

Evaluation of sequential extraction procedures for soluble and insoluble hexavalent chromium compounds in workplace air samples†‡

Kevin Ashley,^{*a} Gregory T. Applegate,^{§a} A. Dale Marcy,^{bc} Pamela L. Drake,^b Paul A. Pierce,^b Nathalie Carabin^d and Martine Demange^d

Because toxicities may differ for Cr(VI) compounds of varying solubility, some countries and organizations have promulgated different occupational exposure limits (OELs) for soluble and insoluble hexavalent chromium (Cr(VI)) compounds, and analytical methods are needed to determine these species in workplace air samples. To address this need, international standard methods ASTM D6832 and ISO 16740 have been published that describe sequential extraction techniques for soluble and insoluble Cr(VI) in samples collected from occupational settings. However, no published performance data were previously available for these Cr(VI) sequential extraction procedures. In this work, the sequential extraction methods outlined in the relevant international standards were investigated. The procedures tested involved the use of either deionized water or an ammonium sulfate/ammonium hydroxide buffer solution to target soluble Cr(VI) species. This was followed by extraction in a sodium carbonate/sodium hydroxide buffer solution to dissolve insoluble Cr(VI) compounds. Three-step sequential extraction with (1) water, (2) sulfate buffer and (3) carbonate buffer was also investigated. Sequential extractions were carried out on spiked samples of soluble, sparingly soluble and insoluble Cr(VI) compounds, and analyses were then generally carried out by using the diphenylcarbazide method. Similar experiments were performed on paint pigment samples and on airborne particulate filter samples collected from stainless steel welding. Potential interferences from soluble and insoluble Cr(III) compounds, as well as from Fe(II), were investigated. Interferences from Cr(III) species were generally absent, while the presence of Fe(II) resulted in low Cr(VI) recoveries. Two-step sequential extraction of spiked samples with (first) either water or sulfate buffer, and then carbonate buffer, yielded quantitative recoveries of soluble Cr(VI) and insoluble Cr(VI), respectively. Three-step sequential extraction gave excessively high recoveries of soluble Cr(VI), low recoveries of sparingly soluble Cr(VI), and quantitative recoveries of insoluble Cr(VI). Experiments on paint pigment samples using two-step extraction with water and carbonate buffer yielded varying percentages of relative fractions of soluble and insoluble Cr(VI). Sequential extractions of stainless steel welding fume air filter samples demonstrated the predominance of soluble Cr(VI) compounds in such samples. The performance data obtained in this work support the Cr(VI) sequential extraction procedures described in the international standards.

^aU.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Mail Stop R-7, Cincinnati, OH, 45226-1998, USA. E-mail: KAshley@cdc.gov; Tel: +1(513)841-4402

^bU.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, 315 E. Montgomery Avenue, Spokane, WA, 99207, USA

^cNorth Idaho College, 1000 W. Garden Avenue, Coeur d'Alene, ID, 83814, USA

^dInstitut National de Recherche et de Sécurité, Département Métrologie des Polluants, Rue du Morvan, CS 60027, 54519 Vandœuvre-les-Nancy, France

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§ Current Address: Procter & Gamble Company, 5299 Spring Grove Ave., St. Bernard, Ohio 45217, USA

Introduction

Worldwide, millions of workers are potentially exposed to hexavalent chromium, Cr(VI), during their work activities. Occupational exposures to Cr(VI) can cause lung cancer and/or numerous other deleterious health effects, primarily through inhalation.^{1,2} In recognition of the carcinogenic properties of inhaled chromate compounds, the Occupational Safety and Health Administration (OSHA) recently effected new regulations that reduced (by more than tenfold) the Permissible Exposure Limit (PEL) for Cr(VI) in the United States.³

Besides carcinogenic effects, some Cr(VI) compounds also can act as contact allergens, for instance in leather tanning and in work activities involving cement.⁴ In occupational settings, Cr(VI) exposures have been associated with numerous industries including metal plating, chemical production, refining, chromite ore processing, spray painting, and welding operations, to name a few.⁵ Occupational exposure to Cr(VI) remains a serious

problem in the U.S. and internationally, and there is a need to reduce or eliminate these exposures.

Exposure assessment methods are necessary to assist in the prevention or reduction of worker exposures to Cr(VI). Thus sampling and analytical methods have been developed in order to provide needed tools for exposure assessment purposes.⁶ For many years, sampling and analytical methods for airborne Cr(VI) have been developed and refined so as to provide means for occupational exposure assessment of this highly toxic species. Monitoring methods for Cr(VI) are continually being optimized in terms of sensitivity, speed, reliability, robustness, field portability, and so on. Improved monitoring methods are required in order to meet the challenges associated with measuring airborne Cr(VI) at trace levels, and the recent literature includes a number of examples thereof.⁶⁻¹⁶

Because toxicities may differ for Cr(VI) compounds of varying solubility,^{4,5} some organizations and countries have established different occupational exposure limits (OELs) for soluble and insoluble Cr(VI) compounds.^{17,18} Recently, international standards have been published describing methods for determining these compounds in workplace air samples.^{7,8} Sequential extraction procedures are described in ASTM D6832⁷ and ISO 16740⁸ and are meant to enable serial measurement of soluble and insoluble Cr(VI) compounds collected onto workplace air filter samples. Separate measurement of soluble and insoluble Cr(VI) compounds has been successfully demonstrated^{6,9} and sequential extraction procedures have been applied to workplace samples for subsequent determination of elemental chromium and other metals.¹⁰ Other work reported the use of sequential extraction followed by voltammetric measurement of chromium species.¹¹ However, supporting validation data for the standardized sequential extraction methods for subsequent measurement of Cr(VI) have not been previously reported in the peer-reviewed literature. In an effort to fill this data void, the aim of the present work was to evaluate and validate the sequential extraction procedures for Cr(VI) that are described in the relevant published international standards.^{7,8}

Experimental

Reagents and materials

Reagent grade potassium chromate, chromic nitrate, chromic oxide, sodium hydroxide and phosphoric acid were obtained from Sigma-Aldrich (Milwaukee, WI, USA). Spectroscopic grade Cr(VI) standard solution (1,000 mg l⁻¹) came from Inorganic Ventures (Lakewood, NJ, USA). Ammonium sulfate, ammonium hydroxide, lead chromate, strontium chromate, ferrous sulfate, sodium carbonate, sodium bicarbonate, 1,5-diphenylcarbazine (DPC), methanol, and acetonitrile (used for dissolution of DPC), all reagent grade, were obtained from Fisher Scientific (Waltham, MA, USA). Nitric, hydrofluoric and hydrochloric acids were spectroscopic grade and were also purchased from Fisher Scientific. Paint pigments were obtained from a local hardware store (Nancy, France).

Polypropylene centrifuge ("Falcon") tubes with screw caps (15 ml and 50 ml) were purchased from Becton Dickinson (Franklin Lakes, NJ, USA). Two- and three-piece polystyrene air sampling cassettes, polyvinyl chloride (PVC) filters (37 mm

diameter, 5 µm pore size), glass fiber filter backup pads (37 mm diameter), and binder-free quartz fiber filters (37 mm diameter) were obtained from SKC (Eighty-Four, PA, USA). Strong anion-exchange solid-phase extraction (SAE-SPE) cartridges, containing 1 g of quaternary amine-bonded silica sorbent (with chloride as counterion), were obtained from Varian (Palo Alto, CA, USA). Where applicable, Büchner funnel filtration was performed using plastic filtration funnels (Fisher Scientific) and 47 mm diameter polytetrafluoroethylene (PTFE) filters (SKC) to fit the funnels. Plastic or borosilicate glass laboratory ware was used in all procedures. Deionized water (18 MΩ cm resistivity), prepared using a Millipore MilliQ[®] water purification system (Billerica, MA, USA), was used for all experiments.

Instrumentation and equipment

Spectrophotometric measurements at 540 nm (sample path length 1 cm) were carried out using a Hach DR/2800 spectrophotometer (Loveland, CO, USA). Plastic cuvettes, 1 cm path length, were also obtained from Hach. Where required, an Accumet 50 pH meter (Chicago, IL, USA), calibrated using pH 4.0, 7.0 and 10.0 buffers (Fisher Scientific), was used to measure solution pH. Where applicable, materials were weighed to the nearest 0.0001 g using a Mettler Model AE 163 analytical balance (Greifensee, Switzerland). Mechanical pipettes of various sizes (100 µl to 10 ml, with corresponding plastic pipette tips) were obtained from Eppendorf (Hamburg, Germany). A Labquake[®] rotator (Barnstead, Dubuque, IA, USA), placed in a Precision Model 45EG laboratory oven (Winchester, VA, USA) set at 37 ± 1 °C, was used for mechanical agitation of samples undergoing the soluble extraction procedure. For extraction of insoluble Cr(VI) compounds, sonication at 40 ± 2 °C was performed using a Branson Ultrasonics Model 3510 ultrasonic bath (Danbury, CT, USA).

A 12-port solid-phase extraction (SPE) manifold, used in some experiments, was purchased from Supelco (Bellefonte, PA, USA). Disposable PTFE valve liners (Supelco) were used for the ports of the SPE manifold. The manifold was connected to a Gast vacuum pump (Benton Harbor, MI, USA) through a pressure control valve. For some samples, inductively coupled plasma – atomic emission spectrometry (ICP-AES) was performed using an Applied Research Laboratories 34000 instrument (Sunland, CA, USA). Where applicable, ion chromatographic (IC) experiments were carried out with a Dionex Series 4500i system (Sunnyvale, CA, USA).

Collection of air samples

Airborne particulate samples containing Cr(VI) were collected onto PVC filters, which were housed in plastic air sampling cassettes, from fumes produced during stainless steel welding. Fumes were generated from manual metal arc welding for various periods between 5 and 15 minutes using AWS A5.4 E312-16 rods (Harris Welco, Kings Mountain, NC, USA) on a section of AISI Type 304 stainless steel rail (NIOSH, Spokane, WA, USA). Stainless steel welding fume samples were collected using a homemade cylindrical multi-port sampler (16.5 cm inner diameter with a 38 cm tall mixing chamber; overall height of 86.4 cm). The sampler was connected to a Gilian AirCon2

high-volume sampling pump (Clearwater, FL, USA) calibrated to an airflow of up to 15 l min^{-1} . The multi-port sampler contained eight separate sampling ports, with each port calibrated to a flow rate of $1.7 \pm 0.1 \text{ l min}^{-1}$, and enabled simultaneous collection of uniform welding aerosol loadings onto the filters. Previous work has reported that the precision of the mass of Cr(vi) collected onto separate filters using this multiport sampler was 1.3% to 3.8% relative standard deviation (RSD) for measured Cr(vi) masses of $\sim 1.5 \mu\text{g}$ to $\sim 8 \mu\text{g}$ per filter.⁹

Sample preparation and analysis

Airborne particulate samples containing Cr(vi) that were collected onto PVC filters from stainless steel welding fumes were prepared in accordance with procedures described in international standards for separate or sequential extraction of soluble and insoluble Cr(vi) compounds.^{7,8} PVC filters spiked with potassium chromate, lead chromate and combinations thereof were prepared similarly by using procedures for soluble extraction, insoluble extraction, or both (in series). In order to investigate the potential influence of trivalent chromium on extraction and analysis, some experiments also included spikes of chromic nitrate and/or chromic oxide (soluble and insoluble Cr(III) compounds, respectively), along with spikes of the aforementioned soluble and/or insoluble Cr(vi) compounds. For some experiments, ferrous sulfate was spiked onto the filters (along with Cr(vi) compounds, but in a separate area of each filter) in order to investigate analytical interference from Fe(II) present in solution. Spiking levels were generally in the range of 0.5 to 3 mg of each material per filter sample.

Details regarding sample preparation procedures for soluble and insoluble Cr(vi) compounds are described in the published international standards.^{7,8} Briefly, soluble extraction entailed treatment of the filter samples in either water or in a buffer of 0.05 M ammonium sulfate and 0.05 M ammonium hydroxide. To do this, the filters were placed into 15 ml centrifuge tubes and 5 ml of extraction solution (water or ammonium sulfate buffer) was added; the centrifuge tubes were then capped. Alternatively, 5 ml of extraction solution was added directly to the sampling cassette housing the filter (and glass fiber filter backup pad, if applicable), and the sampler was capped. The centrifuge tubes or cassettes were then affixed to the rotator, which itself was placed in the laboratory oven held at $37 \text{ }^\circ\text{C}$. The rotator was turned on to effect mechanical agitation and extraction was carried out for a period of one hour. To extract insoluble Cr(vi) compounds, the filters (either within centrifuge tubes or sampling cassettes) were treated by sonication in a buffer of 3% (m V^{-1}) sodium carbonate and 2% (m V^{-1}) sodium hydroxide for 30 minutes at $\sim 40 \text{ }^\circ\text{C}$. Filters that underwent sequential extraction were first subjected to soluble extraction in either water or sulfate buffer. Removal of the soluble extraction solution was afforded by means of a Büchner suction filtration apparatus⁸ or *via* direct filtration through the PVC filter housed within the cassette.¹² An alternative procedure entailed, after carrying out extraction within a 15 ml centrifuge tube, careful manual removal of the soluble extract by decantation/pipetting. Then the remaining undissolved residue and filter were treated as outlined above by ultrasonic extraction in carbonate buffer (either in the 15 ml centrifuge tube or within the sampling cassette).

In order to investigate the application of a three-step sequential extraction procedure, some experiments were carried out which entailed: (1) extraction of filter samples with water to dissolve soluble Cr(vi) compounds (*e.g.*, potassium chromate), (2) extraction in sulfate buffer to target sparingly soluble Cr(vi) species (*e.g.*, strontium chromate), and (3) extraction in carbonate buffer to dissolve insoluble Cr(vi) compounds (*e.g.*, lead chromate). This three-step procedure was applied to filter samples spiked with the above representative soluble, sparingly soluble and insoluble Cr(vi) compounds, and also to some samples of stainless steel welding fumes.

Analysis of aliquots of extract solutions for Cr(vi) content by the diphenylcarbazide (DPC) method was carried out in accordance with one of three techniques: (1) a German procedure that includes phosphoric acid in the DPC detection solution, which eliminates potential measurement interferences from iron after extraction has taken place;¹³ (2) a NIOSH procedure that entails SAE-SPE prior to DPC detection to eliminate potential metallic ion interferences;^{14–16} or (3) a standardized IC procedure that is used to isolate Cr(vi) from other potential interferants prior to detection with DPC.^{7,8,19} Aliquots from both soluble (whether water or sulfate buffer) and insoluble (*i.e.*, carbonate buffer) extract solutions were analyzed by one of these three DPC detection methods; sample aliquots were diluted in water prior to analysis, if necessary. The equivalence of the SAE-SPE and IC methods for Cr(vi) determination has been previously demonstrated.²⁰ For purposes of comparison, selected samples were analyzed for chromium content by ICP-AES after hotplate digestion in *aqua regia*.²¹

Results and discussion

Extraction of soluble Cr(vi) from spiked filter samples

To verify the performance of water to extract soluble Cr(vi), initial experiments were carried out on spiked samples of potassium chromate (in both liquid[¶] and solid forms) on PVC filters; spiking levels were in the range of 0.5–1.5 mg. Extractions were carried out using 5 ml of water either in 15 ml centrifuge tubes or directly within the sampling cassettes, as described in the experimental section. After water extraction, Cr(vi) measurements were carried out using the detection technique described in the German procedure.¹³ High recoveries (ranging from 94% to 122%) of soluble Cr(vi) were obtained in all instances, including situations where insoluble Cr(vi) (as lead chromate) was also present. These trials served as an initial check of the soluble extraction with water. Extraction of potassium chromate with the 0.05 M ammonium sulfate/0.05 M ammonium hydroxide buffer has been previously demonstrated to be effective,^{9,22} and additional experiments with this buffer that were carried out here for verification purposes yielded quantitative recoveries of soluble Cr(vi) (98% to 104%). These experiments served to demonstrate that, in the absence of interferants, water could indeed be used successfully to obtain quantitative recoveries of soluble Cr(vi) from spiked PVC filters.

[¶] *Note:* It was found that Cr(vi) recoveries from liquid spikes that were allowed to air dry were significantly low, presumably due to reduction to Cr(III). This phenomenon was observed with several different lots of PVC filters.

Further water extraction experiments in the presence of soluble and insoluble Cr(III) compounds (as chromic nitrate and chromic oxide, respectively) revealed no apparent influence of these Cr(III) compounds on recoveries of soluble Cr(VI). In these trials, water extractions were carried out within sampling cassettes using PVC filters with glass fiber filter backup pads. Cr(VI) measurements after extraction of PVC filters were performed using the SAE-SPE method described in NIOSH method 7703.¹⁵ Observed recoveries of Cr(VI) from potassium chromate spikes in the presence of soluble and/or insoluble Cr(III) remained quantitative (*i.e.*, 89% to 106%). Similar results have been reported for the use of the ammonium sulfate/ammonium hydroxide buffer, where recoveries of soluble Cr(VI) were quantitative and were unaffected by the presence of Cr(III) species.^{9,14,23} These experiments demonstrated that quantitative recoveries of soluble Cr(VI) can be obtained in the presence of other chromium compounds, both trivalent and hexavalent, of varying solubility. This work also verified that sulfate buffer can be used successfully to extract soluble Cr(VI) in the presence of insoluble Cr(VI), as previously reported.⁹

However, extractions with water that were carried out on quartz fiber filters spiked with soluble Cr(III) and soluble Cr(VI) produced low recoveries of soluble Cr(VI) (29–33%); extracts from these filters were analyzed in accordance with the French (INRS) method.¹² It was found after further investigation that a water-insoluble Cr(VI) species was produced in this case.²⁴ Transformations between Cr(III) and Cr(VI) species have been reported in isotope dilution mass spectrometry studies,²⁵ but the generation of a water-insoluble Cr(VI) compound from soluble predecessors is surprising and not clearly explained. However, this water-insoluble Cr(VI) compound was soluble in the ammonium sulfate/ammonium hydroxide extraction solution, the use of which gave the “true” soluble Cr(VI) measurement in this case.

As a further performance check of the chromium mass balance on spiked PVC or glass fiber filters, measurements of total chromium concentrations were carried out on filter samples containing various combinations of potassium chromate, lead chromate, chromic nitrate and chromic oxide. In these trials, total chromium in PVC filters was determined in accordance with the NIOSH *aqua regia* digestion/ICP-AES method,²¹ while chromium in quartz fiber filters was measured by using the

sonication/ICP-AES procedure described in an INRS procedure.²⁶ Observed recoveries of chromium in all cases were found to be quantitative (96% to 107%). These experiments provided verification that all sources of chromium were accounted for during the analysis.

Interference from Fe(II) to the soluble extraction of Cr(VI) was investigated by spiking ~250 µg of ferrous (Fe(II)) sulfate onto PVC filters in the presence of ~10 µg of soluble chromate (as K₂CrO₄); spikes of ferrous sulfate and potassium chromate were placed onto different areas of the filters. Extraction with water in the presence of Fe(II) resulted in poor recoveries (24–32%) of soluble Cr(VI). Extraction with sulfate buffer in the presence of Fe(II) yielded better recoveries of soluble Cr(VI), albeit not quantitative (66–88%). Previous work has shown that the presence of Fe(II) during ultrasonic extraction of lead chromate in carbonate buffer leads to lower recoveries of insoluble Cr(VI) in that instance as well.⁹ The use of sulfate buffer for soluble extraction assists in alleviating the interference from Fe(II) due to its redox reaction with Cr(VI), but does not completely eliminate it.

Sequential extraction of Cr(VI) from spiked PVC filters

Results from the sequential extraction of potassium chromate and lead chromate spiked onto PVC filters, using mechanical extraction in first (A) water or (B) ammonium sulfate buffer, with subsequent sonication in carbonate buffer, are summarized in Table 1. As explained previously, these procedures are options described for sequential extraction of Cr(VI) in relevant international standards.^{7,8} Analysis of both soluble and insoluble Cr(VI) extracts was performed in accordance with the German detection procedure;¹³ spiking levels of the chromate compounds were 0.5 to 1.5 mg per filter.

As described earlier, experiments carried out entailed one of three procedures: (1) manual decanting/pipette removal of the solution after soluble extraction of the spiked PVC filters within 15 ml centrifuge tubes; (2) Büchner funnel filtration after soluble extraction within 15 ml centrifuge tubes;^{7,8} or (3) vacuum filtration through the filter itself after soluble extraction within the sampling cassette.¹² These procedures enabled separation of the soluble extract and isolation of undissolved lead chromate (along with the PVC filter) after initial treatment with the soluble

Table 1 Recovery data for Cr(VI) from two-step sequential extraction of potassium chromate and lead chromate spiked onto PVC air sampling filters; ± values are standard deviations for *n* = number of samples analyzed using the DPC method

Sequential extraction sequence	Filtration/isolation method	Cr(VI) recovery from K ₂ CrO ₄ (%)	Cr(VI) recovery from PbCrO ₄ (%)
(1) Water	Decanting/pipetting	107 ± 8 (<i>n</i> = 6)	99 ± 6 (<i>n</i> = 6)
(2) Carbonate buffer			
(1) Water	Büchner funnel filtration	100 ± 4 (<i>n</i> = 6)	79 ± 7 (<i>n</i> = 6)
(2) Carbonate buffer			
(1) Water	Within-cassette filtration	102 ± 1 (<i>n</i> = 5)	99 ± 9 (<i>n</i> = 5)
(2) Carbonate buffer			
(1) Sulfate buffer	Decanting/pipetting	98 ± 2 (<i>n</i> = 6)	96 ± 7 (<i>n</i> = 6)
(2) Carbonate buffer			
(1) Sulfate buffer	Büchner funnel filtration	95 ± 6 (<i>n</i> = 6)	90 ± 8 (<i>n</i> = 6)
(2) Carbonate buffer			
(1) Sulfate buffer	Within-cassette filtration	101 ± 1 (<i>n</i> = 7)	98 ± 4 (<i>n</i> = 7)
(2) Carbonate buffer			

extraction medium (water or sulfate buffer), thereby enabling subsequent treatment with the insoluble extraction solution (carbonate buffer).

Quantitative recoveries of soluble and insoluble Cr(vi) species were obtained in almost all situations tested (Table 1). However, Büchner funnel filtration after soluble extraction with water resulted in lower insoluble Cr(vi) recoveries. Yet this phenomenon was not observed if sulfate buffer is used for soluble extraction. Experiments with a different Büchner filtration apparatus led to even lower recoveries of insoluble Cr(vi) ($66\% \pm 5\%$) after initial soluble extraction with water. Unfortunately no satisfactory explanation can be surmised for these surprising results.

It was considered of interest to investigate the use of a three-step extraction procedure employing the above extraction media. PVC filters were spiked (0.5 to 1.5 mg of solid material per sample) with potassium chromate, strontium chromate and lead chromate to represent soluble, sparingly soluble and insoluble Cr(vi) compounds, respectively. Sequential extraction was carried out within the sampling cassettes, in accordance with the INRS method.¹² As above, aliquots of sample extracts were analyzed by the German detection method employing phosphoric acid.¹³ Results obtained from three-step sequential extraction of spiked PVC filters using first water, secondly sulfate buffer and lastly carbonate buffer, are illustrated in Table 2. It is noted that total Cr(vi) determined from similarly spiked samples,

Table 2 Recovery data for Cr(vi) from three-step sequential extraction of potassium chromate, strontium chromate and lead chromate spiked simultaneously onto PVC air sampling filters; and total Cr(vi) measurement by carbonate extraction from PVC filters spiked with all three compounds; \pm values are standard deviations for n = number of samples analyzed using the DPC method

Extractant(s)	Target Cr(vi) compound(s) by extractant	Cr(vi) recovery from target compound(s) (%)
(1) Water	K ₂ CrO ₄	121 \pm 23 (n = 6) ^a
(2) Sulfate buffer	SrCrO ₄	44 \pm 11 (n = 6) ^a
(3) Carbonate buffer	PbCrO ₄	107 \pm 6 (n = 6) ^a
Carbonate buffer only	K ₂ CrO ₄ + SrCrO ₄ + PbCrO ₄	97 \pm 6 (n = 3) ^b

^a Sequential extraction. ^b Single extraction.

Table 3 Cr(vi) analysis results from sequential extraction of paint pigment samples^a using (1) water and (2) carbonate buffer, followed by DPC analysis; and (3) total chromium analysis by acid digestion/ICP-AES analysis

Pigment	% Soluble Cr(vi) (water extraction)	% Insoluble Cr(vi) (carbonate extraction)	% Total Cr (acid digestion)
Zinc chromate	0.6	22.5	21.5
Zinc chromate	7.8	15.2	25.0
Zinc tetraoxychromate	0.1	9.7	9.7
Chrome yellow	<0.01	8.4	7.8
Chrome yellow	0.3	12.4	14.4
Chrome yellow	0.1	14.2	12.8
Molybdenum orange	2.2	10.2	13.4
Molybdenum orange	7.3	3.3	13.5
Molybdenum red	5.3	6.7	12.4
Strontium chromate	2.7	21.5	22.6
Barium chromate	1.3	14.6	19.7

^a Pigments listed are primary constituents of the paint samples analyzed.

extracted using carbonate buffer and measured by the DPC method, yielded quantitative Cr(vi) recoveries (Table 2). These results demonstrate that water extracts sparingly soluble Cr(vi) species to an appreciable extent, thus the three-step extraction method is not appropriate for its intended purpose.

Sequential extraction of Cr(vi) from paint pigment samples

Sequential extraction with first water and secondly carbonate buffer were carried out on samples of paint pigment (~1 mg) spiked onto quartz fiber filters. Cr(vi) was determined by the INRS DPC method,¹² and total chromium in parallel spiked paint pigment samples was determined by the INRS ultrasonic extraction/atomic spectrometry procedure.²⁶ The results of these trials are presented in Table 3. In all but one of the pigment samples analyzed, insoluble Cr(vi) is the preponderant Cr(vi) species found. It can be seen that in all cases (Table 3), the percentage of total chromium determined is roughly equal to the sum of the percentages of soluble and insoluble hexavalent chromium measured: [(percent total Cr(vi))/(percent total Cr)] \times 100% ranges from 79% to 112% (mean = 97%; standard deviation = 11%). However, even for similar pigments, significant differences were observed in the percentages of soluble and insoluble Cr(vi) obtained. This is probably due to the presence of other constituents within the paint samples, which can influence solubility and, as a result, the sequential extraction of target Cr(vi) compounds. Nevertheless, as the total percentage of chromium is similar to the percentage of total Cr(vi) obtained by summing the percentages of soluble and insoluble Cr(vi) (Table 3), the measurement of total Cr(vi) species appears to remain unaffected.

Sequential extraction of Cr(vi) from welding fume samples

Sequential extraction experiments were carried out on stainless steel welding fume samples generated and collected using the multiport sampler as described in the experimental section. Because aerosol loadings were uniform for each set of eight filter samples,⁹ this enabled reliable comparisons to be made between individual samples within a given sample set which were treated by different extraction and/or analysis procedures. Different options for sample preparation that were investigated for various sets and subsets of welding fume samples included the following:

(A) two-step sequential extraction with (1) water and (2) carbonate buffer; (B) two-step sequential extraction with (1) sulfate buffer and (2) carbonate buffer; (C) three-step sequential extraction with (1) water, (2) sulfate buffer and (3) carbonate buffer; and (D) single extraction using carbonate buffer only. For these experiments, water or sulfate buffer extractions were carried out with mechanical agitation at 37 °C, while carbonate buffer extraction was performed using an ultrasonic bath, as described previously for Cr(vi)-spiked samples. Also in these trials, extractions were carried out directly within the sampling cassettes. Unless otherwise indicated, Cr(vi) in aliquots of extract solutions was measured using the German DPC method.¹³

Results from the above experiments are summarized in Tables 4–6 for ten different sample sets collected onto PVC filters during stainless steel welding. If possible, measurement of total Cr(vi) was carried out on selected filter samples from each set. This allowed for comparisons of data for total Cr(vi) to Cr(vi) analysis results from other samples within the same set that were treated by using sequential extraction procedures. Measured Cr(vi) amounts ranged between 5 and 35 µg per sample (Tables 4–6) and depended largely on the fume generation and sampling time, which varied from ~5 to ~15 minutes.

Table 4 demonstrates results from two-step sequential extraction with (1) water and (2) carbonate buffer, along with data from the single extraction procedure using carbonate buffer. In each case, the total Cr(vi) measured in parallel samples from the same sample set is close to the sum of soluble and insoluble Cr(vi) fractions. The percentage of soluble Cr(vi) measured in these welding fume samples ranged from 84% to 98%. Similar results have been previously reported, where predominately

Table 4 Cr(vi) analysis data from stainless steel welding fume samples: two-step sequential extraction with (1) water (to target soluble Cr(vi)) and (2) carbonate buffer (to target insoluble Cr(vi)), and (3) single extraction with carbonate buffer (to obtain total Cr(vi)); Cr(vi) analyses by DPC method. *n* = number of samples run for each subset

Sample set/extractant(s)	Measured Cr(vi) content
<i>Set I</i>	
(1) Water	5.9 ± 0.5 µg (<i>n</i> = 5) ^a
(2) Carbonate buffer	1.1 ± 0.2 µg (<i>n</i> = 5) ^a
Carbonate buffer only	6.6 ± 0.3 µg (<i>n</i> = 3) ^b
<i>Set II</i>	
(1) Water	10.1 ± 0.3 µg (<i>n</i> = 4) ^a
(2) Carbonate buffer	0.6 ± 0.3 µg (<i>n</i> = 4) ^a
Carbonate buffer only	9.9 ± 1.2 µg (<i>n</i> = 4) ^b
<i>Set III</i>	
(1) Water	13.9 ± 0.7 µg (<i>n</i> = 5) ^a
(2) Carbonate buffer	1.3 ± 0.2 µg (<i>n</i> = 5) ^a
Carbonate buffer only	15.1 ± 0.5 µg (<i>n</i> = 3) ^b
<i>Set IV</i>	
(1) Water	19.1 ± 1.0 µg (<i>n</i> = 3) ^a
(2) Carbonate buffer	0.42 ± 0.09 µg (<i>n</i> = 3) ^a
Carbonate buffer only	19.3 ± 1.8 µg (<i>n</i> = 5) ^b
<i>Set V</i>	
(1) Water	23.6 ± 0.3 µg (<i>n</i> = 4) ^a
(2) Carbonate buffer	0.27 ± 0.03 µg (<i>n</i> = 4) ^a
Carbonate buffer only	25.6 ± 1.0 µg (<i>n</i> = 4) ^b

^a Sequential extraction. ^b Single extraction.

Table 5 Cr(vi) analysis data from stainless steel welding fume samples: (A) two-step sequential extraction with (1) sulfate buffer (to target soluble Cr(vi)) and (2) carbonate buffer (to target insoluble Cr(vi)); and (B) single extraction with carbonate buffer (to obtain total Cr(vi)); Cr(vi) analyses by DPC method. *n* = number of samples run for each subset

Sample set/extractant(s)	Measured Cr(vi) content
<i>Set VI</i>	
(1) Sulfate buffer	8.8 ± 0.6 µg (<i>n</i> = 3) ^b
(2) Carbonate buffer	None detected ^a (<i>n</i> = 3) ^b
Carbonate buffer only	7.7 ± 0.4 µg (<i>n</i> = 2) ^c
<i>Set VII</i>	
(1) Sulfate buffer	8.6 ± 0.5 µg (<i>n</i> = 3) ^b
(2) Carbonate buffer	None detected (<i>n</i> = 3) ^b
Carbonate buffer only	10.7 ± 0.3 µg (<i>n</i> = 2) ^c
<i>Set VIII</i>	
(1) Sulfate buffer	14.6 ± 0.8 µg (<i>n</i> = 4) ^b
(2) Carbonate buffer	None detected (<i>n</i> = 4) ^b
Carbonate buffer only	11.9 ± 0.7 µg (<i>n</i> = 4) ^c

^a Limit of detection = 0.1 µg Cr(vi) per sample. ^b Sequential extraction. ^c Single extraction.

soluble Cr(vi) was measured (vs. insoluble Cr(vi)) in welding fumes collected during work activities.^{27,28} These data demonstrate the robustness of the sequential extraction procedure as carried out within sampling cassettes.

Table 5 shows data from two-step sequential extraction with (1) sulfate buffer and (2) carbonate buffer, and also includes single extraction results with carbonate buffer. In these cases no

Table 6 Cr(vi) analysis data from stainless steel welding fume samples: (A) three-step sequential extraction with (1) water (to target soluble Cr(vi)), (2) sulfate buffer (to target sparingly soluble Cr(vi)), and (3) carbonate buffer (to target insoluble Cr(vi)); or (B) single extraction with carbonate buffer (to obtain total Cr(vi)); Cr(vi) analyses by DPC method. *n* = number of samples run for each set/subset

Sample set/extractant(s)	Measured Cr(vi) content
<i>Set VI</i>	
(1) Water	8.3 ± 0.4 µg (<i>n</i> = 3) ^b
(2) Sulfate buffer	None detected ^a (<i>n</i> = 3) ^b
(3) Carbonate buffer	None detected (<i>n</i> = 3) ^b
Carbonate buffer only	7.7 ± 0.4 µg (<i>n</i> = 2) ^c
<i>Set VII</i>	
(1) Water	8.0 ± 0.8 µg (<i>n</i> = 3) ^b
(2) Sulfate buffer	None detected (<i>n</i> = 3) ^b
(3) Carbonate buffer	None detected (<i>n</i> = 3) ^b
Carbonate buffer only	10.7 ± 0.3 µg (<i>n</i> = 2) ^c
<i>Set VIII</i>	
(1) Water	13.0 ± 1.2 µg (<i>n</i> = 8) ^b
(2) Sulfate buffer	0.61 ± 0.07 µg (<i>n</i> = 8) ^b
(3) Carbonate buffer	1.03 ± 1.2 µg (<i>n</i> = 8) ^b
Carbonate buffer only	– ^c
<i>Set IX</i>	
(1) Water	31.6 ± 1.8 µg (<i>n</i> = 8) ^b
(2) Sulfate buffer	0.14 ± 0.08 µg (<i>n</i> = 8) ^b
(3) Carbonate buffer	0.18 ± 0.02 µg (<i>n</i> = 8) ^b
Carbonate buffer only	– ^c

^a Limit of detection = 0.1 µg Cr(vi) per sample. ^b Sequential extraction. ^c Single extraction.

insoluble Cr(vi) is measured, and results for total Cr(vi) from parallel samples are similar to results for soluble Cr(vi). Insoluble Cr(vi) cannot be measured here because the sulfate buffer effectively dissolves all of the Cr(vi) species present. The implication is that the sulfate buffer is completely dissolving both soluble and sparingly soluble Cr(vi) compounds. Thus if it is known that no insoluble Cr(vi) species are present in test samples, the sulfate buffer is a useful option for extracting total Cr(vi). However, it must be recognized that extraction with sulfate buffer will extract more than just water-soluble Cr(vi) compounds. Hence if only water-soluble Cr(vi) species are of interest and interfering reducing agents are largely absent, the use of water for extraction is the obvious choice.

Table 6 presents data from three-step sequential extraction with (1) water, (2) sulfate buffer and (3) carbonate buffer, along with single extraction results for two sample sets by using the carbonate buffer only. As in the above cases (Tables 4 and 5), the majority of the Cr(vi) species present in stainless steel welding fume samples are water-soluble. However, data for sparingly soluble Cr(vi) should be viewed as unreliable, since it is known from experiments previously described (Table 2) that water partially dissolves sparingly soluble Cr(vi) species during the initial step of the extraction sequence.

Conclusion

This work has demonstrated the utility of sequential extraction procedures for determining soluble and insoluble Cr(vi) species in workplace air samples. Two-step extraction involving either water or sulfate buffer for the dissolution of soluble Cr(vi) compounds, followed by sonication in carbonate buffer to obtain insoluble Cr(vi) species, yielded results that demonstrated acceptable performance. However, three-step extraction with first water, then sulfate buffer, and lastly carbonate buffer is not recommended, owing to partial dissolution of sparingly soluble Cr(vi) species by water during the first step of the sequence. Applications of sequential extraction procedures to paint pigment samples and to stainless steel welding fume samples were successfully demonstrated. It is recognized that airborne Cr(vi) compounds can react with other chemicals in workplace atmospheres, e.g., species emanating from stainless steel welding fumes,^{6,10,27-30} nevertheless, our efforts here have focused on analyses of particulate Cr(vi) samples that have been collected using filtration and stabilized to the extent possible. Another advantage of two-step sequential extraction (with either water or sulfate buffer) is that in the first extraction step, soluble Cr(III) is largely extracted along with soluble Cr(vi), so there is minimized possibility of oxidizing soluble Cr(III) to Cr(vi) during the second extraction step. Despite some pitfalls, the results of this study have served to provide performance data in support of the procedures described in the international standard methods,^{7,8} for which such results were previously unavailable in the peer-reviewed literature.

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