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Determination of chromium(III) in water by solid-phase microextraction with a polyimide-coated fiber and gas chromatography-flame photometric detection

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Abstract

A method for the determination of trace Cr(III) in aqueous solution by solid-phase microextraction (SPME) coupled with gas chromatography (GC)-flame photometric detection (FPD) was developed. Aqueous Cr(III) was first converted to the volatile chromium trifluoroacetylacetonate ($Cr(tfa)_3$) by derivatization with 1,1,1-trifluoroacetylacetone (Htfa), followed by SPME extraction using a polyimide-coated silica fiber. The distribution constants (K) of derivatized *cis*- and *trans*-$Cr(tfa)_3$ between the polyimide phase and aqueous phase were 2012 and 2214, respectively. The two $Cr(tfa)_3$ isomers extracted can be efficiently separated by a DB-210 GC column within 9 min. Selective detection of Cr was performed by a FPD equipped with a 385-nm long-pass filter. Linearity ($r > 0.99$) over the concentration range 5–300 ng ml^{-1} Cr was obtained and the limit of detection was 2 ng ml^{-1} Cr. The relative standard deviation was 7% at 10 ng ml^{-1} Cr ($n = 5$). Applicability of this method to water analysis was tested by analyzing the chromium content in a reference standard water sample and an industrial effluent.

Keywords: Chromium; Solid-phase microextraction; Gas chromatography-flame photometric detection

1. Introduction

Solid-phase microextraction (SPME), first introduced by Pawliszyn and co-workers more than a decade ago [1], can be regarded as a combination of sampling, extraction, preconcentration, matrix removal, and gas chromatographic (GC) introduction techniques. Due to its simple, solventless, selective and flexible properties, SPME has become an attractive alternative to some of the conventional sampling techniques and has gained a widespread acceptance in many areas such as food, botanical, clinical, pharmaceutical, forensic and environmental analyses [2,3]. The main drawbacks of SPME are that the fibers are expensive and have a limited lifetime, particularly in samples of complex matrix. Besides, SPME is a relatively slow extraction process due to its equilibrium-based characteristic.

Although SPME has been mainly used for gas chromatographic analysis of volatile and semi-volatile organic compounds, it also has been applied to the analysis of metal ions or organometallic compounds after derivatization [4,5]. Polydimethylsiloxane (PDMS) is the most common fiber coating for the extraction of derivatized volatile metal species. The most studied elements include Hg [6–8], Sn [9–12], Pb [13,14], As [15,16] and Se [17]. Recently, SPME also has been used for sampling of ionic metal species from aqueous phase followed by high-performance liquid chromatographic (HPLC) analysis. SPME fibers modified with a liquid ion exchanger (for Bi(III)) [18], polypyrrole polymer (for anionic As and Se species) [19], crown ethers (for Hg(II)) [20] and a sol-gel coating (for organo-Hg, organo-Sn and organo-As) [21] have been reported. A conductive extraction phase covered fiber (e.g., Au-coated carbon-steel wire [22], poly(3-

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methylthiophene)-coated Pt wire [23], poly(pyrrole-sulfated β-cyclodextrin) film electrode [24]) coupled with electrochemical deposition also has been employed to the SPME of metal ions from aqueous solution. Using SPME as a tool for trace element speciation analysis has been reviewed by Mester et al. recently [25].

Chromium occurs naturally in trace amounts in natural waters through weathering of rocks and erosion of soils. Chromium exists in two oxidation states, viz. Cr(III) and Cr(VI). Although Cr(III) is the more stable form in natural waters, Cr(VI) is always present to some extent [26,27], and their ratio depends upon the pH and E_h values of the water. Speciation of chromium has attracted a great deal of interest in view of the toxic properties of Cr(VI) as compared with Cr(III). Cr(III) is recognized as an essential trace element for human [28,29], while Cr(VI) is extremely irritating and toxic [30]. For chromium speciation in aqueous samples, various techniques have been described in the literature, e.g., flow injection (FI) analysis followed by inductively coupled plasma-atomic emission spectrometric (ICP-AES) detection [31], FI on-line preconcentration and flame atomic absorption spectrometric (FAAS) detection [32], on-line preconcentration and FAES detection [33], and complexation followed by graphite furnace AAS determination [34]. More recently, the sophisticated ICP-mass spectrometry (MS) technique has become the most common method for trace and ultratrace chromium determination [35–37]. Alternatively, chromium also can be determined at trace levels by GC methods. The procedure generally involves chelation of the Cr(III) with a β-diketone, 1,1,1-trifluoro-2,4-pentanedione (also known as trifluoroacetylacetone, Htfa). The formed $Cr(tfa)_3$ chelates are volatile enough for GC analysis. Various techniques, e.g., AAS [38], MS [39], flame photometric detection (FPD) [40], and electron capture detection (ECD) [41,42], have been coupled to GC for detection of $Cr(tfa)_3$.

Despite its wide application to metal ion analyses, SPME has not been commonly employed to the analysis of chromium. To date, there have been only three papers of SPME of chromium published. Boyd-Boland [43] first reported using a Carbowax-templated resin (CWAX-TR) coating combined with EDTA complexation for the SPME of chromium, followed by HPLC with UV detection. Recently, Yang et al. [44] and Abranko et al. [45] reported the determination of total Cr in seawater by GC with ECD, electron impact (EI)-MS and isotope dilution sector field (IDSF)-ICP-MS detection. Commercial PDMS fibers were used in both works to extract preformed $Cr(tfa)_3$. In this paper, we describe an alternative SPME-GC method for the determination of Cr(III) in aqueous solution. The ionic Cr(III) is converted to the volatile $Cr(tfa)_3$, followed by SPME using a polyimide-coated silica fiber. The extracted $Cr(tfa)_3$ is then determined with GC-FPD. To our knowledge, determination of chromium in water by SPME using a polyimide-coated fiber and GC-FPD method has not been reported in the literature.

2. Experimental

2.1. Apparatus

A HP 5890 series II gas chromatograph (Hewlett–Packard, Avondale, PA, USA) equipped with a flame photometric detector and a 385-nm long-pass filter (Edmund Scientific, Barrington, NJ, USA) was used for this study. The separation was carried out on a J&W DB-210 capillary column (15 m × 0.25 mm i.d. × 0.5 μm film thickness). Separation and detection parameters had been optimized previously [46]. In brief, the column temperature was initially held at 60 °C for 3 min, and then programmed at 40 °C/min to a final temperature of 140 °C, which was held for 5 min. Nitrogen was used as the carrier gas at a flow-rate of 4 ml/min. The injector and detector temperatures were set at 210 °C. Injection was performed in the splitless mode using a 0.75 mm i.d. inlet liner for SPME (Supelco, Bellefonte, PA, USA). After 3 min desorption period, the solenoid valve was switched to the purge on mode for injector venting. The detector was operated with an air–hydrogen flame. The flow-rates were 120 and 80 ml/min, respectively.

2.2. Reagents

1,1,1-Trifluoroacetylacetone (Htfa) was obtained from Fluka (Buchs, Switzerland). Chromium trifluoroacetylacetonate ($Cr(tfa)_3$) was purchased from Tokyo Kasei Kogyo (Tokyo, Japan). Standard solutions of $Cr(tfa)_3$ were prepared in acetone. All concentrations of $Cr(tfa)_3$ reported in this work were relative to the content of inorganic chromium. Certified atomic absorption standard for Cr(III) (Aldrich, Milwaukee, WI, USA) was used to prepare appropriate extraction standards. Suprapur acetic acid, sodium acetate and sodium hydroxide (Merck, Darmstadt, Germany) were used for preparation of buffer solution. All other chemicals were of extra pure grade. Distilled water was further purified by passing it through a Nanopure II deionization system (Barnstead/Thermolyne, Dubuque, IA, USA).

2.3. Preparation of SPME fiber

A polyimide-coated silica optical fiber (140 μm o.d. × 10 μm film thickness; part no. FIP100120140; Polymicro Technologies Inc., Phoenix, AZ, USA) was cut into 2 cm piece. One end of the fiber was cemented into the tip of an 8-cm 30-gauge stainless steel tubing (SST) (Hamilton, Reno, NV) with high temperature glue (Epoxy Technology Inc., Billerica, MA, USA), leaving 1.0 cm fiber extruding from the SST end. The unattached end of the SST was then threaded through the stainless steel piercing needle of an used commercial SPME fiber assembly (Supelco), followed by inserting this end into a plain hub also removed from the used SPME fiber assembly. The tensioning spring was finally attached to the fiber assembly. The commercial

SPME device could be used simply by replacing the fiber with the laboratory-made SPME fiber.

2.4. General procedure

2.4.1. Chromium(III)

Aqueous samples containing μg ml^{-1} to ng ml^{-1} Cr(III) were prepared in 0.5 M sodium acetate buffer at pH 6.0. Aliquot of the sample solution (30 ml) was transferred to a clean (acid washed) glass vial, in which 200 μl of 50% Htfa (in methanol) was added. The capped sample vial was placed in an oil bath heated at 75 °C for 60 min. The vial was removed from the oil bath and allowed to cool down to the room temperature. The vial cap was changed with a Teflon-coated silicone rubber septum. The SPME fiber was inserted into the sample solution through the septum, and direct sampling of the aqueous phase was performed for 20 min at 1000 rpm stirring rate. The fiber was then transferred to the injection port of a GC for analyte desorption, followed by GC-PFD analysis. Desorption temperature was set at 210 °C, and desorption time was 3 min.

2.4.2. Total chromium

The reaction between Htfa and chromium is specific for Cr(III); for total chromium determination it is necessary to convert Cr(VI) to Cr(III) before chelation can occur. For non-acidified water, e.g., industrial effluent, the sample was filtered through a 0.45-μm pore-size membrane, followed by 50-fold dilution with 0.5 M sodium acetate buffer (pH 6.0). Aliquot of the sample (30 ml) was added with 1 ml of 1 M sodium sulphite reducing agent. For samples which were stored acidified at pH < 2, e.g., NIST SRM 1643d, Cr(VI) had been totally reduced to Cr(III) [41,42], and thus no reducing agent was required. These samples were then treated in a similar manner as described for the Cr(III) samples above.

3. Results and discussion

3.1. Selection of SPME fiber

During preliminary study, both commercial PDMS and PA fibers were found to be able to extract $Cr(tfa)_3$ from aqueous solution by SPME method. Use of PDMS fibers for extraction of $Cr(tfa)_3$ from seawater also has been reported by other workers recently [44,45]. However, we found that the extraction efficiency of both PDMS and PA fibers deteriorated rapidly (reduction of peak size > 30% after single use). Under a microscope, swelling of the polymer phase as well as roughness on the fiber surface could be observed, presumably due to dissolution of polymer phase by the excess chelating agent in the sample solution during extraction. This was further confirmed by the observation of serious damage to the fiber coating after a 10-min immersion of a PDMS or a PA fiber in a 50% methanolic Htfa solution. In order to overcome this problem, a more robust polymer phase is required. Polyimide is known to have extremely high thermal stability and chemical inertness, which does not dissolve in most organic solvents [47]. Therefore, a silica optic fiber coated with polyimide buffer was tested for its suitability as a SPME fiber. Preliminary results indicated that polyimide phase can efficiently extract $Cr(tfa)_3$ from aqueous solution. Moreover, it also can resist damage from excess Htfa. Typical chromatograms of $Cr(tfa)_3$ from a 100 ng ml^{-1} Cr(III) solution and a reagent blank obtained by GC-FPD following SPME with a polyimide-coated fiber are shown in Fig. 1A and B, respectively. Prior to extraction, $Cr(tfa)_3$ was formed by adding 50 μl of 50% (v/v) methanolic Htfa to 10 ml of sample solution, followed by reaction at 75 °C for 60 min. In Fig. 1A, two peaks corresponding to the *trans*- and *cis*-$Cr(tfa)_3$ appeared at ca. 7.5 and 8.1 min, respectively. The ratio of peak areas of *trans*:*cis* $Cr(tfa)_3$ was about 84:16, which agrees well with the literature value [48]. Quantitative determination was performed by summing up the areas of the two peaks.

3.2. Complexation of Htfa with Cr(III)

Complexation reaction between Htfa and Cr(III) depends on solution pH, reaction time and temperature. It has been reported that the optimal pH range for complexation of Htfa and Cr(III) is 5.6–6.5 [42]. Besides, the complexation kinetics is very slow at room conditions [41,42]. In order to examine the effect of time and temperature on complexation reaction, a sample solution containing 100 ng ml^{-1} Cr(III) and excess Htfa (~0.01 M) was prepared in 0.5 M sodium acetate at pH 6.0. The solution was subjected to different reaction condi-

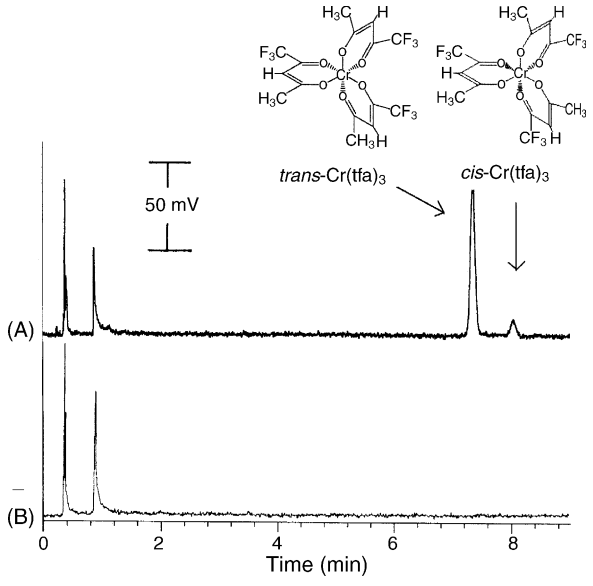

Fig. 1. Chromatograms of $Cr(tfa)_3$ in aqueous solution obtained by GC-FPD following SPME with a polyimide-coated fiber. Samples: (A) 10 ml of 100 ng ml^{-1} Cr(III) solution and (B) 10 ml of reagent blank, both were added with 50 μl of 50% (v/v) methanolic Htfa. SPME conditions: liquid phase extraction mode; 20 min at 25 °C and 1000 rpm stirring. GC-FPD conditions, see Section 2.

tions, followed by SPME and GC-FPD analysis. The variation of obtained peak areas of $Cr(tfa)_3$with reaction time and temperature are schematically depicted in Fig. 2A and B, respectively. From the results in both figures, quantitative formation of $Cr(tfa)_3$ in solution at pH 6.0 can be achieved in 60 min at 75–80 °C. These conditions were adopted as the optimal throughout the following studies.

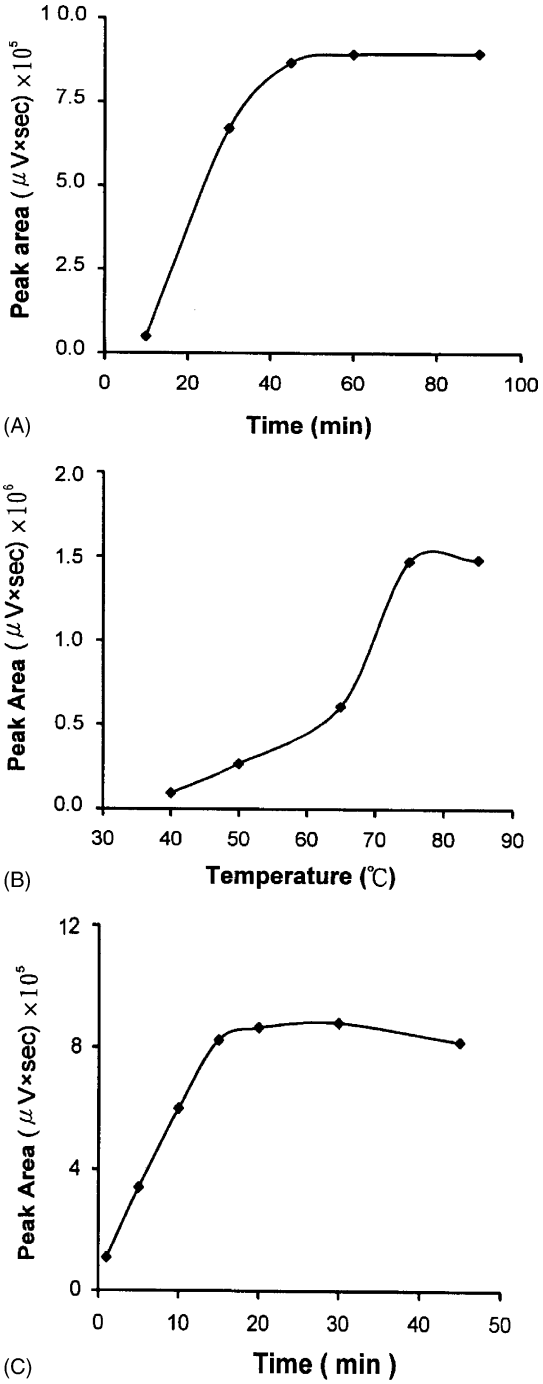

Fig. 2. Variation of peak area of $Cr(tfa)_3$ with: (A) derivatization time, (B) derivatization temperature, and (C) extraction time. Conditions in (A) and (B): $[Cr(III)] = 100\,ng\,ml^{-1}$; [Htfa] = 0.01 M; derivatization temperature in (A), 70 °C; derivatization time in (B), 60 min. Sample in (C): 30 ml of $50\,ng\,ml^{-1}$ $Cr(tfa)_3$ (as Cr). SPME-GC-FPD conditions as in Fig. 1. Each point represents the average of two determinations.

3.3. SPME extractions

SPME procedure was optimized with respect to the extraction mode and extraction time. Although $Cr(tfa)_3$ is volatile enough for GC analysis, its volatility is still not suitable for headspace (HS)-SPME, even at an extraction temperature of 80 °C (data not shown). In the present study, SPME was carried out by direct extraction of $Cr(tfa)_3$ from aqueous solution. Variation of $Cr(tfa)_3$ peak area with extraction time at 25 °C is shown in Fig. 2C. From the extraction time profile, extraction equilibrium was found to achieve at 20 min. Further increasing the extraction time did not increase the amount of $Cr(tfa)_3$ collected on the fiber.

Under equilibrium condition, the distribution constants of *cis*- and *trans*-$Cr(tfa)_3$ between the polyimide fiber coating and the aqueous sample can be calculated following the procedure reported by Buchholz and Pawliszyn [49]. Assuming 16% of the chelate $Cr(tfa)_3$ presented as *cis* isomer, the distribution constants for *cis*-$Cr(tfa)_3$ (K_{cis}) and *trans*-$Cr(tfa)_3$ (K_{trans}) between polyimide phase and aqueous phase were calculated to be 2012 and 2214, respectively. The difference between these two *K* values is only about 10%, which means the two isomers show very similar affinity toward the nonpolar polyimide coating, with *trans* isomer having a slightly larger distribution constant than that of *cis* isomer. This is understandable because the *cis* isomer is somewhat more polar than the *trans* isomer [47].

3.4. Interference

Htfa is not a specific chelating agent for Cr(III). It may form neutral chelates with many di- and trivalent metal ions, e.g., Be(II), Ru(II), Pd(II), AI(III), Co(III), Ga(III), Fe(III), Mn(III), etc. [47]. ECD is a highly sensitive detector for fluorinated metal chelates, but one of its major drawbacks is the non-specificity toward $Cr(tfa)_3$. Other metal–tfa chelates, electron-capturing species extracted from the samples, or minor degradation products of the fluorinated ligand which have been extracted onto the SPME fiber will also give detector responses. Although EI-MS, ICP-MS, or atomic emission detector (AED) [50] can be coupled to GC as an element specific detector for Cr, these detection schemes are very expensive. On the other hand, the low-cost FPD can be made selective toward a specific element by installing a suitable optical filter in front of the PMT. In this study, a 385-nm long-pass filter was used to monitor the major emission lines of Cr (425 nm) and CrO (580–640 nm) [51] in an air–hydrogen flame. No recognizable chromatographic signal was observed from $1\,\mu g\,ml^{-1}$ Be(II), Cu(II), Ni(II), Co(II), Zn(II), Mn(II), AI(III), Fe(III) and Ru(III) under the same Htfa chelation and SPME-GC-FPD conditions as described above for Cr(III). While some of the elements tested do have their characteristic emission spectral maxima (λ_{em})

above 400 nm, which should also be detected by FPD in the present situation, selectivity ratio among different elements in the FPD often varies in accordance with the geometric, chemical, and spectral conditions of the detector [52]. Poor extraction of the metal chelates onto the SPME fiber or decomposition of some of the organometallics before reaching the detector might be another reason for the negligible responses of these test elements. Besides, no change in peak size of 100 ng ml^{-1} Cr(III) was found with a 10-fold spiking of each possible interfering metal ion, if an excess amount (~0.02 to 0.04 M) of Htfa was present during complexation reaction to compensate for the extra chelating agent required.

Due to the high concentration (0.5 M) of background buffer used in the derivatization step, the purity of the reagents (e.g., acetic acid, sodium acetate and sodium hydroxide) is an issue of concern. It was found that analytical reagent grade chemicals were unsuitable for use because of their relatively high level of Cr contamination. Only ultra-pure or Suprapur (Merck) grade chemicals were used for preparation of buffer solution. Besides, all glassware and sample vials were thoroughly cleaned by immersion in a 5 M nitric acid solution for at least 3 days before use. No detectable contamination of Cr was observed in the chromatograms of reagent blank solutions (see Fig. 1B).

In order to assess the possible loss of $Cr(tfa)_3$ to the wall of sample vial during SPME, experiments were carried out to examine the chromatographic peak areas obtained from a 10 ng ml^{-1} Cr(III) solution contained in 20-ml sample vials made from glass and polypropylene. Following the same derivatization, SPME and GC-FPD procedures, no significant difference (95% confidence level, $n = 3$) in GC peak areas of $Cr(tfa)_3$ was found between the two types of sample vials used, if the formed $Cr(tfa)_3$ was immediately extracted by SPME. This result agrees with that of other workers where no loss of analyte from 10 ml of 1 ng ml^{-1} (as Cr) standard $Cr(tfa)_3$ solution contained in a 25-ml glass vial was reported during their investigation of the kinetics of SPME sorption [45]. However, we did observe significant loss (>50%) of $Cr(tfa)_3$ if the aqueous solution of 10 ng ml^{-1} $Cr(tfa)_3$ (as Cr) was kept in a glass vial at room temperature for 24 h before SPME extraction. This is probably due to adsorption of $Cr(tfa)_3$ onto the glass wall. Plastic vials are generally required for aqueous samples containing chromium at sub-part-per-billion level (e.g. sea water) in order to avoid contamination and/or loss of analyte [42,44,45].

3.5. Analytical figures of merit

The calibration curve of the Cr(III) solution was linear over the concentration range 5–300 ng ml^{-1} Cr. The equation of a typical calibration line was $y = 24569x + 16357$ with an $R = 0.9985$ ($n = 5$). The precision of the method was evaluated by performing replicate analysis of a 10 ng ml^{-1} Cr(III) solution. Five replicate analyses gave a relative standard deviation of 7%. Limit of detection (LOD; 3 s) for Cr(III) was 2 ng ml^{-1}. This value is about 10 times lower than that of the SPME-HPLC-UV method [43], but about two orders of magnitude higher than that of the SPME-GC/SF-ICPMS method [44,45] or the SPME-GC-ECD method [45]. Table 1 provides a comparison of the LOD, precision and experimental time (including derivatization, SPME and chromatography) of various methods for chromium analysis. Sample preparation steps, viz., derivatization and SPME, are still the most time-consuming stage in the whole analytical process. Although the sensitivity of FPD is inferior to those of ICP-MS and ECD, the present method is sensitive enough for the analysis of chromium in ground water and drinking water, in which the maximum contaminant level (MCL) for total chromium was set at 100 ng ml^{-1} by U.S. Environmental Protection Agency (EPA) [53].

The accuracy of the method was assessed by the analysis of Cr in a trace element water reference standard, SRM 1643d, from the National Institute of Standards and Technology (NIST, USA). Although this sample matrix also contains many other elements, only a few extraneous peaks appear in the chromatogram, which evidences the high selectivity of this method. The measured value, 19.6 ± 1.7 ng ml^{-1} Cr ($n = 5$), agrees well with the certified value, 18.5 ± 0.2 ng ml^{-1} Cr, which provides proof for the accuracy of the method.

3.6. Application

The developed SPME-GC-FPD method was applied to the determination of chromium in an effluent collected from the water treatment plant of a local industrial park. Sample preparation was as described in the Experimental Section. Fig. 3 shows the chromatograms of Cr in original sample

Table 1
Comparison of SPME-HPLC and SPME-GC methods for chromium analysis

Method	LOD (ng ml^{-1} Cr)	Precision (%)	Analysis time (min)			Reference
			Derivatization	SPME	Chromatography	
SPME-HPLC-UV	17 (Cr(III)); 5 (Cr(VI))	5	–	60	15	[43]
SPME-GC-ICP-MS	0.004–0.02	3–9	120	25	<1[a]; 15	[44]
SPME-GC-ECD	0.01	n.e.	60	25	18	[45]
SPME-GC-FPD	2	7	60	20	9	This work

n.e.: Not established.
[a] GC column (0.5 m).

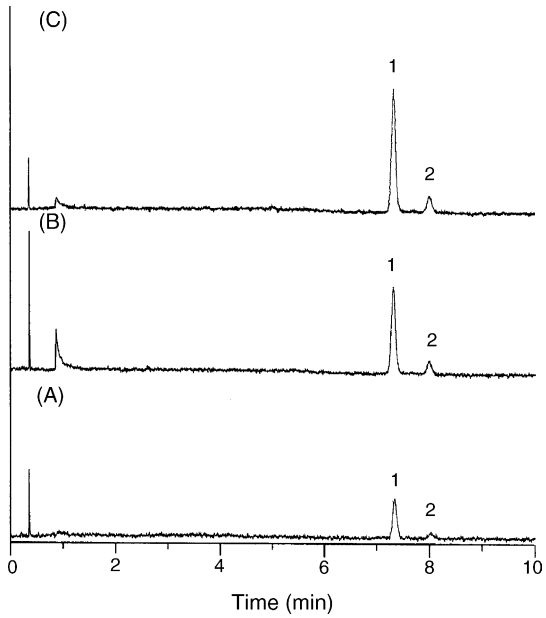

Fig. 3. Chromatograms of Cr in an industrial effluent sample obtained by derivatization-SPME-GC-FPD method. (A) 50-fold diluted sample; (B) 25 ng ml^{-1} Cr(III) added into (A); (C) 50 ng ml^{-1} Cr(III) added into (A).

(50-fold diluted, Fig. 3A) as well as spiked samples (Figs. 3B and C) obtained by the developed method. Calibration was performed using the method of standard addition. Based on triplicate analyses, a value of 1032.0 ± 97.1 ng ml^{-1} Cr (95% confidence interval) was obtained. Total chromium in this sample was also analyzed by another laboratory using the standard ICP-AES method [54], which obtained a value of 915 ng ml^{-1} Cr. The agreement between the two results is reasonably good.

4. Conclusion

A simple method for the determination of Cr(III) in aqueous solution using derivatization-SPME-GC-FPD was developed. A silica fiber coated with polyimide stationary phase was suitable for SPME extraction of Cr(III) as neutral $Cr(tfa)_3$ chelates from aqueous sample. The optimal extraction time was 20 min. The two volatile $Cr(tfa)_3$ isomers extracted can be efficiently separated by a DB-210 GC column within 9 min. Selective detection of Cr was performed by using a FPD equipped with a 385-nm long-pass filter. The limit of detection was 2 ng ml^{-1} Cr. The most time-consuming step in this method was the derivatization of Cr(III) into $Cr(tfa)_3$, which took about 60 min at 75 °C. However, the lengthy reaction time may be significantly reduced by using a microwave oven [42]. Although the sensitivity of the present method is not high enough for direct determination of Cr in seawater which typically has a Cr concentrations of 0.1–0.2 ng ml^{-1} [42,44,45], this method should be suitable for rapid and accurate determination of Cr at ppb level in most natural waters.

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