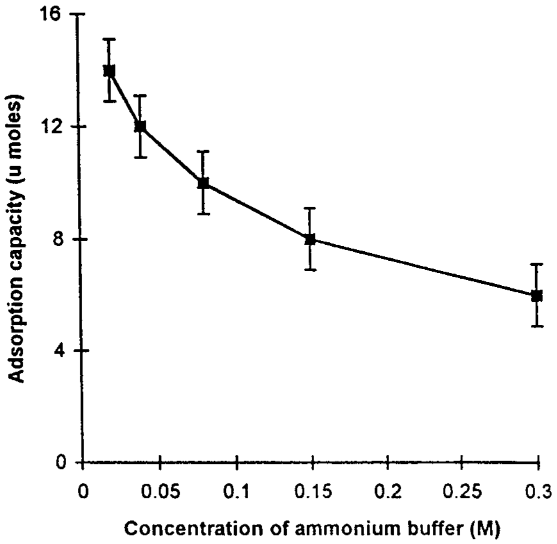

Figure 1. Strong anion-exchange adsorption capacity for hexavalent chromium as a function of the concentration of ammonium sulfate buffer solution.

As indicated above, Cr^{VI}, apart from other heavy metals, is anionic in basic solution, while all other species of chromium (principally Cr^{III}) are present as cations in base. Consequently, Cr^{VI} can be directly and quickly isolated and purified from other chromium species and metal cations by a strong anion-exchange solid-phase extraction procedure in a single step. The method involves (1) ultrasonic extraction of Cr^{VI} from solid matrixes with ammonium buffer solution; (2) SAE-SPE of Cr^{VI} from other chromium species and interferences; (3) elution/acidification of the eluate; (4) complexation with 1,5-diphenylcarbazide (DPC); and (5) spectrophotometric determination of the colored Cr^{VI}−diphenylcarbazone complex.

Adsorption Capacity of Strong Anion-Exchange Cartridge. In the method outlined above, several critical variables affecting the performance of SAE-SPE procedures were investigated. To evaluate strong anion-exchange adsorption and eluting capacity and efficiency, two factors were considered: (1) the percentage of the Cr^{VI} not adsorbed on the SAE cartridge, termed "breakthrough", and (2) the percentage of the adsorbed chromate eluted from the cartridge, termed "recovery".

To evaluate the adsorption capacities of the strong anion-exchange cartridge, spiked Cr^{VI} solutions were loaded onto the cartridges, washed with 3 mL of water, eluted with 9 mL (three 3-mL fractions) of 0.5 M ammonium sulfate buffer solution, and analyzed in triplicate to establish the reproducibility of the procedure. Breakthrough of the analyte was determined by analysis of the solution (following complexation with DPC) that passed through the SAE cartridge after loading of sample aliquots. Figure 1 shows the relationship between the adsorption capacities (micromoles) and concentration of ammonium sulfate/ammonium hydroxide buffer solutions (molar) used in sample preparation. The initial breakthrough was observed at various mass loadings of Cr^{VI}, with the flow rate controlled at 2 mL/min. Similar results were obtained with matrix spikes of MCE filters.

It was also observed that the adsorption capacities of SAE cartridges for Cr^{VI} decreased with increasing concentration of the

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Table 1. Hexavalent Chromium Recoveries (%) Obtained from Strong Anion-Exchange Solid-Phase Extraction, Eluted with 0.5 M $(NH_4)_2SO_4$ + 0.1 M NH_4OH (pH 8) Buffer and Collected from Eluting Fractions

Cr^{VI} standard solutions (μg)	recovery (%) of Cr(VI) ± RSD[a] fractions collected			
	2 (6 mL)	3 (9 mL)	4 (12 mL)	5 (15 mL)
10.0	85.3 ± 2.7	95.3 ± 3.3	95.5 ± 2.7	96.3 ± 2.4
20.0	83.1 ± 3.4	94.1 ± 3.7	94.9 ± 4.1	95.0 ± 2.9
40.0	83.9 ± 4.8	93.3 ± 3.6	94.5 ± 3.2	94.8 ± 2.8
80.0	82.5 ± 4.5	93.0 ± 4.2	94.1 ± 3.7	94.6 ± 3.4

[a] Relative standard deviation.

ammonium sulfate/ammonium hydroxide buffer in the sample solutions (Figure 1). This is because SO_4^{2-} in the sample solution can occupy active sites of the strong anion-exchange resin, thereby causing a decrease in adsorption capacity. The adsorption capacities of SAE cartridges were also related to sample loading flow rates. The percentage breakthrough increased with increased loading rate, and an optimum flow rate of 2 mL/min was arrived at by trial and error. These trials (Figure 1) have demonstrated that reducing the concentrations of ammonium sulfate/ammonium hydroxide buffer in sample solution can improve the adsorption capacity and minimize cartridge breakthrough.

When air samples containing chromium were tested to study SAE cartridge breakthrough, they were treated in an identical manner as spiked Cr^{VI} solutions. The effects of ammonium sulfate/ammonium hydroxide buffer solution (pH 8) used in the extraction procedure were evaluated. In these trials, the samples were treated with ultrasonication for 30 min at ambient temperature (<40 °C bath temperature) in ammonium sulfate buffer solution. The results demonstrated no significant breakthrough of Cr^{VI} when an ammonium sulfate/ammonium hydroxide buffer solution ($\leq$0.05 M) was used to extract Cr^{VI} from samples via sonication.

Eluting Hexavalent Chromium from Strong Anion-Exchange Cartridge. The effectiveness of ion-exchange in eluting solutions for the retention of Cr^{VI} on SAE cartridges was studied. Some of the variables governing the recoveries were investigated. Table 1 shows the recoveries obtained from spiked Cr^{VI} solutions with various elution volumes. The data in Table 1 show that no significant improvement of recoveries could be gained by increasing the number of (3-mL) eluting fractions by more than three. Under these optimum conditions, recoveries from duplicate spiked solutions exhibited reproducible results (Table 1).

Studies of Ultrasonic Extraction of Soluble and Insoluble Cr^{VI}. Although the soluble fractions of Cr^{VI} are useful parameters for estimating levels of hexavalent chromium that may be directly absorbed by human beings, quantifying insoluble forms of Cr^{VI} is pertinent to occupational hazards (such as $PbCrO_4$ in chromate ore processing and painting) associated with airborne respirable dust. Therefore, an effective and reliable method for extracting both soluble and insoluble forms of Cr^{VI} without inducing Cr^{III} oxidation or Cr^{VI} reduction is required. In this section, the research was focused on the study of ultrasonic extraction for the dissolution of soluble Cr^{VI} (K_2CrO_4) and insoluble Cr^{VI} ($PbCrO_4$) with ammonium sulfate/ammonium hydroxide buffer (pH 8) and/or Tris-HCl buffer solutions (with adjustment to pH 8 using NH_4OH).

To maximize dissolution of Cr^{VI} while minimizing method-induced oxidation and reduction, an extraction protocol was employed using 0.05 M ammonium sulfate/ammonium hydroxide buffer solution with sonication at temperatures below 40 °C. These conditions maintain a low activity of Cr^{III}, thereby minimizing oxidation of this species to Cr^{VI}.[16] Lead chromate ($PbCrO_4$, $K_{sp} = 1.8 \times 10^{-14}$) was used to represent insoluble Cr^{VI}; lead chromate has been used as a representative insoluble chromate species in other studies.[30] Potassium chromate was used as a representative soluble chromate species, and Cr_2O_3 was used as a source of trivalent chromium. In initial trials, 300 μg of $PbCrO_4$, K_2CrO_4, and Cr_2O_3 were spiked into triplicate samples of the 10-mL 0.05 M ammonium sulfate/ammonium hydroxide buffer solution. Since this method does not employ high temperatures, it was hypothesized that the procedure would minimize method-induced oxidation (of Cr^{III}) and reduction (of Cr^{VI}) while effectively dissolving Cr^{VI}.

Despite the demonstrated efficacy of the ammonium sulfate solution to dissolve soluble and insoluble forms of Cr^{VI}, a procedure employing Tris-HCl buffer (with ammonium hydroxide adjustment to pH 8) ultrasonication dispersion was also tested in an attempt to quantify total Cr^{VI} in spiked solutions. As Tris-HCl buffer contains ammonia, this ion can complex with Cr^{III} and, therefore, may help in stabilization of the trivalent chromium species.

Table 2 shows the results for soluble Cr^{VI} recoveries from ammonium sulfate and Tris-HCl buffer solutions. In these experiments, recoveries were between 93.3% and 95.5%. No significant differences in recoveries were observed upon increasing the ultrasonic extraction period from 30 to 60 min. Similar patterns were observed for recoveries of soluble Cr^{VI} spiked in Tris-HCl buffer solutions (Table 2).

A similar investigation was carried out for insoluble chromate ($PbCrO_4$) and allowed for comparisons to be made between recoveries from insoluble and soluble chromate spiked solutions. The results in Table 3 indicate that (not surprisingly) Cr^{VI} is more difficult to extract from lead chromate than from potassium chromate under the same ultrasonication time and temperature conditions (compare recoveries to values in Table 2). In both ammonium sulfate/ammonium hydroxide buffer and Tris-HCl buffer solutions, increasing the sonication time to 1 h (from 30 min) resulted in a slight increase in recovery (Table 3). The recovery in ammonium sulfate buffer (92.5%) was slightly greater than that obtained when using Tris-HCl buffer (89.5%) under the same ultrasonic extraction conditions (Table 3); however, these values are not statistically different (*t*-test, 95% confidence interval). Visual observation of the ultrasonication process revealed that lead chromate crystals were slowly dissolved, and this is evident in the nearly quantitative recoveries obtained from insoluble Cr^{VI}.

It was also noted from these experiments (Tables 2 and 3) that the presence of Cr^{III} in solution did not affect recoveries of Cr^{VI}. These results indicate that the conditions used for sample preparation stabilized both Cr^{III} and Cr^{VI} species. The data of Tables 2 and 3 reveal that method-induced reduction of Cr^{VI} or oxidation of Cr^{III} was not observed under the experimental conditions.

Analysis of Reference Materials. Three certified reference materials were chosen to evaluate the basic isolation and deter-

Table 2. Hexavalent Chromium Recoveries (%) Obtained from Spiking of Soluble Cr^{III} into Triplicate K_2CrO_4 Solutions in $(NH_4)_2SO_4 + NH_4OH$ (pH 8) and/or Tris (pH 8) Buffer

	recovery (%) of Cr(VI) ± RSD[a]		
spiked solutions	spiked K_2CrO_4 (300 μg/10 mL) (30-min sonication)	spiked K_2CrO_4 (300 μg/10 mL) + soluble Cr^{III} (300 μg/10 mL) (30-min sonication)	spiked K_2CrO_4 (300 μg/10 mL) (60-min sonication)
0.02 M $(NH_4)_2SO_4$ + 0.02 M NH_4OH	94.5 ± 3.5	94.0 ± 2.6	94.4 ± 3.8
0.05 M $(NH_4)_2SO_4$ + 0.05 M NH_4OH	95.3 ± 2.4	95.1 ± 3.9	95.5 ± 4.1
0.02 M Tris + NH_4OH (pH 8)	93.9 ± 3.8	93.3 ± 2.8	94.1 ± 4.7
0.05 M Tris + NH_4OH (pH 8)	94.7 ± 2.5	94.0 ± 3.6	94.9 ± 4.9

[a] Relative standard deviation.

Table 3. Hexavalent Chromium Recoveries (%) Obtained from Spiking of Cr^{III} (Cr_2O_3) into Triplicate $PbCrO_4$ Solutions in $(NH_4)_2SO_4 + NH_4OH$ (pH 8) and/or Tris (pH 8) Buffer

	recovery (%) of Cr(VI) ± RSD[a]		
spiked solutions	spiked $PbCrO_4$ (300 μg/10 mL) (30-min sonication)	spiked $PbCrO_4$ (300 μg/10 mL) + soluble Cr_2O_3 (300 μg/10 mL) (30-min sonication)	spiked $PbCrO_4$ (300 μg/10 mL) (60-min sonication)
0.02 M $(NH_4)_2SO_4$ + 0.02 M NH_4OH	86.5 ± 3.1	85.2 ± 3.7	90.4 ± 3.9
0.05 M $(NH_4)_2SO_4$ + 0.05 M NH_4OH	90.5 ± 2.9	89.2 ± 4.1	92.5 ± 4.7
0.02 M Tris + NH_4OH (pH 8)	82.5 ± 4.3	83.0 ± 4.8	82.1 ± 3.8
0.05 M Tris + NH_4OH (pH 8)	85.9 ± 3.6	85.1 ± 3.7	89.5 ± 5.3

[a] Relative standard deviation.

mination procedure. One certified reference material (CRM), U.S. EPA CRM 013-050 paint chips, contained relatively high levels of total chromium (reference value 617.6 μg/g, with a 95% confidence interval of 595−670 μg/g). Another bulk standard reference material, NIST SRM 1633a, coal fly ash, contained a much lower level of total chromium (196 ± 6 μg/g). A third reference material, IRMM CRM 545, contained approximately 3 mg of total welding dust, with about 100 μg of Cr^{VI}/filter sample. This last reference material has recently become available and is the only known CRM for particulate Cr^{VI} in the world.

In operation, 10 mL of 0.05 M ammonium sulfate/0.05 M ammonium hydroxide (pH 8) buffer solution was added to ~1 g of U.S. EPA CRM 013-050 or ~2 g of NIST SRM 1633a to dissolve Cr^{VI}. Sonication was performed in 15-mL plastic centrifuge tubes. For the IRMM CRM 545, the filters were sonicated in the same buffer solution after introducing them into 15-mL centrifuge tubes. Following sonication, aliquots of extraction solution were subjected to solid-phase extraction, elution, and subsequent complexation with DPC, and finally spectrophotometric detection, as described previously. The analysis results showed that the Cr^{VI} content was 54.4 ± 2.3 μg/g for U.S. EPA CRM 013-050, and 0.19 ± 0.01 μg/g for NIST SRM 1633a. These values are virtually identical to those found in our previous work using a flow injection analysis procedure.[24] The recovery results for Cr^{VI} from IRMM CRM 545 are shown in Table 4; these results show that the recoveries are quantitative (99%).

Table 4. Determination of Hexavalent Chromium in IRMM Certified Reference Material (CRM 545, Cr^{VI} in Welding Dust Loaded on Filters)

	Cr^{VI} contents (μg/filter)		
filter CRM 545	CRM 545 certified value[a]	determined value[b]	recovery (%)
1	114.3	112.2	98.1
2	116.6	115.2	98.8
3	120.5	119.5	99.1
4	118.2	117.4	99.3
5	116.1	115.5	99.5
av ± RSD[c]	117.1 ± 1.98	115.9 ± 2.33	99.0 ± 0.55

[a] The CRM 545 purchased from Commission of the European Communities (IRMM); certified value for total leachable Cr^{VI}. [b] The value of Cr^{VI} content determined by the method under investigation. [c] Relative standard deviation.

Simultaneous Processing of Multiple Occupational Exposure Air Samples. Simultaneous processing of multiple samples was accomplished by following the method described in the Analytical Methodology section. Optimization of the wavelength for spectrophotometric detection was based on scanning the absorbance of the complexing reagent and the chromium complex in the visible wavelength range. An optimum absorbance wavelength of 540 nm for Cr−diphenylcarbazone complex was found (some reports have cited 520 nm[4]). This wavelength was chosen to ensure maximum sensitivity and eliminate interference of excess (uncomplexed) DPC complexing reagent.

The linearity, precision, sensitivity, and detection limit of the method were also investigated. The reproducibility of the system was tested by running three replicate measurements on each standard and sample solution. The resulting relative standard deviations were between 0.55% and 5.3%. The limit of detection (LOD), estimated as the mass of analyte which gives a signal that is 3σ above the mean blank signal (where σ is the standard deviation of the blank signal), was 1.0 ng/mL for the spectrophotometric determination. By using SAE-SPE, a minimum quantity of 0.08 μg Cr^{VI}/sample can be determined.

The method was applied to the determination of Cr^{VI} in workplace air samples collected from military aircraft maintenance

Table 5. Determination of Hexavalent Chromium in Occupational Exposures Workplace Air Samples

sample no.	Cr(VI) content μg/sample	air (L)	μg/m^3	source being sampled (aircraft painting and maintenance)
1	0.664	147.1	4.51	alodining F 16
2	0.707	72.67	9.73	alodining spray on F 16
3	1.034	126.1	8.19	cutting and grinding steel
4	0.643	117.2	5.48	sanding C-130 beaver tail
5	0.521	73.01	7.14	sanding F 16 bare metal
6	2.952	191.5	15.41	sanding F 16 under wing & under couch
7	4.175	192.1	21.73	sanding to bare metal under wings
8	4.523	173.1	26.12	sanding F 16 landing gear
9	2.678	72.45	36.97	sanding C-130 door edges
10	2.224	59.03	37.67	sanding F 16 air intake
11	3.641	36.04	101.02	priming F 16 yellow spray
12	4.341	39.11	110.99	priming C-130 door
13	6.922	67.01	103.32	priming F 16
14	6.567	39.53	166.12	priming F16
15	8.535	48.91	174.51	priming C-130
16	34.41	136.5	252.08	priming F 16
17	20.84	79.01	263.76	priming C-130 cargo door sides
18	6.822	25.28	269.86	priming water base
19	14.18	39.02	363.65	priming F 16 landing gear
20	8.011	19.86	403.37	priming small parts and panels

operations at U.S. Air Force bases. The sample preparation and analysis procedures were conducted as described above for the CRMs. Quantification of Cr^{VI} for the air filter samples was done by the standard addition method. An unexposed filter was used as a blank sample which was subjected to the same procedure as all other air samples and analyzed with the same technique to check for any influence of baseline shift and to ensure matrix matching. The linear dynamic range was from 10 μg/L to 3.0 mg/L, with a correlation coefficient (R^2) of 0.9991−0.9998 for all quality assurance/quality control samples (clean filters spiked with known quantities of Cr^{VI}). The calibration equation for the external standard or standard addition was calculated by linear regression.

Viscous or highly concentrated (with Cr^{VI}) samples may demonstrate greater breakthrough through the SPE cartridge. Therefore, diluting the sample solution prior to solid-phase extraction might yield better recoveries. For a viscous sample, dilution could improve the mass transfer to active sites on the cartridge. Also, dilution can overcome the shortage of active sites for samples having high concentrations Cr^{VI}. Therefore, for a few samples having high dust loadings, diluting the sample solution prior to loading onto the cartridge was employed.

The results in Table 5 show the Cr^{VI} contents in air samples that were collected from military aircraft maintenance operations. It can be seen from Table 5 that the amount of Cr^{VI} generated in workplace air varies greatly, depending on the work practice. The highest exposures of Cr^{VI} were detected in paint priming operations, and the lowest Cr^{VI} exposures were observed in alodining (metal surface preparation) and cutting operations. Sanding gave rise to Cr^{VI} exposures in an intermediate range between those exposures found in the above work practices.

CONCLUSIONS

A simple, fast, sensitive, and quantitative field method was developed for the extraction, isolation, and determination of hexavalent chromium in occupational exposure air samples. Ultrasonic extraction in basic ammonium buffer solution without deliberate heating was shown to give quantitative recoveries for Cr^{VI} and prevented method-induced oxidation of Cr ^{III} or reduction of Cr^{VI}. The main advantages of SAE-SPE in this procedure are the following: (1) solvent consumption is minimized; (2) throughput time is short; (3) recoveries are quantitative; (4) handling of multiple samples simultaneously is easy; and (5) the cost is low (less than \$10 per sample). This approach avoids the use of complicated instrumentation and large quantities of organic solvents in the analysis and affords efficiency and simplicity.

As demonstrated from these results, the method was sensitive and suitable for the determination of trace Cr^{VI} content in industrial hygiene air samples. Aside from the obvious time savings offered by an on-site method, the ability to conduct Cr^{VI} measurements in the field enables samples to be analyzed before there is a chance for sample degradation. It is known that Cr^{VI} air filter samples are unstable over time,[40] so the field method can help to alleviate this contribution to method bias. Furthermore, the method was selective, because all typical interferences, including Cr^{III}, Fe^{III}, and Cu^{II},[41,42] were eliminated in the SAE-SPE procedure. The procedure offers a novel and effective approach for the on-site determination of Cr^{VI} in environmental and workplace samples. The technique offers promise for field-based occupational exposure measurements of Cr^{VI} in a variety of settings, e.g., factories, repair shops, construction, and maintenance of aircraft and ships.

Disclaimer. Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention or the U.S. Air Force.

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