Speciation of Chromium via Laser-Induced Breakdown Spectroscopy of Ion Exchange Polymer Membranes

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A new method for the speciation of ng/mL concentrations of Cr(III) and Cr(VI) solutions with analysis by laser-induced breakdown spectroscopy (LIBS) is reported. Speciation is achieved by pre-concentration of the chromium onto commercially available cation exchange polymer membranes. Chromium(III) is removed directly by cation exchange; chromium(VI) in the filtrate is reduced to Cr(III) and concentrated onto a second cation exchange membrane, affording independent measurement of both species. Large volumes of waters containing Cr(III) and Cr(VI) can be concentrated onto the membranes and directly analyzed by laser-induced breakdown spectroscopy. The estimated limit of detection corresponds to 500 ng of Cr on the membrane: if a solution volume of 1 L is used, then the detection limit corresponds to a solution concentration of 0.5 ng/mL. Excellent separation of the chromium species is attained. Results show that overall method efficiencies range from 94–116% and are independent of the matrix. The influence of pH has been measured, and although Cr(VI) converts to Cr(III) in acidic solutions, the total Cr recoveries are not appreciably influenced by pH over the range of natural waters (4 to 9). In addition, speciation was performed in the presence of a number of different cations and showed that the method is robust in many different and complex matrices.

Index Headings: **Laser-induced breakdown spectroscopy; LIBS; Chromium speciation; Hexavalent chromium; Ion exchange polymer membranes.**

INTRODUCTION

Trivalent and hexavalent chromium species play vastly different roles in mammalian systems. Trivalent chromium is considered an essential element to human survival. Chromium(III) deficiency has been linked to problems with growth and fertility as well as a diabetic-like state associated with impaired glucose tolerance.[1] Conversely, hexavalent chromium can be extremely toxic to mammalian systems. The toxicity of chromium(VI) is attributed to the strong oxidative properties of the hexavalent complexes and the ease of their transmission through cellular membranes.[2] Hexavalent chromium complexes are known to cause tumors, tissue damage, and lesions of the skin and respiratory tract in laboratory animals.[1]

The Toxic Release Inventory (TRI) reports the environmental release of chromium and chromium containing compounds between 1988 and 1999 at 134 million pounds and 527 million pounds, respectively.[3] Current regulations for chromium in potable water place the minimum reporting level (MRL) at 10 ng/mL and the maximum contaminant level (MCL) at 100 ng/mL. The U.S. Environmental Protection Agency (EPA) estimate 917 000 people are exposed annually to levels exceeding the MRL and 3000 people are exposed to levels exceeding the MCL.[3] While these values may be alarming, it should be noted that none of the surveys in the Occurrence Summary and Use Support Document for the Six-Year Review of National Primary Drinking Water Regulations differentiate between the (III) and (VI) chromium oxidation states.[3]

Presently, there is a critical need for a rapid, accurate, and sensitive method for the speciation of chromium. However, speciation proves difficult since the typical concentrations of chromium in natural waters lie in the low ng/mL range.[4] Determination of chromium species at very low concentrations requires the use of expensive hyphenated techniques such as liquid chromatography–inductively coupled plasma mass spectrometry (LC-ICP-MS)[5] and ion chromatography–inductively coupled plasma mass spectrometry (IC-ICP-MS).[6] Many labs prefer to use conventional workhorse instruments such as electrothermal atomic absorption spectrometry (ETAAS)[7] and inductively coupled plasma atomic emission spectrometry (ICP-AES)[8] in conjunction with a separation and preconcentration step.

The EPA has approved several methods for the speciation of chromium. EPA methods for chromium analyze either total chromium or the hexavalent species, but none of the approved methods allow for direct speciation of both oxidation states. Approved methods analyze Cr(VI) by chelation/extraction FAAS,[9–11] ion chromatography,[12,13] co-precipitation ETAAS,[14,15] differential pulse polarography,[16] and complexation/colorimetry.[17] Total chromium is determined by either FAAS[18,19] or by ETAAS.[20,21] Table I provides a summary of EPA approved methods for chromium analysis.

Several pre-concentration techniques have been developed for chromium speciation with conventional instruments, but these methods all measure total chromium, one of the two ionic species, and then infer the concentration of the remaining species by difference, rather than by direct analysis.[8,22–24] Methods that are capable of simultaneous analysis often rely on chelation or derivatization to create ionic species of the same charge, thus allowing for speciation on a single ion exchange column.[25–27] For example, ethylenediaminetetraacetic acid (EDTA) converts the cation Cr^{3+} to the anionic $Cr(EDTA)^{-}$ for simultaneous analysis with chromate (CrO_4^{2-}) on an anion exchange column.[26]

Other speciation methods rely on the pre-concentration of one oxidation state onto ion exchange resins. Following pre-concentration, either reduction or oxidation converted the remaining form for analysis on the same resin. Under normal conditions, Cr(III) is found in aqueous solutions as the Cr^{3+}, $Cr(OH)^{2+}$, and $Cr(OH)_2^{+}$ cations and

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TABLE I. Summary of methods approved by the USEPA.

Method	Description	Range	Interferences	Reference
218.3	Cr(VI) analyzed by	1.0–25	High metal concentrations	9
218.4	chelation/	ng/mL		10
7197	extraction FAAS			11
218.6	Cr(VI) analyzed by ion	0.23–5000	Column overload in highly	12
1636	chromatography	ng/mL	anionic solutions	13
218.5	Cr(VI) analyzed by	5.0–100	Sulfate or chloride > 1000	14
7195	$PbCrO_4/PbSO_4$ co-precipitation followed by ETAAS	ng/mL	μg/mL	15
7198	Cr(VI) analyzed by differential pulse polarography	10.0–5000 ng/mL	Copper ion concentration > [Cr(VI)]	16
7196A	Cr(VI) analyzed by complexation/ colorimetry	0.5–50 μg/mL	Molybdenum, vanadium, and mercury salts	17
218.1	Cr total analyzed by	0.5–10	Ionization interferences in	18
7190	direct aspiration FAAS	μg/mL	highly alkaline solutions	19
218.2	Cr total by direct	5.0–100	Low concentration calcium	20
7191	ETAAS	ng/mL	and/or phosphate	21

as the amorphous precipitate $Cr(OH)_3$; Cr(VI) is found as anions, typically CrO_4^{2-}, $HCrO_4^-$, or $Cr_2O_7^{2-}$, depending on pH and reduction potential.[28] The difference in charge is the basis for the separation and concentration. Excellent results have been achieved by sequential speciation ETAAS[29,30] and FAAS,[31] but no attempts have been made to extend chromium speciation to laser-induced breakdown spectroscopy.

Laser-induced breakdown (LIBS) refers to the process by which the focused energy of a laser beam exceeds the breakdown threshold value at the focal point and forms a plasma.[32,33] When the energy from a laser is properly focused onto an analytical sample, the resulting plasma may be used for mass removal and as an excitation source in atomic emission spectroscopy. Atoms of analyte are raised to an excited state in the high-temperature plasma and emit characteristic radiation as they return to the ground state. Recently LIBS was used for the analysis of the metals regulated by the Resource Conservation and Recovery Act (RCRA), including Cr^{3+}, bound to ion exchange polymer membranes. The calculated limit of detection was 130 ng/mL.[34]

In this paper, results from the direct pre-concentration of hexavalent and trivalent chromium onto commercially available cation exchange polymer membranes are reported. We also show the first use of laser-induced breakdown spectroscopy for elemental speciation. The use of the ion exchange membranes offers many distinct advantages for the speciation of chromium. Previous experiments done in our lab found that the limit of detection can be extended to lower concentrations by increasing the volume of solution drawn through the ion exchange membrane.[34] Additionally, the limited number of reagents needed for conditioning the membrane and the field portable capability of LIBS suggests that separation of the chromium species may be performed on location. LIBS is inherently a real-time technique that requires minimal sample pretreatment. It may take several minutes to filter samples, but only seconds to perform LIBS measurements. Extending this process to on-site analysis would minimize problems encountered when acidic preservatives change the speciation of chromium in natural waters. Finally, matrix effects present in the original sample are alleviated; analyte atoms all enter the common matrix of the extraction membrane.

EXPERIMENTAL

Ion Exchange Membrane. Chromium solutions can be speciated using ion exchange membranes by taking advantage of the difference in charge between the two naturally occurring oxidation states, Cr(III) and Cr(VI). Cation exchange was performed on 10 mm round segments of 3M Empore™ High Performance Extraction Disks–Chelating (3M Corp, St. Paul, MN). The cation exchange polymer has a poly(styrenedivinylbenzene) copolymer support functionalized by iminodiacetic acid groups. Filtration was performed using a locally fabricated 25-mL borosilicate glass funnel with an 8.2 mm inner diameter. The membranes were conditioned according to the manufacturer's instructions, and the sample was directly filtered. No pretreatment was required. The resulting membranes were dried and analyzed by LIBS.

Apparatus. A Continuum Surelite II-10 Nd:YAG laser (Santa Clara, CA) operated at 1064 nm with 120 mJ pulses was used as the ablation source. The laser beam was focused by a plano-convex quartz lens with a focal length of 75 mm. The focal point was set at the surface of the sample to minimize breakdown above the surface. Low power density and narrow focus minimized burning. Samples were placed on a mechanical X–Y stage, model 451P Ball Slide (Del-Tron Precision, Inc., Bethel, CT) and stage movement was controlled by model K92111-P2 digital linear actuated stepper motors. Emission from the plasma was collected using a 25 mm diameter plano-convex quartz lens with a focal length of 100 mm and was transferred into a fiber-optic cable. The fiber-optic cable transmitted the emission radiation to a Mechelle 7500 DiCAM-PRO echelle spectrometer (Multichannel Instruments AB, Stockholm, Sweden). Camera control and spectral data collection were accomplished by a Dell OptiPlex GX1 computer running Multichannel Instruments software. Spectra were displayed by GRAMS/AI version 7.01 spectroscopic data analysis software (Galactic Industries Corporation, Salem, NH). A block diagram

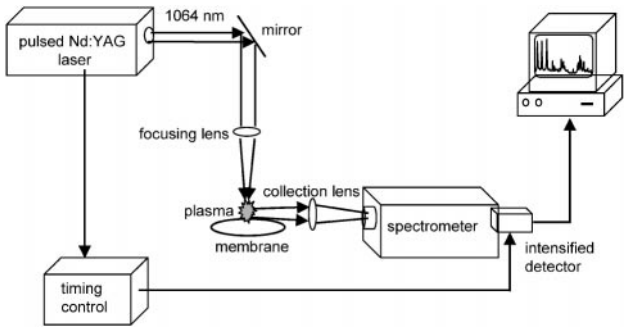

FIG. 1. Block diagram of the LIBS instrumentation.

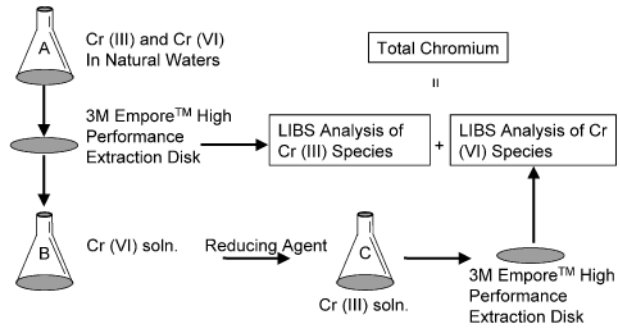

FIG. 2. Block diagram of speciation process.

of the LIBS instrumentation is shown in Fig. 1, and individual components are specified in Table II.

Materials. Chromium solutions with Cr(III) and Cr(VI) concentrations similar to those found in natural waters (5–200 ng/mL) were pre-concentrated onto ion exchange membranes. Calibration standards were also made in dilute solutions and pre-concentrated onto ion exchange membranes. Membranes were then analyzed for chromium content by LIBS. Stock solutions of chromium (III) nitrate (Mallinckrodt Specialty Chemicals Co., Paris, KY) and potassium dichromate (Fisher Scientific Co., Fair Lawn, KY) were prepared and diluted in deionized water. Daily working solutions were prepared by dilution from the stock. The extraction membranes were conditioned according to the manufacturer's instructions using the reagents as follows: hydrochloric acid, ammonia, and ammonium acetate (all from Fisher Scientific Co., Fair Lawn, KY). Cr(VI) species were reduced using hydroxylamine sulfate (Fisher Scientific Co., Fair Lawn, KY).

TABLE II. LIBS instrumentation.

Laser components	
Laser	Continuum Surelite II-10 Nd:YAG laser (Santa Clara, CA)
Laser pulse	120 mJ, 7 ns
Ablation spot	0.3 mm diameter
Mirrors	25 mm dia., 45° high energy, 1064 nm, 99.9% R (Newport, Irvine, CA)
Optics	25 mm dia., 75 mm focal length plano-convex lens (Coherent, Auburn, CA)
Power meter	Molectron Detector, Inc. Model EPM1000 Single-Channel Joulemeter/Powermeter (Portland, OR)
Spectroscopic components	
Optics	25 mm dia., 100 mm focal length plano-convex lens (Coherent, Auburn, CA)
Detector	Mechelle 7500 DiCAM-PRO with echelle spectrophotometer and Mechelle Software (Multichannel Instruments AB, Stockholm, Sweden)
Wavelength range	200–1000 nm
Delay time	3 μs
Integration time	30 μs
Data analysis	
Computer	Dell OptiPlex GX1 (Dell Computers Corporation, Round Rock, TX)
Software	GRAMS/AI version 7.01 Spectroscopic Data Analysis Software (Galactic Industries Corporation, Salem, NH)
	Microsoft Excel 2000 (Microsoft Corporation, Redmond, WA)

Samples made in matrices other than deionized water were spiked standards (High-Purity Standards, Charleston, SC) unless otherwise stated.

Pre-Concentration Procedure. Chromium solutions were filtered through conditioned extraction membranes (~10 mL/min) using suction from an aspirator and allowed to dry. Suction was broken and the membranes (now containing Cr(III) species) were removed for analysis of Cr(III) species. The resulting 50 mL filtrates (free from Cr(III) species) were treated with hydroxylamine sulfate and filtered through a second conditioned extraction membrane, dried, and removed for analysis of Cr(VI) species. Figure 2 shows a block diagram for the speciation process.

It is possible to remove Cr(VI) with an anion exchange membrane, thus eliminating the reduction step. Anion exchange membranes, however, function on the ion-exchange principles and lack the selectivity of the cation (chelation) system, increasing the potential for matrix interferences in high-salt solutions.

RESULTS AND DISCUSSION

Optimization of Parameters. The emission signal from a LIBS plasma is time dependent, and most researchers use the time dependence to optimize signal-to-noise ratio (S/N). A delay of 3 μs was used to discriminate against the early-occurring continuum emission, and the emission was integrated for 30 μs following the delay. These times were chosen based on the results shown in Fig. 3. Although S/N remains high up to 12 μs after the laser pulse, spectra earlier in time allow an internal standard ratio to the H_α line emission from hydrogen in the poly(styrenedivinylbenzene) copolymer support on the membrane.

Power density, measured as irradiance (GW/cm^2), was

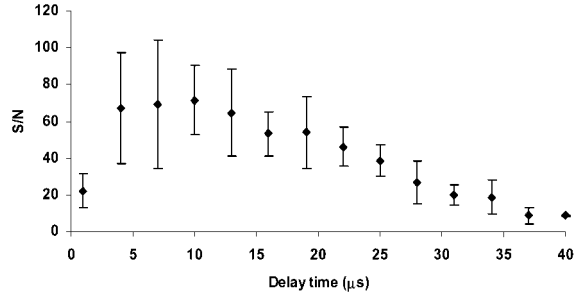

FIG. 3. Signal-to-noise ratio as a function of delay time. Each point was integrated for 3 μs. Error bars represent ± one standard deviation.

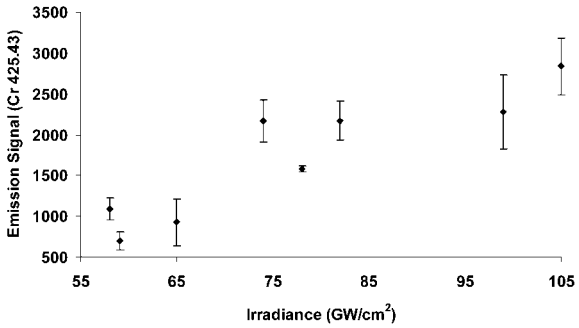

FIG. 4. Optimization of irradiance. Optimum conditions correspond to energy of about 120 mJ focused at the surface of the membrane. Error bars represent ± one standard deviation.

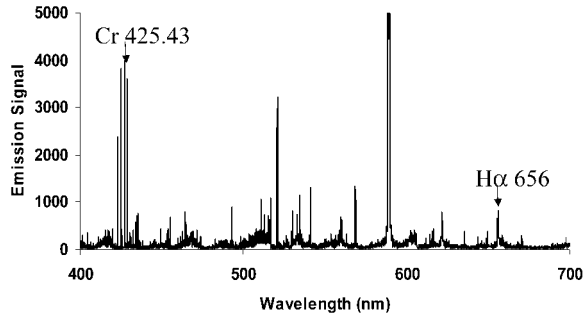

FIG. 6. Representative LIBS spectrum. The Cr 425.43 and the Hα lines are used for calibration. Other important lines include Ca 422.67, Cr 427.48, Cr 428.97, Cr 520.84, and the sodium doublet: Na 588.99 and Na 589.59.

optimized using the 3 μs delay and 30 μs integration. As can be seen in Fig. 4, the emission signal increases proportional to increased irradiance. Above 105 GW/cm^2 significant burning occurs on the membrane surface. An irradiance of 95–100 GW/cm^2 was used for all analyses, corresponding to an energy of about 120 mJ focused at the surface of the membrane.

Last, the optimum number of unique laser shots was determined based on the increase in signal-to-noise ratio in relation to the number of measurements taken. Raster patterns were used to collect multiple laser shots at unique locations. As can be seen in Fig. 5, no significant enhancements in S/N were observed after 10 shots per spectrum, presumably due to source flicker noises. For all analytical samples, 10 unique locations were ablated and averaged to represent a single spectrum.

Calibration. Membranes containing Cr(III) were prepared for calibration following the procedure outlined in the pre-concentration section above. Emission was collected for 30 μs following a 3 μs delay. Ten laser shots were collected per spectrum and emission from the Cr 425.43 line was monitored. Then, the ratio (Cr 425/H_α) was used as an internal standard correction to minimize shot-to-shot variability. A representative spectrum generated at optimum conditions is shown in Fig. 6. Standard solutions containing 1 to 40 μg of Cr were analyzed at optimum conditions; a full-range calibration plot is shown in Fig. 7A. The response is linear in the 1–10 μg range (Fig. 7B), and regression parameters for calibration graphs in this range were very reproducible over the course of several weeks.

Identical signals were obtained from solutions containing 1.0 μg of Cr(III) in 50, 100, and 1000 mL samples. These results are similar to previous studies in which the effect of analyte volume was studied in detail in the range from 5 to 1000 mL.[34]

Effect of pH. The iminodiacetic acid functional group on the membrane is sensitive to changes in pH. At very low pH, the carboxylate groups of the iminodiacetic acid are neutral and the membrane is inactive. At pH ≥ 5, both carboxylate groups are deprotonated, allowing the membrane to function as a bidentate chelator. The following experiment was conducted to determine the membrane performance in different pH solutions.

Two trivalent cations, Cr^{3+} and Sc^{3+} were added to solutions buffered in the range of natural waters (4–9). The solutions were filtered through conditioned membranes, the cations were removed from the membranes by acid digestion, and the resulting extract was diluted to 50 mL with deionized water. Chromium and scandium recoveries were calculated based on comparison to a spiked DI reference that had not been filtered; Fig. 8 shows the results. There is no discernable trend in recovery as a function of pH and the method is applicable over the pH range of natural waters.

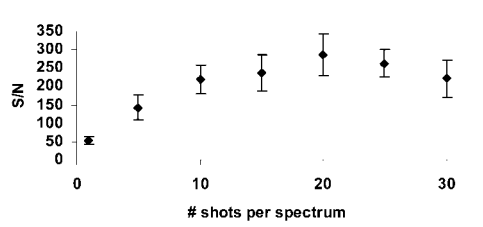

FIG. 5. Optimization of the number of shots per spectrum. No significant enhancement was seen after 10 shots per spectrum, presumably due to source flicker noises. Error bars represent ± one standard deviation.

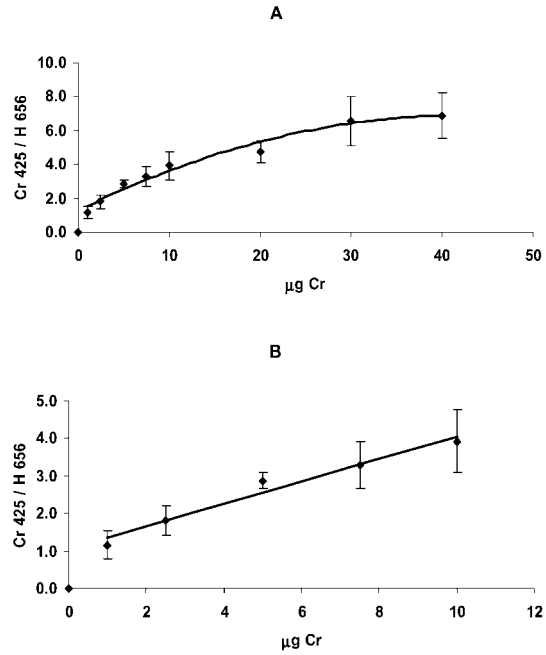

FIG. 7. Typical calibration obtained from LIBS analysis at optimum conditions. Error bars represent ± one standard deviation.

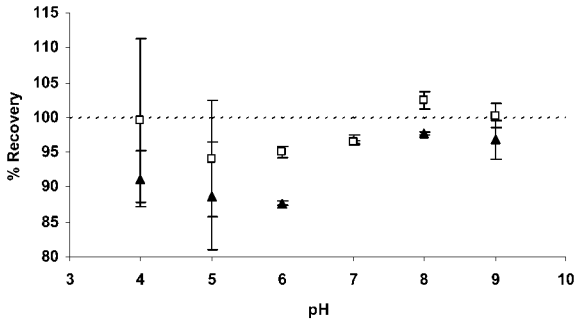

FIG. 8. Chromium (▲) and scandium (□) recovery as a function of pH. There is no discernable trend in recovery as a function of pH and the method is applicable over the pH range of natural waters. Error bars represent ± one standard deviation.

Method Performance in Spiked Matrices. The influence of the sample matrix was evaluated with 50 mL each of simulated rainwater and certified wastewater (High-Purity Standards, Charleston, SC), tap water (City of Columbia, SC), Instant Ocean®, and pH 9 buffer all spiked with 4 μg Cr(III) and 4 μg Cr(VI). Recoveries from these matrices are shown in Table III. Net recoveries from the mass balance of both species ranged from 94–116% with a mean of 107%. Since Cr(VI) is stable at higher pH,[28] excellent speciation is achieved in the pH 9 system: 117% Cr(III), 103% Cr(VI), and 110% net Cr. Inter-conversion of chromium species was prevalent in low pH samples. The simulated rainwater was buffered at pH 4.5 and showed 162% Cr(III), 55% Cr(VI), and 108% net Cr. Certified wastewater samples were preserved in 10% nitric acid and understandably showed no detectable Cr(VI). Tap water lacks buffering capacity and addition of acidified Cr(III) stock solution caused inter-conversion: 207% Cr(III), 4% Cr(VI), and 106% net Cr. Instant Ocean, while buffered, also contains significant amounts of dissolved organic matter,[35] providing a reducing environment and no detected Cr(VI): 233% Cr(III), 0% Cr(VI), and 116% net Cr. Precision ranged from ±5 to 40 %RSD, with a mean of 22 %RSD. These values (shown in Table III) are comparable to the ranges expected for LIBS.[36]

Speciation in spiked matrices also allowed investigation of matrix-induced errors caused by competitive binding of multi-valent cations. Specifically, recoveries from simulated wastewater (94%) and Instant Ocean (116%) prove that the method is robust in complex matrices. Simulated wastewater samples contained 50 μg each Al, Co, Fe, Mo, Sr, and V, and 12.5 μg each Be, Cd, and Ni. Instant Ocean samples contained 64 800 μg Mg, 21 250 μg Ca, and 350 μg Sr. Minor multi-valent and all monovalent ions are omitted since the iminodiacetic acid functional groups are not sensitive to singly charged species.

Comments on Limit of Detection. The method limit of detection in terms of concentration cannot be readily defined because passing a larger volume of sample through the membrane will increase spectroscopic response. The limit of detection on the membrane is estimated to be 500 ng of chromium (half the amount in the lowest standard). If a solution volume of 1 L is used, then the detection limit corresponds to a concentration of 0.5 ng/mL. Decreasing the limit of detection by increasing the sample volume increases the time of analysis; it takes about 1.5 h to filter a 1-L sample, and most labs are unwilling to spend more time on an individual sample. A 100 mL sample with Cr content at the EPA's MRL (10 ng/mL) would match the lowest calibration standard, 1 μg. The upper limit is the total amount of chromium that may be added to a membrane before saturation. Chromium was added to the ion exchange membrane until the resulting filtrate began to show detectable amounts of chromium. The membrane was saturated after 4000 μg of Cr was added. The highest point of the linear calibration (10 μg) was well below the saturation point.

TABLE III. Chromium recovery from spiked matrices.

Matrix	% Recovery Cr (total) ± 1 σ	Cr(III)	Cr(VI)
pH 9	110 ± 13	117	103
Simulated rainwater	108 ± 38	162	55
Certified wastewater	94 ± 5	188	ND
Tap water	106 ± 40	207	4
Instant Ocean	116 ± 7	233	ND
Mean	107 ± 21		

CONCLUSION

Cation exchange membranes pre-concentrate chromium and provide accurate and sensitive speciation. The technique provides a unique advantage in that no preservatives, derivatizing agents, or matrix modifiers are required. Also, a limited number of reagents are needed for conditioning the membranes, and the field portable nature of LIBS analysis suggest that separation may be performed on location.

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