Determination of chromium(VI) and lead in water samples by on-line sorption preconcentration coupled with flame atomic absorption spectrometry using a PCTFE-beads packed column

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Abstract

A new time-based flow injection on-line solid phase extraction method for chromium(VI) and lead determination using flame atomic absorption spectrometry was developed. The use of hydrophobic poly-chlorotrifluoroethylene (PCTFE)-beads as absorbent in on-line preconcentration system was evaluated. Effective formation of ammonium pyrrolidine dithiocarbamate complexes and subsequently retention in PCTFE packed column, was achieved in pH range 1.0–1.6 and 1.5–3.2 for Cr(VI) and Pb(II) ions, respectively. The sorbed analyte was efficiently eluted with isobutyl-methyl-ketone for on-line FAAS determination. The proposed packing material exhibited excellent chemical and mechanical resistance, fast kinetics for adsorption of Cr(VI) and Pb(II) permitting the use of high sample flow rates at least up to 15 mL min⁻¹ without loss of retention efficiency. For a preconcentration time of 90 s, the sample frequency was 30 h⁻¹, the enhancement factor was 94 and 220, the detection limit was 0.4 and 1.2 \( \mu \text{g} \text{L}^{-1} \), while the precision (R.S.D.) was 1.8% (at 5 \( \mu \text{g} \text{L}^{-1} \)) and 2.1% (at 30 \( \mu \text{g} \text{L}^{-1} \)) for chromium(VI) and lead, respectively. The applicability and the accuracy of the developed method were estimated by the analysis spiked water samples and certified reference material NIST-CRM 1643d (Trace elements in water) and NIST-SRM 2109 (chromium(VI) speciation in water).

Dedicated to Professor John A. Stratis for his 35 years contribution in analytical chemistry.

Keywords: Chromium; Lead; Polychlorotrifluoroethylene; Solid phase extraction; Atomic absorption spectrometry; On-line

1. Introduction

Nowadays, it is well known that the toxicological and biological properties of many elements depend upon their chemical forms. Chromium(III) is considered an essential element controlling glucose lipid and protein metabolism in mammals, while chromium(VI) is definitely highly toxic for biological systems, with mutagenic and potential carcinogenic properties [1]. In addition, there is an increasing interest in determination hazardous substances at trace level, such as heavy metals, because of persistent and bio-accumulative effect in the environment and living organisms. Determination of trace amount of lead in natural water samples plays an important role in the environmental pollution monitoring the environmental pollution. Due to the constant interest for monitoring of toxic elements such as Cr(VI) and lead, extended reviews about the analytical methodologies for their determination are recently published [2,3].

Although, flame atomic absorption spectrometry (FAAS) is one of the most popular techniques, with significant precision and accuracy, a preconcentration and/or separation step prior the final measurement, is usually required, in order to bring the analyte concentration into the dynamic range of the detector or to isolate the analyte from the desirable matrix constituents. The hyphenation of flow injection (FI) on-line solid phase extraction (SPE) with FAAS has proved to be a powerful tool for trace elements determination in a variety of matrices in terms of the enhanced sensitivity, efficient matrix removal, high sampling frequency and low cost of equipment [4].

On-line column preconcentration/separation is based predominantly on the incorporation of mini-columns packed with
various polar or non-polar sorbent materials. The nature and the properties of the packing materials are of prime importance for effective retention of analyte [5], while some basic requirements for them should be met, like fast and quantitative adsorption, effective elution, negligible swelling and shrinking, regeneration ability, high capacity, accessibility and high chemical resistibility [4].

Several methods have been developed for FI on-line column preconcentration of Cr(VI) and lead for atomic spectrometric determination. These procedures mainly utilize various packing materials like: octadecyl functional groups bonded on silica gel, C18 [6–10]; ion-exchange resins, cellex-T [11] packing materials like: octadecyl functional groups bonded on silica gel, C18 [6–10]; ion-exchange resins, cellex-T [11]; activated alumina [14,15]; activated carbon [16]; C60-fulerenes [17]; polyurethane foam [18–20]; polymers amberlite XAD-16 [21], XAD-2 [22], chromosorb-102 [23]; and polytetrafluoroethylene (PTFE) as turnings [24,25], as beads [26] as grafted fiber [27] and as knotted reactor [28,29].

Polychlorotrifluoroethylene, PCTFE (Neoflon® or Kel-F®) is a hydrophobic porous, non-reactive and solvent-resistance polymer, which has been used as packing material for reverse phase column chromatography [30]. Although, it has been reported in batch procedures that PCTFE can effectively adsorb some metal complexes, which can be easily eluted with hydrochloric acid or methanol without any swelling or shrinking effect [31,32], it has not be used for FI-FAAS on-line preconcentration systems.

Various chelating agents containing sulphur, nitrogen or oxygen donor atoms as weak Lewis bases were reported for lead and chromium determination [10,33]. Ammonium pyrrolidine dithiocarbamate (APDC), which is usually employed for metal determination in FAAS, has proved to be suitable for the determination of lead with on-line sorbent extraction and FAAS [16]. Although, it is well known that Cr(III) reacts with APDC ligand under mild conditions to give the complex tris[pyrrolidine-1-dithioato-S,S']-Cr(III) [6], the extraction of Cr(III) by APDC-IBMK system under the conditions usually employed for the extraction of Cr(VI) has been found to be inefficient, due to the difficulty of displacing by APDC the coordinated water from the strongly hydrated Cr(III) ion [34,35]. On the other hand, Cr(VI) is reduced easily and quickly by APDC to Cr(III), which subsequently forms complexes easily extracted. This differentiation on complex formation of Cr(III) and Cr(VI) with APDC can be easily applied in on-line preconcentration systems for chromium speciation [6].

In the present work the performance of APDC/PCTFE-beads/IBMK scheme for on-line preconcentration and determination of chromium(VI) and lead was investigated. The applicability of PCTFE as packing material in FI-FAAS systems for trace metal preconcentration and separation was evaluated. All main analytical parameters such as sample acidity, ligand concentration, sample loading and elution flow rate and the preconcentration time were examined thoroughly. The effect of potential interferents occurring in environmental samples also studied. The developed method was applied for chromium(VI) and lead determination in natural water samples and certified reference materials.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer, Norwalk, Connecticut, USA model 5100 PC flame atomic absorption spectrometer equipped with a deuterium arc background corrector was used as a detector. A chromium hollow cathode lamp (Perkin-Elmer), operated at 30 mA and a lead electrodeless discharge lamp (EDL) operated at 10 W, were used as light sources. The wavelength was set at 357.9 nm resonance line and at 283.3 nm for chromium and lead determination, respectively. The monochromator spectral bandpass was set at 0.7 nm and a 0.2 s time-constant was used for peak height evaluation. The flame composition was optimized, in order to compensate for the effect of IBMK, which serves as additional fuel. A flow spoiler was used into the spray chamber for all measurements. The nebulizer free uptake rate was 5.6 mL min⁻¹. An Orion EA 940 pH-meter was employed for the pH measurements.

The flow injection system, which is shown schematically in Fig. 1, was coupled to the nebulizer system of the above spectrometer with a short PTFE capillary 12 cm length, 0.35 mm i.d., to minimize the analyte dispersion. The manifold consisted of two peristaltic pumps (Watson Marlow, Cornwall, England model 205U/BA) and an injection valve two-position six-port (Labpro, Reodyne, USA). Peristaltic pump tubing of “Tygon” type was adopted to deliver the aqueous solutions, while due to the incompatibility of organic solvents with the peristaltic tubes, a displacement bottle (Tecator, Hoganas, Sweden) was used for the IBMK transportation. PTFE tubing of 0.5 mm i.d. was used for all connections.
A special adapter to the nebulizer (Fig. 1) called flow compensation (FC) in the shape “T” was used in order to compensate the lack of nebulizer free uptake flow rate. The benefit of FC unit was the very good reproducibility of the recorded signal especially at elution flow rate lower than 2 L min\(^{-1}\). In addition, no gas bubbles are produced in the tubing, during the step 1, where the peristaltic pump P2 is inactive as it is described in Section 2.3.

The preconcentration column (C) was made from a glass tube, with an effective length of 70 mm and inner diameter of 3.5 mm. An amount of 950 mg, fraction 100–600 µm (Fig. 2) of PCTFE beads were firmly packed into the column. The ends of each side of the column were plugged with glass wool for keeping the packing material in place. The PCTFE-beads were washed thoroughly by 2.0 mol L\(^{-1}\) HNO\(_3\) followed by ethanol and finally with water. As it is proved from the present study, the performance of the column was stable at least over 500 preconcentration cycles.

2.2. Reagents and samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany). Ultra-pure quality water was used throughout which was produced by a Milli-Q system (Millipore, Bedford, USA). Working standard solutions of chromium(VI) and lead(II) were prepared by stepwise dilution of 1000 mg L\(^{-1}\) stock standard solution (Titrisol, Merck) to the required µg L\(^{-1}\) levels. The acidity of the standards was adjusted with dilute HNO\(_3\). The chelating reagent, 0.08% (m/v) APDC was prepared fresh daily by dissolving the appropriate amount of ammonium pyrrolidine dithiocarbamate in water. Isobutyl methyl ketone (IBMK) was used after saturation with water, without any other purification. The poly-chlorotrifluoroethylene (PCTFE) powder (Aldrich, Steinheim, Germany) was sieved to obtain the PCTFE-beads fraction between 100 and 600 µm.

Two standard reference materials were used in order to validate the accuracy of the developed method: NIST CRM 1643d (National Institute of Standard and Technology, Gaithersburg, MD, USA) containing trace elements in water and NIST SRM 2109 (Cr(VI) standard reference solution). The SRM 2109 is a standard reference solution with a certified Cr(VI) content of 1000 mg L\(^{-1}\), which was properly diluted (three steps dilution) to a final Cr(VI) concentration of 20.0 µg L\(^{-1}\). Natural water samples were collected from Axios River, Volvi Lake, and seawater from Thermaikos Gulf, which were located in Northern Greece. All water samples were filtered through 0.45 µm membrane filters, acidified to ca. pH 1.6 with dilute HNO\(_3\) and stored at 4 °C in acid-cleaned polyethylene bottles, in order to determine the “dissolved metal” fraction.

2.3. Operational procedure

The on-line FI-manifold of the developed method for the metal preconcentration and determination and the operation sequences are presented in Fig. 1 and Table 1, respectively. The FI-procedure runs through a cycle of two steps. A complete cycle of the operation lasts 120 s. In the preconcentration step (Fig. 1a), the injection valve V is in the “load position” and pump P1 is activated for 90 s. The pump P2 is inactive and the nebulizer aspirates air through the flow compensation adapter (FC). The on-line complex formed is subsequently retained on the surface of the PCTFE-beads in the column. During the elution step, the injection valve V is in the “injection position”. The pump P1 is stopped, while pump P2 propels the IBMK through the column in order to elute the sorbed complex and to transport into the nebulizer of spectrometer. For minimum dispersion, the eluent IBMK pumped through the column in reverse direction than that of the sample. The peak height of the transient signal was proportional to metal concentration in the sample, and was used for all measurements. The recorded peaks were sharp and the baseline was stable. Five replicate measurements per sample were made in all instances.

3. Results and discussion

3.1. Optimization of experimental parameters

In order to improve the performance characteristics of the on-line preconcentration procedure for Cr(VI) and Pb(II) determination, all chemical and flow variables were investigated in
detail, using the FI-FAAS manifold shown in Fig. 1. Standard solutions of 20.0 μg L⁻¹ Cr(VI) and 50.0 μg L⁻¹ Pb(II) and a preconcentration period of 90 s were used for each study.

The sample acidity and the APDC concentration affect significantly the on-line complex formation and its adsorption on the sorbent surface. The effect of the pH was studied within the range of 0.1–5.3 and it was achieved through adjusting the concentration of nitric acid or ammonia in the sample solution. The sample solution and the effluent in step 1 had the same pH value, indicating that the influence of the APDC solution on the acidity of the system was not significant. As shown Fig. 3, optimum absorption signal occurred within the pH range of 1.0–1.6 and 1.5–3.2 for Cr(VI) and Pb(II), respectively. Hence, the sample solution was adjusted to pH 1.6 for the on-line preconcentration in further experiments. This fact enables the use of the method directly in water samples after common acid preservation without any laborious precise pH adjustment.

APDC concentration was examined from 0.001 to 0.2% (m/v) at fixed 0.6 mL min⁻¹ flow rate. For all studied metals the maximum absorbance was recorded in the range of 0.05–0.2% (m/v). Therefore a 0.08% (m/v) APDC solution in water was adopted for further study. The preconcentration of Cr(III) has been found to be inefficient, while in absence of the chelating agent, no detectable amounts of the two analytes could be retained in the PCTFE-beads packed column.

Organic solvents like IBMK, methanol and ethanol have been proved more effective as eluents at on-line preconcentration systems using hydrophobic packing materials, than acidic or alkaline solutions. In addition, IBMK is practically immiscible with water, less polar solvent than alcohols and also contributes in the rising of the flame temperature. Hence, IBMK produces lower dispersion, better elution of the retained complexes and higher atomization of the analyte. Preliminary experiments between ethanol and IBMK as eluents showed that the last one produced higher and sharpest signals, while the baseline was stable. Thus, IBMK was chosen as eluent, while the elution time was fixed at 50 s for complete elution. The flame composition of the FAAS nebulizer was adjusted properly to have an acetylene–air mixture of 2.0–9.0 L min⁻¹, during this study. The effect of IBMK flow rate was studied within the range 2.5–6.0 mL min⁻¹. Maximum absorbance was achieved within the range 2.5–3.5 mL min⁻¹ for all analytes, while above 3.5 mL min⁻¹ the absorbance slightly decreases, mainly due to the higher dispersion. Thus, 2.8 mL min⁻¹ flow rate of IBMK was used in further experiments as a compromise between the eluent consumption and sampling frequency. At this flow rate the necessary elution time was 30 s for complete elution.

The effectiveness of the on-line time-based preconcentration systems is influenced both by the loading flow rate and the reaction (complex formation) rate. At fixed 0.6 mL min⁻¹ APDC flow rate, the effect of the sample flow rate was studied in the range 2.5–15 mL min⁻¹. The absorbance was found to increase linearly up to 12 mL min⁻¹ and practically linear into the whole examined range, proving that the kinetic of the complex formation was very fast and the contact time for complete sorption was sufficient. This is a significant advantage over other on-line preconcentration column or knotted reactors, because different loading flow rates can be used with proportional sensitivity. At 90 s preconcentration time a flow rate of 12.0 mL min⁻¹ was selected for high sensitivity.

The influence of preconcentration time (loading time) was investigated in the range from 15 to 180 s. As it is shown in Fig. 4, the absorption increased linearly up to 180 s for Cr(VI) and up to 120 s for Pb(II). For longer time, the analytical signal increases with lower rate, probably due to a partial leaching of the complexes. Finally, a 90 s preconcentration time was chosen for all metals as a compromise between medium sample consumption, sufficient sensitivity and high sampling frequency.

3.2. Interference studies

Generally, ammonium pyrrolidine dithiocarbamate is a chelating agent for many transition metals. Thus, interferences from coexisting ions should be considered. The effect of potential interferents occurring in environmental water samples on the on-line determination of chromium(VI) and lead were tested using the optimized on-line preconcentration system for 90 s preconcentration time. The recovery of 10 μg L⁻¹ Cr(VI) and

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Fig. 3. Effect of sample acidity on the absorbance of 20.0 μg L⁻¹ Cr(VI) (□) and 50.0 μg L⁻¹ Pb(II) (○). All other conditions as in Table 1.

Fig. 4. Effect of preconcentration time on the absorbance of 20.0 μg L⁻¹ Cr(VI) (□) and 80.0 μg L⁻¹ Pb(II) (○). All other conditions as in Table 1.
Table 2
Analytical performance of the FI on-line solid phase extraction FAAS method for chromium(VI) and lead determination

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Chromium(VI)</th>
<th>Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preconcentration time (s)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Sampling frequency (h⁻¹)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Enhancement factor</td>
<td>94</td>
<td>220</td>
</tr>
<tr>
<td>Linear range (µg L⁻¹)</td>
<td>1–50</td>
<td>3–150</td>
</tr>
<tr>
<td>Regression equation, n = 5</td>
<td>A = 0.0047[Cr(VI)] + 0.0014</td>
<td>A = 0.0017[Pb(II)] + 0.0022</td>
</tr>
<tr>
<td>Correlation coefficient, r</td>
<td>0.9995</td>
<td>0.9993</td>
</tr>
<tr>
<td>Detection limit, 3 s (µg L⁻¹)</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Precision, R.S.D., n = 10 (%)</td>
<td>1.8 (5.0 µg L⁻¹)</td>
<td>2.1 (30.0 µg L⁻¹)</td>
</tr>
</tbody>
</table>

30 µg L⁻¹ Pb(II) was tested with individual interferents added. Taking as criterion for interference the deviation of the recovery more than ±5%, the obtained results showed that the tolerance concentrations for each interference were the following, Al(III) at 10 mg L⁻¹, Cd(II) at 0.2 mg L⁻¹, Co(II) at 1.0 mg L⁻¹, Cr(III) at 10.0 mg L⁻¹, Cu(II) at 1.0 mg L⁻¹, Fe(III) at 10.0 mg L⁻¹, Hg(II) at 0.5 mg L⁻¹, Mn(II) at 10.0 mg L⁻¹, Ni(II) at 0.5 mg L⁻¹ for Cr(VI), Ni(II) at 2.0 mg L⁻¹ for Pb(II), Zn(II) at 2.0 mg L⁻¹, Cr(VI) at 5.0 mg L⁻¹ for Pb(II) and Pb(II) at 2.0 mg L⁻¹ for Cr(VI), do not interfere. High concentrations of alkali and alkaline earth metals, which are usually found in natural water, were tested. Na⁺ and K⁺ up to 1500 mg L⁻¹, Ca²⁺, Mg²⁺, Ba²⁺ up to 500 mg L⁻¹ and NaCl up to 30 g L⁻¹ did not cause any interference.

Table 3
Analytical results for the determination of chromium(VI) and lead in the certified reference materials and water samples (determination in “dissolved metal” fraction)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Sample (µg L⁻¹)</th>
<th>Certified value</th>
<th>Added</th>
<th>Founda</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>SRM 2109</td>
<td>20.0</td>
<td></td>
<td>19.3 ± 0.8</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>River water</td>
<td>–</td>
<td>10.0</td>
<td>12.9 ± 0.7</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>Lake water</td>
<td>–</td>
<td>10.0</td>
<td>9.8 ± 0.5</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>Seawater</td>
<td>–</td>
<td>10.0</td>
<td>11.5 ± 0.9</td>
<td>102</td>
</tr>
<tr>
<td>Pb</td>
<td>CRM 1643d</td>
<td>18.15 ± 0.64</td>
<td></td>
<td>17.6 ± 0.9</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>River water</td>
<td>–</td>
<td>10.0</td>
<td>16.7 ± 0.8</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>Lake water</td>
<td>–</td>
<td>10.0</td>
<td>14.7 ± 0.5</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>Seawater</td>
<td>–</td>
<td>10.0</td>
<td>12.7 ± 0.8</td>
<td>95</td>
</tr>
</tbody>
</table>

a Mean ± S.D. based on three replicate determinations.

Table 4
Comparison of the characteristic data between selected on-line solid phase extraction methods and the developed one for Cr(VI) and Pb(II) determination with FAAS

<table>
<thead>
<tr>
<th>Reference</th>
<th>Analyte</th>
<th>Sorbent material</th>
<th>Reagent</th>
<th>Eluent</th>
<th>PT (s)</th>
<th>SC (mL)</th>
<th>f (h⁻¹)</th>
<th>c₁ (µg L⁻¹)</th>
<th>s₁ (%)</th>
<th>EF</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>Cr</td>
<td>PCTFE-beads</td>
<td>APDC</td>
<td>IBMK</td>
<td>90</td>
<td>18.0</td>
<td>30</td>
<td>0.4</td>
<td>1.8</td>
<td>94</td>
</tr>
<tr>
<td>[14]</td>
<td></td>
<td>Activated alumina</td>
<td>–</td>
<td>NH₄OH</td>
<td>35</td>
<td>3.0</td>
<td>55</td>
<td>0.8</td>
<td>1.3</td>
<td>25</td>
</tr>
<tr>
<td>[18]</td>
<td></td>
<td>PUF</td>
<td>APDC</td>
<td>IBMK</td>
<td>60</td>
<td>12.0</td>
<td>36</td>
<td>2.0</td>
<td>3.6</td>
<td>28</td>
</tr>
<tr>
<td>[25]</td>
<td></td>
<td>PTFE-turnings</td>
<td>APDC</td>
<td>IBMK</td>
<td>180</td>
<td>37.8</td>
<td>18</td>
<td>0.8</td>
<td>3.2</td>
<td>80</td>
</tr>
<tr>
<td>[29]</td>
<td></td>
<td>KR-MSP</td>
<td>APDC</td>
<td>EtOH</td>
<td>180</td>
<td>36.0</td>
<td>12</td>
<td>0.4</td>
<td>2.1</td>
<td>59</td>
</tr>
<tr>
<td>This work</td>
<td>Pb</td>
<td>PCTFE-beads</td>
<td>APDC</td>
<td>IBMK</td>
<td>90</td>
<td>18.0</td>
<td>30</td>
<td>1.2</td>
<td>2.1</td>
<td>220</td>
</tr>
<tr>
<td>[8]</td>
<td></td>
<td>C-18 silica gel</td>
<td>DDPA</td>
<td>EtOH</td>
<td>60</td>
<td>3.6</td>
<td>40</td>
<td>11</td>
<td>&lt;6</td>
<td>36</td>
</tr>
<tr>
<td>[16]</td>
<td></td>
<td>Activated carbon</td>
<td>APDC</td>
<td>IBMK</td>
<td>120</td>
<td>6</td>
<td>25</td>
<td>10</td>
<td>2.3</td>
<td>50</td>
</tr>
<tr>
<td>[18]</td>
<td></td>
<td>PUF</td>
<td>APDC</td>
<td>IBMK</td>
<td>60</td>
<td>12.0</td>
<td>36</td>
<td>1.8</td>
<td>3.4</td>
<td>131</td>
</tr>
<tr>
<td>[19]</td>
<td></td>
<td>PUF loaded</td>
<td>TAM</td>
<td>HCl</td>
<td>120</td>
<td>11.6</td>
<td>27</td>
<td>2.2</td>
<td>2.4</td>
<td>45</td>
</tr>
<tr>
<td>[22]</td>
<td></td>
<td>Amberlite XAD-2</td>
<td>BTAC</td>
<td>HCl</td>
<td>120</td>
<td>4.5</td>
<td>–</td>
<td>3.7</td>
<td>4.4</td>
<td>27</td>
</tr>
<tr>
<td>[23]</td>
<td></td>
<td>Chromosorb-102</td>
<td>NH₄-DDC</td>
<td>EtOH</td>
<td>120</td>
<td>4.4</td>
<td>25</td>
<td>2.5</td>
<td>2.5</td>
<td>25</td>
</tr>
<tr>
<td>[24]</td>
<td></td>
<td>PTFE-turnings</td>
<td>APDC</td>
<td>IBMK</td>
<td>180</td>
<td>39</td>
<td>15</td>
<td>0.8</td>
<td>2.6</td>
<td>330</td>
</tr>
<tr>
<td>[27]</td>
<td></td>
<td>PTFE-fiber grafted</td>
<td>Acrylic acid</td>
<td>HNO₃</td>
<td>45</td>
<td>7.5</td>
<td>55</td>
<td>0.26</td>
<td>1.9</td>
<td>49</td>
</tr>
<tr>
<td>[28]</td>
<td></td>
<td>KR-MSP</td>
<td>APDC</td>
<td>HCl</td>
<td>120</td>
<td>28.8</td>
<td>24</td>
<td>8</td>
<td>1.4</td>
<td>57</td>
</tr>
</tbody>
</table>

TAM: 2-(2-thiazolyloazo)-5-dimethylaminophenol; BTAC: 2-(2-benzoazolyloazo)-2-p-cresol; NH₄-DDC: ammonium diethyl-dithiocarbamate. EF: enhancement factor; PT: preconcentration time; f: sampling frequency; c₁: detection limit; s₁: precision (R.S.D.); SC: sample consumption.
3.3. Analytical performance of the FI-FAAS method

The characteristics data on the performance of the on-line column preconcentration coupled with FAAS under the optimum conditions for the determination of chromium(VI) and lead are listed in Table 2. The calculation of the enhancement factor was based on the ratio of the slope of the calibration curve obtained with on-line preconcentration to the slope without preconcentration (using aqueous standards solutions in batch mode). The obtained batch slopes using FAAS were $5 \times 10^{-5}$ and $7 \times 10^{-6} \text{L} \cdot \text{µg}^{-1}$ for Cr(VI) and Pb, respectively. The accuracy of the proposed method was estimated by analyzing the standard reference solution SRM 2109 and the certified water reference materials CRM 1643d (trace elements in water) for chromium(VI) and lead determination, respectively. The proposed method was applied also to the analysis of local natural water samples (river, lake and seawater) and was validated by spiking the samples with known amounts of Cr(VI) or Pb(II). The obtained results are presented in Table 3, and the recoveries were varied in the range 95–102%.

For comparative purposes, the performance characteristics of the proposed method and other selected on-line solid phase extraction preconcentration FAAS methods reported in the literature are given in Table 4. The proposed method shows good sensitivity ($c_T$) and precision ($s_T$) with reasonable preconcentration time (PT) over other online preconcentration methods.

4. Conclusions

The use of PCTFE in the shape of beads as column packing material for FI-FAAS preconcentration and determination of trace chromium(VI) and lead, was successfully performed. The chemical inertness, the excellent swelling and shrinking resistance, the hydrophobic nature and the fast kinetics of the proposed sorbent material make it very attractive for on-line column preconcentration systems. A high sample loading flow rate in conjunction with longer preconcentration time resulted in a more pronounced improvement in retention efficiency. The proposed method proved to be simple, rapid and accurate for chromium and lead determination.

References