Ultrasonic extraction of hexavalent chromium in solid samples followed by automated analysis using a combination of supported liquid membrane extraction and UV detection in a flow system

Kuria Ndung’u, Niï-Koteï Djane, Fredrik Malcus and Lennart Mathiasson*

Department of Analytical Chemistry, Lund University, P.O. Box 124, S-221 00, Lund, Sweden

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A simple and sensitive supported liquid membrane (SLM) extraction technique for the determination of Cr(vi) in occupational hygiene and environmental samples has been developed. Solid samples were ultrasonicated for 30 min at 40 °C in ammonium or phosphate buffers. The samples containing Cr(vi) were extracted using the SLM technique for 20 min and Cr(vi) was determined on-line in a flow system by reaction with 1,5-diphenylcarbazide (DPC). The detection limits after a 20 min SLM enrichment at a flow rate of 1 ml min⁻¹ were 0.63 μg l⁻¹ using a 5 mM phosphate buffer at pH 7.0 and 1.18 μg l⁻¹ using a 10 mM ammonium buffer at pH 8.0. The corresponding detection limits for an alternative approach using electrothermal atomic absorption spectrometry (GFAAS) oфф-line after 20 min SLM enrichment were 0.04 μg l⁻¹ and 0.03 μg l⁻¹ for ammonium and phosphate buffers, respectively. The method was validated using a new certified reference material for Cr(vi) and total leachable Cr in welding dust, CRM 545, from the European Commission’s Community Bureau of Reference (BCR). The method should be adaptable for both field sampling and analysis.

Introduction

Chromium(vi) is an established human carcinogen and many workers are exposed to this form of the element in a variety of industries. Hexavalent chromium compounds on contact with skin, generally as liquids, mists or dusts, may act as both irritants and sensitizers. Allergic dermatitis is well known in metal, cement and textile workers, printers and leather tanners. Chromium fumes are also formed during stainless steel welding, and these fumes are known to cause a variety of respiratory injuries, including cancers. At concentrations below those resulting in irritation, skin sensitivity is the most common effect following exposure to chromium compounds. Hexavalent chromium is such a potent carcinogenic agent for the respiratory tract that continuous monitoring is imposed, as stated in the Directive 90/394/EEC on exposure to carcinogenic substances. In occupational health, the occupational exposure limits (OEL) for water-soluble and certain water-insoluble compounds in indoor air are as low as 0.5 mg m⁻³ for chromium, 0.5 mg m⁻³ for Cr(III) and 0.05 mg m⁻³ for Cr(vi). This reflects the different toxicity of the two species.

Samples requiring the determination of Cr(vi) often have a matrix in which the Cr(III) concentration is 10 to 1000 times higher than the concentration of Cr(vi). Thus preservation and stabilization of the oxidation states are essential for an accurate analysis. In this case, the pH is an important factor determining the relative stabilities of Cr(vi) and Cr(III) in aqueous systems. An alkaline medium favours the stabilization of Cr(vi). The thermodynamic standard electrochemical reduction potential for Cr(vi) to Cr(III) at high pH is −0.12 V. In acidic medium, the standard reduction potential for Cr(vi) to Cr(III) is +1.10 V. The irony is that, when Cr(vi) is stabilized with respect to pH, Cr(III) is in an unstable environment. One must consider the stability of both valences when performing an analysis.

A variety of methods exist for the determination of chromium, atomic absorption spectrometry (AAS) being the most commonly used technique for final determination. Other analytical methods for elemental chromium include inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). These spectroscopic techniques are used in methods such as 7024 (AAS) and 7300 (ICP-AES) from the National Institute for Occupational Safety and Health (NIOSH) for the determination of chromium in workplace air samples. These methods can only determine the total chromium, and a separation method prior to detection is necessary to obtain any speciation information. Cr(vi) can also be measured using electrochemical methods, with voltammetric techniques being the most prevalent. Turyan and Mandler recently reported a self-assembled monolayer-based Cr(vi) ion selective electrode.

A number of spectrophotometric and colorimetric techniques have also been developed for Cr(vi) determination. The most sensitive and widely used colorimetric method employs the selective reaction of Cr(vi) with 1,5-diphenylcarbazide (DPC) under acidic conditions. Although most standard analytical methods for Cr(vi) speciation use ion chromatography, including method 3060A from the Environmental Protection Agency (EPA), and method 7604 from the NIOSH, they are limited to laboratory-based analysis of samples. Supported liquid membranes (SLM) have been used for the extraction of anionic contaminants including chromium in ground water and industrial effluents. However, their analytical applications have been scarce. Recently, we presented an SLM-based method for chromium speciation in natural waters using two serially connected SLM units. Ultrasonic extraction has previously been utilized for extraction of Cr(vi) in solid samples. In this study, we have combined a fast off-line sample work-up step for Cr(vi) extraction from solid samples, based on ultrasonic extraction, with an automated determination using SLM in a flow system with spectrophotometric detection. The automated system has been developed with a long-term goal of applying it for field analysis. We have therefore avoided complicated instrumentation.
**Experimental**

**Equipment**

**Supported liquid membrane device.** The SLM device used was similar to that described previously. It consists of two circular poly(tetrafluoroethylene) (PTFE) blocks (with a diameter of 120 mm and a thickness of 30 mm). Each block contains machined grooves like an Archimedes spiral (depth 0.25 mm, width 1.5 mm and length 250 cm, giving a total volume of ca. 0.95 ml). The membrane used was a porous PTFE membrane (pore size 0.2 μm, total thickness 175 μm, of which 115 μm is polyethylene backing, porosity 0.70, FG Millipore, Bedford, MA, USA). It was impregnated by soaking for at least 15 min in a Petri dish containing the membrane liquid (5% m/m Aliquat® in di-n-hexyl ether). The membrane was then placed between the two PTFE blocks and clamped with six stainless steel screws. The stainless steel screws were covered with PTFE to prevent any contact with the solution in the membrane channels.

**Flow injection system.** The flow injection system consisted of peristaltic pumps (Minipuls, Gilson, Villiers-le-Bel, France), an injector and a variable wavelength detector (Kontron Instruments, Milan, Italy). The reagent DPC and the carrier (2 M HNO₃) were pumped at a flow rate of 0.8 ml min⁻¹ using acid resistant tubing (Elkay, Shrewsbury, MA, USA). Samples of 130 μl were injected into the carrier stream by means of an injector assembled from two pneumatically actuated valves (Cheminert, LDC, FL, USA). PTFE tubing (id 0.5 mm) was used. After mixing, the absorbance of the Cr-diphenylcarbazon complex was monitored at 540 nm.

**Atomic absorption spectrometry.** The electrothermal atomic absorption spectrometry (GFAAS) system was a Varian AA-1475 (Varian, Springvale, Australia), connected to a GTA-95 graphite tube atomizer. No background correction was made.

Sample solutions (20 μl) were delivered into the furnace using a Varian programmable autosampler. Pyrolytic graphite tubes were used exclusively and absorbance measurements were recorded on a computer. Parameter settings, such as lamp current and wavelength, were those recommended by the manufacturer.

**Reagents**

All solutions were prepared from suprapur or analytical grade reagents and high purity water was obtained from a MilliQ-RO4 unit (Millipore, Bedford, MA, USA). All glassware and bottles used were cleaned in 4 M HNO₃ for 4 days and rinsed with high purity water before use. Nitric acid solutions were made from 65% suprapur HNO₃ (Merck, Darmstadt, Germany). Chromium(III) and chromium(VI) standard solutions were prepared from 1000 mg l⁻¹ stock solutions using chromium(III) chloride or potassium dichromate (BDH Chemicals, Poole, Dorset, UK). The extractant in the membrane was 5% m/m methyltricapryl ammonium chloride (Aliquat®, Merck) in di-n-hexyl ether (Sigma Aldrich, St. Louis, MO, USA). The Cr(VI) complexing reagent solution, DPC (BDH Chemicals), was prepared by dissolving 0.05 g of DPC in 40 ml methanol and diluting to 100 ml with water. Ammonium chloride, ammonium sulfate, ammonia solution, dipotassium hydrogen phosphate and potassium dihydrogen phosphate, p. a. grade, were purchased from Merck.

**Experimental procedures**

**Experimental set-up.** Fig. 1 shows the automated experimental set-up for on-line SLM extraction/enrichment and final analysis after off-line Cr(VI) ultrasonic extraction. After ultrasonic extraction, the sample solution is pumped using pump P1 through the donor channel of the SLM device containing 5% m/m Aliquat® in di-n-hexyl ether in the pores. After enrichment, pump P2 is used to pump out the selectively
enriched analyte from the stagnant acceptor solution into a 2 ml collection loop. At the same time, pump P3 is automatically turned on to set the baseline of the UV/VIS detector before injection of the sample. After filling the collection loop, valve V2 switches to bypass the SLM, and 130 μl of the 2 ml acceptor eluate is loaded into the injection loop. The excess volume goes to the waste through valve V6. To minimize the dilution effect, valve V3 is switched in such a way that the 2 ml collection loop is emptied from an opposite direction to that of loading. The sample is injected into the carrier stream using P3 and passes via V5 and V7 to the T-connection, where it is mixed with the complexing reagent. P3 also delivers the complexing reagent, DPC, to the sample via the same T-connection. The absorbance of the coloured complex formed is measured on the UV/VIS detector at 540 nm and recorded as a peak height on a chart recorder. Pump P2 is used to wash the membrane acceptor channels with fresh acceptor solution and empty the 2 ml collection loop before the next enrichment commences.

For off-line GFAAS chromium determination, a fraction collector was incorporated into the set-up: 2 ml of the enriched sample was transferred into a vial in the fraction collector instead of the 2 ml collection loop.

Blank determination. Blank determinations were performed by enriching either ammonium (10 mM, pH 8.0) or phosphate (5 mM, pH 7.0) buffer solutions. The initial Cr(vi) concentration in the blank was then calculated from the measured Cr(vi) after enrichment and the extraction efficiency value determined from a standard solution.

Sample preparation. Twenty millilitres of 10 mM ammonium [10 mM (NH₄)₂SO₄–10 mM NH₃, pH 8.0] or phosphate (5 mM K₂HPO₄–5 mM KH₂PO₄, pH 7.0) buffer solution was added to the sample followed by ultrasonication in a bath (220 V, 340 W, 47 kHz: Branson Ultrasonics, Danbury, CT, USA) for 30 min at 40 °C. After ultrasonication, the supernatant was pumped through the SLM device. Cr(vi) was determined online by flow injection analysis (FIA)-UV/VIS using the set-up shown in Fig. 1 or off-line by GFAAS. The reference material used for method validation was CRM 545, a glass fibre filter (ECV, Brussels, Belgium).

Results and discussion

Ultrasonic extraction optimization

Cr(vi) is normally extracted at pH ≈ 7 where it is thermodynamically stable. Cr(III) is, however, thermodynamically unstable in basic medium. Ammonia has been shown to inhibit the oxidation of Cr(III) to Cr(vi) in aqueous alkaline media through complexation. An ammonium [(NH₄)₂SO₄–NH₃] buffer was therefore chosen for Cr(vi) extraction in this work. A phosphate buffer (5 mM K₂HPO₄–5 mM KH₂PO₄, pH 7) is normally used to quantify and define operationally soluble and exchangeable forms of Cr(vi). In order to determine the optimum conditions for ultrasonic extraction of Cr(vi) from solid samples, the effects of the ultrasonic bath temperature, sonication time, ammonium buffer concentration and pH were evaluated. Sonication temperature and time were investigated from 30 to 60 °C and 20 min to 1 h respectively. A sonication time of 30 min at 40 °C of spiked filter paper and washed sea sand samples was found to give quantitative (above 98%) recovery of Cr(vi). Fig. 2 shows the effect of pH and ammonium buffer concentration on the extraction of Cr(vi). Fig. 2 indicates that there is a gradual decrease in recovery with increasing buffer concentration and pH. pH 8 was chosen as the digestion pH due to the possible instability of Cr(vi) at lower pH values. The optimum pH for the donor solution using SLM for the extraction of Cr(vi) in ammonium buffer was also 8.0.

Cr(vi) stability

Experiments were carried out to investigate the efficiency of the ammonium buffer in leaching out Cr(vi) and the possibility of Cr(vi) reduction or Cr(III) oxidation. Filter and acid washed sand samples were spiked with solutions of known concentration of Cr(vi) and a tenfold excess of Cr(III). Table 1 gives a summary of Cr(vi) extracted from such samples. The results in Table 1 show that, with the chosen conditions, 10 mM ammonium buffer at pH 8.0 and 5 mM phosphate buffer at pH 7.0, the tendency for Cr(vi) reduction or Cr(III) oxidation is minimal.

SLM optimization studies

Extraction efficiency and donor flow rate. The extraction efficiency, E, is an analytically important quantitative parameter for describing the SLM extraction process. For a flowing sample solution in the donor channel and a stagnant acceptor solution, it is expressed as:

\[
E = \frac{C_A V_A}{C_D F_D} \tag{1}
\]

Table 1 Determination of Cr(vi) in the presence of excess Cr(III) in spiked filter paper (40 mg) and acid washed sand (0.2 g) after ultrasonic extraction using ammonium (pH 8.0) and phosphate (pH 7.0) buffers. Each concentration is a mean of three determinations (standard deviation in parentheses). The samples were ultrasonicated for 30 min at 40 °C in 20 ml of buffer solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added Cr(vi) + 250 (μg g⁻¹) Cr(III)</th>
<th>Recovered Cr(vi)/μg g⁻¹</th>
<th>Cr(vi) recovery (%)</th>
<th>Added Cr(vi) + 250 (μg g⁻¹) Cr(III)</th>
<th>Recovered Cr(vi)/μg g⁻¹</th>
<th>Cr(vi) recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid washed sand</td>
<td>2.50 (0.13)</td>
<td>2.46 (0.13)</td>
<td>98</td>
<td>2.50 (0.13)</td>
<td>2.65 (0.10)</td>
<td>106</td>
</tr>
<tr>
<td>Filter paper</td>
<td>25.0</td>
<td>25.9 (3.6)</td>
<td>104</td>
<td>25.0</td>
<td>25.8 (1.0)</td>
<td>104</td>
</tr>
</tbody>
</table>

Fig. 2 Recovery values for Cr(vi) ultrasonic extraction at different pH values and (NH₄)₂SO₄–NH₃ buffer concentrations. All experiments were performed at a temperature of 40 °C for 30 min using a buffer volume of 20 ml.
where $C_A$ and $V_A$ are the concentration and volume of analyte collected in the acceptor phase, and $C_D$ is the analyte concentration in the incoming donor phase, pumped with the volume flow rate $F_D$ during time $t$ min. The mass transfer kinetics in an SLM extraction have been described by Jönsson et al. and in a recent review of the basic principles of membrane extraction. The extraction efficiency approaches unity as the flow rate approaches zero. Although the most efficient extractions are obtained at low donor flow rates, sometimes it is more important to maximize the enrichment factor, i.e., the amount of sample accumulated in the acceptor per given time, rather than maximize the extraction efficiency. The enrichment factor $E_e$ is defined as:

$$E_e = \frac{E S / V_A}{E D / V_A}$$

where $E_S$ and $V_A$ are the donor and acceptor volumes respectively.

Fig. 3 shows the variation in $E$ and $E_e$ at different donor flow rates in the extraction set-up for Cr(vi) with an acceptor solution of 1 M HNO$_3$. As shown in Fig. 3, the enrichment factor, $E_e$, increases with donor flow rate in the investigated system. However, at high flow rates, larger sample volumes are consumed and hence the choice of operational flow rate might be dictated by the available sample volume, $V_S$. There are also mechanical limitations due to the narrow donor channel in the membrane device to obtain a high mass transfer between the donor solution and the membrane liquid. High flow rates will increase the pressure drop along the channel, which may affect the long-term stability of the system. With the membrane construction used here, which is similar, to that used elsewhere, a flow rate of 5–6 ml min$^{-1}$ should not be exceeded. In this work, $V_S$ was limited by the volume used during ultrasonic extraction of Cr(vi) from the solid samples. Normally, a flow rate of 1 ml min$^{-1}$ has been used, leading to an enrichment factor of 3–4 times. If higher enrichment factors are desired, it would be better to increase the sample size used in the ultrasonic extraction step rather than decrease the flow rate.

**Acceptor solution.** Cr(vi) species (HCrO$_4$–, CrO$_2$$^{2–}$ or Cr$_2$O$_7$$^{2–}$) are extracted into the organic membrane by forming neutral ion-pair complexes with Aliquat® at the donor–membrane interface. These diffuse to the membrane–acceptor interface, where the Cr(vi) anion in the Aliquat®–Cr(vi) ion-pair is substituted with another anion. The driving force is therefore the anion concentration on the acceptor side of the membrane. In a previous study, $\text{NO}_3^–$ (as HNO$_3$) was found to be a suitable acceptor solution for Cr(vi) extraction from natural water samples, where GFAAS was used for final determination. However, HNO$_3$ could not be used for on-line FIA Cr(vi) determination due to the risk of reduction of Cr(vi) to Cr(III) in acidic media. Several ions (SO$_4^{2–}$, NO$_3^–$ and Cl$^–$), present as anions in salts, were evaluated as acceptor solutions in the SLM device for stripping of Cr(vi) from phosphate or ammonium buffer donor solutions. Chloride ion, as NH$_4$Cl, gave the best results. Hence, Cl$^–$ was used for trapping Cr(vi) in the acceptor prior to on-line FIA. It should be noted that the influence of Cl$^–$ on analyte extraction efficiency could be attributed to the presence of Cl$^–$ in the complexing reagent (Aliquat®). The mass transfer kinetics are likely to be enhanced more by Cl$^–$ in the ion exchange process compared to NO$_3^–$ or SO$_4^{2–}$. In order to determine the optimum acceptor Cl$^–$, the concentration of this solution was varied from 0.25 to 1.0 M, with each concentration also made 50 mM in NH$_3$ to stabilize Cr(vi).

Fig. 4 shows the variation in extraction efficiency at different acceptor NH$_4$Cl concentrations with ammonium or phosphate buffer as the donor solution. As expected, there is a steady increase in extraction efficiency as the NH$_4$Cl concentration increases up to 0.25 M for the 5 mM phosphate buffer and 0.5 M for the ammonium buffer. A further increase in the NH$_4$Cl concentration does not increase the flux of the Cr(vi) species. The extraction efficiency using 10 mM ammonium buffer as the donor is lower compared to the phosphate buffer for all concentrations investigated. The reduced flux could result from NH$_4$$_2$PO$_4$ complexation with Cr(vi) which slows the diffusion of Cr(vi) to the donor–membrane interface. The exact explanation for the drop in extraction efficiency when extracting Cr(vi) from the ammonium buffer into NH$_4$Cl is not clear, as higher $E$ values were obtained when using NO$_3^–$ as nitric acid at similar concentrations (Fig. 6, see later). It could depend on the fact that, in the system used here, the NH$_4$$^+$ ion is present on both sides of the membrane.

**Donor concentration and SLM stability.** For reliable quantification, it is important that the extraction efficiency at different analyte concentrations in the sample should remain constant. In a previous study, a similar SLM (6% m/m Aliquat® in di-n-hexyl ether) was used for Cr(vi) speciation in natural waters. The extraction efficiency was constant in the concentration range 2–40 $\mu$g l$^{-1}$ Cr(vi) in spiked river water. In this work, a 20 min enrichment period at a flow rate of 1 ml min$^{-1}$ was performed using an SLM containing 5% m/m Aliquat® in di-n-hexyl ether. The extraction efficiency was constant (RSD < 5%) for Cr(vi) concentrations in the range 2–20 $\mu$g l$^{-1}$ when HNO$_3$ was used as trapping solution prior to GFAAS analysis and for 10–50 $\mu$g l$^{-1}$ in NH$_4$Cl solutions prior to DPC-FIA. The long-term stability of the SLM will depend on the type of carrier and its solubility in water, the pore size of the membrane support and the flow rate. Membranes impregnated with hydrophobic liquids with small pore sizes are stable over a long period. The membranes in this work could be used at the normal

**Fig. 3** Variation in extraction efficiency, $E$, and enrichment factor, $E_e$, at different flow rates in the donor channel and with a stagnant acceptor solution. SLM: 5% Aliquat® in di-n-hexyl ether. Donor: 10 $\mu$g l$^{-1}$ Cr(vi), 5 mM KH$_2$PO$_4$–K$_2$HPO$_4$ buffer at pH 7.0. Enrichment time: 20 min. Acceptor: 1.0 M HNO$_3$.

**Fig. 4** Optimization of the buffer concentration in the acceptor for SLM extraction of Cr(vi). Acceptor: different concentrations of NH$_4$Cl each containing 50 mM of NH$_3$ adjusted to pH 8.0. Flow rate: 1 ml min$^{-1}$. All other conditions as in Fig. 3.
operating conditions for at least 4 days without showing a significant decrease in extraction efficiency.

**DPC-FIA detection**

The UV/VIS detector was investigated for on-line Cr(VI) detection. The reaction between Cr(VI) and DPC is the basis of the most sensitive spectrophotometric method for the determination of trace amounts of Cr(VI) and is widely used for routine determination of Cr(VI). The use of a continuous flow injection technique (FIA) has the potential of making routine determinations easier, faster and more reliable. The reproducibility of the FIA system was investigated by making three replicate measurements on each standard and samples. The resulting RSDs were 2.6% and 4.0% for the standards and replicate measurements on each standard and samples. The limits of detection (LODs), calculated as three times the standard deviation of the blank signal, were 4.1 µg l⁻¹ using a phosphate buffer and 8.0 µg l⁻¹ using an ammonium buffer.

The calibration curve was obtained by plotting the peak heights as a function of the standard concentration of Cr(VI). A linear dynamic range was observed for the concentration range 50–400 µg l⁻¹ Cr(VI) with a correlation coefficient of 0.998 (Fig. 5, see below), using a carrier solution of 2 M HNO₃ and 0.05% m/v DPC in 40% methanol and an injection volume of 130 µl.

**On-line SLM-DPC-FIA**

Cr(VI) samples were analysed on-line after ultrasonic extraction using the automated set-up shown in Fig. 1. This set-up is similar to that used for speciation analysis of chromium in natural waters with off-line GFAAS determination after SLM extraction and enrichment.19 In that set-up, the enriched analyte in the stagnant acceptor solution of the membrane device was pumped into a vial in a fraction collector after the enrichment step. A volume of 2 ml was normally used to ensure a complete transfer of the enriched sample from the acceptor channel (volume, 1 ml) to the vials. In the on-line set-up used here, we have followed the same guidelines and the enriched sample is eluted from the acceptor side of the membrane device into a 2 ml collection loop. After filling the loop, 130 µl of this acceptor eluate is loaded into the FIA injection loop and injected into the FIA system for detection. The SLM eluate in the 2 ml collection loop is pushed out into the FIA injection loop from a direction opposite that of loading to minimize dilution. To minimize carry-over effects, the acceptor channel is washed with fresh acceptor solution before starting a new enrichment.

Fig. 5 shows four on-line replicate determinations of Cr(VI) (peaks A–D) using the system. The calibration part of the analysis was performed off-line with manual injection of standards into the injection loop of the FIA system. During this time, the reagent/carrier pump was turned off (pump 3 in Fig. 1). The rise in the baseline before peaks A–D in Fig. 5 is due to the absorbance of the stagnant DPC-carrier complex in the detector flow cell during this time. The small variations in the heights of peaks A–D are due to random errors in the determinations.

The SLM extraction time can be chosen with respect to the initial Cr(VI) concentration in the sample. If the concentration of the analyte in the sample is low, the detection limit can be improved by extending the enrichment time (which will need a larger sample size during the off-line ultrasonic extraction step).

The LOD for Cr(VI) in a solution of 0.25 M NH₄Cl–0.05 M NH₃ using the SLM-DPC-FIA technique with a 20 min SLM extraction was 0.63 µg l⁻¹ using the phosphate extraction buffer at pH 7.0 and 1.18 µg l⁻¹ in 0.5 M NH₄Cl–0.05 M NH₃ solution using the pH 8.0 ammonium extraction buffer. Instrumentation in the current FIA set-up was chosen with application to field analysis in mind. However, if the system is to be used for laboratory-based real time analysis, which is important in industrial process control, an auto-injector can easily be connected. Thus the only off-line step in the analytical procedure would be the ultrasonic extraction step.

**SLM-GFAAS analysis**

Chromium(VI) determination by GFAAS is sometimes necessary when the concentration in the samples is below the detection limit of the SLM-DPC-FIA method. However, since the determination of Cr(VI) by AAS, unlike the DPC method, is not Cr(VI) specific, a separation step to selectively extract anionic Cr(VI) species in the presence of Cr(III) is necessary. This is achieved by SLM in the same way as in the DPC-FIA method. We have previously used NO₃⁻ (added as nitric acid) in the acceptor solution to selectively trap Cr(VI) from natural water samples prior to GFAAS determination.19 A reduction of Cr(VI) to Cr(III) in acidic medium on the acceptor side of the membrane does not pose a problem since GFAAS gives the total Cr concentration, which in this case is equal to the Cr(VI) concentration in the sample. Experiments were performed to determine the optimum nitric acid concentration for trapping Cr(VI) from the two buffers used during the ultrasonic extraction step. Fig. 6 shows the extraction efficiency at different nitric acid concentrations in the acceptor. The trend is similar to that for NH₄Cl, with the extraction efficiency showing no further increase after a nitric acid concentration of 1.0 M for both donor buffer solutions. In a previous study,19 the optimum nitric acid concentration for trapping Cr(VI) from water samples was found to be about 0.75 M compared to 1.0 M in the present study. This might depend on the ionic strength of the solution used for the ultrasonic extraction of solid samples, resulting in a higher ionic strength in these samples compared to the natural water samples.19 The blank concentration and standard deviation (s) after 20 min SLM extraction (in 1.0 M HNO₃) were 0.32 and 0.015 µg l⁻¹ for the phosphate buffer, and 0.16 and 0.01 µg l⁻¹ for the ammonium buffer, respectively. The corresponding LODs, expressed as three times the s, will then be 0.04 µg l⁻¹ and 0.03 µg l⁻¹ for the phosphate and ammonium buffers, respectively. The blank values are small compared to the values expected in polluted solid samples. For
The SLM methodology for Cr(vi) determination was validated using a new certified reference material: CRM 545. The material is certified for Cr(vi) and total leachable chromium in welding dust loaded on filter paper from the Standards, Measurements and Testing Programme (formerly BCR) of the European Commission. Until now, there has been no known certified reference standard material available for particulate Cr(vi). The results of the validation are shown in Table 2. The values for total leachable Cr shown in Table 2 were determined by direct GFAAS injections (no SLM extraction) after ultrasonic extraction and appropriate dilution. Generally, a good agreement was achieved between the certified values and those obtained using both SLM-GFAAS and SLM-DPC-FIA. Christiansen et al., 28 who were involved in the certification of CRM 545, attribute the fact that the total leachable Cr content of the welding dust is somewhat lower than the Cr(vi) content to the uncertainty of the results used for calculation of the certified values.

Conclusion

In this work, we have presented a simple, inexpensive and sensitive method for the determination of Cr(vi) in workplace samples and in environmental samples. Using a simple computer-controlled system consisting of a membrane device, peristaltic pumps, low-pressure pneumatic valves and a UV/VIS detector, Cr(vi) in particulate samples was determined on-line at the sub-ppb level after ultrasonic extraction. By combining a Cr(vi)-selective SLM extraction step with a Cr(vi)-specific spectrophotometric detection, a highly specific on-line method

<table>
<thead>
<tr>
<th>Buffer</th>
<th>Certified value</th>
<th>SLM-GFAAS</th>
<th>SLM-DPC-FIA</th>
<th>Certified value</th>
<th>Direct GFAAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate</td>
<td>40.16 (0.60)</td>
<td>40.02 (0.63)</td>
<td>40.22 (0.81)</td>
<td>39.47 (1.30)</td>
<td>40.87 (1.29)</td>
</tr>
<tr>
<td>Ammonium</td>
<td>40.16 (0.60)</td>
<td>40.23 (0.34)</td>
<td>40.13 (0.82)</td>
<td>39.47 (1.30)</td>
<td>42.56 (2.33)</td>
</tr>
</tbody>
</table>

*Calculated after subtraction of the blank values.

References