Determination of Cr(VI) in Water, Wastewater, and Solid Waste Extracts

Key Words

Chromium, Environmental Samples, Oxidation States, Speciation, Metal Toxicity

Goal

To develop a precise Cr(VI) detection method that meets U.S. Environmental Protection Agency (EPA) Method 218.6 requirements and is capable ofhandling the high-ionic-strength sample matrices generated through leaching, impinging, and digestion procedures

Introduction

Chromium, while not unique in its properties, is commonly used in various industries because of the characteristics of the metal and its compounds. The predominant use of chromium in industry introduces an environmental concern. Chromium exists almost exclusively in the Cr(III) oxidation state or in the Cr(VI) oxidation state.

In the environment, Cr(III) is typically not a problem. The uncomplexed trivalent species is the chromic ion, Cr^{3+}, and although it is soluble in acidic solutions, it typically precipitates as the hydroxide in alkaline solutions. It shares the quality with all other metals of being toxic to biological systems at some level. Its relative toxicity is low because of the slow ligand exchange kinetics of Cr(III) that cause it to be fairly unreactive. Actually, Cr(III) is essential to mammalian systems, admittedly at low concentrations, for the maintenance of several metabolic pathways. In contrast, Cr(VI) seems to serve no useful biological purpose to living things.

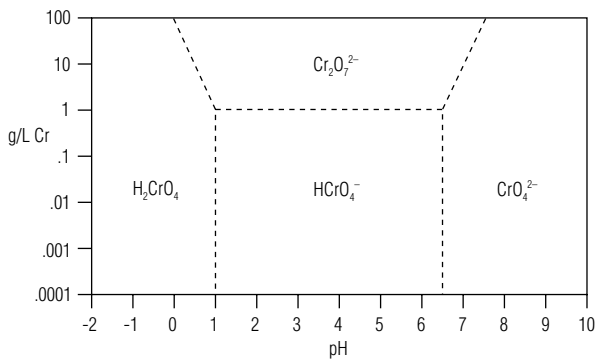

Figure 1. Relative distribution of Cr(VI) species in water as a function of pH and Cr(VI) concentration.

The hexavalent species exists primarily as chromic acid (H_2CrO_4) and its salts—hydrogen chromate ion ($HCrO_4^-$) and chromate ion (CrO_4^{2-})—depending on the pH. The predominant species present, as a function of the pH, are H_2CrO_4 at pHs less than ~1, $HCrO_4^-$ at pHs between 1 and 6, and CrO_4^{2-} at pHs above ~6 (Figure 1). The dichromate ion ($Cr_2O_7^{2-}$) is a dimer of $HCrO_4^-$, less a water molecule, which forms when the concentration of chromium exceeds approximately 1 g/L.

Cr(VI) is a strong oxidizer and, therefore, harmful in biological systems. This fact warrants its regulation in the environment. As is typical, the oxidizing power of Cr(VI) is a function of pH. As the pH becomes lower, Cr(VI) is more inclined to oxidize something. Fortunately, environmental samples are typically alkaline and, because the reduction potential of Cr(VI) decreases as the pH increases, Cr(VI) is less reactive at these higher pHs.

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The contrast in qualities of Cr(III) and Cr(VI) is the reason it is critical to differentiate between the two oxidation states when analyzing environmental or process samples. Various industries urge environmental regulation efforts to focus on Cr(VI) instead of on the relatively harmless Cr(III). This position has credence but, whether one wants or needs to determine one or both species in a sample, the analytical method must be capable of differentiating between the two. Speciation of various oxidation states of a metal in a sample is not always easy. Even after an analytical method has been developed, the question of whether or not the sample preparation procedure has altered the relative concentration of the species of interest still remains.

These issues combine to make a difficult analytical situation. To date, the study of sampling and sample preparation procedures for the speciation of chromium is an area of considerable activity. Existing sample preparation procedures (extraction, digestion, filtration) are undergoing critical review. They have proven to be imprecise, incomplete, and can alter the relative oxidation state concentrations.

Sample digestion and extraction procedures can provide values for dissolved (free) Cr(VI) or total chromium as Cr(VI). Examples of these are the toxicity characteristic leaching procedure (TCLP) extraction and alkalinepersulfate digests, both of which generate high-ionic-strength matrices; not matrices of choice for most instrumental analytical methods.

Although analytical method development is ongoing, the methods are dependent on the sample preparation procedures to determine the ultimate applicability of the techniques. Most spectroscopic and electrochemical methods are not specific enough. Because of these inadequacies, substantial sample preparation is required to yield useful analytical results.

The method presented here overcomes many analyte interference problems by separating the two chromium using a detection method specific for Cr(VI) that is capable of handling the high-ionic-strength sample matrices generated in many leaching, impinging, and digestion procedures. This method is consistent with U.S. EPA Method 218.6 and is described in several other publications.[2–5]

Equipment

- A DX-500 Chromatography System, including:
  - GP40 Gradient Pump or IP20 Isocratic Pump
  - AD20 Absorbance Detector
  - PC10 Postcolumn Pneumatic Delivery Package
  - Thermo Scientific™ Dionex™ OnGuard™-P Sample Pretreatment Cartridges

Reagents and Standards

All reagents are analytical reagent grade or better.

- Deionized (DI) water, 18 MΩ-cm
- Sulfuric Acid, 96%
- Methanol, HPLC grade
- Ammonium Hydroxide, 29%
- Ammonium Sulfate
- 1,5-DPC
- Potassium Dichromate

Conditions	
Guard Column:	Thermo Scientific™ Dionex™ IonPac™ NG1
Analytical Column:	Dionex IonPac AS7
Eluent:	250 mM Ammonium sulfate 100 mM Ammonium hydroxide
Eluent Flow Rate:	1.5 mL/min
Postcolumn Reagent:	2 mM DPC, 10% Methanol, 1 N Sulfuric acid
Postcolumn Reagent Flow Rate:	0.5 mL/min
Detection Wavelength:	520 nm
Sample Volume:	50–100 µL

Preparation of Reagents and Standards

Eluent

- 250 mM Ammonium Sulfate
- 100 mM Ammonium Hydroxide

Dissolve 33.0 g of ammonium sulfate in ~500 mL of water. Add 6.5 mL of 29% ammonium hydroxide. Mix well and dilute to 1 L in a volumetric flask. Transfer the solution to the eluent bottle. If a larger volume of the eluent is desired, multiply the weight and volumes listed for the eluent by an appropriate factor to prepare.

Postcolumn Reagent

- 2.0 mM DPC
- 10% Methanol
- 1 N Sulfuric Acid

Dissolve 0.5 g of 1,5-DPC in 100 mL of HPLC-grade methanol. Add to about 500 mL of water containing 28 mL of 98% sulfuric acid. Dilute, with stirring, to 1 L in a volumetric flask. Transfer the solution to the pressurized reagent container. The solution will be stable for several days, but must be prepared only as it is used, one liter at a time.

Chromium Stock

- 1000 ppm Cr(VI)

Dissolve 0.283 g of potassium dichromate ($K_2Cr_2O_7$ dried at 100 °C for one hr) in water. Dilute to 100 mL in a volumetric flask.

Chromium Standard

Prepare standards by appropriate dilutions of the stock solution. As an example, for a 1 mg/L Cr(VI) standard, pipet 1 mL of the Chromium Stock solution into a 1 L volumetric flask. Dilute to volume with water.

Sample Preparation

Collect samples in amber glass bottles with plastic lined caps. Clean the bottles with 1:1 HNO_3 and rinse well with DI water before use.

Because Cr(VI) is an oxidizer, care must be taken in sampling and sample preparation procedures. Sampling and preservation procedures often involve changing the sample pH, which may result in changes in the relative concentrations of the oxidation states.

Refrigeration of the samples, minimal sample handling, and immediate analysis are suggested as the best protocol for maintaining the integrity of the samples. After collecting the samples, store at 4 °C to minimize chemical reactivity. Analyze within 24 h.

Analyze drinking water, rain water, and air particulate extract solutions directly with no sample preparation (other than possible dilution). Filter ground water and wastewater samples through 0.45 µm filters before injection.

Pass samples such as ground water, wastewater, and solid waste extracts, which may contain high concentrations of organic contaminants, through Dionex OnGuard-P syringe cartridges before injection. Although this procedure is not necessary, it helps prevent premature fouling of the column. Be sure to follow the instructions for the use of the cartridges, which are enclosed with the cartridge package.

Discussion of Method

The method allows the detection of low-µg/L levels of Cr(VI) in typical high ionic strength matrices. As discussed, most analysts are concerned with free Cr(VI) only, or total chromium as Cr(VI), so the method is specific for Cr(VI).

Using this method, hexavalent chromium is separated as the divalent CrO_4^{2-} anion on the Dionex IonPac column using a well-buffered ammonium sulfate, ammonium hydroxide eluent (Figure 2). After the separation, Cr(VI) reacts with the color reagent diphenylcarbohydrazide (DPC) in the following reaction:

$$2\ CrO_4^{2-} + 3\ H_4L + 8\ H+ \times Cr(III)\ (HL)_2+ + Cr^{3+} + H_2L + 8\ H_2O$$

where:

H_4L = diphenylcarbazide
H_2L = diphenylcarbazone

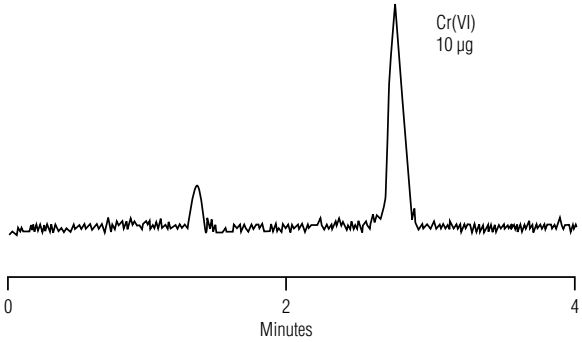

Figure 2. Determination of Cr(VI) in water, wastewater, and solid waste extracts.

The reaction consists of the simultaneous oxidation of diphenylcarbazide to diphenylcarbazone, reduction of Cr(VI) to Cr(III), and the chelation of Cr(III) by diphenylcarbazone. The actual structure of the chelate is not known, but it is detected by visible absorbance using a photometric detector at 520 to 530 nm. A diagram of the system flow path is shown in Figure 3.

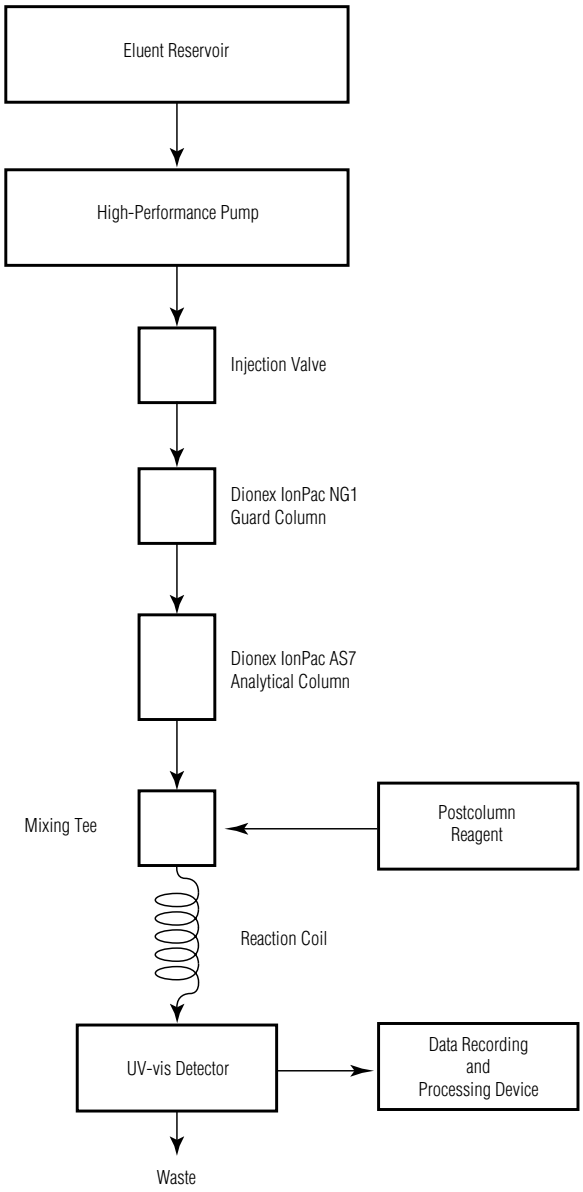

Figure 3. System flow diagram.

The analysis time is ~5 min. The method has a linear detection response from the detection limit, which is ~50 pg or 1 µg/L using a 50 µL loop and up to ~0.5 µg or 10 mg/L using a 50 µL loop (Figure 4). The RSDs from multiple injections of the same sample are 1% to 3% at concentrations above 10 µg/L.

The method can handle samples of up to 5% sodium sulfate, 2% sodium chloride, 1 M acetate buffer, or 0.5 M carbonate buffer without adverse effects on the analysis. Figure 5 illustrates the responses of 100 µg/L Cr(VI) spikes in various concentrations of these sample matrices.

Increasing the matrix ionic strength is illustrated in Figure 6 for the acetate buffer. This eventually causes column overload and compromises the chromatography and detection.

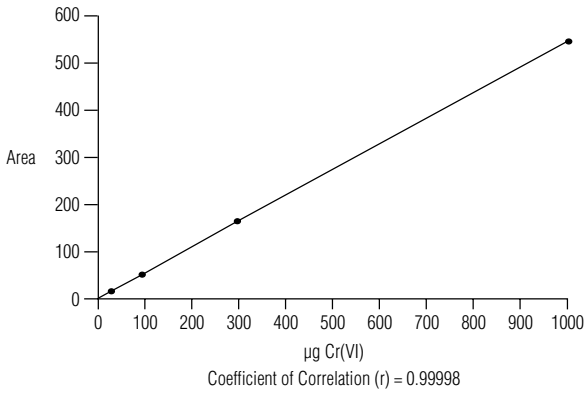

Figure 4. Area response for colorimetric chromium detection.

Troubleshooting

This method is simple and rugged, but a troubleshooting guide is included to minimize downtime. The guide lists the symptoms of potential problems as well as their likely causes and remedies.

Symptom: No peak observed

- Possible Cause: No sample injected.
  - Remedy: Ensure that the pressurized gas used to switch the injection valve is turned on.
  - Remedy: Ensure that the sample is loaded from the autosampler or syringe.
- Possible Cause: Recording device not properly connected.
  - Remedy: Check that the computer interface is turned on, or that the recording device is connected to the detector.
- Possible Cause: No postcolumn reagent flow.
  - Remedy: Check that the flow rate out of the cell is 2.0 mL/min and that the backpressure past the mixing tee is less than 50 psi.
- Possible Cause: Wrong detector wavelength.
  - Remedy: Check that the wavelength readout is 530 nm.

Symptom: Noisy baseline

- Possible Cause: Air bubble in cell.
  - Remedy: Disconnect line cell inlet, replace with a Luer-type adapter, and flush the cell with a few mL of methanol or ispropanol.

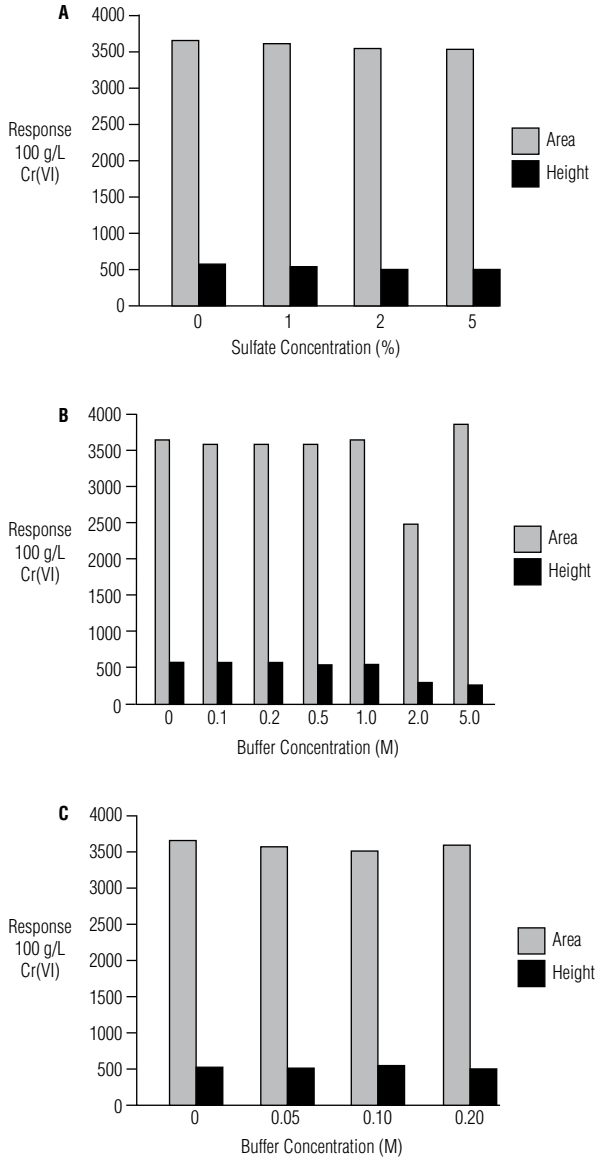

Figure 5. The responses of spikes in (A) alkaline sulfate, (B) acetate buffer, and (C) carbonate buffer samples.

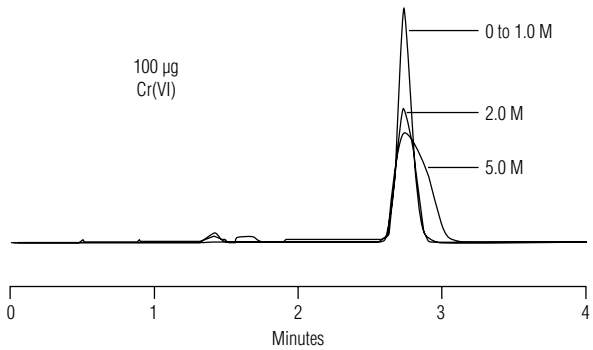

Figure 6. Cr(VI) in acetate buffer.

Symptom: Low column pressure

- Possible Cause: Air in pump head.
  - Remedy: Prime the pump with eluent (see pump instruction manual).
- Possible Cause: Leak in system.
  - Remedy: Tighten or replace leaking fitting.

Symptom: Excessive pressure on column

- Possible Cause: Improper flow rate.
  - Remedy: Check that the pump flow rate is 1.5 mL/min.
- Possible Cause: Fitting is plugged.
  - Remedy: With the pump off, remove the columns and reconnect the eluent lines. Turn on the pump and check that the system pressure is less than 100 psi when the valve is in either the LOAD or INJECT position.
- Possible Cause: Column bed support plugged.
  - Remedy: Replace the bed support on the column. See the column manual for instruction.

Symptom: Peak response too high or too low

- Possible Cause: Incorrect detector range (applies when using analog output only).
  - Remedy: Check that the detector range is correct.
- Possible Cause: Incorrect sample loop size.
  - Remedy: Ensure that the sample loop volume is 50 µL or 100 µL.
- Possible Cause: Low postcolumn reagent flow rate.
  - Remedy: Check that the flow rate from the detector waste line is 2.0 mL/min.

Symptom:
Poor peak shape — reasonable retention time

- Possible Cause: Column is overloaded with a sample concentration that is too high.
  - Remedy: Dilute the sample so that the peak response is below that expected for a 1 µg injection.

Symptom:
Poor peak shape — incorrect retention time

- Possible Cause: The eluent was prepared incorrectly.
  - Remedy: Prepare new eluent with a pH of approximately 8 to 9.
- Possible Cause: The column is contaminated with strongly retained anions, metals, or organics.
  - Remedy: Pump acetonitrile through only the Dionex IonPac NG1 guard column for ~30 min, and then rinse with DI water for ~15 min. Pump 1 N HCl through all of the columns for one hr, rinse with DI water for 30 min, and re-equilibrate with eluent for 30 min.

Reference

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