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Solid phase microextraction for the determination of chromium in sea-water†

László Abrankó, Lu Yang, Ralph E. Sturgeon, Péter Fodor and Zoltán Mester

Institute for National Measurement Standards, National Research Council of Canada, Ottawa, ON, Canada K1A 0R6. E-mail: zoltan.mester@nrc.ca; Fax: 613 9932451

BKÁÉ-ET, Department of Applied Chemistry, 1118 Budapest, Villányi út 29-33, Hungary

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Application of solid phase microextraction (SPME) to the extraction of Cr from sea-water after derivatization with the β-diketonate ligand 1,1,1-trifluoro-2,4-pentadione (trifluoroacetylacetone) is reported. The chelation reaction was conducted in a single (aqueous) phase medium. Both liquid phase and headspace extraction were studied by employing a 100 μm PDMS (polydimethylsiloxane) coated SPME fiber. Capillary gas chromatography (GC) coupled to electron capture detection (ECD), electron impact-mass spectrometry (EI-MS) and inductively coupled plasma-mass spectrometry (ICP-MS) were compared for the quantitation of Cr. Except for the ECD, isotope dilution calibration was applied, using 53Cr enriched spikes. Detection limits between 0.011–0.015 ng ml⁻¹ as Cr were achieved with all three systems. Accuracy was assessed using CASS-4 Nearshore Seawater Certified Reference Material (CRM) from the National Research Council of Canada (NRCC). The developed method provided accurate results with EI-MS and ICP-MS detection, while significant bias was experienced with the ECD.

Introduction

Since inductively coupled plasma mass spectrometry (ICP-MS) has become commercially available, it has risen to dominance as a sensitive multielement technique for elemental trace analysis. Nevertheless, its use for the determination of some elements, such as chromium and iron, that may suffer from matrix/spectral interferences, remains challenging. This problem is most pronounced when the analyte of interest is present in the ng l⁻¹ range in a highly complex matrix. In the case of sea-water, accurate results can be obtained for several trace elements using HR-ICP-MS, following a simple dilution of the sample, but the application of a reaction/collision cell (as Cr) as an alternative, some type of matrix separation/analyte preconcentration or step prior to quantitation was required with low resolution ICP-MS in order to eliminate/minimize spectral interferences.

Another possible approach used to overcome matrix related limitations is the application of vapour generation, wherein initially non-volatile (usually ionic) analyte compounds are converted to volatile metal species. The main advantages of this approach for trace element analysis over sample introduction via solution nebulization include efficient matrix separation and virtually 100% sample introduction efficiency. Although most metallic elements are not amenable to conventional vapour generation approaches such as hydride formation, volatile/semi-volatile metal chelates can be formed by many metallic elements, and have been extensively studied from the late fifties until the early eighties.

The roots of inorganic GC, first suggested by Lederer, go back to 1955. Early successes greatly contributed to establishing this technique as a useful approach for elemental trace analysis. Thus, numerous elements coupled with different ligands have been studied and the extensive knowledge gained in this field was first summarized in a monograph by Mosher and Sievers in 1965. Subsequent reviews have been published on separation of metal chelates with GC: Rodriguez-Va ´zquez, in 1974, Henderson and Uden in 1977, Uden in 1984 and Dilli et al. in 1987 to mention a few.

For the gas chromatographic measurement of chromium, trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentadione, hereafter denoted as HTFA) has emerged as one of the most commonly used chelating agents because of its (i) quantitative reaction with the analyte, (ii) sufficient volatility and thermal stability and (iii) relative inertness towards undesirable on-column reactions. In addition to these features, which are essential for quantitative GC analysis, several other practical considerations, such as (i) exceptional sensitivity with electron capture detection (ECD) of the fluorinated complex and (ii) ease of synthesis for calibration purposes, have made HTFA the most commonly used ligand for several decades. The product of derivatization of Cr with HTFA is Cr-tris[1,1,1-trifluoro-2,4-pentanedione], hereafter denoted as Cr(TFA)₃. As a consequence of its desirable properties, HTFA was chosen as the chelating agent in this study for the determination of chromium in sea-water.

The application of SPME to the determination of trace metal concentrations has been recently reviewed by the authors. Most published SPME methods employ derivatization to convert the aquo metal ions to volatile organometallic compounds, hydride formation and aqueous phase alkylation being the most commonly employed derivatization techniques. However, halide generation methods have also been reported. The application of SPME-GC for the determination of metal chelates has not been reported earlier. Sample preparation for GC application was generally based on the following procedure: free ligand, either dissolved in solvent or as a pure compound, was added to the aqueous sample solution; after completion of the complexation reaction, the metal chelates were transferred to an organic solvent by performing a liquid-liquid extraction (LLE). Microliter volumes of the organic phase containing the derivatized analyte were introduced to the GC. Unlike conventional solvent extraction SPME, as a solid sorbent based extraction technique, eliminates the LLE step.

ECD has been the most frequently applied detection method for the determination of metal-(TFA)₃ complexes...
during the early days of its development: however application of MS detection,\textsuperscript{21} often using magnetic sector analysers, has also been reported. The enhanced selectivity of MS compared with ECD decreases the demand for chromatographic resolution and allows faster temperature programming on the GC. Moreover, with mass selective detectors, isotope dilution (ID) calibration can also be performed, which may significantly improve the quality of the generated data.\textsuperscript{22}

In this study, the development of an SPME-GC based method for determination of Cr as Cr(TFA)\textsubscript{3} in sea-water is reported, along with a performance comparison of ECD, electron impact mass spectrometry (EI-MS) and ICP-MS as detectors.

### Experimental

#### Instrumentation

A manual SPME device, equipped with a fused silica fiber coated with a 100 μm film of polydimethylsiloxane (PDMS) (Supelco, Bellefonte, PA, USA), was used for chelate extraction in all experiments. A 10 μl liquid sampling syringe (Hamilton Company, Nevada, USA) was used for the injection of standard solutions of Cr(TFA)\textsubscript{3} for the optimization of the GC response.

For GC-ECD measurements, a Hewlett-Packard HP 5890 Series II GC (Agilent Technologies Canada, Mississauga, Canada), equipped with a 63Ni electron capture detector was used. The instrument was fitted with a 30 m × 0.32 mm id, 1.5 μm film thickness DB-5 capillary column (Sigma–Aldrich Canada Ltd., Oakville, Ontario, Canada).

GC-MS measurements were performed on a Hewlett-Packard HP 6890 GC coupled to a HP 5973 mass-selective detector (Agilent). In this GC, a DB-5MS column (Iso-Mass Scientific, Calgary, Canada) was used. Single ion monitoring (SIM) data acquisition was performed, peak hopping to the m/z 358, 359, 511 and 512, corresponding to \textsuperscript{52}Cr(TFA)\textsubscript{3}\textsuperscript{+}, \textsuperscript{53}Cr(TFA)\textsubscript{3}\textsuperscript{+}, \textsuperscript{52}Cr(TFA)\textsubscript{3}\textsuperscript{2+}, and \textsuperscript{53}Cr(TFA)\textsubscript{3}\textsuperscript{2+}, respectively.

A ThermoFinnigan Element2 ICP-MS (Bremen, Germany) (Elemental Scientific, Omaha, NE, USA) was used following optimization and dead time correction as recommended by the manufacturer. A Varian 3400 GC (Varian Canada Inc., Georgetown, Ontario, Canada), equipped with an MXT-5 metal column (5% diphenyl, 95% polydimethylsiloxane, 30 m × 0.28 mm id with a 0.5 μm film thickness), was coupled to the ICP-MS using a home-made interface and transfer line, described in detail previously.\textsuperscript{21} For all determinations with the ICP-MS, \textsuperscript{52}Cr and \textsuperscript{53}Cr were monitored in low resolution mode. Operating conditions for all instruments are summarized in Table 1.

### Table 1 Operating parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GC-parameters</th>
<th>GC-ECD</th>
<th>GC-MS</th>
<th>GC-ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet port temperature</td>
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<td>He, 1.5 ml min\textsuperscript{-1}</td>
<td>He, 1.5 ml min\textsuperscript{-1}</td>
<td>Ar, 1.5 ml min\textsuperscript{-1}</td>
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<td>Carrier gas</td>
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<td>25 to 270 °C (1 min)</td>
<td>25 to 270 °C (1 min)</td>
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<tr>
<td>Initial temperature</td>
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<td>150 °C</td>
<td>230 °C</td>
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<td>Ramp/° min\textsuperscript{-1}</td>
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<td>80 °C (3 min)</td>
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<td>25 to 270 °C (1 min)</td>
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<tr>
<td>Detector temperature</td>
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<tr>
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<td>ICP MS parameters</td>
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<td>1.05 l min\textsuperscript{-1}</td>
<td>0.30 l min\textsuperscript{-1}</td>
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<td>0.005 s sample time</td>
<td>0.005 s sample time</td>
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<td>E-scan, 4500 passes, 5% mass window</td>
<td>E-scan, 4500 passes, 5% mass window</td>
<td>E-scan, 4500 passes, 5% mass window</td>
</tr>
</tbody>
</table>

Reagents

Nitric and acetic acids were purified in-house by sub-boiling distillation of reagent grade feedstock in a quartz still prior to use. Ammonia was purchased from Anachemia Science (Montreal, Quebec, Canada). High purity de-ionized water (DIW) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp., IA, USA). DIW saturated with sulfur dioxide was prepared by bubbling SO\textsubscript{2} (Air Products, Ontario, Canada) through high purity DIW overnight at room temperature. A buffer solution used for optimization purposes was prepared by adjusting a 1 mol l\textsuperscript{-1} sodium acetate (Fisher Chemicals) solution to pH 5.2 by addition of acetic acid. A different solution was used for the pH adjustment of sea-water samples because of the requirement for higher purity. A pH 9.5 solution was prepared by dissolving appropriate amounts of (20–22%) NH\textsubscript{4}OH and sub-boiling distilled glacial acetic acid in high purity DIW. Working solutions of Cr\textsuperscript{3+} (natural isotope abundance and \textsuperscript{53}Cr enriched) were diluted from stock solutions. A 1000 μg ml\textsuperscript{-1} stock solution of natural abundance Cr was prepared by dissolution of the high purity metal (Johnson, Matthey & Co. Limited, London, UK) in HCl. Working standards, which were used for \textsuperscript{53}Cr reverse spike isotope dilution, were prepared by serial dilution of the stock with DIW containing 1% HNO\textsubscript{3}. Enriched \textsuperscript{53}Cr isotope was purchased from Oak Ridge National Laboratory (USA) as Cr\textsubscript{2}O\textsubscript{3}. A \textsuperscript{53}Cr stock solution of approximately 310 μg ml\textsuperscript{-1} was prepared by dissolution of the metal oxide in a few millilitres of perchloric acid followed by dilution with DIW. A working spike solution containing 0.40 μg ml\textsuperscript{-1} Cr was prepared by volumetric dilution of the stock in 1% HNO\textsubscript{3}. All inorganic Cr working solutions were acidified to 1% v/v HNO\textsubscript{3} with sub-boiling, quartz distilled acid. Crystalline Cr(TFA)\textsubscript{3} and HTFA (purum) were purchased from Sigma–Aldrich Canada Ltd. (Oakville, ON, Canada). National Research Council of Canada (NRCC, Ottawa, Canada) Nearshore Seawater certified reference material CASS-4 was used for method validation. Zero grade He (for GC) (Praxair Products Inc., Mississauga, ON) was used throughout. High capacity gas purifiers (Supelco) were employed for the removal of moisture and O\textsubscript{2} content from the carrier and make-up (N\textsubscript{2}) gases for the GC-ECD.

#### Analytical procedures

Vials and stirring bars were cleaned by soaking in 50% v/v analytical grade HNO\textsubscript{3} for at least 48 h and then in 5% v/v sub-boiling distilled HNO\textsubscript{3} until use. A 20 g subsample of...
sea-water (density = 1.03 g ml\(^{-1}\)) or 0.03 M HNO\(_3\) solution (as blank) was measured into a clean 30 ml polyethylene (HDPE) vial. Samples intended for GC-MS or ICP-MS measurement were spiked with 50 \(\mu\)l of \(^{53}\text{Cr}\) enriched solution having a nominal concentration of 38.83 \(\mu\)g ml\(^{-1}\). In order to reduce Cr(vi) to Cr(III), 200 \(\mu\)l of the sulfur dioxide solution was added to all samples and allowed to react for 15 min. The pH was then adjusted to 5.2 by adding 1 ml of ammonia-acetic acid solution. Finally, 50 \(\mu\)l of 25% v/v HTFA solution was pipetted into all samples. After closing the vials, they were placed in an open water bath for 1 h at 75 °C to complete derivatization. After cooling, vials were opened in a class 100 environment and pre-cleaned Teflon coated stirring bars were added to each. The original cap was replaced with a PTFE coated disc. While the solution was being stirred on a magnetic stirring plate at ambient temperature, the SPME fiber was immersed into the liquid phase for 25 min to effect analyte extraction. The fiber was then introduced into the injector of the GC. GC-MS or the GC-ICP-MS. The highest desorption temperature no higher than the accessible limit of many GC systems. Separation characteristics were studied by injecting the authentic compound dissolved in toluene when SPME extraction was carried out. In spite of the congruence of the retention times for the authentic and derivatized compounds obtained with the GC-ECD, the identity of the species was also confirmed by GC-MS and GC-ICP-MS measurements.

### SPME optimization

Fluorinated diketonates, such as Cr(TFA)\(_3\), are usually considered to be volatile compounds\(^3\) for the purpose of gas chromatography. As a general rule, if the vapor pressure of an analyte compound is greater than 0.1 Hg mm at column temperatures no higher than the accessible limit of many GC stationary phases (i.e., of 250 °C) it has sufficient volatility for determination\(^5\) by GC. There was no attempt made to determine the vapor pressure of the Cr(TFA)\(_3\) at 250 °C in this study; nevertheless, the above described requirement must have been met because elution temperatures of approximately 140–160 °C were satisfactory. At lower temperatures, the vapor pressure of Cr(TFA)\(_3\) decreases significantly (the pure compound has a vapour pressure of 0.001 Hg mm at 100 °C) and may be the reason why headspace SPME extraction of Cr(TFA)\(_3\) at ambient temperature is less efficient than liquid phase sampling. A comparison of headspace and liquid phase extraction is presented in Fig. 1.

Several attempts were made to characterize the kinetics of headspace extraction of Cr(TFA)\(_3\). The determination of the time dependence of the headspace concentration resulted in ambiguous data in all experiments. After approximately 40 min extraction time, efficiency significantly decreased; moreover, the uncertainty of the data was unacceptably high. The reason for this is not yet clear, as such inconsistencies were not experienced during liquid phase extraction. The equilibrium (e.g., the maximum) concentration of the analyte on the fiber could not be reached within a practical time-frame. The concentration of the analyte on the fiber continuously increased over a period of 100 min. An arbitrary extraction time of 25 min was chosen for subsequent experiments, which provided sorption of sufficient mass of extracted analyte to achieve the required detection limits. Moreover, it was compatible with the time required for GC separation (i.e., during a GC run the subsequent sample could be extracted).

The mass of analyte absorbed onto the fiber coating after

![Fig. 1 Comparison of the kinetics of headspace and liquid phase extraction of 1 ng ml\(^{-1}\) Cr(TFA)\(_3\) (as Cr) using a 100 \(\mu\)m PDMS fiber at ambient temperature.](image-url)
25 min was not an exhaustive extraction technique, only a finite portion of the analyte present in the sample solution is extracted. The ratio of the \( \text{Cr(TFA)}_3 \) extracted into the fiber to that originally present in the solution can be calculated. For a 10 ml solution containing 10 ng ml\(^{-1}\) Cr, 4% of the total amount of analyte is absorbed into the coating. Since the influence of the sample volume to the amount extracted is not significant under the described conditions,\(^{24}\) the calculated extraction efficiency is valid only for the 10 ml sample volume considered (the larger the sample volume, the smaller the calculated extraction efficiency). The calculated 4% extraction efficiency is quite high, especially considering the volume ratio of the phases.\(^{25}\)

**Derivatization**

Normally, the \( \text{Cr(TFA)}_3 \) complex formed in an aqueous medium is solvent extracted into an organic phase and then injected into the GC. Using SPME sampling, LLE is eliminated. This alteration required reconsideration of the vehicle used for introduction of the chelating agent to the aqueous solution. Conventionally, the ligand, which has only very limited water solubility, is dissolved in the organic solvent which is subsequently employed as the extraction medium (i.e., hexane, benzene, etc.). However, the solid phase extraction protocol does not require phase separation in the liquid medium. The ‘organic phase’ required for the partitioning of the analyte is the solid phase itself. Additionally, the SPME protocol is not compatible with low polarity organic solvents as they would immediately saturate the fiber, inhibiting the extraction of the target compound. Consequently, in this study a water miscible solvent, methanol, was chosen for dissolution of the ligand and appropriate volumes were added to the aqueous samples, thereby retaining the characteristics of a single phase system. However, another aspect of the addition of methanol had to be considered. The methanol present in the aqueous phase leads to decreased polarity and consequently decreased extraction efficiency. This polarity difference is the driving force for the extraction and has now been reduced. Therefore, the volume of the methanolic ligand solution added to the sample was kept to a minimum (50 \( \mu l \) methanolic ligand to 20 ml of aqueous sample). Thus, the final methanol concentration in each sample was 0.25% v/v, independent of the ligand concentration dissolved in the methanol. In general, if the solvent content of an aqueous solution is less than 1% v/v, the performance of SPME sampling is not significantly influenced.\(^{24}\)

According to the prior art, the amount of free ligand, temperature, derivatization time, and pH are the major factors which affect the derivatization reaction. In our study, despite the absence of the organic phase, the optimum conditions for temperature\(^{26}\) and pH\(^{27}\) are not expected to change. Therefore, these values were adopted from the literature.

For the optimization of the HTFA concentration, 10 ml of a 2 ng ml\(^{-1}\) \( \text{Cr(m)} \) solution at pH of 5.2 were prepared in a manner similar to the procedure used for the SPME study of extraction kinetics. Additionally, 50 \( \mu l \) of 0.1–25% v/v HTFA solution was added and allowed to react for 2 h at 75 °C in an open water bath, while moderate stirring was employed. Results are shown in Fig. 2.

Based on these results, a 2 mmol l\(^{-1}\) concentration of HTFA was chosen for future experiments, although a slight increase in response can still be observed at higher concentrations. Therefore, 50 \( \mu l \) of 5% v/v methanolic HTFA was chosen as optimum, resulting in a ligand concentration of 2.06 mmol l\(^{-1}\) in the final sample volume.

The time dependence of derivatization was also studied. A set of standard solutions having a concentration of 0.5 ng ml\(^{-1}\) \( \text{Cr(m)} \) was prepared, similar to those described earlier. All samples were subjected to derivatization. During the course of the reaction, liquid phase SPME was performed for a period of 25 min on every vial, but each sampling was delayed over increasing time intervals following mixing of the reagents. Results are presented in Fig. 3.

The derivatization reaction equilibrated after one hour at 75 °C, faster than the previously reported reaction times obtained using a similar setup\(^{21}\) (LLE sampling). This two-fold improvement is probably due to the easier availability of the complexing agent in the single phase system.

**Determination of chromium in sea-water**

When trace and ultra-trace measurements are attempted, special consideration must be given to the blank/background control issues. Consequently, the sodium acetate-acetic acid

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**Fig. 2** Optimization of the amount of chelating agent (HTFA). Ligand concentration is calculated based on the final volume of the test solution.
buffer solution used throughout the optimization was changed to a solution derived from sub-boiling acetic acid and ammonia, eliminating the use of inorganic salts. Glass vials were substituted with disposable polyethylene flasks. A magnetic stirring bar was added to the sample solution only after the high temperature derivatization procedure was completed. There was no mechanical agitation (i.e., stirring, shaking) during the derivatization. By comparing signals, it was concluded that the lack of agitation caused no reduction in the derivatization efficiency (i.e., signal decrease). On the other hand, SPME extraction could not be implemented within 25 min without stirring. All sample preparation manipulations were performed in a clean room (class 100 environment). As a result, significant improvement was achieved in the blank values.

The chelation reaction of chromium with HTFA is not element specific, as the ligand reacts with other elements present in the sample solution. Several potentially HTFA complexable ions, such as Al, Be, Fe and Ni, are present in sea-water and this is likely the reason why the ligand concentration had to be increased when sea-water samples were processed. The minimum required concentration was found to be 10.3 mmol l⁻¹ (50 μl 25% v/v HTFA solution in methanol added to 20 g of sea-water), which is 5-fold higher than needed for DIW standards. No attempt was made to eliminate the excess unreacted ligand from the aqueous sample after derivatization. Since SPME is not an analyte specific extraction method, unreacted ligand molecules along with several ‘electron capturing’ species (i.e., halide rich impurities originating from the chelating agent) would also be absorbed onto the fiber coating.

Figures of merit for ECD, MS and ICP-MS detection

The chelation-SPME sample preparation procedure was evaluated by applying GC-ECD, GC-MS and GC-ICP-MS for separation and detection. ECD is the simplest and least expensive detection technique. It provided exceptional sensitivity for the Cr(TFA)₃ due to the presence of 9 fluorine atoms in a single complex molecule. However, as a less specific detector, it can be prone to interferences. In this study, baseline separation of the analyte could be achieved with the GC-ECD using the conditions shown in Table 1. Typical chromatograms obtained with GC-ECD for blank and sea-water samples are presented in Fig. 4.

Based on the combined peak area of both Cr(TFA)₃ isomers, a limit of detection (LOD) of 0.011 ng ml⁻¹ (as Cr) could be achieved using ECD, calculated as three times the standard deviation of the blank sample (n = 3) divided by the slope of the calibration curve. In the case of EI-MS and ICP-MS detection, calibration was achieved by applying isotope dilution (ID) using ⁵²Cr enriched spikes. The ID calculations are described elsewhere. Using GC-MS, detection limits (3σ, n ~ 4) of 0.012 and 0.014 ng ml⁻¹ (as Cr) calculated from m/z 358/359 and 511/512 ratios, respectively, were obtained. Owing to the lack of interference at the monitored m/z values of 358, 359, 511 and 512, exceptionally low background noise was observed with GC-MS; consequently a further 100-fold improvement could be achieved in the instrumental detection limits. However, the method detection limits reported earlier are blank limited. A LOD of 0.015 ng ml⁻¹ was calculated for the SPME-GC-ICP-MS system, based on the ⁵²Cr/⁵³Cr signal.
Table 2  Chromium in CRM CASS-4 Nearshore Seawater, ng ml⁻¹
(once standard deviation, n = 3)*

<table>
<thead>
<tr>
<th>Certified value</th>
<th>GC-ECD</th>
<th>GC-MS (ID)*</th>
<th>GC-ICP-MS (ID)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.144 ± 0.029</td>
<td>0.384 ± 0.030</td>
<td>0.161 ± 0.011 (a)</td>
<td>0.152 ± 0.016 (b)</td>
</tr>
<tr>
<td>0.160 ± 0.014</td>
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<td></td>
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</tbody>
</table>

* Calculations based on m/z: (a) 358/359; (b): 511/512. * All confidence intervals are calculated at 95% significance level.

ratios. It is evident that all three systems show practically the same performance.

The accuracy of this approach was verified using CASS-4 Nearshore Seawater CRM. For quantitation, ID was applied with both GC-MS and GC-ICP-MS, while standard additions were used for GC-ECD. Standard additions were implemented by adding 100 μl of a 100 ng ml⁻¹ Cr(III) solution to the sample. Calculation of the concentrations is based on the summed responses for both isomers. Results obtained for the sea-water CRM are given in Table 2. Except for the GC-ECD, confidence intervals are calculated at 95% significance level. With GC-ECD, significant deviation from the certified values is evident. Because of the non-selectivity of the detector, it is conceivable that chelates formed from other ions present in the sample co-eluted with the analyte when the sea-water was analyzed. In order to verify this assumption, the ratios of the peaks corresponding to the trans and cis isomers were calculated for all replicates. A Student’s t-test was performed on the average (n = 3) ratio values obtained for the sea-water samples and the spiked sea-water samples. The homologous isomer ratio values for both (unspiked and spiked) samples were proven to be different from the original peaks for the sea-water sample that were produced only by the isomers of Cr(TFA)₃. In other words, if co-elution was responsible for the inaccurate results, it should affect the two Cr isomers differently. Based on peak area calculations, ratios were significantly different (significance level 95%), thus proving the assumed co-elution.

Conclusions

Here we report the successful utilization of SPME for the solvent free extraction of Cr(TFA)₃ and its application to the quantitative determination of total Cr in sea-water. Most of the early experiments involving metal chelates were performed using packed GC columns. Here we have shown that Cr(TFA)₃ can survive the extended interaction which occurs in a capillary GC column compared with a packed column. With modern instrumental detection methods, such as ICP-MS, a 10–1000-fold improvement in detection capability can be realized compared with the classical FID and ECD based detection systems. Although the present study deals exclusively with total chromium determination in sea-water, the potential of the described chelation-based methodology goes far beyond this application. The capability for highly sensitive multielemental speciation applications is evident.

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References