

Field Method for the Determination of Insoluble or Total Hexavalent Chromium in Workplace Air

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National Institute for Occupational Safety and Health method 7703 is a portable field procedure for the analysis of workplace air filter samples for hexavalent chromium (Cr^{VI}) content immediately after the samples are collected. The field method prescribes Cr^{VI} extraction from air filter samples with an ammonium sulfate/ammonium hydroxide extraction buffer using ultrasonic extraction (UE). Strong anion-exchange solid-phase extraction (SAE-SPE) is then used to separate Cr^{VI} from trivalent chromium and other interferences. Portable spectrophotometric measurement of Cr^{VI} is then conducted using the 1,5-diphenylcarbazide (DPC) method. However, it has been found that the ammonium extraction buffer does not adequately bring insoluble Cr^{VI} compounds into solution during the UE process. Thus, it was deemed necessary to modify the field method so that it would provide acceptable recoveries for insoluble Cr^{VI} compounds. To this end, a more alkaline extraction solution—sodium carbonate/sodium bicarbonate buffer—was investigated. The modified procedure using the highly alkaline extraction solution was demonstrated to be compatible with SAE-SPE cartridges when determining insoluble Cr^{VI} in air filter samples. It was found that the carbonate/bicarbonate buffer was equally effective for complete dissolution of both insoluble and soluble forms of Cr^{VI}. Furthermore, the modified procedure met desired performance criteria established for air sampling and analytical methods.

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The carcinogenic risks from chromium exposure are linked closely to the specific valence states of chromium compounds.⁽¹⁾ In the environment the most common chromium valences found are trivalent

(Cr^{III}) and hexavalent (Cr^{VI}). While Cr^{III} is an essential trace element for both animals and humans,^(2,3) Cr^{VI} compounds are considered harmful, owing to observations of carcinogenic and/or allergenic responses.⁽¹⁾ Primary routes of exposure to Cr^{VI} include inhalation, absorption through the skin, and ingestion.⁽²⁾ Cr^{VI} is readily absorbed by the body via many routes, but Cr^{III} is not as easily absorbed.^(2,4) Metabolic breakdown of Cr^{VI} involves its reduction to Cr^{III} by various enzymes, with concomitant generation of reactive species such as peroxides.⁽¹⁾ Toxic effects can be caused by the reaction of these reactive species with various biomolecules, notably DNA.^(1,4)

In the body the highest concentrations of chromium are found in the liver, kidney, and lungs.⁽²⁾ The capacity of Cr^{VI} compounds to cause cancer as a result of occupational exposure has been well documented.^(3,4) Although lung cancer is most frequently caused by occupational exposure to Cr^{VI}, other cancers such as oral, nasal, and gastrointestinal tumors have also been reported.⁽¹⁾ Water-insoluble Cr^{VI} compounds are thought to have the greatest capability for causing cancer, but water-soluble Cr^{VI} compounds also appear to be carcinogenic and allergenic.^(3,5)

While occupational exposure to Cr^{VI} occurs predominantly as a result of inhalation,⁽²⁾ dermal contact is another potential route of worker exposures.⁽⁵⁾ The primary manufacturing processes that involve exposure to Cr^{VI} are stainless steel welding, chromate production, chrome plating, ferrochrome production, spray painting, and tanning and leather working.⁽³⁾ Airborne concentrations of Cr^{VI} in these industrial processes range anywhere from 0.005 to 1 mg/m³.⁽²⁾

The American Conference of Governmental Industrial Hygienists (ACGIH[®]) has set threshold limit values (TLVs[®]) for water-soluble and water-insoluble Cr^{VI} compounds at 0.05 mg/m³ and 0.01 mg/m³, respectively.⁽⁶⁾ Given the severity and extensive health effects that Cr^{VI} compounds can cause, analytical methods are needed that can be used to assess exposure levels quickly and accurately. Furthermore, since the

TLVs for Cr^{VI} are different for water-soluble and insoluble Cr^{VI} compounds, analytical methods that can differentiate between the two are needed.

BACKGROUND

Field sampling and determination of airborne Cr^{VI} employ a collection method that uses sampling filter materials such as polyvinylchloride (PVC) or mixed cellulose ester (MCE) filters.⁽⁷⁾ However, since MCE filters and some PVC filters have been found to promote the reduction of Cr^{VI} to Cr^{III},⁽⁸⁾ on-site field methods that can be used to assess occupational exposure immediately would help to bypass the problem of sample instability.

In previous work a quick and effective field method for determination of soluble Cr^{VI} was developed.⁽⁹⁾ This method uses ultrasonic extraction (UE) to extract Cr^{VI} from the sampling media, and strong anion-exchange solid-phase extraction (SAE-SPE) to separate Cr^{VI} from Cr^{III} and other interferences. SAE-SPE has proved to be a reliable separation and isolation technique for the subsequent determination of Cr^{VI} in workplace samples.⁽⁷⁻¹⁰⁾

For some matrices and elements, UE has been shown to be an effective means of aiding in the extraction of the metal analytes from filter samples.^(11,12) Earlier studies have shown that UE is an effective technique for dissolution of Cr^{VI} compounds collected from workplace atmospheres.^(9,13) For chromates, basic buffer solutions have been used for extraction,⁽¹²⁻¹⁴⁾ since Cr^{VI} compounds are strongly oxidizing in acidic conditions and may become reduced to Cr^{III}.⁽²⁾ In basic solutions, Cr^{VI} species are relatively stable and exist as anions, in contrast to other heavy metal ions, which are ordinarily cationic under such conditions.^(3,5) Therefore, Cr^{VI} is easily separated from other metal cations by SAE-SPE.⁽⁹⁾

Using the National Institute for Occupational Safety and Health (NIOSH) field method,⁽¹⁰⁾ after extracted Cr^{VI} is retained on the SAE cartridges (while potential interferences are washed through), the isolated Cr^{VI} is eluted with a 0.50 M (NH₄)₂SO₄/0.10 M NH₄OH elution buffer. The eluate solution containing Cr^{VI} is subsequently acidified, and 1,5-diphenylcarbazide (DPC) is added to form a colored complex ion, that can be measured with high sensitivity using visible spectrophotometry.^(9,10,14)

Although the field method using the ammonium sulfate/ammonium hydroxide extraction buffer is effective for the extraction of soluble and sparingly soluble Cr^{VI} compounds,^(9,12,13,15) this buffer been found to be inadequate for dissolving insoluble Cr^{VI} compounds.⁽¹⁶⁾ The NIOSH procedure is therefore not capable of providing accurate quantitative determination of total Cr^{VI} if insoluble chromate compounds are present in the sampled matrix. Because of this limitation a modified version of the NIOSH field method was developed using a sodium carbonate/sodium bicarbonate extraction buffer, which is known to dissolve insoluble Cr^{VI} compounds.^(14,16) The modified method enables measurement of total Cr^{VI} in occupational air samples. Alternatively, sepa-

rate on-site measurement of soluble and insoluble Cr^{VI} species in workplace atmospheres is possible by using different extraction buffer systems in sequence. To our knowledge no other field method is capable of measuring insoluble hexavalent chromium compounds.

EXPERIMENTAL SECTION

Instrumentation and Equipment

Sonication was carried out with a Crest Ultrasonics (Trenton, N.J.) 117-V, 50-Hz ultrasonic bath. The 12-port solid-phase (SPE) extraction manifold used in this work was purchased from Supelco (Bellefonte, Pa.). Disposable polytetrafluoroethylene (PTFE) valve liners (Supelco) were used for the ports of the SPE manifold. The manifold was connected to a Gast (Benton Harbor, Mich.) vacuum pump through a pressure control valve. Strong anion-exchange solid-phase extraction (SAE-SPE) cartridges were purchased from Varian (Palo Alto, Calif.). The cartridges contained 0.5 g (lower capacity) or 1 g (higher capacity) of quaternary amine-bonded silica sorbent with chloride ion functioning as the counterion. A portable, battery-powered spectrophotometer (Hach DR/2000, Loveland, Colo.) was used for spectrophotometric measurements at 540 nm (sample path length 1 cm). A Fisher Scientific (Chicago, Ill.) Accumet 50 pH meter was used to measure solution pH. Where applicable, materials were weighed to the nearest 0.0001 g using a Mettler (Greifensee, Switzerland) Model AE 163 analytical balance.

Reagents and Materials

Reagent grade chromic oxide and potassium chromate solids, as well as Cr(III), Fe(II), and Cr(VI) standard solutions (~1000 µg/mL), were obtained from Aldrich (Milwaukee, Wis.). Ammonium sulfate, ammonium hydroxide, lead chromate, sodium carbonate, sodium bicarbonate, 1,5-diphenylcarbazide (DPC), acetonitrile (used to dissolve DPC), and hydrochloric acid were reagent grade and were obtained from Fisher Scientific. Additionally, 15 mL polypropylene centrifuge tubes, scintillation vials, and volumetric flasks were all purchased from Fisher Scientific. Certified reference material (CRM) filters, consisting of glass fiber filters containing certified amounts of hexavalent and total chromium in welding dust (CRM 545), were obtained from the Institute for Reference Materials and Measurements (IRMM) of the European Commission (Brussels).⁽¹⁷⁾ Preloaded plastic filter cassette samplers housing mixed cellulose ester (MCE) or polyvinyl chloride (PVC) filters with cellulose backup pads were obtained from SKC (Eighty Four, Pa.).

Air Sample Collection

Air samples containing Cr^{VI} were collected onto air filters from fumes generated during welding stainless steel. The samples were collected using a homemade multi-port sampler connected to a Gilian (Clearwater, Fla.) AirCon2, high-volume, air-sampling pump calibrated up to an airflow rate of 15 L/min. The multiport sampler contained eight separate ports with each port calibrated at a flow rate of approximately

1.7 L/min. Gravimetric analysis using PVC filters had previously demonstrated the precision of the mass collected onto separate filters using the multiport sampler to be less than 5% relative standard deviation (RSD) for aerosol loadings ranging from ~0.5 to ~5 mg/filter. After the samples were collected, they were immediately prepared for analysis.

Preparation of Air Filter Samples

Ultrasonic Extraction

Air filter samples were removed from the sampling cassettes and placed into 15-mL centrifuge tubes using PTFE-coated forceps. Clean plastic or glass rods were used to push the filters to the bottom of each centrifuge tube. Next, 10 mL of 0.10 M Na₂CO₃/0.02 M NaHCO₃ extraction buffer was added to each centrifuge tube; the extraction buffer had a measured pH of 10.7 (±0.1). The centrifuge tubes containing the filter samples were then immersed in the ultrasonic bath and subjected to sonication for 30 min at ambient temperature. The water level in the bath was adjusted so that it was above the level of sample solution inside the centrifuge tubes. In some experiments, an alternative buffer was used (i.e., 0.05 M ammonium sulfate/0.05 M ammonium hydroxide, pH 8.0).⁽¹⁰⁾

Strong Anion-Exchange Solid-Phase Extraction

SAE-SPE cartridges were first conditioned with 3 mL of distilled water,⁽¹⁸⁾ thereby activating the functional groups of the sorbent. Aliquots of each sample solution were subsequently loaded onto separate SAE-SPE cartridges. Each SAE-SPE cartridge had a sorbent mass of 0.5 g or 1 g and accommodated a sample volume of 3 mL or 6 mL. Distilled water was used in three 1-mL fractions to wash away Cr^{III} and other interferences, and scintillation vials were used to collect extraction solution and water. Afterward, these vials were removed and replaced with clean scintillation vials, which were used to collect eluted Cr^{VI}. For elution, 9 mL of 0.50 M (NH₄)₂SO₄/0.10 M NH₄OH elution buffer was used in three 3-mL fractions to elute Cr^{VI} from the SAE-SPE cartridges.

Analysis

The eluate was acidified with 100 μL of 37.5% (v/v) HCl solution, and DPC indicator solution added. The colored chromous-diphenylcarbazone complex ion develops within minutes after the addition of 2 mL of 20-mM DPC complexing solution. The absorbance of each sample was then measured at 540 nm using the Hach DR/2000 spectrophotometer. Distilled water blanks were used to zero the instrument.

RESULTS AND DISCUSSION

Extraction Buffers for Cr^{VI} Compounds

The composition of the carbonate/bicarbonate extraction buffer mixture was varied in order to determine the concentration ratio that was most compatible with the SAE-SPE cartridges, while also giving good recoveries of insoluble Cr^{VI}. Through trial and error (by trying buffer mixtures of different ratios and strengths), a buffer consisting of 0.10 M Na₂CO₃/

0.02 M NaHCO₃ was found to meet both criteria. Using this carbonate/bicarbonate buffer system, sonication of known masses of lead chromate and/or potassium chromate was investigated.

Calibration

A calibration line was prepared from concentrations of Cr^{VI} ranging from ~0.05 to ~3.0 μg/mL Cr^{VI} (prepared from lead chromate in carbonate/bicarbonate buffer), and from a reagent blank. Aliquots from a solution of 20 μg/mL Cr^{VI} in 0.10 M Na₂CO₃/0.02 M NaHCO₃ were taken and pipetted into 15-mL centrifuge tubes, and then diluted up to 10 mL with the Na₂CO₃/NaHCO₃ extraction buffer to yield the desired concentrations. These samples were then prepared using SAE-SPE, acidified and complexed with DPC, and measured spectrophotometrically. The resulting calibration line is described by the expression: Absorbance $A = 0.7789[\text{Cr}^{\text{VI}}] + 0.0006$; $R^2 = 0.9999$.

Buffer Compatibility with SAE-SPE

In NIOSH Method 7703,⁽¹⁰⁾ SAE-SPE cartridges with a sorbent mass of 500 mg and a retention capacity of 25 mg are used. However, the 0.10 M Na₂CO₃/0.02 M NaHCO₃ extraction buffer is more alkaline than the 0.05 M (NH₄)₂SO₄/0.05 M NH₄OH (pH 8) extraction buffer used for soluble Cr^{VI} compounds. It was found that larger cartridges with a sorbent mass of 1 g and a retention capacity of 50 mg performed well in the method modified for insoluble chromates. Spiked Cr^{VI} samples were prepared from potassium chromate standards, and a test was run to compare the 1-g and 500-mg cartridges under all conditions specified by NIOSH method 7703. A t-test⁽¹⁹⁾ revealed no significant differences in the recoveries of soluble Cr^{VI} using both the 1-g and 500-mg cartridges ($p = 0.9936$), indicating the equivalent performance of the cartridges.

As no breakthrough was observed, the 0.10 M Na₂CO₃/0.02 M NaHCO₃ extraction buffer did not exceed the capacity of the 1-g SAE cartridges. The performance of this extraction buffer for the determination of insoluble Cr^{VI} was investigated using the following modification of NIOSH method 7703. A 20 μg/mL Cr^{VI} (from PbCrO₄) solution was prepared by sonication in 0.10 M Na₂CO₃/0.02 M NaHCO₃, while a 20-μg/mL Cr^{VI} (from K₂CrO₄) solution was prepared by sonication in 0.05 M (NH₄)₂SO₄/0.05 M NH₄OH. To test the effectiveness of the carbonate/bicarbonate buffer for the analysis of soluble Cr^{VI}, a 20-μg/mL Cr^{VI} solution (from K₂CrO₄) in 0.10 M Na₂CO₃/0.02 M NaHCO₃ was also prepared. Aliquots were taken from each of these stock solutions to make up Cr^{VI} solutions with concentrations of 0.1 μg/mL, 0.5 μg/mL, 1.0 μg/mL, and 2.0 μg/mL in a total of 10 mL of the corresponding extraction buffer. Aliquots (3 mL) from each sample were then prepared using SAE-SPE and analyzed by portable visible spectrophotometry, as described previously.

Table I presents the results for Cr^{VI} measurements from the above experiments. Plots of absorbance versus concentration for each of the three different solutions yielded coefficients

TABLE I. Comparison of Extraction Buffers on Chromate Compounds of Different Solubility

	Absorbance 0.1 $\mu\text{g/mL Cr}^{\text{VI}}$	Absorbance 0.5 $\mu\text{g/mL Cr}^{\text{VI}}$	Absorbance 1.0 $\mu\text{g/mL Cr}^{\text{VI}}$	Absorbance 2.0 $\mu\text{g/mL Cr}^{\text{VI}}$
20 $\mu\text{g/mL Cr}^{\text{VI}}$ (PbCrO_4) in carbonate/bicarbonate buffer	0.023	0.117	0.206	0.406
				$R^2 = 0.9986$
20 $\mu\text{g/mL Cr}^{\text{VI}}$ (K_2CrO_4) in carbonate/bicarbonate buffer	0.025	0.113	0.211	0.397
				$R^2 = 0.9986$
20 $\mu\text{g/mL Cr}^{\text{VI}}$ (K_2CrO_4) in sulfate/bisulfate buffer	0.023	0.114	0.199	0.399
				$R^2 = 0.9988$
Mean absorbance \pm SD ^A	0.024 \pm 0.001	0.115 \pm 0.002	0.205 \pm 0.006	0.401 \pm 0.005
RSD ^B	4.9%	1.8%	2.9%	1.2%

Note: Results from calibration solutions prepared after treatment with extraction buffers for insoluble (PbCrO_4) and soluble (K_2CrO_4) Cr^{VI} compounds. (Carbonate/bicarbonate buffer for insoluble chromates: 0.10 M Na_2CO_3 /0.02 M NaHCO_3 ; sulfate/bisulfate buffer for soluble chromates: 0.05 M $(\text{NH}_4)_2\text{SO}_4$ /0.05 M NH_4OH .)

^AStandard deviation.

^BRelative standard deviation.

of determination (R^2) approaching 0.999 (Table I). As can be seen from the near-unity correlation for each solution and high precision (as demonstrated by low relative standard deviations), there are no significant differences in the performances of the carbonate/bicarbonate buffer for extracting insoluble Cr^{VI} and that of the ammonium sulfate/ammonium hydroxide buffer for the extraction of soluble Cr^{VI} . Thus, the 0.10 M Na_2CO_3 /0.02 M NaHCO_3 buffer was found to be effective in using SAE-SPE for isolation of insoluble Cr^{VI} .

Soluble and Insoluble Cr^{VI}

The results of Table I also indicate that the carbonate/bicarbonate extraction buffer can be used in concert with SAE-SPE to measure both soluble and insoluble Cr^{VI} . Furthermore, the agreement of the results indicates acceptable compatibility of the carbonate/bicarbonate extraction buffer with the ammonium sulfate/ammonium hydroxide elution buffer. In the field, these buffer systems could be used separately to measure (1) soluble + sparingly soluble Cr^{VI} , or (2) soluble + sparingly soluble + insoluble = total Cr^{VI} .⁽²⁰⁾

Cr^{VI} – Spiked Filters at 0.1–2.0 \times TLV

To validate the method according to criteria previously established for air sampling and analytical method development,⁽²¹⁾ replicates of each loading level of interest (0.1, 0.5, 1.0, and 2.0 times the TLV for insoluble Cr^{VI}) were prepared. For the method to meet NIOSH accuracy criteria, observed percent recoveries must be within $\pm 25\%$ of the true concentration at least 95% of the time. Amounts of PbCrO_4 yielding the desired concentrations of Cr^{VI} when diluted in 10 mL of carbonate/bicarbonate extraction buffer, i.e., 0.0010, 0.0050, and 0.0100 mg (giving 1, 5, 10 and 20 $\mu\text{g}/\text{filter}$) were spiked onto two types of filters (PVC and MCE). (These amounts correspond to desired levels with respect to the TLV, assuming 8-hour time-weighted-averaged sampling at a flow rate of about 2 L/min). These filters were prepared and analyzed as already described. After correcting for the media blank, percent Cr^{VI} recoveries were calculated from the absorbance values.

Results from these experiments are presented in Table II. Calculated percent recoveries (within 100% \pm 10%) satisfied performance criteria established for the development of air sampling and analytical methods.⁽²¹⁾

TABLE II. Percent Cr^{VI} Recoveries

Filter Medium	Percent Recovery @ 0.1 \times TLV	Percent Recovery @ 0.5 \times TLV	Percent Recovery @ 1.0 \times TLV	Percent Recovery @ 2.0 \times TLV
PVC ^A	92.2 \pm 1.6	102 \pm 4.3	98.7 \pm 2.1	101 \pm 2.9
MCE ^B	97.9 \pm 3.6	99.8 \pm 3.4	97.6 \pm 2.8	95.1 \pm 5.0

Note: Percent Cr^{VI} mean values \pm standard deviations, $n \geq 3$; obtained from air filters spiked with PbCrO_4 (extracted in carbonate/bicarbonate buffer) at ~ 0.1 to ~ 2.0 times the ACGIH[®] TLV[®] for insoluble Cr^{VI} . Samples were subjected to ultrasonic extraction in 0.10 M Na_2CO_3 /0.02 M NaHCO_3 (carbonate/bicarbonate buffer) prior to SAE-SPE treatment and DPC spectrophotometric measurement.

^APolyvinylchloride.

^BMixed cellulose ester.

TABLE III. Analysis of Air Samples for Cr^{VI} Collected from Fumes Generated When Welding Stainless Steel

Mean Mass of Cr ^{VI} ± SD, ^A Expt. 1 (PVC; ^B n = 8)	Mean Mass of Cr ^{VI} ± SD, ^A Expt. 2 (MCE; ^C n = 8)	Mean Mass of Cr ^{VI} ± SD, ^A Expt. 3 (MCE; ^C n = 8)	Mean Mass of Cr ^{VI} ± SD, ^A Expt. 4 (MCE; ^C n = 8)
7.71 ± 0.24 μg RSD ^D = 3.1%	6.48 ± 0.21 μg RSD ^D = 3.2%	2.89 ± 0.11 μg RSD ^D = 3.8%	1.56 ± 0.02 μg RSD ^D = 1.3%

Note: Samples were subjected to ultrasonic extraction in 0.10 M Na₂CO₃/0.02 M NaHCO₃ (carbonate/bicarbonate buffer) prior to SAE-SPE treatment and DPC spectrophotometric measurement.

^AStandard deviation.

^BPolyvinylchloride.

^CMixed cellulose ester.

^DRelative standard deviation.

Analysis of Welding Fume Samples

The method described above was used to determine the mass of total Cr^{VI} in air samples produced from fumes generated while welding stainless steel (UNS-304). Filter cassettes housing MCE or PVC filters were attached to the multiport sampler, which was connected to the air sampling pump. The multiport sampler was positioned above the welding location in order to collect the fumes produced. Four trials were performed in which either two or three welding rods (AWS A5.4 Class E 312-16) were used, and the air samples were collected for different time periods, in order to obtain a range of Cr^{VI} filter loadings.

After sample collection the cassettes were removed from the multiport sampler, and the filters were then subjected to the sample preparation and analysis procedure described above (for total, including insoluble, chromates). Calculated mean Cr^{VI} masses from all four trials are shown in Table III. Determined masses of Cr^{VI} in the welding fumes collected ranged from ~1.5 μg for Trial 4 to ~7.7 μg for Trial 1. Although these data cannot be used to assess overall method accuracy, the high precision of the method over a range of Cr^{VI} measurements is demonstrated by observed RSDs of less than 5%.

Analysis of Reference Materials

A certified reference material (CRM) was used to evaluate the effectiveness of the field procedure for determining either total Cr^{VI}. This reference material, IRMM CRM 545,⁽¹⁷⁾ contains approximately 3 mg of total welding dust loaded onto glass fiber filters, with ~100 μg of Cr^{VI} per sample. Table IV shows Cr^{VI} recoveries obtained from CRM 545 samples which were prepared using the carbonate/bicarbonate extraction buffer and analyzed by SAE-SPE and DPC spectrophotometry. Recoveries of over 90% were obtained from all but one of the CRMs. The lowest value of ~82% was identified as a statistical outlier (*Q*-test, *p* = 0.05),⁽¹⁹⁾ but was nonetheless not discarded from the sample set.

Investigation of Interferences

Test for Oxidation of Cr^{III}

A positive interference could potentially result from air oxidation of Cr^{III} during sample extraction at higher tempera-

tures.⁽²²⁾ Hence, experiments were conducted in order to test for conversion of Cr^{III} during sonication in the carbonate/bicarbonate buffer. Solutions of different concentrations of Cr^{III} in the 0.10 M Na₂CO₃/0.02 M NaHCO₃ extraction buffer were prepared after sonication of ~0.005 g Cr₂O₃ plus MCE or PVC filter material. Aliquots of the test solutions were then subjected to SAE-SPE, eluted and measured as above using the DPC portable spectrophotometric technique.

Table V shows results from these trials. It can be seen that the measured absorbance is not significantly different from that of blank solutions, thus showing no discernable oxidation of Cr^{III} to Cr^{VI} as a result of sonication in the more alkaline extraction buffer.

Cr^{III} Interference Check

Tests were conducted to investigate potential interference from Cr^{III} if this species were present in solution along with Cr^{VI}. About 0.002 g PbCrO₄ and ~0.003 g Cr₂O₃, plus PVC or MCE filters, were sonicated in 0.10 M Na₂CO₃/0.02 M NaHCO₃ extraction buffer. Solutions were then prepared over a range of concentrations, and aliquots were analyzed by

TABLE IV. Percent Recoveries of Cr^{VI} Obtained from IRMM CRM 545 Filter Samples

Sample No.	Certified Value (μg Cr ^{VI})	Measured Value (μg Cr ^{VI})	Percent Cr ^{VI} Recovery
1	116.86 ± 1.74	107.84	92.3
2	121.33 ± 1.81	114.36	94.3
3	115.50 ± 1.72	94.46	81.8
4	116.54 ± 1.74	109.23	93.7
5	119.47 ± 1.78	115.60	96.8
6	122.85 ± 1.83	117.97	96.0
			Mean ± SD ^A = 92.4% ± 5.5%

Note: Samples were subjected to ultrasonic extraction in 0.10 M Na₂CO₃/0.02 M NaHCO₃ (carbonate/bicarbonate buffer) prior to SAE-SPE treatment and DPC spectrophotometric measurement.

^AStandard deviation.

TABLE V. Absorbance Measurements from Cr^{III} Solutions

[Cr ^{III}], $\mu\text{g/mL}$	Absorbance (PVC) ^A	Absorbance (MCE) ^B
0 (media blanks)	0.003	0.003
0.1	0.005	—
1.5	0.006	0.003
3.0	0.004	0.005
6.0	—	0.004
Mean \pm SD ^C	0.005 \pm 0.001	0.004 \pm 0.001

Note: Solutions (n = 3), with PVC or MCE filters, sonicated in carbonate/bicarbonate buffer, treated using SAE-SPE, and measured by DPC spectrophotometry.

^APolyvinylchloride.

^BMixed cellulose ester.

^CStandard deviation.

SAE-SPE and DPC spectrophotometry in the same manner as described above.

Results from these experiments are given in Table VI. The calculated Cr^{VI} recoveries for MCE and PVC filters are 92–103%, indicating no apparent interference from Cr^{III} on these filter media.

Fe^{II} Interference Check

Similar experiments as described above were carried out in order to investigate interferences from Fe^{II} if this species were present in the carbonate/bicarbonate extraction buffer solution along with Cr^{VI}. About 0.003 g of ferrous ammonium sulfate and ~0.002 g of lead chromate were sonicated in the carbonate/bicarbonate buffer along with MCE or PVC filters. Results of these trials are shown in Table VII. It can be seen that Cr^{VI} recoveries are appreciably below 90%, thereby showing a significant interference from Fe^{II} to Cr^{VI} measurement if

TABLE VI. Results from [Cr^{III}] = [Cr^{VI}] Solutions

[Cr ^{III}] + (Cr ^{VI}), $\mu\text{g/mL}$	Percent Cr ^{VI} Recovery (PVC) ^A	Percent Cr ^{VI} Recovery (MCE) ^B
0 (media blanks)	ND ^C	ND ^C
0.1	92.5	101.1
0.5	103.1	94.7
1.0	100.3	98.1
2.0	99.4	99.8
4.0	101.6	101.3
Mean \pm SD ^D	99.4 \pm 4	99.0 \pm 2.7

Note: Solutions (with PVC or MCE filters) sonicated in carbonate/bicarbonate buffer, treated using SAE-SPE, and measured by DPC spectrophotometry.

^APolyvinylchloride.

^BMixed cellulose ester.

^CNone detected.

^DStandard deviation.

TABLE VII. Results from [Fe^{II}] = [Cr^{VI}] Solutions

[Fe ^{II}] + (Cr ^{VI}), $\mu\text{g/mL}$	Percent Cr ^{VI} Recovery (PVC) ^A	Percent Cr ^{VI} Recovery (MCE) ^B
0 (media blanks)	ND ^C	ND ^C
0.1	65.7	65.4
0.5	71.6	66.6
1.0	72.4	64.6
2.0	74.1	69.1
Mean \pm SD ^D	70.9 \pm 3.7	66.4 \pm 1.9

Note: Solutions (with PVC or MCE filters) sonicated in carbonate/bicarbonate buffer, treated using SAE-SPE, and measured by DPC spectrophotometry.

^APolyvinylchloride.

^BMixed cellulose ester.

^CNone detected.

^DStandard deviation.

these species are present in the extraction solution at similar concentrations. These observations are similar to results from analogous experiments where hot plate extraction was used.⁽¹⁴⁾ Thus, it is shown that UE in carbonate/bicarbonate extraction buffer does not prevent reduction of Cr^{VI} by Fe^{II}.

CONCLUSION

The field method for insoluble Cr^{VI}, using an extraction buffer consisting of 0.10 M Na₂CO₃/0.02 M NaHCO₃, was found to meet NIOSH accuracy criteria established for workplace air sampling methods. The method was shown to be effective for of Cr^{VI} in air samples generated from welding fumes. The method was also demonstrated to be effective for the determination of Cr^{VI} in CRM welding dust samples. This procedure offers an alternative to NIOSH method 7703 for the on-site analysis of Cr^{VI} compounds when the Cr^{VI} species of interest are insoluble. It is pointed out that the ammonium sulfate/ammonium hydroxide buffer can be used to extract soluble and sparingly soluble Cr^{VI} compounds from air filter samples. Thus, by taking side-by-side samples, the field method using either extraction buffer would enable separate determination of Cr^{VI} compounds of different solubility in workplace air. If desired, total chromium concentration could be determined in the field by oxidizing Cr^{III} with Ce^{IV}, as has been described in previous work.^(13,23)

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REFERENCES

1. **Chang, L.W., L. Magos, and T. Suzuki:** *Toxicology of Metals*, vol. I. L.W. Chang (ed.). Boca Raton, Fla.: CRC Press, 1996, pp. 48–229.
2. **Bertholf, R.I., M.R. Wills, and J. Savory:** *Handbook on Toxicity of Inorganic Compounds*, H.G. Seiler and H. Sigel (eds.). New York: Marcel Dekker, 1988, pp. 239–250.
3. **Hayes, R.B.:** *Biological and Environmental Aspects of Chromium*. Amsterdam: Elsevier, 1982.
4. **Langård, S.:** One hundred years of chromium and cancer—A review of epidemiological evidence and selected case reports. *Am. J. Ind. Med.* 17:189–215 (1990).
5. **U.S. Agency for Toxic Substances and Disease Registry (ATSDR):** *Toxicological Profile for Chromium*. Atlanta, Ga.: ATSDR, 2000.
6. **American Conference of Governmental Industrial Hygienists (ACGIH®):** *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*. Cincinnati, Ohio: ACGIH, 2003, p. 22.
7. **Marlow, D., J. Wang, T.J. Wise, and K. Ashley:** Field test of a portable method for the determination of hexavalent chromium in workplace air. *Am. Lab.* 32(15):26–28 (2000).
8. **Carlton, G.N., L. Chaloux, J. Reichert, E.C. England and K. Greebon:** *Hexavalent Chromium (Cr^{VI}) Field Analytical Method for Bioenvironmental Engineers*. Brooks Air Force Base, Texas: Air Force Institute for Environment, Safety and Occupational Health Risk Analysis, 1999.
9. **Wang, J., K. Ashley, D. Marlow, E.C. England, and G. Carlton:** Field method for the determination of hexavalent chromium by ultrasonication and strong anion-exchange solid-phase extraction. *Anal. Chem.* 71:1027–1032 (1999).
10. **National Institute for Occupational Safety and Health (NIOSH):** Method 7703, Hexavalent Chromium by Portable Visible Spectrophotometry. In *NIOSH Manual of Analytical Methods*, 4th Edition (3rd Suppl.), P.C. Schlecht and P.F. O'Connor (eds.). Cincinnati, Ohio: NIOSH, 2003.
11. **Ashley, K.:** Ultrasonic extraction of heavy metals from environmental and industrial hygiene samples for their subsequent determination. *Trends Anal. Chem.* 17:366–372 (1998).
12. **Ashley, K., R.N. Andrews, L. Cavazos, and M. Demange:** Ultrasonic extraction as a sample preparation technique for elemental analysis by atomic spectrometry. *J. Anal. At. Spectrom.* 16:1147–1153 (2001).
13. **Wang, J., K. Ashley, E.R. Kennedy, and C. Neumeister:** Determination of hexavalent chromium in industrial hygiene samples using ultrasonic extraction and flow injection analysis. *Analyst* 122:1307–1312 (1997).
14. **Occupational Safety and Health Administration (OSHA):** “Hexavalent Chromium in Workplace Atmospheres,” OSHA Method No. ID-215. Salt Lake City, Utah: OSHA, 1998.
15. **Boiano, J.M., M.E. Wallace, W.K. Sieber, J.H. Groff, J. Wang, and K. Ashley:** Comparison of three sampling and analytical methods for the determination of airborne hexavalent chromium. *J. Environ. Monit.* 2:329–333 (2000).
16. **Goodman, W.F., A.M. Howe, and M. Martinez:** *Revision of MDHS 61 (Total Hexavalent Chromium in Air): Investigation of Sample Dissolution Methods* (HSL Report IEAS/01/02). Sheffield, U.K.: Health and Safety Laboratory, 2002.
17. **Vercoutere, K., R. Cornelis, J.M. Christensen, K. Byrialsen, and P. Quevauviller:** *The Certification of the Contents of Cr(VI) and Total Leachable Cr Loaded on a Filter (CRM 545)*. Luxembourg: European Commission, 1997.
18. **American Society for Testing and Materials (ASTM):** ASTM D1193, standard specification for reagent water. In *Annual Book of ASTM Standards*, vol. 11.01. West Conshohocken, Pa.: ASTM International, 2003.
19. **Miller, J.C., and J.N. Miller:** *Statistics for Analytical Chemistry*. Chichester, U.K.: Halstead Press, 1984.
20. **American Society for Testing and Materials (ASTM):** ASTM D6832, standard test method for the determination of hexavalent chromium in workplace air by ion chromatography and spectrophotometric measurement using 1,5-diphenylcarbazide. In *Annual Book of ASTM Standards*, vol. 11.03. West Conshohocken, Pa.: ASTM International, 2003.
21. **Kennedy, E.R., T.J. Fischbach, R. Song, P.M. Eller, and S.A. Shulman:** *Guidelines For Air Sampling and Analytical Method Development and Evaluation* (DHHS [NIOSH] Pub. No. 95-117). Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1995.
22. **Zatka, V.J.:** Speciation of hexavalent chromium in welding fumes—Interference by air oxidation of trivalent chromium. *Am. Ind. Hyg. Assoc. J.* 46:327–331 (1985).
23. **Grate, J.W., and R.H. Taylor:** Sequential injection method with on-line soil extraction for determination of Cr(VI). *Field Anal. Chem. Technol.* 1:39–48 (1996).