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Determination of Total Chromium in Seawater by Isotope Dilution Sector Field ICPMS Using GC Sample Introduction

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A method for the accurate determination of total Cr in seawater by isotope dilution (ID) sector field inductively coupled plasma mass spectrometry (SF-ICPMS) using GC as a means of sample introduction is described. Chromium was reduced to Cr^{III} by addition of SO_2-saturated water and derivatized with trifluoroacetylacetonate (TFA) to form volatile $Cr(TFA)_3$. Derivatized analyte was either extracted into hexane or directly sampled by solid-phase microextraction (SPME) using a poly(dimethylsiloxane)-coated fused-silica fiber for GC/SF-ICPMS analysis. With medium resolution required to efficiently separate argide, argon chloride and oxide interferences, a concentration of 0.154 ± 0.013 ng mL^{-1} (1 SD, $n = 4$) was obtained for Cr in NRCC seawater CRM CASS-4 using a 1-μL hexane extract, in agreement with the certified value of 0.144 ± 0.029 ng mL^{-1} (95% confidence interval). A detection limit of 20 pg mL^{-1} was achieved. Low-resolution GC/SF-ICPMS in combination with solvent-free SPME sampling effectively eliminated spectroscopic interferences, yielding a concentration of 0.132 ± 0.004 ng mL^{-1} (1 SD, $n = 4$) for Cr in CASS-4 with a method detection limit of 3.9 pg mL^{-1}. By comparison, SPME sampling with GC/SF-ICPMS in medium-resolution mode provided a concentration of 0.146 ± 0.013 ng mL^{-1} (1 SD, $n = 4$) and a method detection limit of 9.1 pg mL^{-1}.

Trace element determinations in seawater provide a challenge for analytical chemists because of high concentrations of dissolved solids (3.5 wt %) and typically less than nanogram-per-milliliter concentrations of analytes. Over the past decade, clean sampling techniques developed by researchers such as Bruland et al.[1] have been combined with modern developments in sensitive instrumentation to make reliable and robust determinations possible.

Chromium has entered the environment via many industrial applications, including the galvanization, steel, leather, and paint industries. Interest in measuring chromium in natural waters is significant because of concerns over the toxicity of Cr^{VI} as a carcinogen and Cr^{III} as an essential element.[2−4] Cr^{VI} is a major form of inorganic Cr that exists in natural waters.[5]

Currently, only few reports address the determination of total Cr in seawater.[5−12] Commonly used techniques for total Cr assessment often involve some mode of preconcentration, such as chelation extraction,[5,9−11] followed by quantitation using gas chromatography (GC), GC/mass spectrometry (GC/MS), and graphite furnace atomic absorption spectrometry (GFAAS) or following sorption on columns[6−8,12] with GFAAS, inductively coupled plasma atomic emission spectrometry (ICPAES), and inductively coupled plasma mass spectrometry (ICPMS) detection.[12]

ICPMS has been used as a sensitive detector for Cr^{III} and Cr^{VI} determination in combination with chromatographic separation,[2,4,12−18] but little information is available on the determination of total Cr in seawater by ICPMS,[12] in which concentrations are typically[5−12] in the range of 100−200 pg mL^{-1}. One of the most attractive features of ICPMS is its capability for determination of elemental isotopic composition. If two interference-free isotopes of a given element can be found, isotope dilution ICPMS (ID ICPMS) can be applied to yield enhanced accuracy and precision over other calibration techniques.[19,20]

Samples having high dissolved solid content, such as seawater, are still preferably not analyzed directly by ICPMS, because

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blockage of the cones and deposition of the sample matrix on ion lenses typically degrade analytical results. Furthermore, polyatomic interferences arising from matrix constituents must be corrected for in order to ensure accuracy. Simple dilution of the seawater prior to ICPMS analysis can minimize the former effects to some extent, but this approach was avoided in this study because of the already very low concentration of analyte. Fortunately, polyatomic interferences from $^{40}Ar^{12}C$, $^{40}Ar^{13}C$, $^{36}Ar^{16}O$, $^{36}Ar^{17}O$, $^{35}Cl^{17}O$, and $^{35}Cl^{18}O$ present with quadrupole ICPMS can be overcome using sector field (SF) ICPMS or reaction cell technology, as demonstrated by recent studies relating to Cr speciation.[4,16]

Enhanced detection power and elimination of many interferences can be achieved using various column separation methods.[6−8,12] Additionally, application of vapor generation, which converts nonvolatile/ ionic compounds to gaseous species,[21] permits gaseous sample introduction, which may provide a 50-fold improvement in sample introduction efficiency over conventional nebulizer-based systems. Since the late 1950s until the early 1980s, volatile metal chelates were commonly used for quantitation by gas chromatography,[22] and a vast knowledge base of volatile metal chelates exists which is currently grossly underutilized. Because most metals can form volatile chelates, their use for gas-phase separation/ preconcentration/ sample introduction remains to be explored.

Determination of Cr based on volatile chelate formation and GC detection has been employed by many research groups, including this laboratory. An earlier method[9] for quantitation of total Cr in seawater utilized derivatization with trifluoroacetylacetonate (TFA) to form volatile $Cr(TFA)_3$ which was extracted into hexane for GC/ MS detection with isotope dilution calibration. In general, sample preparation for GC analysis is usually time-consuming, and organic solvents used in the liquid−liquid extraction may be toxic and require waste processing. In an effort to simplify sample preparation and minimize the use of organic solvent while retaining the merits of GC, solid-phase microextraction (SPME) was introduced by Pawliszyn and co-workers[23,24] in the early 1990s. Since 1993, following the commercialization of SPME, this sampling technique has enjoyed widespread acceptance as a consequence of its simplicity, relatively low cost, and ease with which analytes can be transferred to the GC column. The application of SPME to inorganic analysis was recently reviewed by Mester et al.[25] and was recently evaluated for use in the determination of total Cr in seawater by GC-ECD and GC/ MS.[10] One drawback noted in the study was the lengthy analysis time needed (at least 15 min per run) when a 30-m length of column was typically used for GC separation.

The objective of this study was to evaluate the advantages of the high sensitivity, high resolution, and capability for isotope dilution offered by SF-ICPMS in combination with a short (0.5-m) GC column for the rapid and accurate determination of Cr in seawater.

EXPERIMENTAL SECTION

Instrumentation. The sector field inductively coupled plasma mass spectrometry (SF-ICPMS) instrument used was a ThermoFinnigan Element2 (Bremen, Germany) equipped with a Scott-type double-pass glass spray chamber and a PFA self-aspirating nebulizer (Elemental Scientific, Omaha, NE). A plug-in quartz torch with a sapphire injector and a Ag guard electrode were used. Optimization of the Element2 was performed as recommended by the manufacturer. Detector dead time was determined following the procedure of Nelms et al.[26] (method 2); i.e., a plot of $^{238}U/^{235}U$ ratio versus U concentration was constructed using solution concentrations of 0.5, 1.0, and 2.5 ng mL^{-1}, from which a dead time of 18 ns was derived.

A Varian 3400 gas chromatograph (Varian Canada Inc. Georgetown, ON, Canada) equipped with either a 0.5-m MXT-5 metal column (5% diphenyl, 95% poly(dimethylsiloxane), 0.28 mm i.d. with a 0.5-μm film thickness) or standard 30-m column was used for introduction of the derivatized analyte. The GC was coupled to the SF-ICPMS instrument using a homemade interface and a transfer line similar to that described previously.[27,28] The latter was maintained at 220 °C using a flexible heating cable.

A 10-μL liquid sampling syringe (Hamilton Company, NV) was used for the injection of samples of the hexane extract.

A manual SPME device, equipped with a fused-silica fiber coated with a 100-μm film of poly(dimethylsiloxane) (Supelco, Bellefonte, PA) was used for the direct sampling of derivatized $Cr(TFA)_3$ from aqueous solutions. For convenience, SPME sampling was conducted in a regular fume hood. The influence of SPME extraction time, pH of sample, concentration of derivatization agent, and GC injection port temperature were all optimized using a standard 30-m length of column based on both electron capture and MS detection,[10] and as such, conditions utilized in this study were as follows: SPME extraction time, 25 min; pH of sample, 5.2; sample volume, 20 mL; TFA concentration, 25% (v:v) in methanol; injector temperature, 250 °C.

Reagents and Solutions. Acetic acid, nitric acid, and methanol were purified in-house prior to use by subboiling distillation of reagent grade feedstock in a quartz still. Environmental grade ammonium hydroxide was purchased from Anachemia Science (Montreal, PQ, Canada). OmniSolv methanol (glass-distilled) and hexane were purchased from EM Science (Gibbstown, NJ). High-purity deionized water (DIW) was obtained from a NanoPure mixed-bed ion-exchange system fed with reverse osmosis domestic feedwater (Barnstead/ Thermolyne Corp, Dubuque, IA). Trifluoroacetylacetonate (TFA) and chromium trifluoroacetylacetonate, $Cr(TFA)_3$, were purchased from Sigma Aldrich Canada Ltd. (Oakville, ON, Canada). A TFA solution (25% v/ v) was prepared by dissolving an appropriate amount of pure compound in methanol. A 1000 μg mL^{-1} stock solution of natural abundance

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Cr was prepared by dissolution of the high-purity metal (Johnson, Matthey & Co. Limited, London, U.K.) in HCl. Working standards, which were used for ^{53}Cr reversed-spike isotope dilution, were prepared by serial dilution of the stock with DIW containing 1% HNO_3.

Enriched ^{53}Cr isotope was purchased from Oak Ridge National Laboratory as Cr_2O_3. A ^{53}Cr stock solution of ~310 μg mL^{-1} was prepared by dissolution of the metal oxide in a few milliliters of perchloric acid, followed by dilution with DIW. A working spike solution containing 0.40 μg mL^{-1} Cr was prepared by volumetric dilution of the stock in 1% HNO_3.

A pH 9.5 ammonium acetate solution (NH_4Ac) was prepared by mixing 10 mL of NH_4OH (20−22%) with 4 mL of glacial acetic acid and diluting to 100 mL with DIW. Water, saturated with sulfur dioxide, was prepared by bubbling sulfur dioxide gas (Air Products, Ottawa, ON, Canada) through 100 mL of DIW at room temperature in a fume hood until the solution was saturated.

Coastal seawater CRM CASS-4, used as test sample for method development, was obtained from the Institute for National Measurement Standards, National Research Council Canada (Ottawa, ON, Canada).

Sample Preparation for SPME. All polyethylene bottles, septa, and stirring bars were first cleaned with a few percent decon solution and then soaked in 1:1 reagent grade nitric acid for several days. After rinsing with DIW, these bottles were filled with 1% ultrapure nitric acid until used. The derivatization and extraction procedure selected was similar to that reported previously.[9−10] Sample preparation was undertaken in a class-100 clean room. Three procedural blanks and four samples of CASS-4 were prepared. Aliquots of 20 mL of CASS-4 (or 20 mL of DIW, acidified to a pH of 1.5, used for blanks) were spiked with appropriate amounts of ^{53}Cr-enriched spike and 200 μL of saturated SO_2 solution and allowed to stand for 15 min. The concentration of ^{53}Cr-enriched spike was verified by reversed-spike isotope dilution analysis using two independently prepared natural abundance Cr standards and SF-ICPMS detection with pneumatic sample aspiration. Samples were pH-adjusted to 5.2 with 2.5 mL of NH_4Ac solution. After 50 μL of 25% TFA in MeOH was added, the bottles were capped and heated in a water bath at 75 °C for 2 h. After cooling, a precleaned stirring bar was introduced, and the bottle was capped with a PTFE-coated silicone rubber septum. The SPME needle was inserted through the septum, and direct sampling of the aqueous phase was performed for 25 min during stirring. The collected derivatized analyte was then desorbed from the SPME fiber onto the GC column and transported to the SF-ICPMS for measurement.

Sample Preparation for Liquid−Liquid Extraction. Derivatization of Cr was as described above. Three procedural blanks and four samples of CASS-4 were prepared. After derivatization, 2 mL of hexane was added, and liquid−liquid extraction was completed by manual shaking for 5 min. The organic layer was transferred to a small precleaned glass vial and evaporated on a hot plate at 70 °C in a class-10 fume hood to a volume of ~50 μL. One microliter of this extract was injected for GC/SF-ICPMS analysis.

Data acquisition on the Element2 was manually triggered prior to the injection of the sample onto the GC. Both ^{52}Cr and ^{53}Cr were simultaneously monitored. A mass bias correction solution of 500 ng mL^{-1} natural abundance $Cr(TFA)_3$ was introduced between samples to permit a mass bias correction factor to be determined. At the end of the chromatographic run, the acquired raw data were transferred to an off-line computer for further processing using in-house software, which yields both background-corrected peak height and peak area information. Peak height response was used to optimize performance, but only peak areas were used to generate $^{52}Cr/^{53}Cr$ ratios, from which the analyte concentration in the seawater was calculated.

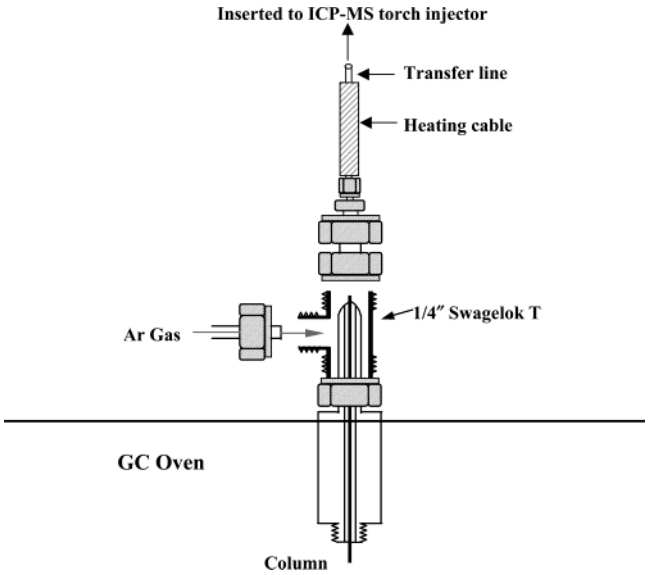

Figure 1. Schematic of the GC/SF-ICPMS interface.

RESULTS AND DISCUSSION

Optimization of the GC/SF-ICPMS System. Optimization of the SF-ICPMS system was undertaken as recommended by the manufacturer using liquid sample introduction of a 1 ng mL^{-1} multielement standard to achieve stable and high sensitivities for Li, In, and U. Mass calibration was performed only once per week because of the good stability of the Element2. The plasma was then extinguished, and the spray chamber and nebulizer assembly were replaced with the heated GC transfer line and its ball joint adapter. The PTFE transfer line was shrouded in a flexible heating cable to permit control of the temperature in the range of 30−300 °C, as shown in Figure 1, and extends from the GC interface to the base of the torch. Thereafter, the inner PTFE transfer line is not heated and terminates 5 mm below the injector tip.

The distance between the injector tip and the end of the transfer line had no significant effect on the resulting sensitivity over the range 0−12 mm; consequently, a 5-mm distance was used in this study. It was also found that the length of the transfer line had little effect on the analyte peak shape, because of a short residence time. Therefore, for flexibility and ease of handling of the GC/SF-ICPMS, a 150-cm-long heated PTFE line was used in this study.

The Ar carrier gas flow rate is related to that of the He effluent from the GC column as it was introduced through a sidearm of the interface and was optimized for a He pressure of 40 psi using the short GC column (0.5 m). Ar carrier gas flow in the range of 0.2−0.45 L min^{-1} was optimized by examining response following

Table 1. GC and ICPMS Operating Conditions

	GC
injection mode	splitless
injection volume	1 μL
injector temperature	250 °C
interface temperature	270 °C
columns	0.5-m column: MXT-5 (0.5 m × 0.28 mm × 0.5 μm); 30-m column: MXT-5 (30 m × 0.28 mm × 0.5 μm)
carrier gas	He at 40 psi, 1.2 mL min^{-1}
oven programs	120 °C (0.1 min) to 200 °C at 30 °C min^{-1} for 0.5-m column and 60 °C (1 min) to 260 °C at 30 °C min^{-1} (5 min) for 30-m column
	Element2
rf power	1150 W
plasma Ar gas flow rate	15.0 L min^{-1}
auxiliary Ar gas flow rate	1.05 L min^{-1}
Ar carrier gas flow rate	0.34 L min^{-1} (0.5-m column) and 0.275 L min^{-1} (30-m column)
sampler cone (nickel)	1.1 mm
skimmer cone (nickel)	0.8 mm
lens voltage	focus, −844 V; *x* deflection, −1.37 V; *y* deflection, 1.67 V; shape, 102 V
dead time	18 ns
resolution	300 and 4000 (mass offset and lock mass features used)
data acquisition	E-scan, 600 passes (4500 passes for 30-m column), 5%(100%for MR) mass window, 0.001-s settling time, 0.0050-s sample time

injections of 1 μL of 500 ng mL^{-1} Cr(TFA)$_3$ standard solution in hexane under medium resolution (MR) to separate argon carbide interferences from the Cr isotopes. Highest sensitivity was found using flow rates in the range of 0.325−0.350 L min^{-1}; sensitivity decreased gradually beyond this range, and thus, an optimum Ar carrier gas flow rate of 0.34 L min^{-1} was selected for the dry plasma conditions when using the 0.5-m column. An optimum Ar carrier gas flow rate of 0.275 L min^{-1} was found for the 30-m column.

The effect of transfer line temperature on the analyte sensitivity and peak shape was investigated in the range of 60−270 °C using injections of 1 μL of 500 ng mL^{-1} Cr(TFA)$_3$ standard solution under MR. As shown in Figure 2a, no significant difference in sensitivity was evident at any temperature; however, a notable effect on peak shape does occur, with pronounced peak tailing at 60 °C. The peak width at 5% peak height decreased from 10 to 8 s as the transfer line temperature increased from 60 to 220 °C, and peak symmetry correspondingly improved. No further improvements were achieved as temperature was increased to 270 °C. Thus, a transfer line temperature of 220 °C was selected for final measurements.

The initial column temperature also had a significant effect on the sensitivity and peak shape using the 0.5-m column. The Cr(TFA)$_3$ is quickly eluted from the 0.5-m column, and thus, a 0.1-min hold at the initial column temperature was used, after which the temperature was quickly ramped to 200 °C at 30 °C min^{-1} to minimize the total analysis time. As shown in Figure 2b, peak height increased significantly from 10 000 to 5 000 000 cps while peak width decreased from 22 to 1 s (at 5% peak height) as the initial column temperature was increased from 60 to 180 °C. Although better sensitivity could be obtained using an initial column temperature above 140 °C, the number of sampling points defining the peak shape above 5% peak height decreased significantly from 46 at 120 °C (8 points over the rising edge) to 26 (4), 5 (2), and 4 (2) at temperatures of 140, 160 and 180 °C, respectively. A compromise condition of 120 °C was selected for initial column temperature in the final study to ensure accurate sampling of peak shape and best sensitivity. Optimized conditions are summarized in Table 1.

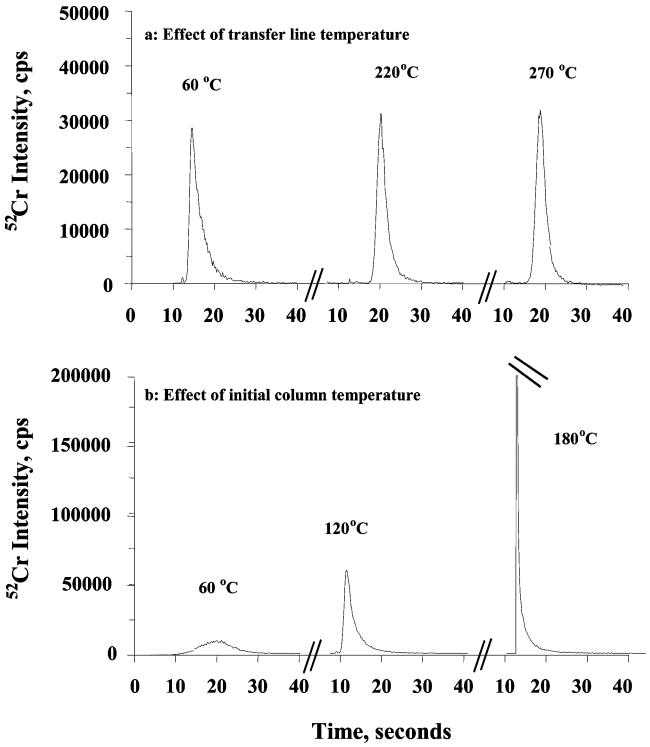

Figure 2. Chromatograms obtained from 1-μL injection of a 500 ng mL^{-1} Cr(TFA)$_3$ standard solution in hexane with GC/SF-ICPMS short column under MR: a, effect of transfer line temperature; b, effect of initial column temperature.

Optimization of SPME with GC Sample Introduction. Optimization of SPME sampling was previously undertaken;[10] hence, only the initial column temperature was varied for SPME GC/ SF-ICPMS using the 0.5-m column and a transfer line temperature of 220 °C with an Ar carrier gas flow rate of 0.340 L min^{-1} and He pressure of 40 psi.

A 20-mL volume of 100 ng mL^{-1} Cr(TFA)$_3$ standard solution buffered to a pH of 5.2 (1 mL of NH_4Ac buffer), to which 50 μL of 25% of TFA solution in methanol was added, was used for SPME immersion sampling for 5 min. Response from this sample was used to optimize column temperature. As shown in Figure 3, peak

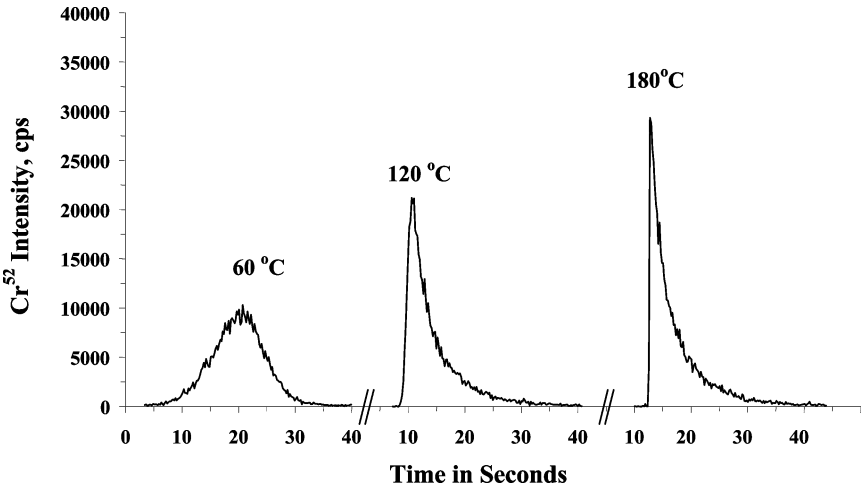

Figure 3. Effect of initial column temperature; chromatograms obtained with direct SPME sampling of a 100 ng mL^{-1} $Cr(TFA)_3$ standard solution with GC/SF-ICPMS 0.5-m column under MR.

height response increased from 10 000 to 30 000 cps while peak width decreased from 23 to 16 s (at 5% peak height) as the initial column temperature increased from 60 to 180 °C. Although slightly better sensitivity could be obtained using an initial column temperature over 140 °C, the number of sampling points decreased significantly from 14 at 120 °C, defining the rising edge of the transient above 5% peak height to 7, 4, and 2 points at temperatures of 140, 160, and 180 °C, respectively. Thus, an initial column temperature of 120 °C was selected in the final study to avoid recording distorted transients as well as for achieving the best sensitivity.

A 1-min hold time at the initial column temperature was used for SPME injection; a shorter hold time of 0.1 min was tested at 120 °C in an effort to further reduce analysis time with this 0.5-m column. Identical chromatograms in terms of retention time, peak shape, and sensitivity were obtained using either hold time. Thus, 0.1 min was selected for the final measurement protocol.

Determination of Cr in CASS-4 Using Liquid Extraction. A large solvent peak manifest as polyatomic interferences from $^{40}Ar^{12}C^+$ and $^{40}Ar^{13}C^+$, generated during injection of a $Cr(TFA)_3$ standard in hexane using a 30-m length of column and the SF-ICPMS operated in low-resolution (LR) mode, could be resolved from the analyte peak, as evident in Figure 4; however, this solvent peak coeluted with the $Cr(TFA)_3$ peak in LR mode when the 0.5-m column was used, prohibiting determination of Cr. Thus, medium resolution (MR) mode was required to resolve the interferences from $^{40}Ar^{12}C^+$ and $^{40}Ar^{13}C^+$ on the ^{52}Cr and ^{53}Cr isotopes. As shown in Figure 5, successful separation of these interferences from the analyte isotopes was achieved. The $^{52}Cr/^{53}Cr$ ratio arising from a 500 ng mL^{-1} $Cr(TFA)_3$ standard solution in hexane was measured using the 0.5-m column to confirm the separation of interferences, yielding 8.816 ± 0.091 (1 SD, $n = 5$), which is not significantly different from the expected natural abundance ratio of 8.819. This confirmed that no significant spectroscopic interference on either isotope arises from the sample matrix (hexane), permitting accurate analytical results to be obtained.

ID-MS is capable of compensating for any loss of analyte during sample derivatization and extraction, suppression of ion intensities by concomitant elements present in the sample matrix, and for instrument drift, providing isotopic equilibrium is achieved

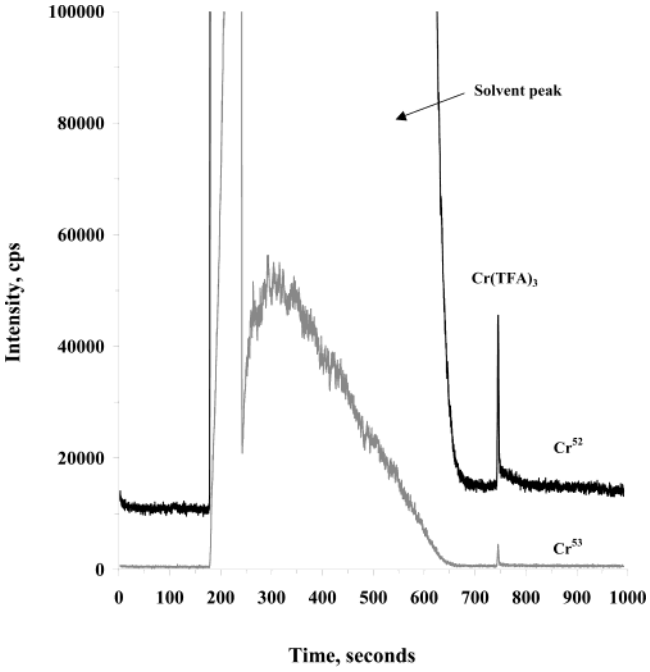

Figure 4. Chromatogram obtained with GC/SF-ICPMS 30-m column in LR, 1-μL injection of 50 ng mL^{-1} $Cr(TFA)_3$ in hexane.

between the added spike and the endogenous analyte in the sample. Results would be biased if equilibration between the spike and the sample was not achieved prior to the ratio measurements. In practice, validation of the achievement of equilibrium of the enriched spike and the sample is not easy. In an effort to verify that equilibration has been achieved following analyte reduction and derivatization, a spiked sample was prepared and divided into two portions. Reduction and derivatization were performed immediately on the first portions, and these steps were performed on the second portions after it was maintained at 60 °C for one week. No significant difference was found between the $^{52}Cr/^{53}Cr$ ratios measured in both portions, suggesting that equilibration between the added spike and the endogenous Cr in the sample was achieved prior to the measurements. Seawater CRM CASS-4 was used to validate the proposed method. The final determination of Cr was undertaken by isotope dilution GC/SF-ICPMS based on a 1-μL injection of hexane extract using MR mode and the

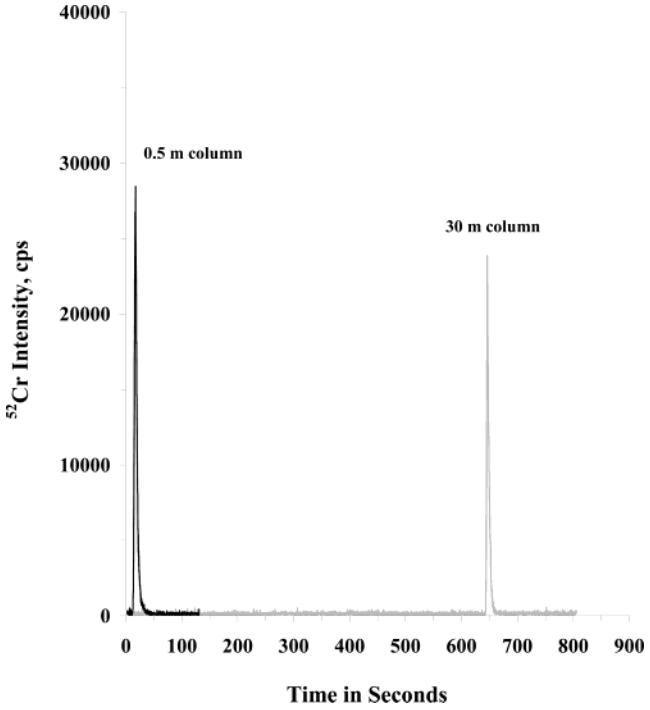

Figure 5. Chromatograms obtained with GC/SF-ICPMS in MR, 1-μL injection of 500 ng mL^{-1} Cr(TFA)$_3$ in hexane. Black trace, 0.5-m column; grey trace, 30-m column.

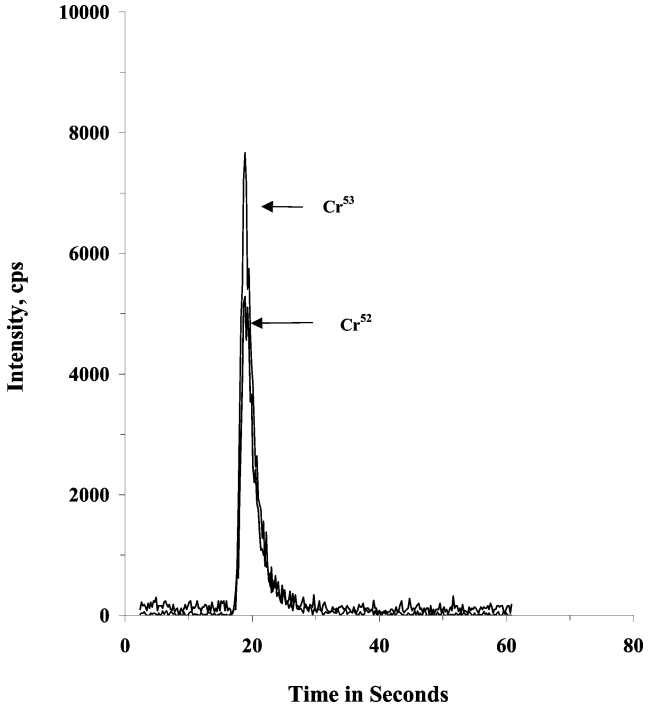

Figure 6. Chromatogram obtained from a spiked CASS-4 extract, 1-μL injection, using GC/SF-ICPMS 0.5-m column in MR.

0.5-m column. One analysis can be completed in <2 min, as shown in Figure 6. To achieve best accuracy and precision for the ratio measurement, a natural abundance 500 ng mL^{-1} Cr(TFA)$_3$ standard solution in hexane was repeatedly introduced between samples to permit calculation of the mass bias correction factor. A mass bias correction factor of 1.0004 ± 0.0098 (mean and one standard, n = 5) was obtained. The following equation was used for the quantitation of Cr in CASS-4:

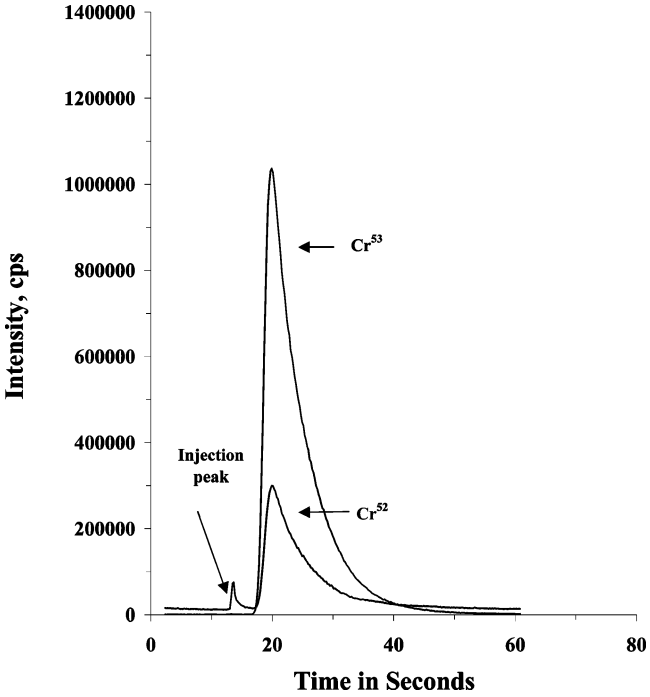

Figure 7. Chromatogram obtained from a spiked CASS-4 sample with SPME sampling and GC/SF-ICPMS 0.5-m column in LR.

$$C_x = C_y \frac{v_y}{v_x} \frac{A_y - B_y R_n}{B_x R_n - A_x} \frac{\mathrm{AW}_x}{\mathrm{AW}_y} \quad (1)$$

where C_x is Cr concentration (ng mL^{-1}) in seawater, C_y is the concentration (ng mL^{-1}) of enriched ^{53}Cr spike, v_y is the volume (mL) of spike used to prepare the blend solution of sample and spike, v_x is the volume (mL) of sample used, A_y is the abundance of the reference isotope (^{52}Cr) in the spike, B_y is the abundance of the spike isotope (^{53}Cr) in the spike, A_x is the abundance of the reference isotope in the sample, B_x is the abundance of the spike isotope in the sample, R_n is the measured reference/ spike isotope ratio (mass bias corrected) in the blend solution of sample and spike, AW$_y$ is the atomic weight of the analyte in the spike, and AW$_x$ is the atomic weight of the analyte in the sample. A blank corrected total Cr concentration of 0.154 ± 0.013 ng mL^{-1} (1 SD, n = 4) was obtained in CASS-4, in agreement with the certified value of 0.144 ± 0.029 ng mL^{-1} (95% confidence interval).

The method detection limit for ID GC/ SF-ICPMS using the 0.5-m column with liquid injection, calculated from three ^{53}Cr-spiked blanks (3SD, three times the standard deviation), was 0.020 ng mL^{-1}.

Determination of Cr in CASS-4 Using SPME Sampling. As noted earlier, SPME can be used for GC sample preparation as an elegant, solvent-free sample extraction technique, eliminating the large solvent peak observed in LR arising from injection of hexane. As shown in Figure 7, a chromatogram of a spiked CASS-4 obtained using SPME GC/ SF-ICPMS in LR reveals that only a small perturbation occurs in the baseline, which is associated with the injection process. A ^{52}Cr/ ^{53}Cr ratio in an unspiked CASS-4 seawater was measured using the 0.5-m column with SPME GC/ SF-ICPMS in LR to confirm that no significant spectroscopic interferences were present with SPME sampling. A mass bias corrected ratio of 8.82 ± 0.12 (1 SD, n = 4) obtained in an unspiked CASS-4 seawater is not significantly different from the

expected natural abundance ratio of 8.819, confirming this. The concentration of total Cr in CASS-4 was measured using SPME sampling in LR to yield a value of 0.132 ± 0.004 ng mL^{-1}, with a RSD of 3.0% (1 SD, $n = 4$).

For comparison, the Cr concentration in CASS-4 was also measured using SPME sampling in MR, and a concentration of 0.146 ± 0.013 ng mL^{-1} with a RSD of 8.9% (1 SD, $n = 4$) was obtained.

An average concentration of 0.0053 ± 0.0013 ng mL^{-1} (1 SD, $n = 3$), obtained from processing three blanks in LR, is insignificant compared to the concentration of Cr in CASS-4, confirming that contamination is effectively under control during sample preparation and yielding detection limits (3 SD) of 0.0091 and 0.0039 ng mL^{-1} for MR and LR, respectively. Superior detection power is offered with LR using SPME GC/ SF-ICPMS with the 0.5-m column because better sensitivity is achieved in the LR mode.

CONCLUSIONS

An accurate method for the determination of total Cr in seawater using GC/ SF-ICPMS or SPME GC/ ICPMS with a 0.5-m GC column as a means of sample introduction was developed. Analysis time decreased significantly from 15 min with a 30-m column to ,2 min using the 0.5-m column. It should be noted that the only "chromatographic" separation required in this system is the minimization of overlap of the hexane vapor plug arising from liquid−liquid extraction with the analyte peak because of its manifestation as polyatomic ArC interference. This is effectively eliminated in LR mode at the expense of throughput if a 30-m column is used or by reverting to MR with a 0.5-m column. Alternatively, SPME sampling eliminates these interferences, permitting operation in LR mode, even with a 0.5-m column, suggesting its use with quadrupole-based MS instruments, as well. In such a case, the 0.5-m column simply serves as an extension of the transfer line. Enhanced detection power (0.0039 ng mL^{-1}) is realized with SPME GC/ SF-ICPMS in LR, as compared to MR, as a result of the greater sensitivity afforded in LR with the SF-ICPMS. Use of MR also degrades precision of determination, as expected, as a result of decreased sensitivity. In general, metal chelation combined with SPME sampling and element-specific detection may offer viable alternatives for the determination of numerous transition metals and many other metallic elements.

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