

New Cation-Exchange Method for Field Speciation of Hexavalent Chromium

INTRODUCTION

Chromium (Cr) is usually present in surface and ground water in either the +3 or the +6 oxidation state. Because Cr(III) is considered an essential nutrient and Cr(VI) is considered a toxin and a carcinogen, it is important to distinguish between oxidation states of Cr. Hexavalent chromium [Cr(VI)] concentration limits for drinking water now being considered by the California Environmental Protection Agency present analysts with the need for quantitation limits in the sub-parts-per-billion (ppb or $\mu\text{g/L}$) range. Existing methods for accurately determining Cr(VI) in natural waters have one or more of the following weaknesses: (1) poor sensitivity, (2) time-instability of the Cr redox species, (3) necessity for expensive instrumentation that is not commonly available. A new cation-exchange method for field speciation of Cr(VI) has been developed to meet the stringent regulatory standards and to improve upon the weaknesses of existing methods. The capability of the new technique compares favorably with existing methods such as the diphenylcarbazide direct colorimetric and EPA 218.6 ion-chromatographic/colorimetric methods.

APPARATUS AND SUPPLIES

Cation-exchange cartridges (IC-H, Alltech), disposable syringes, and suitable containers (centrifuge tubes) of size appropriate to process and hold sample volumes consistent with the analytical technique are needed. Syringe filters [25-millimeter (mm), 0.2-micrometer (μm)] are needed for unfiltered samples. Separated (speciated) samples are preserved with concentrated hydrochloric acid (HCl) or nitric acid (HNO_3), American Chemical Society Reagent grade, for later measurement in the laboratory. The sampling supplies are shown in figure 1, and a photograph of the separation procedure is shown in figure 2. An elemental analysis instrument capable of determining total Cr at concentrations in the range sought is needed for

the measurement step. The cation-exchange method was developed for analysis using graphite furnace atomic absorption spectrometry (GFAAS), with a detection limit of



Figure 1. Hexavalent chromium field speciation supplies.

approximately $0.05 \mu\text{g/L}$ using end-capped transversely heated graphite tubes. Consequently, sample volumes of 2 mL were collected using a 10-mL disposable syringe and stored in 2-mL centrifuge tubes. If a different analytical instrument were to be used, such as inductively coupled plasma-mass spectrometry (ICP-MS) with a conventional nebulizer, larger sample volumes would be required, necessitating use of larger syringes and storage containers, and possibly larger cation-exchange cartridges.

FIELD SPECIATION PROCEDURE

Aspirate about 8 mL sample into a 10-mL disposable plastic syringe. If the sample has not been filtered, attach a syringe filter. Invert the assembly and purge of all air. Collect a sample for Cr(total) by filling one 2-mL centrifuge tube. Attach an IC-H cartridge to the syringe/filter assembly. At no more than two drops per second, force about 3 mL sample through the assembly to waste. Again at no more than two drops per second, force about 2 mL sample through the assembly into the second 2-mL centrifuge tube. The sample issuing from the cation-exchange cartridge contains only Cr(VI), and because Cr(total) is determined in the laboratory measurement step, the oxidation state of Cr is no longer critical. Preserve the samples by acidifying to $\text{pH} < 2$ with about 10 μL HCl or HNO_3 .



Figure 2. Hexavalent chromium field separation.

COMPARISON OF METHODS

The diphenylcarbazide direct colorimetric method (Hach Company, 1992) uses a portable spectrophotometer and a 1-inch measuring cell. The cell is filled with sample, and then a packet of powdered reagent is added. After color development, the absorbance of the solution is read and the Cr(VI) concentration is displayed in milligrams per liter (mg/L). The two most important limitations of this method are its higher detection limit compared with other methods and the potential for interferences by unknown solution components.

The steps taken to collect and preserve samples must be compatible with the intended analytical technique that will be used later in the laboratory. The most commonly used method is USEPA method 218.6 (Arar and others, 1991). This method specifies that samples be preserved in the field and adjusted to a pH of 9 to 10 with ammonium sulfate/ammonium hydroxide buffer solution to ensure that the distribution of the dissolved Cr redox species remains unchanged. Samples are analyzed in the laboratory by ion chromatography with post-column derivatization with diphenylcarbazide and absorbance detection within 24 hours of collection.

In contrast to the other two methods, the new cation-exchange method is not

as time-sensitive. Because only Cr(VI) remains in the sample after the cation-exchange separation and Cr(total) is determined in the analytical step, samples can be processed up to several weeks after collection. The determination starts with field sampling using the cation-exchange system. Strong acid cation-exchange resin (AG50W-X8) will retain Cr(III), whereas Cr(VI) will pass into the effluent (Johnson, 1990). Care is needed to prevent contamination and to ensure a clean separation. Sample pH is not critical, but must be between 2 and 11, so that all Cr(VI) is present as either hydrogen chromate (HCrO_4^-) or chromate

($\text{Cr}(\text{OH})_2^+$). Although the selectivity of the AG50W-X8 resin for $\text{Cr}_{(\text{aq})}^{3+}$ is very high, the flow rate through the cartridge should be no greater than two drops per second so that Cr(III) species will be quantitatively retained.

The USEPA method 218.6 and the new cation-exchange method also differ in the availability of laboratory instrumentation. The ion chromatograph equipped with an absorbance detector and a small-volume sample cell is specialized instrumentation that is not commonly available, and older ion

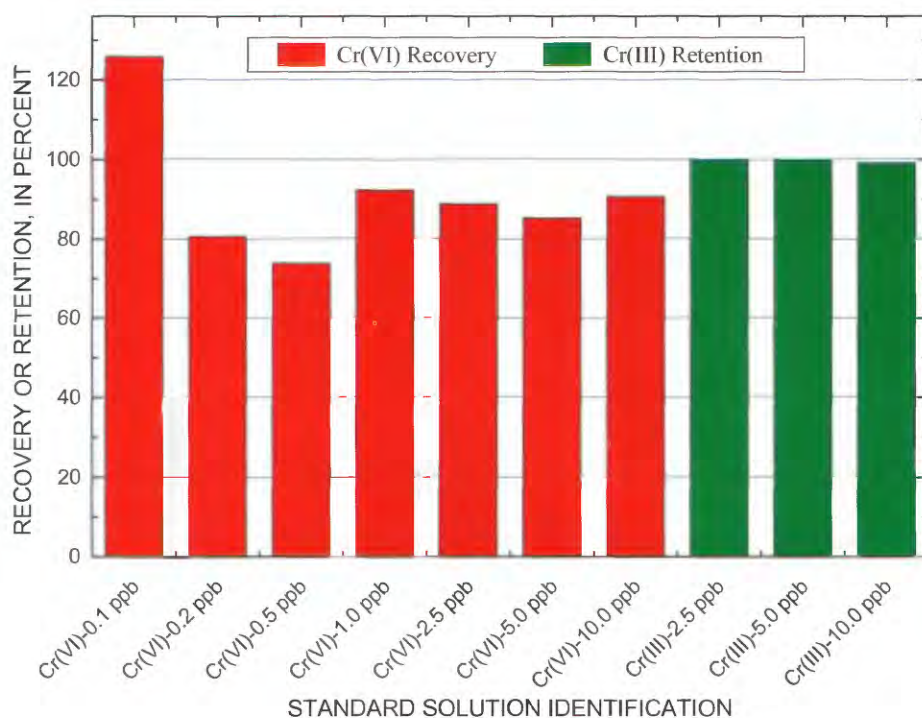


Figure 3. Recovery or retention from cation-exchanged Cr(III) and Cr(IV) standard solutions.

(CrO_4^{2-}) and all Cr(III) is present as $\text{Cr}_{(\text{aq})}^{3+}$, chromic monohydroxide ($\text{Cr}(\text{OH})_2^+$), or chromic dihydroxide

chromatographs cannot be retrofitted. The graphite furnace atomic absorption spectrometer (GFAAS), although similar in cost, is commonly available. Thus, typically no new instrument purchase is necessary to

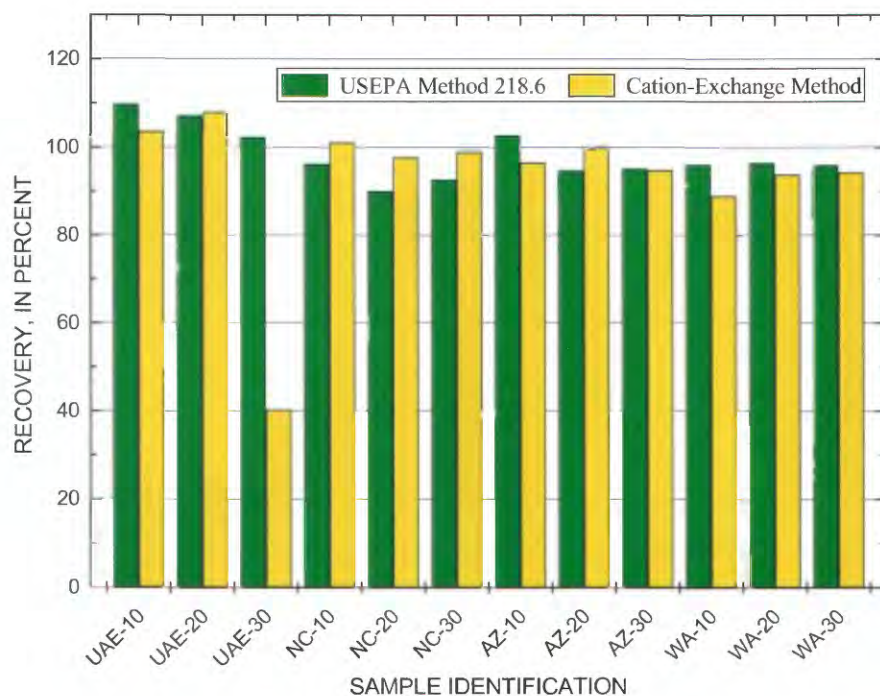


Figure 4. Results of analyses of four CR-containing samples spiked with varying concentrations of Cr(III).

implement the analytical step of the new cation-exchange method.

Limitations of the cation-exchange method

In the field when processing water samples through the cation-exchange cartridges, the capacity of the resin must be considered. Samples of high ionic strength or high Cr(III) concentration may displace Cr(III) from the cartridge and cause erroneously high results for Cr(VI). In such cases larger amounts of cation-exchange resin must be used, and the volume of sample passed through the cartridge must be minimized. Cartridges are available in several sizes and may be connected in series to achieve increased capacity. Any modifications made to the described conditions should be tested and verified before use.

Waters high in dissolved organic carbon may complex Cr(III) (Icopini

and Long, 2002) and prevent its retention by the cation-exchange resin. If waters to be tested are known or suspected to contain dissolved organic carbon at concentrations exceeding several mg/L, this should be tested by adding known amounts of Cr(III) standard to the sample. Higher than expected Cr(VI) concentrations are an indication that Cr(III) is not being retained by the resin.

Accuracy of the method: standards and spike recoveries

Demonstrating accuracy of the cation-exchange separation is challenging because no reference standards exist for redox species, and low concentrations of prepared standards may be difficult to maintain in their initial redox state. A series of standard solutions of single redox state was prepared in the laboratory, and Cr redox species were separated using the new method. The results, presented in figure 3, demonstrate that recoveries

were variable for the Cr(VI) solutions, with an average recovery over the concentration range tested of about 91 percent. Retention of Cr(III) appears to be excellent, with an average Cr(III) retention of about 99.8 percent.

Four Cr-containing samples, one each from the United Arab Emirates, North Carolina, Arizona, and the state of Washington, were prepared for analysis by spiking separate aliquots in the laboratory with 10, 20, or 30 µg/L Cr(III). Each solution was then divided into two subsamples. One set of 12 subsamples was separated by the cation-exchange method and analyzed by GFAAS. The second set of 12 subsamples was preserved, and then analyzed by ion chromatography according to USEPA method

218.6. Results, shown in figure 4, demonstrate that even for this diverse set of samples the two preservation and analysis methods have virtually equivalent capabilities to distinguish between Cr(VI) and Cr(III). The average recovery of Cr(VI) by USEPA method 218.6 was 98.3 percent, whereas the average recovery by the cation-exchange method was 98.0 percent. The anomalous result for sample UAE-30 from the cation-exchange method was not included in the recovery calculations. This sample is saline water with a specific conductance of more than 55,000 microSiemens per centimeter (µS/cm), for which procedural modifications may be needed to achieve good cation-exchange separation of the Cr redox species.

Comparison of results with those from alternative methods

Several groundwater samples from the Mojave Desert in California were analyzed for Cr(VI) using a modification of the Hach Company (1992) diphenylcarbazide direct colorimetric method, and for Cr(VI) and total Cr using the new cation-exchange method. Because some of the water samples may not have been preserved for optimal stabilization of Cr redox species, Cr redox species distributions may not always represent concentrations that were present at the time of collection. However, comparisons between the two analytical approaches are valid and may be illustrative. The results (data not shown) demonstrated favorable comparability with the modified diphenylcarbazide method, suggesting that, to the extent the diphenylcarbazide method is accurate, the new cation-exchange method is at least as accurate and is at least 10 times as sensitive.

Many samples from diverse sources were analyzed using the new cation-exchange method and using USEPA Method 218.6 (Arar and others, 1991). The results (fig. 5) illustrate that, for these samples and over the Cr(VI) range covered, the proposed method produces Cr(VI) concentrations virtually identical to EPA method 218.6.

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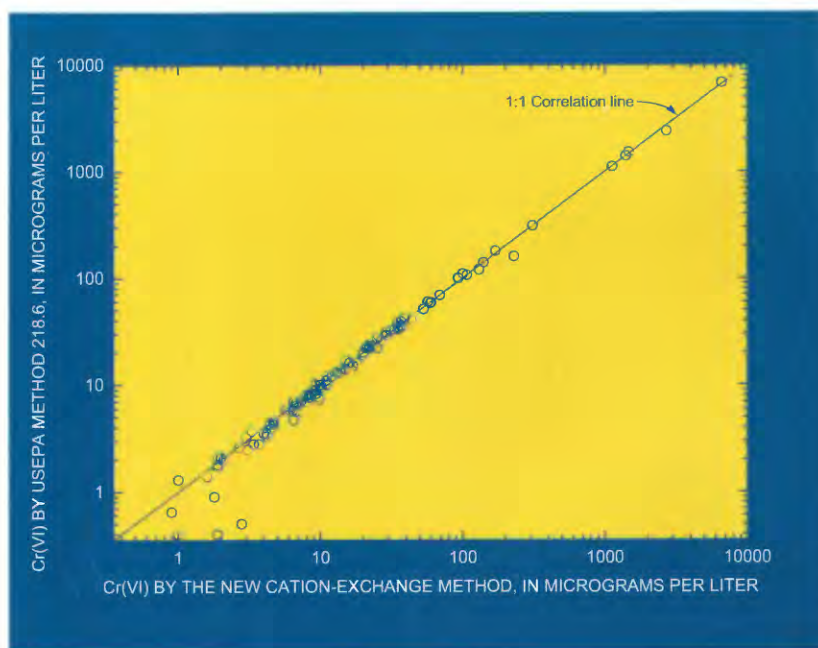


Figure 5. Comparison of Cr(VI) determinations by USEPA method 218.6 with determinations by the new cation-exchange method.

Additional details on the development of this method can be found in:

Ball, J.W., McCleskey, R.B., 2003, A New Cation-Exchange Method for Accurate Field Speciation of Hexavalent Chromium: U.S. Geological Survey Water-Resources Investigations Report 03-4018, 17 p.

Acrobat pdf versions of this fact sheet and the above report can be found at the Project web site:

http://wwwbr.cr.usgs.gov/projects/GWC_chemtherm/

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