

Determination of Hexavalent Chromium in Industrial Hygiene Samples Using Ultrasonic Extraction and Flow Injection Analysis

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A simple, fast, and sensitive method was developed for the determination of hexavalent chromium (Cr^{VI}) in workplace samples. Ultrasonic extraction in alkaline solutions with 0.05 M $(\text{NH}_4)_2\text{SO}_4$ –0.05 M NH_3 provided good extraction efficiency of Cr^{VI} from the sample and allowed the retention of Cr^{VI} on an ion-exchange resin (95%). The Cr^{VI} in the sample solution was then separated as an anion from trivalent chromium [Cr^{III}] and other cations by elution from the anion-exchange resin with 0.5 M $(\text{NH}_4)_2\text{SO}_4$ in 0.1 M NH_3 (pH 8) buffer solution. The eluate was then acidified with hydrochloric acid and complexed with 1,5-diphenylcarbazide reagent prior to flow injection analysis. By analyzing samples with and without oxidation of Cr^{III} to Cr^{VI} using Ce^{IV} , the method can measure Cr^{VI} and total Cr. For optimizing the separation and determination procedure, preliminary trials conducted with two certified reference materials (CRMs 013–050 and NIST 1633a) and three spiked samples (ammonia buffer solution, cellulose ester filters and acid washed sand) indicated that the recovery of Cr^{VI} was quantitative (>90%) with this method. The limit of detection for FIA–UV/VIS determination of the Cr–diphenylcarbazone complex was in the sub-nanogram range (0.11 ng). The technique was also applied successfully to a workplace coal fly ash sample that was collected from a power plant and paint chips that were collected from a heating gas pipe and a university building. The principal advantages of this method are its simplicity, sensitivity, speed and potential portability for field analysis.

Keywords: Hexavalent chromium; ultrasound; base extraction; anion exchange; flow injection; industrial hygiene

Hexavalent chromium (Cr^{VI}) has been shown to be a human respiratory carcinogen in epidemiological studies^{1–3} when humans are exposed to relatively high levels in the workplace. High exposures may also induce dermal sensitization. Hexavalent chromium emission has been associated with a number of industrial sources, including metal plating, tanning, chromate ore processing and spray painting operations, combustion sources, such as automobiles and incinerators, and fugitive dusts from contaminated soils.^{4,5}

Chromium occurs primarily in two valence states, hexavalent and trivalent. The toxicity of chromium is a function of the oxidation state of the metallic species and its aqueous concentration. Trivalent chromium is relatively non-toxic and is an essential nutrient in the human diet to maintain effective glucose, lipid and protein metabolism.^{6,7} In contrast, hexavalent chromium is primarily man-made and can diffuse as CrO_4^{2-} or HCrO_4^- through cell membranes and oxidize biological molecules with toxic results.⁸ It has been shown to be carcinogenic to humans exposed to relatively high levels in the

workplace. Owing to the large difference in toxicological response for Cr^{VI} compared with Cr^{III} there has been considerable interest^{9–12} within industry and in the regulatory community to assess the potential cancer risks of workers exposed to the former.

Many methods for the determination of chromium are known, with atomic absorption spectrometry (AAS) being the most commonly used technique.^{13,14} Elemental analytical methods that can be used to determine chromium include inductively coupled plasma mass spectrometry (ICP-MS)^{15,16} and atomic emission spectrometry (ICP-AES),^{17–19} X-ray fluorescence,²⁰ charged-particle X-ray emission spectrometry and neutron activation analysis. Additional methods, NIOSH 7024 and 7300, found in the National Institute for Occupational Safety and Health Manual of Analytical Methods (NMAM), use AAS and ICP-AES, respectively, for the determination of chromium in workplace air samples.²¹ However, these methods can only directly determine the total chromium. To obtain speciation information, a method of separating the ionic species of chromium must be applied prior to detection.

A variety of spectrophotometric and colorimetric techniques have been devised for the determination of Cr^{VI} .^{22–24} The most prevalent colorimetric method uses the selective reaction of Cr^{VI} with 1,5-diphenylcarbazide (DPC) under acidic conditions. This reaction involves the oxidation of DPC to yield a red–violet diphenylcarbazone complex. A variation of this technique was used in NIOSH method 7600,²¹ where alkaline extraction was used to help stabilize the Cr^{VI} . Hexavalent chromium can also be measured by an electroanalytical technique with stripping voltammetry.^{25,26} Although an ion chromatographic assay is used extensively for chromium speciation^{27–29} including American Society for Testing and Materials (ASTM) method D 5281–92,³⁰ Environmental Protection Agency (EPA) Methods 218.6³¹ and 3060A,³² and NIOSH 7604,²¹ it is limited to laboratory-based analyses of the samples.

The objectives of this study were to develop a simple, fast and sensitive method for the assessment of exposure to Cr^{VI} in workplace samples and to investigate the feasibility of the technique for field portability. Flow injection analysis (FIA), one of the most rapidly growing analytical methods in the field of automated analyses,^{33,34} was selected as a flexible approach for potential field application. Flow injection allows for high precision and accuracy in comparison with manual methods, with greatly increased sampling frequencies. With a simple system of a pump and autosampler operating under low pressure and computer control, this technique can be used to automate the precise manipulation of microliter amounts of samples and deliver the products to a flow-through detector. The longer term objective is to apply this technique to field tests; in this study colorimetric and electrochemical detectors were employed for the determination of chromium species, since they offered a simple, fast and low-cost detection method that could be made field portable.

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in workplace samples and to investigate the feasibility of the technique for field portability, the research was designed to avoid a high-pressure operation system (HPLC) and to reduce the time and complicated instrumentation required for laboratory-based analyses (such as those employed in the ASTM D5281 and EPA 218.6 methods). The method developed in this study was based mainly on the unique chemical and physical properties of chromium in aqueous solutions, and utilized a solid-phase extraction procedure preceded by alkaline extraction of the sample.^{35–37} Ultrasonic extraction under basic conditions was employed for dissolution of Cr^{VI} in samples.³⁸ Hexavalent chromium, apart from other heavy metals, exists as an anion in a basic solution, whereas all other species of chromium are present as cations in basic solution. Consequently, Cr^{VI} can be directly and quickly separated from other chromium species and interferences in one step by a small amount of a low-cost and disposable anion exchanger.

Experimental*

Instrumentation

The flow injection system consisted of a Waters 600-MS system controller pump, a Waters 717 Plus autosampler (Millipore, Milford, MA, USA) and either a Model 783A programmable ultraviolet absorbance detector set at 540 nm (Applied Biosystems, Ramsey, NJ, USA) or an ESA Coulochem II multi-electrode detector equipped with a Model 5041 flow-through cell (ESA, Bedford, MA, USA). The Model 5041 cell was a reduced volume, thin-film analytical cell and contained a coulometric electrode of large surface area and a solid-state palladium reference electrode. In addition, there was a unique reference electrode compartment that simplified change-over of the mobile phase and eliminated bubbles around the reference electrode. The flow rate of the pump was 1.0 ml min⁻¹ of mobile phase. Upon initial start-up, the system was allowed to equilibrate for about 15 min. A sample volume of 10 µl was used for injections.

Reagents and Samples

All reagents, including hexavalent and trivalent chromium standards, ammonia solution, 1,5-diphenylcarbazide (DPC), cerium(IV) sulfate and hydrochloric, sulfuric and nitric acid, were of analytical reagent grade and were purchased from Aldrich (Milwaukee, WI, USA). Coal fly ash was collected from the electrostatic precipitators of a power company. Paint chips were collected from a heating gas pipe, a laboratory door and a university building. Certified reference materials (CRMs) were used as supplied (paint chips, US EPA Catalog, CRMs 013–050; NIST 1633a, Coal Fly Ash). Mixed cellulose ester filters (0.8 µm pore size, 37 mm) were obtained from SKC (Eighty Four, PA, USA) and acid washed sand was obtained from Aldrich.

A strong anion-exchange resin (Dowex 1-X8; Fluka Chemical, Ronkonkoma, NY, USA) was used for the separation of Cr^{VI} from Cr^{III} and other cations. This resin has a styrene-divinylbenzene polymer skeleton to which tertiary ammonium groups have been bound. The capacity of the resin was 1.2 mequiv ml⁻¹ and the resin was supplied in the chloride form. The resin was cleaned prior to use by slurrying it with 3 M HCl, allowing it to stand for 10 min and then decanting off the acid. This procedure was repeated three times. After pouring off the last portion of the cleaning acid, the resin was slurried with 1 M HCl and dried prior to use.

Breakthrough Studies

Breakthrough of Cr^{VI} was determined using Cr^{VI} and Cr^{III} solutions produced by diluting aliquots of 1000 µg ml⁻¹ standard solution with (NH₄)₂SO₄–NH₃ buffer solutions of various molarity [0.05 M (NH₄)₂SO₄–0.05 M NH₃ to 0.3 M (NH₄)₂SO₄–0.1 M NH₃] to yield 0.5 mM Cr^{VI} and/or 0.5 mM Cr^{III} + 5.0 mM Cr^{III} solutions. The column dimensions were 10 cm × 1.5 cm id and the amount of resin used was 1.0 g. The percentage breakthrough of Cr^{VI} was determined by analyzing the collected eluate as 5 ml aliquots of the spiked solutions of varying buffer strength that were loaded on the column. The eluate from the column generated during the addition of 5 ml of the 0.5 mM Cr^{VI} solutions was sufficient to permit the detection of breakthrough by FIA.

Elution Studies

For elution studies, a 10 cm × 1.5 cm id anion-exchange column was used. To obtain the elution profile, a total of 25 ml of 0.5 M (NH₄)₂SO₄–0.1 M NH₃ (pH 8) buffer solution was used to elute the spiked solution of Cr^{VI} (0.5 mM) from the anion exchanger. During experiments with other chromium-containing samples, the elution volume was reduced to 10 ml.

Sample Preparation

Sample preparation consisted of adding 10 ml of 0.05 M (NH₄)₂SO₄–0.05 M NH₃ (pH 8) buffer solution to the sample, followed by ultrasonication in an ultrasonic bath (115 V, 60 Hz; Sonicator Instruments, Farmingdale, NY, USA) for 30 min at 40 °C. After ultrasonication, the supernatant obtained (10 ml) was loaded on the anion-exchange resin bed. The Cr^{VI} was eluted with 10 ml of 0.5 M (NH₄)₂SO₄–0.1 M NH₃ (pH 8) buffer solution over 8 min. After separation, the eluate was acidified with 2 drops of 37% HCl solution, 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 can remain stable for at least 3 h. The chromium concentration was quantified by FIA. Additional sample pre-treatment after the anion-exchange separation for electrochemical determination included (1) removal of ammonia with H₂SO₄ after acidifying the eluate and (2) removal of the SO₄²⁻ as BaSO₄ by adding BaCl₂.

For total chromium determination, 100 mM cerium(IV) sulfate solution (1 ml) was mixed with 9 ml of 0.05 M ammonium sulfate alkaline extraction solution and added to the samples for ultrasonic extraction for 30 min at 40 °C. The procedures for anion-exchange separation and FIA determination were the same as described above. Alternatively, an aliquot of the sample was digested with 30% nitric acid by ultrasonication for 30 min at 40 °C, filtered and determined by FIA.

Results and Discussion

Because of the significant differences in the behavior of Cr^{VI} and Cr^{III}, the stability of the chromium valences must be considered when evaluating analytical techniques. The thermodynamic standard electrochemical reduction potential from Cr^{VI} to Cr^{III} at high pH is negative [CrO₄²⁻ + 4H₂O + 3e⁻ = Cr(OH)₃(s) + 5OH⁻ (*E*^o = -0.13 V, pH = 14)],³⁴ which indicates that alkaline media favor stabilization of Cr^{VI}. In acidic media, the standard reduction potential for Cr^{VI} to Cr^{III} is positive [HCrO₄⁻ + 7H⁺ + 3e⁻ = Cr³⁺ + 4H₂O (*E*^o = +1.21 V, pH = 1)],³⁹ which favors Cr^{III} stabilization. Therefore, pH is an important factor in the relative stability of Cr^{VI} and Cr^{III} in aqueous systems. Between pH 1 and 6, the monohydrogenchromate ion (HCrO₄⁻) is the primary species. At pH > 6, CrO₄²⁻ predominates in the aqueous solution. Hexavalent chromium

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will be reduced to Cr^{III} in the presence of reducing agents such as oxides of nitrogen and sulfur compounds. Alternatively, Cr^{III} in basic solution will oxidize to Cr^{VI} in the presence of Fe^{III} , oxidized Mn^{VII} or dissolved oxygen.

Earlier studies of anionic Cr^{VI} separation indicated that other anionic species such as Cl^- , HCO_3^- , H_2PO_4^- and NO_3^- did not interfere in the quantitative sorption of Cr^{VI} on an anion-exchange resin.⁴⁰ Since reducing agents may reduce Cr^{VI} to Cr^{III} in acidic matrices, a slightly basic (pH 8) ammonium buffer solution minimized the effect of these interferences. In addition, studies have shown that oxidation of Cr^{III} in alkaline media is reduced by 65–95% on addition of ammonia.⁴¹ This was attributed to the complexation of ammonia and Cr^{III} . These observations indicated that the use of a slightly basic ammonium buffer solution may help stabilization of chromium species in this study.

To evaluate possible anion-exchange separation procedures, two factors were considered: (1) the percentage of the Cr^{VI} not sorbed on the resin, termed 'breakthrough' and (2) the percentage of the sorbed metals eluted from the resin, termed 'recovery.' An anion-exchange resin (Dowex 1-X8) that exhibited high selectivity for Cr^{VI} , Cr^{III} and other ions was chosen for the separation of Cr^{VI} . To attempt to shorten the separation time, a 100–200 mesh resin was selected to offer a greater surface area and therefore accelerate the sorption process.

To evaluate breakthrough and recovery, spiked solutions [0.5 mM Cr^{VI} and/or 0.5 mM Cr^{VI} + 5.0 mM Cr^{III}] of various buffer strengths were introduced on to the column, eluted and analyzed in triplicate to establish the reproducibility of the procedure. The results showed that the breakthrough of Cr^{VI} was below the limit of detection (LOD = 0.11 ng) when the 0.05 M and 0.1 M $(\text{NH}_4)_2\text{SO}_4$ buffer solution (pH 8) was used to load the Cr^{VI} on to the resin bed. However, breakthrough was significant (6.7%, Table 1) when the 0.3 M $(\text{NH}_4)_2\text{SO}_4$ –0.1 M NH_3 buffer solution was used to apply the Cr^{VI} . The percentage breakthrough increased with increasing concentration of ammonium sulfate in the solution used to load the Cr^{VI} on to the column (Table 1).

When workplace samples (coal fly ash and paint chips) were used to study resin bed breakthrough, they were treated in an identical manner to spiked solutions. The effects of various concentrations of $(\text{NH}_4)_2\text{SO}_4$ – NH_3 buffer solution used in the extraction procedure were evaluated. In these trials, the samples were treated by ultrasonication for 30 min at 40 °C in $(\text{NH}_4)_2\text{SO}_4$ – NH_3OH (pH 8) buffer solution. The results demonstrated a significant breakthrough of Cr^{VI} when a 0.2 M $(\text{NH}_4)_2\text{SO}_4$ –0.1 M NH_3 buffer solution was used to extract Cr^{VI} from coal fly ash samples. Additionally, significant break-

through was observed when a 0.1 M $(\text{NH}_4)_2\text{SO}_4$ –0.05 M NH_3 buffer solution was used with the paint chip samples. Therefore, a 0.05 M $(\text{NH}_4)_2\text{SO}_4$ + 0.05 M NH_3 buffer solution was needed not only to extract Cr^{VI} efficiently from workplace samples, but also to reduce the breakthrough from the anion-exchange resin bed during sample introduction.

The elution profile of Cr^{VI} from the anion-exchange resin in Fig. 1 shows that over 95% of Cr^{VI} was eluted from the resin bed by 5 ml of 0.5 M $(\text{NH}_4)_2\text{SO}_4$ –0.1 M NH_3 (pH 8) buffer solution when 0.5 mM Cr^{VI} was loaded on the resin. It is also important to note that when Cr^{III} was present in the Cr^{VI} solution in this experiment, the Cr^{VI} recovery was not affected (Table 1). This indicates that the conditions used stabilized both Cr^{III} and Cr^{VI} species.

Optimization and Calibration of Flow Injection Analysis

Both a Coulochem II multi-electrode detector and a UV/VIS detector were investigated for FIA. For UV/VIS detection, the Cr–diphenylcarbazone complex was found to give excellent results with regard to sensitivity, stability and interferences. An optimum absorbance wavelength was chosen to ensure maximum sensitivity and eliminate interference from excess DPC complexing reagent.

The reproducibility of the FIA system was tested by making three replicate measurements on each standard and sample solution. The resulting RSDs were between 1.5 and 4.5%. The LOD, calculated as the mass of analyte which gives a signal that is 3 σ above the mean blank signal (where σ is the standard deviation of the blank signal), was 0.11 ng for the FIA–UV/VIS determination with MeOH–de-ionized water (1 + 1) as the mobile phase. The calibration curve was obtained by using a linear plot of the peak area as a function of standard concentrations of Cr^{VI} by least-squares regression analysis. The linear dynamic range was from 11 $\mu\text{g l}^{-1}$ to 5.0 mg l^{-1} with a correlation coefficient (r^2) of 0.9965 (Fig. 2).

For the Coulochem II multi-electrode detector determination, the pulse amperometric mode was found to give a better response for Cr^{VI} than the constant mode. Provided that the electrode surface was suitably conditioned and remained stable during the detection process, the technique of pulse amperometry allowed accurate quantification of an electroactive species with an electrochemical detector. In pulse amperometry, there are four processes: (1) measurement of the current from the oxidation or reduction of the compound of interest (analytical pulse); (2) pulse of the potential to a high positive potential (conditioning pulse); (3) pulse of the potential to a

Table 1 Hexavalent chromium recovery (%) and breakthrough (%) obtained from an anion-exchange resin (Dowex 1-X8) with spikes of Cr^{VI} and Cr^{VI} + Cr^{III} in $(\text{NH}_4)_2\text{SO}_4$ – NH_3 (pH 8) buffer solutions, with 5 ml samples

Spike	Recovery of $\text{Cr}^{\text{VI}} \pm \text{RSD}$ (%)			
	0.05 M $(\text{NH}_4)_2\text{SO}_4$ – 0.05 M NH_3	0.1 M $(\text{NH}_4)_2\text{SO}_4$ – 0.05 M NH_3	0.2 M $(\text{NH}_4)_2\text{SO}_4$ – 0.1 M NH_3	0.3 M $(\text{NH}_4)_2\text{SO}_4$ – 0.1 M NH_3
0.5 mM Cr^{VI}	95.5 \pm 1.1*	96.8 \pm 2.2	95.3 \pm 2.3	93.2 \pm 3.1
0.5 mM Cr^{VI} + 5.0 mM Cr^{III}	95.1 \pm 1.5	94.3 \pm 2.7	93.8 \pm 4.4	92.3 \pm 5.1
Spike	Breakthrough of $\text{Cr}^{\text{VI}} \pm \text{RSD}$ (%)			
	0.05 M $(\text{NH}_4)_2\text{SO}_4$ – 0.05 M NH_3	0.1 M $(\text{NH}_4)_2\text{SO}_4$ – 0.05 M NH_3	0.2 M $(\text{NH}_4)_2\text{SO}_4$ – 0.1 M NH_3	0.3 M $(\text{NH}_4)_2\text{SO}_4$ – 0.1 M NH_3
0.5 mM Cr^{VI}	BD*	BD	4.9 \pm 3.1	6.5 \pm 5.1
0.5 mM Cr^{VI} + 5.0 mM Cr^{III}	BD	1.0 \pm 1.1	5.5 \pm 4.1	6.7 \pm 4.1

* BD = Below detection level (LOD = 0.11 ng).

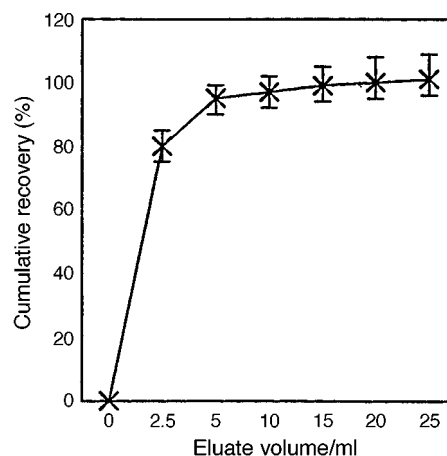


Fig. 1 Elution profile obtained by loading 0.5 mM Cr^{VI} in 5 ml of solution on the 1.0 g Dowex 1-X8 anion-exchange resin bed and eluting with 25 ml of 0.5 M ammonium sulfate (pH 8) alkaline buffer solution.

high negative potential (conditioning pulse); and (4) return to the original potential. The results showed that the higher the detection potential applied, the lower were the limits of detection obtained. Calibration was performed with triplicate injection of six standard solutions. The LOD, calculated 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 2.3 ng for the electrochemical determination with acetonitrile–de-ionized water (8 + 2) as the mobile phase. The correlation coefficient (r^2) of the calibration curve was 0.9948 (Fig. 2).

In a comparison of the results obtained from these two detectors, UV/VIS determination of the chromium–diphenylcarbazone complex yielded lower LODs (more than 20 times, Fig. 2), lower background correction and higher sensitivity, and needed fewer sample pre-treatment steps. Therefore, the UV/VIS detector was chosen for further experimental studies.

Determination of Hexavalent Chromium in Samples

To evaluate the recovery efficiency of this method on simulated workplace samples, solutions of known concentrations of Cr^{VI} were spiked on to mixed cellulose ester filters and acid washed sand samples. The samples were then subjected to the same elution and analysis procedures as described previously. The recoveries (Table 2) were quantitative for spikes of 40 μg of Cr^{VI} on to each filter and also quantitative for spikes of 25 μg of Cr^{VI} per gram of acid washed sand samples. In order to investigate

the possibility of oxidation of Cr^{III} to Cr^{VI} with the current experimental procedure, 25 $\mu\text{g g}^{-1}$ of Cr^{VI} and 250 $\mu\text{g g}^{-1}$ Cr^{III} were spiked on to acid washed sand samples. The procedure involved the same sample preparation, separation and complexation as used for other samples. The measured Cr^{VI} concentrations in the spiked sand samples indicated that no significant amount of Cr^{III} was oxidized to Cr^{VI} . The recovery of Cr^{VI} was quantitative (Table 2). The RSDs of the measured recovery for spiked sand samples (Table 2) were higher than those of the certified reference materials (Table 2). These results may be attributed to the unhomogenized spike of Cr^{VI} in sand samples and/or irreversible adsorption of Cr^{VI} on the sand.

Two CRMs were chosen to evaluate the basic separation and determination procedure. One (US EPA certified, paint chips) contained relatively high levels of total chromium (reference value 617.6 $\mu\text{g g}^{-1}$ with a 95% confidence interval of 595–670 $\mu\text{g g}^{-1}$). The other (NIST 1633a Coal Fly Ash) contained a lower level of total chromium (196 \pm 6 $\mu\text{g g}^{-1}$). In operation, 10 ml 0.05 M $(\text{NH}_4)_2\text{SO}_4$ –0.05 M NH_3 (pH 8) buffer solution was added to 0.1 g of CRMs paint chips or 1.0 g of NIST Coal Fly Ash to extract the Cr^{VI} . Table 2 gives the Cr^{VI} contents determined for the two samples.

Since these results did not account for the total chromium in the sample, an additional analysis was conducted with these samples. Total chromium in the samples can be determined if all the chromium in the sample is first oxidized to the hexavalent state. Acidic cerium(VI) sulfate was effective for this purpose and did not interfere with Cr^{VI} determination by the DPC method. When this modification of the method was applied to the CRM samples, the results (Table 3) were in good agreement with the determination of total Cr by nitric acid digestion and demonstrated that this method can be used to determine total chromium when an oxidation step is applied.

Hexavalent chromium was determined in several real samples from different workplaces, including coal fly ash collected from electrostatic precipitators of a power company, and paint chips collected from a heating gas pipe, a laboratory door and a university building. The sample preparation procedures were conducted as described above for the CRMs. The results (Table 2) show the Cr^{VI} contents determined for the coal fly ash and yellow paint chips sampled from a gas pipe. The Cr^{VI} contents of the paint chips sampled from a laboratory door and a university building were below the detection limit.

There is no known Cr^{VI} particulate reference standard material available, although reference materials are under

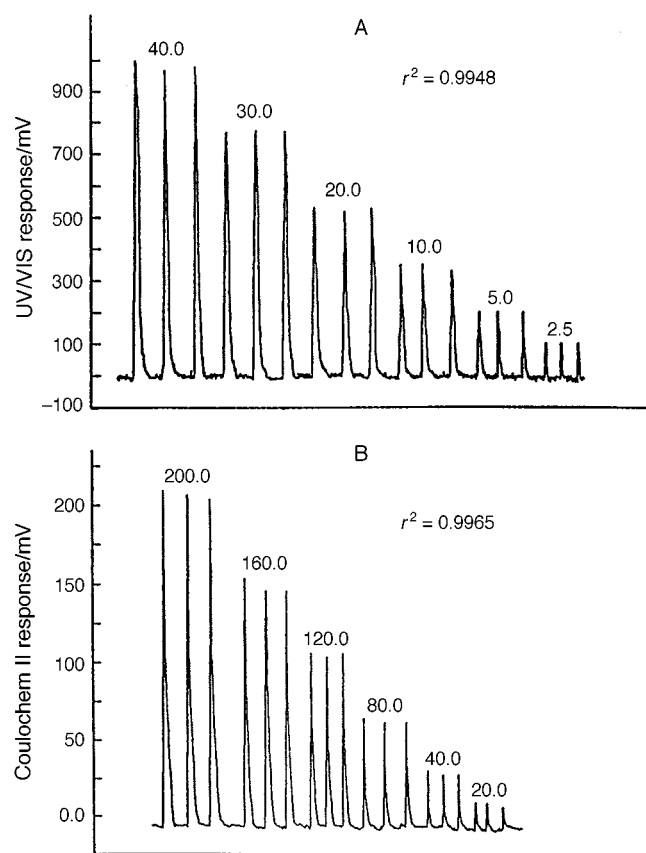


Fig. 2 Typical responses for the flow injection of various amounts (ng) of: A Cr–diphenylcarbazone complex detected by UV/VIS with MeOH–de-ionized (1 + 1) water as mobile phase, and B, Cr^{VI} analyte detected with the Coulchem II with (1) analytical pulse $E_1 = -1500$ mV, conditioning pulses $E_2 = +900$ mV and $E_3 = -900$ mV; (2) pulse width $T_1 = 500$ ms, $T_2 = 500$ ms and $T_3 = 300$ ms; and (3) acetonitrile–de-ionized water (8 + 2) as mobile phase.

Table 2 Determination of hexavalent chromium in spiked cellulose ester filters, spiked acid washed sand, certified reference materials and workplace samples

Sample	Cr^{VI} content/ $\mu\text{g g}^{-1} \pm \text{RSD} (\%)$	Recovery (%) [*]
Spiked filters, 40 $\mu\text{g Cr}^{\text{VI}}$ per filter	37.9 \pm 3.2	95.6
Spiked sand samples, 25 $\mu\text{g g}^{-1}$ Cr^{VI}	23.8 \pm 4.5	95.2
Spiked sand samples, 25 $\mu\text{g g}^{-1}$ Cr^{VI} + 250 $\mu\text{g g}^{-1}$ Cr^{III}	23.3 \pm 7.6	93.8
EPA CRMs, paint chips	54.4 \pm 3.4	N/A [†]
NIST 1633a coal fly ash	0.19 \pm 3.9	N/A
Power company coal fly ash	0.53 \pm 3.4	N/A
Gas pipe paint chips	352.6 \pm 4.4	N/A
Laboratory door paint chips	BD [‡]	N/A
University building paint chips	BD	N/A

^{*} The sample, spiked filter (0.8 μm , 37 mm) and/or 1.0 g of spiked sand in 0.05 M $(\text{NH}_4)_2\text{SO}_4$ –0.05 M NH_3 (10 ml) was treated by ultrasonication for 30 min at 40 °C. The sample was then subjected to anion-exchange separation (1.0 g resin bed). The eluate was acidified and reacted with 2 ml of 20 mM DPC complexing reagent solution. Finally, Cr^{VI} was determined by FIA. [†] N/A, no standard or reference data for Cr^{VI} available.

[‡] BD, below detection level (LOD = 0.11 ng).

development.²⁸ Therefore, generation of a test aerosol of known concentration is not feasible. Test method bias was based on spike recoveries of known concentration of Cr^{VI} in buffer solutions (Table 1), cellulose ester filters and acid washed sand samples (Table 2). In these tests, two concentration levels of three replicates were prepared. After the spiked samples were corrected for the background contribution, the spiked recoveries were quantitative (Table 2). These trials demonstrate that this procedure can be used to determine Cr^{VI} in real samples, and also were consistent with the notion that ammonia can stabilize Cr^{III} and decrease Cr^{III} oxidation due to complexation.

A simple modification based on the unique chemical properties of chromium could allow the development of a practically useful field suitable technique. The technique can solve an important problem related to improvement of throughput in a large number of analyses of real workplace samples, especially in connection with complex and challenging sample matrices. The LOD of 0.11 ng with this method is close to that of EPA method 218.6 (0.10 ng) that was obtained by collaborative work of 22 laboratories. The LOD of the present method is significantly higher than the calculated LOD for ASTM method D 5281 of 0.018 ng. This may be due to the sensitivity of the detector used in the ASTM method being greater than that of the detector used in the present work. Our efforts to reproduce the LOD claimed in the ASTM method were unsuccessful. It is emphasized that the method performance parameters (e.g., precision, bias, detection limit and dynamic range) claimed in ASTM method D5281 were not evaluated by interlaboratory round-robin testing, which is a requirement of ASTM test methods. Hence the performance parameters cited in ASTM method D5281 may be questionable.

Conclusion

A simple, fast, and sensitive method for the determination of Cr^{VI} was developed for workplace samples. The method was suitable for the determination of Cr^{VI} down to low ppb ($\mu\text{g l}^{-1}$) levels. Sonication in 0.05 M (NH₄)₂SO₄–0.05 M NH₃ buffer solution was shown to extract Cr^{VI} efficiently from real samples. This basic buffer solution also serves to reduce the breakthrough from the anion-exchange resin bed during sample introduction. In the flow injection mode, the chromium–diphenylcarbazone complex dynamic range was linear from concentration levels of 11 $\mu\text{g l}^{-1}$ to 5 mg l⁻¹, with good correlation ($r^2 = 0.9965$) using UV/VIS determination. The method was tested with certified reference materials (CRMs

013–050, NIST 1663a), and successfully measured Cr^{VI} concentration in workplace samples, including coal fly ash sampled from a manufacturing process and paint chips sampled from building interiors.

The method was selective, because all typical interferences, including Cr^{III}, Fe^{II} and Cu^{II}, were eliminated in the anion-exchange separation procedure. Spike recovery trials also indicated that Cr^{VI} was stable in this test method, and also showed no interference from Cr^{III}. With the oxidation of Cr^{III} to Cr^{VI} by Ce^{IV}, the total chromium concentration was determined by this method. The experimental data also indicated that pH and ammonia concentration play important roles in the determination of Cr^{VI}. The results were consistent with the idea that ammonia can serve to inhibit the oxidation of Cr^{III} to Cr^{VI} in aqueous alkaline media through complexation under the experimental conditions employed.

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Table 3 Determination of total chromium in certified reference materials and in workplace samples with pre-oxidation and/or nitric acid digestion procedures

Sample	Total Cr/ $\mu\text{g g}^{-1} \pm \text{RSD} (\%)$	
	Oxidation with Ce ^{IV} *	Nitric acid digestion†
EPA CRMs, paint chips	587.9 \pm 4.5	596 \pm 3.8
NIST 1633a coal fly ash	185.0 \pm 5.7	192.0 \pm 4.9
Power company coal fly ash	23.2 \pm 6.3	24.8 \pm 6.7
Gas pipe paint chips	358.2 \pm 7.1	361.1 \pm 5.3

* An aliquot of sample, in 10 mM Ce^{IV}–0.05 M (NH₄)₂SO₄–0.05 M NH₃ (10 ml), was treated by ultrasonication for 30 min at 40 °C. The sample was then subjected to anion-exchange separation (2.0 g resin bed). The eluate was acidified and reacted with 2 ml of 20 mM DPC complexing reagent solution. Finally, Cr was determined by FIA. † An aliquot of sample, in 30% HNO₃, was treated by ultrasonication for 30 min at 40 °C, and then subjected to filtration. The Cr in the sample solution was determined by FIA.

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