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On-line preconcentration and determination of copper, lead and chromium(VI) using unloaded polyurethane foam packed column by flame atomic absorption spectrometry in natural waters and biological samples

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Abstract

A simple, sensitive and low cost, flow injection time-based method was developed for on-line preconcentration and determination of copper, lead and chromium(VI) at sub μg l^{-1} levels in natural waters and biological samples. At the optimum pH, the on-line formed metal–ammonium pyrrolidine dithiocarbamate (APDC) complexes were sorbed on the unloaded commercial polyurethane foam (PUF), and subsequent eluted quantitatively by isobutylmethylketone and determined by flame atomic absorption spectrometry (FAAS). All chemical, and flow injection variables were optimized for the quantitative preconcentration of each metal and a study of interference level of various ions was also carried out. The system offered improved flexibility, low backpressure and applicability to all the studied metals. At a sample frequency of 36 h^{-1} and a 60 s preconcentration time, the enhancement factor was 170, 131 and 28, the detection limit was 0.2, 1.8 and 2.0 μg l^{-1}, and the precision, expressed as relative standard deviation (s_r), was 2.8 (at 10 μg l^{-1}), 3.4 (at 50 μg l^{-1}) and 3.6% (at 50 μg l^{-1}) for Cu(II), Pb(II) and Cr(VI), respectively. The accuracy of the developed method was sufficient and evaluated by the analysis of certified reference materials and spiked water samples. Finally, the method was applied to the analysis of environmental samples.

Keywords: Atomic absorption spectrometry; On-line preconcentration; Polyurethane foam; Copper; Lead; Chromium

1. Introduction

Flame atomic absorption spectrometry (FAAS) is an available technique in most laboratories and one of the most extensively used techniques for various elements determination with significant precision and accuracy. However, there are many difficulties to determine traces of heavy metals in environmental samples due to insufficient sensitivity or matrix interferences. Thus, a preconcentration and/or separation step is necessary. On-line solid phase extraction (SPE) may be used as an alternative to flow injection liquid-liquid extrac-

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tion, in order to improve the sensitivity and selectivity of FAAS. In addition it has some extra advantages: large availability, easy recovery of the solid phase, attainability of large preconcentration factors and facility for separation using various flow injection systems.

In recent years, a fast increasing number of analytical methods for metals determination, which combine on-line packed column preconcentration procedures with FAAS, has been reported. The most convenient sorbent materials for column packing are, C_{18} [1–4], amberlite or Chelex [5–8], activated carbon [9], polytetrafluoroethylene (PTFE) [10,11], or polyurethane foam (PUF) [12–18].

Since Bowen investigated the absorption properties of PUFs in 1970 [19] the interesting about these materials has increased significantly, and they have been used as a solid sorbent for preconcentration and separation of a wide variety of inorganic and organic compounds in different media. Braun [20–22] and Palagyi [23] have published some extended review articles about the importance of PUF in SPE procedures. The PUF is an excellent sorbent material due to high available surface area, cellular structure and extremely low cost. In addition, it is stable in acids (except concentrated nitric and sulfuric acids), bases and organic solvents and also, it will not change its structure when heated up to 180 °C [20]. Thus, it is very suitable material for on-line preconcentration column packing. It can be used directly (unloaded PUF) for polar or nonpolar molecules [12,15,16,24] or with physically immobilized reagents such as chelating agents (with or without plasticizer solution) [25,26] and modified PUF [17,27].

Jesus et al. [12] applied firstly the PUF for on-line preconcentration and determination of zinc in 1998. After this work a number of papers have been cited about the on-line analytical applications of this sorbent material on the determination of the metals Pb [13,14], Ni [15], Zn [16], Cd [17], Co [18]. On-line methods are advantageous as compared with the off-line batch systems, because they are automated, make use of simpler apparatus with easier operation, much cheaper equipment and lower running costs.

An efficient and convenient chelating agent for batch liquid/liquid extraction and preconcentration of metals for FAAS determination in natural waters, is the ammonium pyrrolidine dithiocarbamate (APDC), although a great number of other dithiocarbamates and hydrazones have been employed for this purpose.

In this work a new on-line time-based column preconcentration system for FAAS, was developed capable to determine traces of three toxic metals Cu(II), Pb(II) and Cr(VI), as dithiocarbamate complexes with APDC, in a mini-column packed with unloaded PUF. Due to the hydrodynamic properties of the PUF, it was able to operate the system in high sample flow rates with low backpressure and consequently to achieve high enhancement factors. As far as we know no other papers have been published using the PUF for on-line copper and chromium determination and two papers for lead determination only [13,14]. The proposed method is applicable to routine analysis of natural water samples, with very good analytical performance characteristics, and sensitivity comparable with that obtained by using electrothermal atomic absorption spectrometry (ETAAS). A thorough review of the recent literature on the field of SPE on-line preconcentration systems for FAAS determination of the above three metals is also presented.

2. Experimental

2.1. Instrumentation

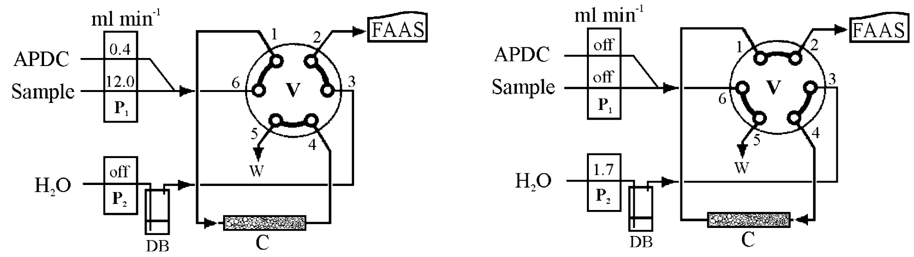
A Perkin–Elmer model 5100 PC flame atomic absorption spectrometer equipped with a flow spoiler in the spray chamber was used. The copper and chromium hollow cathode lamps and the lead electrodeless discharge lamp were operated under the conditions recommended by the manufacturer. The analytical wavelengths were 324.7, 283.3 and 357.9 nm for Cu, Pb and Cr, respectively. A time-constant of 0.2 s was used for peak height evaluation. The flame composition was adjusted properly to compensate for the effect of IBMK, which serves as additional fuel. For copper and lead, the air flow rate was set at 9.0 l min^{-1} and acetylene flow rate at 0.9 l min^{-1}. For chromium the flow rates were adjusted to 9.0 l and 2.0 l min^{-1}, after precise optimization with various IBMK flow rates. The electrothermal atomization mode of the above instrument equipped with zeeman background corrector was used as a standardized method for the analyte determination in the real samples.

The flow injection manifold is shown schematically in Fig. 1. It was adapted directly to the burner nebulizer system of the spectrometer, and was consisted from two peristaltic pumps (Watson Marlow model 205U/BA) equipped with Tygon tubes for delivery of the aqueous streams, a two-position/six-port injection valve (Labpro, Reodyne, USA) and a mini-column packed with PUF for the on-line preconcentration of the analytes. A displacement bottle (Tecator, Hoganas, Sweden) was used to propel the IBMK stream, due to the organic solvent incompatibility with Tygon tubes. The manifold was constructed with PTFE tubes of 0.5 mm i.d. The tube length from the confluence point of sample and APDC streams until the injection valve was as short as possible (ca. 1 cm), because the PTFE material of the tube retains the M-PDC complexes [10,11], affecting, thus, the precision of the determination. The column connection tubes and the capillary between the injection valve with the burner nebulizer were also short (ca. 1 and 10 cm/0.35 mm i.d., respectively) in order to minimize the dispersion. The mini-column was constructed of a plastic syringe, 45 mm length/4.5 mm i.d.

2.2. Reagents

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany) and doubly de-ionized water was used throughout for dilutions. Working standard solutions of copper, lead and chromium(VI) were prepared immediately before use, by stepwise dilution of a 1000 mg l^{-1} stock standard solutions (Merck) to the required µg l^{-1} levels. The chelating reagent, 0.05% mV^{-1} APDC was prepared daily by dissolving the appropriate amount of APDC (Merck) in de-ionized water. Isobutyl methyl ketone (IBMK) was used, after saturation with de-ionized water, without any other purification.

Commercial, open cell, resilient polyether-type PUF (Euroform, GmbH), with 12–14 cells per cm and a density of 22–24 mg cm^{-3}, without any pretreatment was used as sorbent material. The open cells occupy approximately 95% of the volume and distorted into polyhedrons (pentagonal, dodecahedra). This structure contributes to keep the backpressure sufficiently low Fig. 2 shows an image taken by scanning electron microscopy of the structure of the used PUF. It was cut into cylindrical plugs of 50 mm length/6 mm i.d. The appropriate foam plugs were placed in the column (150 mg of PUF) and subsequently washed thoroughly to remove organic and inorganic contaminates, by percolating through the column 1 M HNO_3 solution, for 15 min followed by de-ionized water until the washings were acid free and



a) PRECONCENTRATION b) ELUTION

Fig. 1. FI manifold and its operation sequence for on-line preconcentration and determination of copper, lead and chromium(VI); APDC, 0.05% m m^{-1} APDC solution; FAAS, flame atomic absorption spectrometer; P_1, P_2, peristaltic pumps; V, injection valves; DB, displacement bottle for IBMK; C, mini-column packed with 150 mg PUF; W, waste.

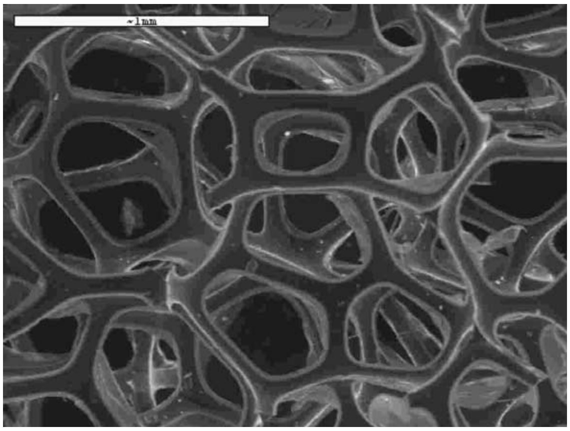


Fig. 2. Image of the open cell PUF obtained, by the scanning electron microscopy. The mean diameter of the cells is about 0.7–0.8 mm with 12–14 cells per cm.

subsequently flushed with IBMK. The performance of the column was stable during all experiments (more than 500).

The following standard reference materials were used to verify the accuracy of the proposed method: NIST SRM 1643d (trace elements in water), NIST SRM 2109 (Cr(VI) standard reference solution), BCR CRM 278R (mytilus edulis, freeze dried), IAEA 350 (tuna fish tissue, lyophilized), IAEA MA-B-3 (fish tissue, lyophilized).

2.3. Procedure

The two main steps of the method (preconcentration and elution) are shown in Fig. 1. In the preconcentration step, the injection valve is in the 'load' position, and the sample or standard solution merges the APDC stream by pump 1. The mixture percolates through the PUF mini-column where generated complexes are retained for a suitable preconcentration time. During the elution step, the above valve is in the 'injection' position, and the elution solution (IBMK) is propelled by pump 2 through the column in reverse direction than that of the sample and reagent, in order to minimize dispersion and consequently the eluted complex is directly delivered to the burner nebulizer. All the measurements were made in peak height, which were proportional to the analyte concentration in sample. The signals were sharp and the baseline was stable. Five replicate measurements per sample were made in all instances.

The natural water samples were filtered before analysis through 0.45 μm filters and acidified to the suitable pH for each analyte with dilute HNO_3. Standard solutions of metals were made up to the working pH by 0.01 mol l^{-1} HNO_3. Finally, the certified reference materials were acidified close to the working pH range.

2.4. Sample treatment

A portion of 0.3 g dry (or 1 g fresh) tissue sample was precisely weighted into sealed Teflon crucibles and 6 ml of concentrated HNO_3 were added. Also a number of sub-samples were spiked with known amount of each analyte. The crucibles were placed in a nine-position steel pressurized bomb and the mixtures were digested under pressure, at 130–140 °C. The pH of the final digests were adjusted to pH $\approx$ 1.6 by suitable addition of 0.5 mol l^{-1} NH_4OH solution, and the mixture was finally diluted to 100 ml by double de-ionized water.

The river water and industrial wastewater samples were initially acidified for storage to pH $\approx$ 1.5–1.8 by HNO_3, and filtered through 0.45 μm Millipore filters, thus, no other pH adjustment was needed. The SRM 1643d certified reference material is a fresh water matrix in 0.5 mol l^{-1} HNO_3, so a preliminary treatment with NH_4OH is needed to adjust the pH to approximately 1.6, and the diluted solutions used for the evaluation of the copper and lead determination. The SRM 2109 is a standard reference solution with a certified Cr(VI) content of 1000 mg l^{-1} and was properly diluted (three steps dilution) to a final Cr(VI) concentration of 20.0 μg l^{-1} and pH $\approx$ 1.6, by dilute HNO_3 solution.

3. Results and discussion

3.1. Optimization of chemical and FI variables

Both chemical and flow variables were thoroughly studied using the manifold shown in Fig. 1, in order to improve the performance characteristics of the method for each analyte separately.

Standard solution of 20.0 μg l^{-1} of Cu(II), 120.0 μg l^{-1} of Pb(II) and 100.0 μg l^{-1} of Cr(VI) for 60 s preconcentration time, are employed for these studies.

The pH value of the sample solution effects significantly the metal-PDC complex formation and its adsorption on the sorbent surface. The effect of the pH was studied within the range of 0.71–6.27 (adjusted with dilute nitric acid). The waste and the sample solution had the same pH value, indicating that the effect of the APDC solution on the acidity was not significant. Maximum absorption signal occurred within the pH range of 1.0–3.0, 1.3–3.9 and 0.8–1.6 for Cu(II), Pb(II) and Cr(VI), respectively, as can be seen in Fig. 3. Thus, the pH 1.6 was established, for every analyte. This fact enables the use of the method directly in various aqueous samples after common acid preservation at pH ≈ 1.6. The optimum pH range for copper and lead was found to be shorter but within the working pH range of the standard batch L/L extraction method (0.1–8 and 0.1–6 for Cu and Pb, respectively). This reduction of the optimum pH was observed probably due to kinetic differences among flow and batch procedure, and the decrease of the efficiency at higher and lower pH values is probably due to non-complete complex formation and sorption.

APDC concentration was studied ranging from 0.01 to 0.1% mV^{-1} (at 0.4 ml min^{-1}). The preconcentration efficiency remained constant on the above range. Therefore, a 0.05% mV^{-1} solution of APDC in water was selected, for further study. In absence of the chelating agent, no detectable amounts of the three analytes could be retained in the column.

Water and acidic solutions were proved less effective as eluents at on-line preconcentration systems using PUF column, than organic ones [16]. On the other hand, IBMK is considered to be a better eluent for FAAS than alcohols (ethanol or methanol), or halogenated hydrocarbons (chloroform). Attiyat and Christian [28] have shown that using IBMK instead of other organic solvents as carrier, highest enhancement factors were obtained. In addition, IBMK is almost completely immiscible with water, less polar solvent and the use as eluent in on-line SPE preconcentration systems may enhance the sensitivity of FAAS due to the fact that increases the flame temperature, producing lower dispersion and better elution of the complexes than aqueous eluents. Preliminary experiments between ethanol, methanol, chloroform and IBMK as eluents showed that the last one produced higher and sharpest signals. In addition with ethanol and methanol as eluents

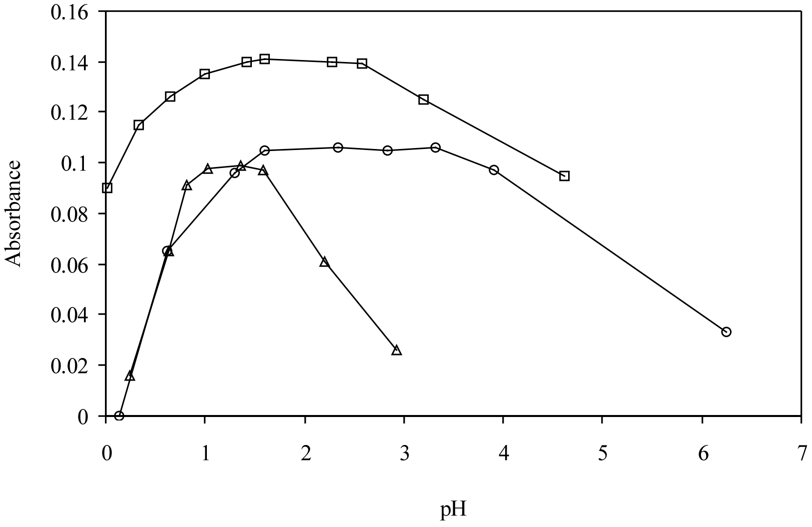


Fig. 3. Effect of pH on the absorbance of 20.0 μg l^{-1} Cu(II) (○), 120.0 μg l^{-1} Pb(II) (⊖) and 100.0 μg l^{-1} Cr(VI) (△) solution, for 60 s preconcentration time. Other FI parameters are as in Fig. 1.

the baseline was unstable and the absorbance was lower because of the greater dispersion. With chloroform the recorded signals were lower although the baseline was stable. Thus, IBMK was chosen as eluent.

The effect of the sample flow rate in the proposed manifold was investigated in the range from 0.83 to 15.31 ml min^{-1}. The absorption was linear up to 12.0 ml min^{-1} and practically linear up to the whole examined range, implying that the complexation is complete and the contact time is sufficient and the kinetic properties of the PUF allow significant retention of the analytes. This fact is a very useful feature of the proposed column, because it permits a higher sample throughout improving the concentration efficiency. Therefore, 12.0 ml min^{-1} was selected as a compromise between high sensitivity and low sample consumption.

The flow rate of the APDC stream was tested in the range of 0.32–1.56 ml min^{-1} and the optimum flow rates were obtained at flow rate above 0.40 ml min^{-1}. This value was chosen for further experiments because it preserves lower sample dilution.

The effect of elution flow rate was studied in the range of 0.7–7.2 ml min^{-1}. The flame composition of the FAAS, which is critical for the atomization of chromium, adjusted properly at the above limits, during the study, as it was described above. At elution flow rate less than 1.0 ml min^{-1}, the analytical signal decreased significantly, became broader and not reproducible, due to gas bubbles formed in the column and the tube between the column and the nebulizer. These gas bubbles produces because the nebulizer free uptake exceeded significantly the elution flow rate. Peak height goes through a maximum, at IBMK flow rate of 1.7–2.1 ml min^{-1} for all analytes, and above this range slightly decreases. This fact is probably due to the higher analyte dispersion and suppression of the obtained signals, and not to the variation of desorption kinetics. The last is not considered significant to the APDC–IBMK system, because IBMK assures rapid elution of the complexes. Consequently, an elution flow rate of 1.7 ml min^{-1} was chosen as optimal for the three metals and at this flow rate the elution time was 40 s.

The preconcentration time was studied in the range from 10 to 180 s. The absorption was increased linearly up to 120 s for Cu(II) and up to 90 s for Pb(II) and Cr(VI). For longer time, the analytical signals increases slightly with smaller rates, due to the fact that the effect from partial leaching of the complexes becomes significant. Finally, a 60 s preconcentration time was chosen for all metals as a compromise between medium sample consumption, high sensitivity and sufficient sampling frequency.

The amount of PUF in the column was investigated in the range 100–300 mg. About 100 mg of PUF were enough to retain the above standards of the analytes. However, 150 mg was used throughout in order to ensure total retention of all metals.

The capacity of the PUF packed column was studied by measuring the maximum quantity of each metal sorbed on PUF surface, when a series of standard solutions with increasing concentrations of each analyte in the range 1.0–100 mg l^{-1} (with sufficient concentration of APDC) were passed through the column, for 1 min at 12.0 ml min^{-1} sample flow rate. The effluent was collected and measured by FAAS, in order to determine the non-sorbed amount of analyte. The obtained maximum sorption capacity of PUF, was 63 μmol g^{-1} for Cu(II), 34 μmol g^{-1} for Pb(II), and 58 μmol g^{-1} for Cr(VI). However, the recovery was satisfactory only when low concentrations for all analytes were passed (<5 mg l^{-1}).

3.2. Analytical features

Under the optimum conditions, the characteristic data for the performance of the on-line preconcentration system for FAAS determination of copper, lead and chromium are summarized in Table 1. Peak height absorption signals were used for the calculation of the calibration curve and the precision of the method. The detection limit was calculated by the S*s* criterion, as the concentration that gives a response equivalent to three times the standard deviation (S.D.) of the blank ($n = 12$). The quantification limit was calculated as the concentration that gives a response equivalent to ten times the S.D. of the blank ($n = 12$), and define the lower limit of the

Table 1
Analytical performance of the on-line preconcentration FAAS method for copper, lead and chromium(VI) determination

Features	Cu(II)	Pb(II)	Cr(VI)
Preconcentration time (s)	60	60	60
Sampling frequency (h)	36	36	36
Enhancement factor	170	131	28
Detection limit (3 s) (μg l^{-1})	0.2	1.8	2.0
Precision (R.S.D., $n = 15$) (%)	2.8% (10 μg l^{-1})	3.4% (50 μg l^{-1})	3.6% (50 μg l^{-1})
Linear range (μg l^{-1})	0.4–40	3–250	3–250
Regression equation (12 standards, $n = 5$; [M] (μg l^{-1})	$A = 0.002 + 0.0068$[Cu(II)]	$A = 0.000 + 0.0009$[Pb(II)]	$A = 0.001 + 0.0010$[Cr(VI)]
Correlation coefficient	$r = 0.9989$	$r = 0.9991$	$r = 0.9987$

range. The calculation of the enhancement factor was based on the ratio of the slopes of the calibration curves, obtained with and without preconcentration, using FAAS. The slopes without preconcentration were 4×10^{-5}, 7×10^{-6} and 4×10^{-5} μg^{-1} l, for Cu, Pb and Cr(VI), respectively. The figures of merit of this and other on-line methods are summarized in Table 2, for comparative purpose. It can be seen that the proposed method is a sensitive, rapid and flexible one, and has some good advantages over other on-line preconcentration FAAS methods reported in the literature. In addition except Cu(II), Pb(II) and Cr(VI), this method is probably applicable to other metals, which form complexes with APDC, after proper optimization of the pH.

3.3. Interference studies

In order to evaluate the selectivity of the proposed on-line preconcentration system the interference of various elements was investigated on the determination of 10 μg l^{-1} Cu(II), 50 μg l^{-1} Pb(II) and 50 μg l^{-1} Cr(VI), taking as a criterion for an interference the deviation of the percentage recovery more than ±5%. High concentrations of alkali and alkaline earth metals, which are usually found in high concentrations in natural waters and other samples, were tested. Na^+ and K^+ up to 1500 mg l^{-1} and Ca^{2+}, Mg^{2+}, Ba^{2+} up to 500 mg l^{-1}, did not caused any interference. A number of common anions like Cl^-, Br^-, I^-, SO_4^{2-}, SCN^-, HCO_3^-, NO_3^- were tested and found that they did not interfere at concentrations up to 1000 mg l^{-1}. On the other hand it is well known that transition metals form complexes with APDC, so the recovery of the analytes was tested in presence of the most common of these metals.

Al(III) (5 mg l^{-1}), Cd(II) (0.2 mg l^{-1}), Co(II) (1.0 mg l^{-1}), Cr(III) (10.0 mg l^{-1}), Fe(III) (10.0 mg l^{-1}), Hg(II) (0.5 mg l^{-1}), Mn(II) (10.0 mg l^{-1}), Ni(II) (0.5 mg l^{-1}), Zn(II) (5.0 mg l^{-1}), Cu(II) (1.0 mg l^{-1} for Pb and Cr), Pb(II) (1.0 mg l^{-1} for Cu and Cr), Cr(VI) (5.0 mg l^{-1} for Cu and Pb), do not interfere.

3.4. Accuracy of the method and analysis of real samples

The accuracy of the proposed method was tested, by determining the copper, lead and chromium content of certified reference materials. All the calibrations were performed using aqueous standard solutions (without further matrix specific optimization for calibration procedure). The certified values and the obtained analytical results are presented in Table 3. The recovery was satisfactory for samples (95–101%) showing that the proposed method is suitable for analysis of waters and biological samples.

Finally the method was applied to the analysis of river water, industrial wastewater and mussel tissue (mytilus galloprovinciallis), and compared with the electrothermal atomization (ETAAS)

Table 2
Comparative data from recent references on copper, lead and chromium determination by various on-line SPE preconcentration FAAS methods

Sorbent material	Eluent	Function group	c_L[b] (μg l^{-1})/s_r[c]			PT[d] (s)	SF[e] (h^{-1})	Reference
			Cu	Pb	Cr(VI)			
PUF	IBMK	APDC	0.2/2.8	1.8/3.4	2.0/3.6	60	36	[a]
C_{18}	EtOH	DDDC	0.2/1.3	3/1.0		20	120	[1]
C_{18}	MeOH	Dithizone	1.2/5	3/6		60	30	[3]
Chellex-100	HNO_3			0.8/2.2		100	60	[6]
Amberlite	HNO_3	TBABr[f]		0.3/2.4		60	30	[7]
Activated carbon	IBMK	APDC		10/2.3		120	25	[9]
C_{18}	EtOH	DDTP		0.3/5.0		4500	< 1	[13]
PUF	EtOH	DDTP		1.2/5.0		4500	< 1	[13]
PUF	HCl	BTAC		1.0/6.0		60	?	[14]
C_{18}	IBMK	DDC		3/3.8		120	24	[29]
C_{60}-fullerenes	IBMK	APDC		15/2.7		120	25	[30]
Muromac	HNO_3	Iminodiacetate		2.1/1.3		240	13	[31]
Activated alumina	HNO_3			0.36/1.4		300	10	[32]
Chromosorb 102	EtOH	DDC		2.5/2.5		120	25	[33]
Amberlite XAD-2	HCl	BTAC		3.7/4.4		120	?	[34]
PTFE	IBMK	APDC		0.8/2.6		180	15	[35]
KR-PTFE	IBMK	Cu(II)-DDTC[g]		3.2/2.0		30	65	[36]
KR-microline	IBMK	Fe(II)-HMDTC[g]		2.0/2.7		30	90	[37]
Silica gel (Pb-02)	EDTA			5/1.9		30	63	[38]
Silica gel (aliquat)	HCl			4.0/6		1800	2	[39]
C_{18}	EtOH	Phenanthroline	0.3/3			30	90	[2]
Amberlite XAD-2	HCl		0.15/6			180	20	[5]
PTFE	IBMK	APDC	0.05/1.5			60	40	[10]
C_{18}	MeOH	DDTC	0.2/1.4			30	85	[40]
KR-PTFE	IBMK	Na-DDC	0.2/3.6			60	46	[41]
Zeolite (Na-LTA)	IBMK	APDC	0.1/2.6			120	?	[42]
Zeolite (Na-Fau)	IBMK	APDC	0.4/2.8			120	?	[42]
C_{18}	Methanol	DDTC			0.02/3.5	300	10	[4]
Cellex T	NaOH				1.4/4.5	150		[8]
PTFE	IBMK	APDC			0.8/3.2	180	18	[11]
KR (PEEK)	IBMK	APDC			0.54/2.9	60		[43]
KR (PEEK)	IBMK	APDC			2.0/2.1	60	30	[44]
Activated alumina	NH_4OH				0.8/1.1	35	55	[45]
Activated alumina	NH_4OH				42/10	2		[46]

[a] This work.
[b] Detection limit.
[c] Relative standard deviation.
[d] Preconcentration time.
[e] Sampling frequency; enhancement factor.
[f] Dual stage preconcentration system.
[g] Co-precipitation procedure.

method. The results are given in Table 4. The recovery obtained for real samples (92–98%) is comparable with that for reference materials, showing the good performance of the method in all types of the examined samples. The relative standard deviation (s_r) for the three metals determination in the examined samples ranged from 3.8 to 7.5%.

Table 3
Analytical results of copper, lead and chromium(VI) determination in various certified reference materials

Analyte	Certified reference material	Unit	Certified[a]	Found[b]	Recovery (%)
Cu	SRM 1643d (fresh water)	μg l^{-1}	20.5±3.8	19.5±1.0	95
	BCR 278R (mussel tissue)	μg g^{-1}	9.45±0.13	9.07±0.66	96
	IAEA 350 (tuna fish tissue)	μg g^{-1}	2.83 (2.55–3.10)	2.74±0.21	97
Pb	SRM 1643d (fresh water)	μg l^{-1}	18.15±0.64	18.3±0.8	101
	BCR 278R (mussel tissue)	μg g^{-1}	2.00±0.04	1.90±0.13	95
	IAEA MA-B-3 (fish tissue)	μg g^{-1}	4.62 (3.85–5.13)	4.45±0.16	96
Cr(VI)	SRM 2109 (Cr(VI) std solution)[c]	μg l^{-1}	20.0	19.6±0.6	98

[a] Certified value and uncertainty as given in the certificate.

[b] Mean value±S.D. based on five replicates ($n = 5$) determinations.

[c] Cr(VI)–NIST standard with certified content of 1000 mg l^{-1}.

Table 4
Recovery of copper, lead and chromium(VI) in environmental samples by the proposed on-line FAAS method and ETAAS

Analyte	Samples	Units	Added	Found[a]	Recovery (%)[b]	ETAAS
Cu	River water	μg l^{-1}	0	8.0±0.4		7.1±1.0
		μg l^{-1}	10.0	17.6±0.9	96	
	Mussel tissue[c]	μg g^{-1}	0	6.2±0.5		6.1±0.7
		μg g^{-1}	5.0	10.9±1.2	94	
Pb	River water	μg l^{-1}	0	4.0±0.6		3.4±0.5
		μg l^{-1}	20.0	23.6±1.3	98	
	Mussel tissue[c]	μg g^{-1}	0	0.35±0.02		0.38±0.07
		μg g^{-1}	0.25	0.58±0.04	92	
Cr(VI)	River water	μg l^{-1}	0	5.3±0.4		6.2±0.8
		μg l^{-1}	20	24.6±1.6	97	
	Waste water	μg l^{-1}	0	26.0±1.0		24.3±3.9
		μg l^{-1}	20	44.3±2.5	92	

[a] Mean value±S.D. based on five replicates ($n = 5$) determinations.

[b] Recovery obtained from spiked samples.

[c] Fresh weight.

4. Conclusions

The use of commercial PUF as a column packing material was successfully applied to the on-line preconcentration and determination of copper, lead and chromium(VI) by FAAS and was found to improve significantly the performance characteristics of the off-line FAAS method. The developed manifold permitted the use of high sample loading flow rates in order to achieve better enhancement factors. The obtained detection limit was also comparable with those obtained by other more sophisticated techniques and manifolds or expensive sorbent materials. The precision and recovery obtained in the analysis of certified reference materials and real samples show the reliability and accuracy of the method. The proposed method proved to be simple, rapid, inexpensive and reliable for copper, lead and chromium(VI) determination in waters and biological samples. The application of open cell polyether type PUF as packing material for construction of mini-columns is recommended. Future research is focused on testing the ability of PUF and its performance for on-line determination of other metals, with various ligands, which are known that they are adsorbed on this material.

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