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Further study on a flow injection on-line multiplexed sorption preconcentration coupled with flame atomic absorption spectrometry for trace element determination

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Abstract

A further study on a newly developed flow injection (FI) on-line multiplexed sorption preconcentration (MSP) using a knotted reactor coupled with flame atomic absorption spectrometry (FAAS) was carried out to demonstrate its applicability and limitation for trace element determination. For this purpose, Cr(VI), Cu(II), Ni(II) and Co(II) were selected as the analytes, and detailed comparison was made between the MSP–FAAS and conventional FI on-line sorption preconcentration FAAS in respect to retention efficiency and linear ranges of absorbance versus sample loading flow rate and total preconcentration time. Introduction of an air-flow for removal of the residual solution in the KR after each sub-injection in the MSP procedure played a decisive role in the improvement of retention efficiency. The linearity of absorbance versus sample loading flow rate or total preconcentration time was extended to a more degree for the metal ions with less stability of their PDC (pyrrolidine dithiocarbamate) complexes than those with more stable PDC complexes. It seems that the MSP procedure behaves advantages beyond the inflection points in the diagrams of absorbance versus total preconcentration time and sample loading flow rate obtained by conventional (a single continuous) preconcentration procedure. With a sample loading flow rate of 6.0 ml min^{-1} and a total preconcentration time of 180 s, the retention efficiencies were increased from 25, 46, 41 and 63% with a single continuous sorption preconcentration to 44, 78, 65 and 75% with a six sub-injection preconcentration procedure for Cr(VI), Co(II), Ni(II), and Cu(II), respectively. The detection limits were 0.40, 0.33, 0.31 and 0.26 μg l^{-1} for Cr(VI), Co(II), Ni(II), and Cu(II), respectively. The precision (R.S.D.) for eleven replicate determination of 2 μg l^{-1} Cr(VI), Co(II) and Ni(II), and 1 μg l^{-1} Cu(II), was 2.1, 4.1, 2.6 and 1.7%, respectively.

Keywords: Multiplexed sorption preconcentration; Knotted reactor; Chromium; Cobalt; Nickel; Copper; Flame atomic absorption spectrometry

1. Introduction

Flow injection (FI) on-line preconcentration and separation based on the sorption of hydrophobic organo-metallic complexes on the wall of the polytetrafluoroethylene (PTFE) knotted reactor (KR) have been successfully coupled with atomic spectrometry for trace element analysis [1–5]. Compared with conventional microcolumn systems, the KR sorption system allows the analysis to be conducted at low cost owing to the nearly unlimited lifetime and the ease of construction of the KR in no need for packing materials, and permits the use of higher sample loading rates for achieving higher sensitivity due to the low hydrodynamic impedance in the KR [1–9].

One of limitations in conventional FI sorption preconcentration procedures in a KR, which have been carried out exclusively with a single continuous sample injection in a certain period, is the relatively low retention efficiency (typically 40–50%) [5,10]. Although the sensitivity of such systems could be improved by properly increasing preconcentration time and/or sample loading flow rate, further improvement of the sensitivity has been limited by the narrow linearity of the relationship between signal intensity and preconcentration time or sample loading flow rate.

Recently, a novel FI on-line multiplexed sorption preconcentration procedure (MSP) was developed with an attempt

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to overcome the above mentioned drawbacks [10]. Contrast to conventional FI preconcentration, the proposed MSP evenly divided a single longer preconcentration step into several shorter sub-steps while the total preconcentration time is still kept constant. Application of the MSP with eight repetitive sample injections for a total preconcentration time of 120 s to flame atomic absorption spectrometric determination of lead improved the retention efficiency by a factor of 2. In addition, the linear ranges of the diagrams of absorbance of lead against sample loading flow rate, and preconcentration time were significantly extended in comparison with previous one single continuous sample injection preconcentration procedure [10].

More recently, Som-Aurn et al. [11] applied this MSP to electrothermal atomic absorption spectrometric determination of Cr(VI) at 1 $\mu g\,l^{-1}$. When dividing the total preconcentration time of 60 s into four sub-preconcentration steps, no significant improvement in retention efficiency for Cr(VI) was observed as compared with the conventional single continuous sample loading. This attributed to a lower retention efficiency of the Cr(VI)—pyrrolidine dithiocarbamate (PDC) complex on the PTFE KR at the lower concentration levels of Cr(VI) used in their work [11].

The main purpose of this work was to make a further study on this newly developed MSP using a knotted reactor coupled with flame atomic absorption spectrometry (FAAS) for its application to trace element determination. To demonstrate its applicability and limitation, Cr(VI), Cu(II), Ni(II) and Co(II) were selected as the analytes, and detailed comparison was made between the MSP and the conventional single continuous sample loading in respect to retention efficiency and linear ranges of the diagrams of signal absorbance against sample loading rate and preconcentration time.

2. Experimental

2.1. Instrumentation

A Hitachi 180-80 polarized Zeeman atomic absorption spectrometer was used for all measurements. Hollow cathode lamps of Cr, Co, Ni and Cu (Ningqiang Light Sources Co. Ltd., Hengshui, China) were used as the light sources. The analytical line and spectral bandpass employed are, respectively, 395.4 and 0.4 nm for Cr, 240.7 and 0.2 nm for Co, 232.0 and 0.2 nm for Ni, 324.8 and 1.3 nm for Cu. The recommended flame conditions were employed. Peak height of the absorption signal was used for quantification.

A Model FIA-3100 flow injection system (Vital Instruments Co. Ltd, Beijing, China) was used for the on-line multiplexed sorption preconcentration. The FIA-3100 consists of two peristaltic pumps and a standard rotary injection valve (eight ports on the rotor, and eight ports on the stator). The rotation speed of the two peristaltic pumps, their stop and go intervals, and the actuation of the injection valve were programmed (see Table 1). The KR used for the preconcentration was laboratory-made of a 0.5-mm i.d. × 250-cm long PTFE tubing by tying interlaced knots. Ismaprene pump tubes were used to deliver the samples and reagents. Small-bore (0.35-mm i.d.) PTFE tubing were used for all connections, which were kept as short as possible to minimize the dead volumes.

2.2. Reagents

All reagents were of the highest available purity and at least of analytical grade. Doubly deionized water (DDW, 18.2 M Ω cm) obtained from a WaterPro water system (Labconco Corporation, Kansas City, MO, USA) was used throughout.

The chelating agent solution was prepared by dissolving APDC (ammonium pyrrolidine dithiocarbamate, Sigma) in DDW just prior to use. Working standard solutions of Cr(VI), Co(II), Ni(II), and Cu(II) were prepared respectively by stepwise dilution of their stock solutions of 1000 $mg\,l^{-1}$ (National Research Center for Standard Materials (NRCSM), Beijing, China) immediately before use. A standard reference material of GBW 08608 (Trace elements in water) (NRCSM) was used to check the accuracy of the developed method.

2.3. Sample pretreatment

Three river-water and three seawater samples were collected locally. Immediately after sampling, the samples were filtered, acidified to pH 1.90 with nitric acid, and stored at

Table 1
Operation sequence of the MSP–FAAS system for the determination of Cr(VI), Co(II), Ni(II), and Cu(II)

Step	Function	Valve position	Duration (s)	Medium pumped	Flow rate ($ml\,min^{-1}$)	
					Pump 1	Pump 2
1 (Fig. 1a)	Sample loading	Fill	30	Sample APDC (0.02%, m/v)	Off	6.0 6.0
2 (Fig. 1a)	Removal of residual solution from KR	Fill	15	Air	3.0	Off
Repeating the above two substeps six times						
3 (Fig. 1b)	Analyte elution	Inject	20	Ethanol	3.3	Off

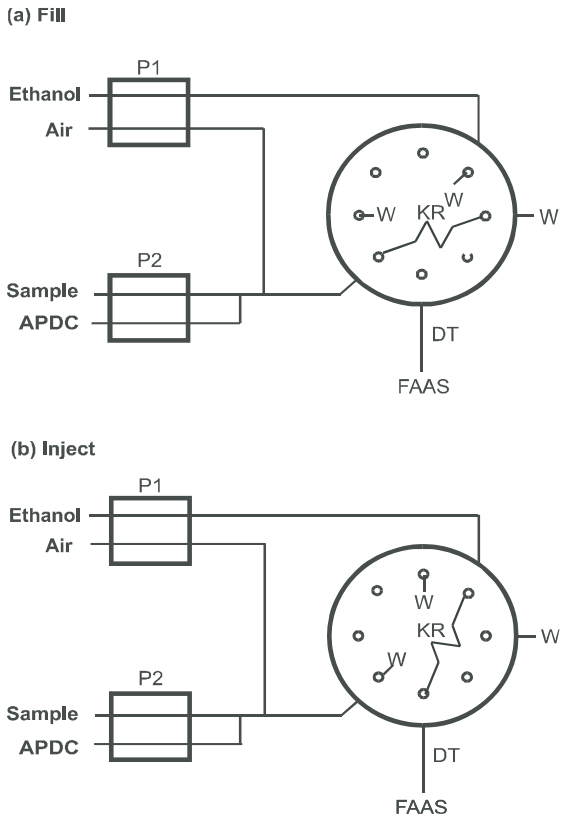

Fig. 1. FI manifold for the on-line multiplexed sorption preconcentration coupled with FAAS: P1, P2, peristaltic pump; W, waste; KR, knotted reactor (0.5-mm i.d. × 250-cm long PTFE tubing); DT, delivery tubing. Injector valve position: (a) fill and (b) injection.

4 °C in low-density polyethylene (LDPE) bottles. The samples were adjusted to the optimum pH values with HNO_3 or $NH_3{\cdot}H_2O$ for the preconcentration of Cr(VI), Co(II), Ni(II), and Cu(II).

2.4. Procedures

Details of the FIA-3100 program and the sequence of operation are given in Table 1. In step 1 (Fig. 1a), pump 2 was actuated and the injection valve was in the fill position, so that the analyte–PDC complex was formed on-line and adsorbed onto the inner surface of the KR. In step 2 (Fig. 1a), the injection valve was still in the fill position whereas pump 2 stopped and pump 1 was active such that an air flow was introduced to remove the residual solution from the KR and the connecting conduits. Steps 1 and 2 were repeated six times, while total preconcentration time was kept 180 s. In step 3 (Fig. 1b), the injection valve turned to the injection position while the status of the two pump was still the same as in step 2. In this step, ethanol was introduced into the KR to elute the sorbed analyte and to deliver the eluate into the FAAS detector. The total period for determination was 290 s including 180 s for sample preconcentration.

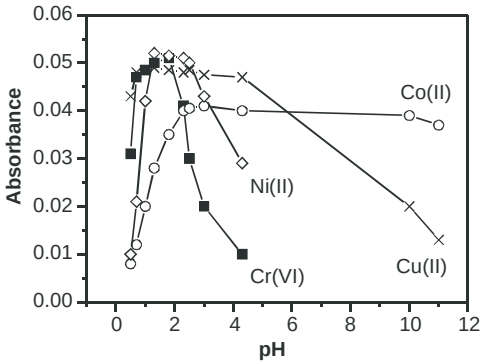

Fig. 2. Effect of sample acidity on the on-line multiplexed sorption preconcentration of 5 μg l^{-1} Cr(VI), Co(II), Ni(II) and Cu(II) with a total preconcentration time of 180 s and a sample loading flow rate of 6.0 ml min^{-1}. All other conditions as in Fig. 1 and Table 1.

3. Results and discussion

3.1. Effects of sample acidity and APDC concentration

The sample acidity and APDC concentration are the most important chemical variables affecting the on-line preconcentration of trace Cr(VI), Co(II), Ni(II) and Cu(II), and therefore investigated in detail. The pH of the effluent in step 1 was monitored as the indication of the pH of the system. The on-line pH adjustment of the reaction mixture in step 1 was achieved through adjusting the concentration of nitric acid or ammonia in the standard solution or sample solution. As shown in Fig. 2, the optimal pH of the system for the on-line sorption preconcentration of Cr(VI), Co(II), Ni(II) and Cu(II) was found to be in the range of 1.0–1.8, 2.3–10.1, 1.3–2.5, and 0.7–4.3, respectively, corresponding to the pH range of 0.8–1.6, 2.0–9.8, 1.0–2.0, and 0.5–4.0 in the sample solution. Hence, the sample solution was adjusted to pH 1.0, 4.5, 2.0 and 3.0, respectively, for the preconcentration of Cr(VI), Co(II), Ni(II) and Cu(II) in further experiments.

The effect of APDC concentration was examined from 0.001 to 1% (m/v). For all of the metal ions studied, the maximum absorbance was found in the range of 0.01–0.5% (m/v) APDC. Accordingly, a 0.02% (m/v) APDC solution was used for further experiments.

3.2. Effect of total preconcentration time and sample loading flow rate

In the present FI on-line multiplexed preconcentration system, the duration for each sub-injection was determined by dividing the total preconcentration time with the number of repetitive sub-injections. Thus, each sub-injection duration increased with the total preconcentration time while the repetitive numbers kept constant. To demonstrate the advantages and applicability of the MSP–FAAS for trace element determination, detailed comparison for preconcentration of Cr(VI), Co(II), Ni(II) and Cu(II) was made between the MSP (six sub-injections) and conventional FI sorption

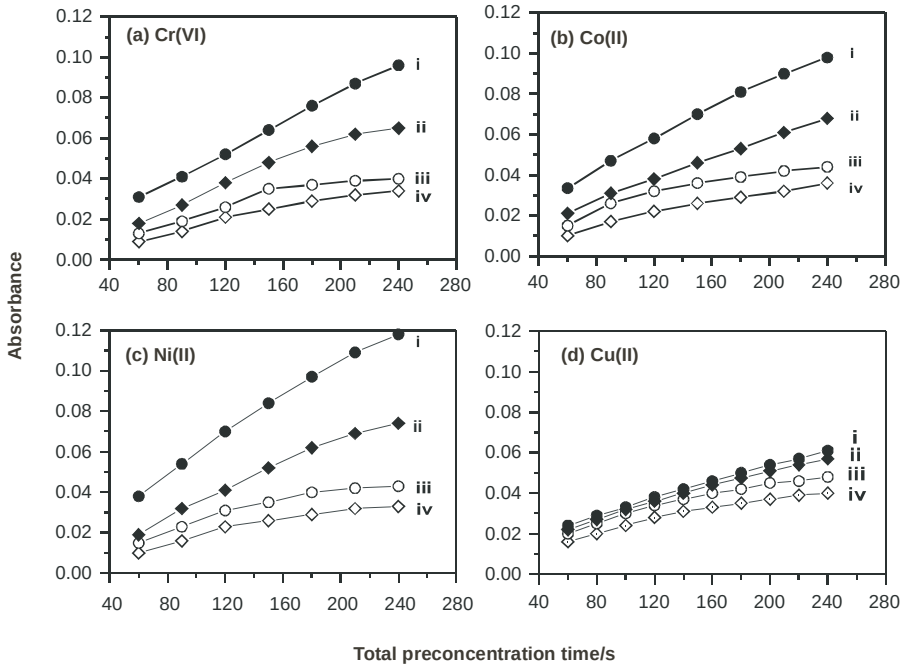

Fig. 3. Effect of the total preconcentration time on the on-line sorption preconcentration of (a) 10 μg l^{-1} Cr(IV), (b) 10 μg l^{-1} Co(II), (c) 10 μg l^{-1} Ni(II), (d) 5 μg l^{-1} Cu(II) with a six sub-injection multiplexed sorption preconcentration (i and ii) or a single continuous injection preconcentration (iii and iv) at a sample loading flow rate of 6.0 ml min^{-1} (i and iii) or 2.0 ml min^{-1} (ii and iv). All other conditions as in Figs. 1 and 2, and Table 1.

preconcentration (i.e. a single continuous injection) in respect to the sensitivity and linearity of absorbance versus total preconcentration time and sample loading flow rate.

Fig. 3 compared the linearity of the absorbance of the four analytes as a function of total preconcentration time for the MSP and conventional FI sorption preconcentration with a sample loading flow rate of either 6 or 2 ml min^{-1}. As can be seen from Fig. 3, besides the enhancement of sensitivity for Cr(VI), Co(II), Ni(II) and Cu(II), the present multiplexed preconcentration procedure with six repetitive sample sub-injections offered a wider linearity in the diagrams of absorbance versus total preconcentration time (also see Table 2).

Fig. 4 compared the linearity of the absorbance of the four analytes as a function of sample loading flow rate for the MSP and for conventional FI sorption preconcentration with a total preconcentration time of 180 s. Clearly, the linear range of absorbance versus sample loading flow rate was significantly improved by the MSP procedure in comparison with conventional preconcentration with one single continuous sample injection (6.0 ml min^{-1} versus 3.8 ml min^{-1} for Cr(VI), Co(II) and Cu(II), 6.0 ml min^{-1} versus 3.2 ml min^{-1} for Ni(II)).

In addition, the present MSP exhibits a rapid increase in absorbance with increasing in total preconcentration time and sample loading flow rate for Cr(VI), Co(II), Ni(II) and Cu(II) (Fig. 3a–d (i, ii) versus Fig. 3a–d (iii, iv), Fig. 4a–d (i) versus Fig. 4a–d (ii)). The extended linearity of the absorbance of the four analytes as a function of total preconcentration time and sample loading flow rate could be attributed to the increased retention efficiencies of the analytes.

3.3. Effect of the number of repetitive sub-injections

To further demonstrate the merits and limitations of the proposed MSP for FAAS, the effect of the number of repetitive sample sub-injections for preconcentration on the

Table 2
Comparison of the linear ranges of total preconcentration time for Cr(VI), Co(II), Ni(II) and Cu(II) obtained by the proposed FI on-line multiplexed sorption preconcentration (MSP) and conventional FI on-line sorption preconcentration (CSP)

Sample loading flow rate (ml min^{-1})	Linear range of total preconcentration time (s)							
	Cr(VI)		Co(II)		Ni(II)		Cu(II)	
	MSP	CSP	MSP	CSP	MSP	CSP	MSP	CSP
2.0	50–180	50–150	50–240	50–120	50–210	50–120	50–200	50–140
6.0	50–240	50–150	50–240	50–120	50–210	50–120	50–240	50–120

Data extracted from Fig. 3.

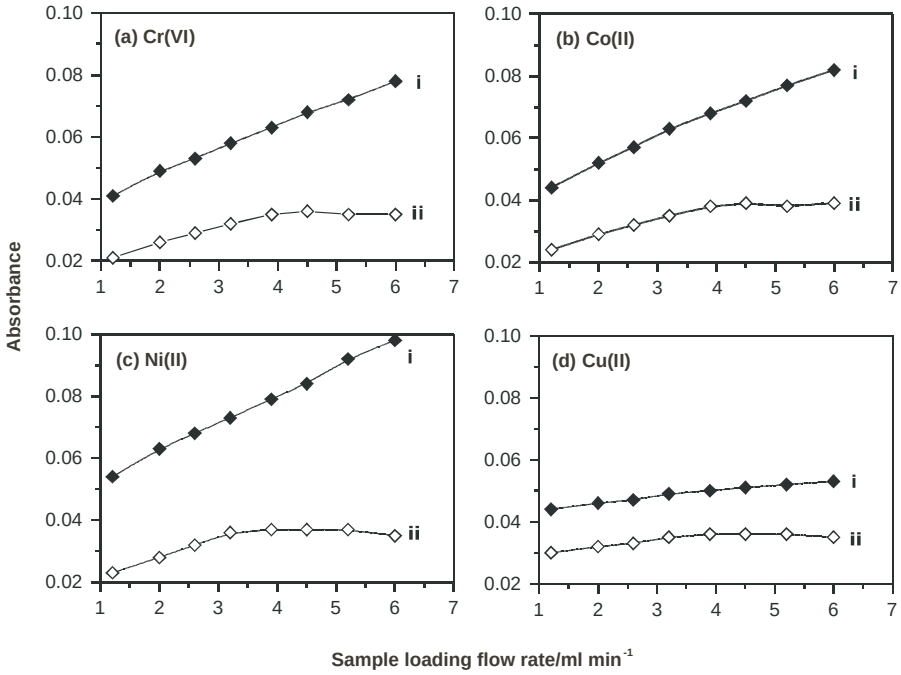

Fig. 4. Effect of the sample loading flow rate on the preconcentration of: (a) 10 μg l^{-1} Cr(IV), (b) 10 μg l^{-1} Co(II), (c) 10 μg l^{-1} Ni(II), (d) 5 μg l^{-1} Cu(II) with (i) a six sub-injection multiplexed sorption preconcentration and (ii) a single continuous injection preconcentration with a total preconcentration time of 180 s. All other conditions as in Figs. 1 and 2, and Table 1.

absorbance of 10 μg l^{-1} Cr(VI), Co(II), Ni(II), and 5 μg l^{-1} Cu(II) was investigated (a) with a total preconcentration time of 180 s and a sample loading flow rate of 6.0 ml min^{-1}, and (b) with a total preconcentration time of 90 s and a sample loading flow rate of 2.0 ml min^{-1}. In the first case, the total preconcentration time and sample loading flow rate were well beyond the linear range of the diagram of the absorbance against total sample precocentration time and sample loading flow rate obtained by conventional preconcentration procedure (see Figs. 3 and 4). However, in the second case the total preconcentration time and sample loading flow rate were fairely within the linear range of the diagram of the absorbance against the sample precocentration time and the sample loading flow rate obtained by conventional preconcentration procedure (see Figs. 3 and 4).

As shown in Fig. 5, the absorbance for all the analytes interested obtained with a total preconcentration time of 180 s and a sample loading flow rate of 6.0 ml min^{-1} increased almost linearly as the number of repetitive sample injections increased from two to at least eight. Although similar trends were observed for Cr(VI), Co(II) and Ni(II) when a total preconcentration time of 90 s and a sample loading flow rate of 2.0 ml min^{-1} were applied, the absorbance of these analytes increased to a much less extent in comparison with the use of a total preconcentration time of 180 s and a sample loading flow rate of 6.0 ml min^{-1}. As to Cu(II), the absorbance had almost no changes for a total preconcentration time of 90 s and a sample loading flow rate of 2.0 ml min^{-1}, but increased by 27% for a total preconcentration time of 180 s and a sample loading flow rate of 6.0 ml min^{-1} with increase in the number of repetitive sub-injections to eight. The above results may indicate that the proposed MSP could not present its virtue if the selected preconcentration time and sample loading flow rate were within the linear range of the diagrams of absorbance versus preconcentration time and sample loading flow rate for a single continuous sample injection preconcentration procedure. Som-Aurn et al. [11] did not observed significant improvement in retention efficiency for 1.0 μg l^{-1} Cr(VI) when dividing a total preconcentration time of 60 s into four sub-preconcentration step as compared with the conventional single continuous sample loading, possibly because the total preconcentration time (60 s) and the loading flow rate (5.0 ml min^{-1}) used did not exceed the linear ranges.

The observed increase in the absorbance of the analytes by the MSP resulted from an improvement of the retention efficiency of the KR for the analytes, probably because the first adsorption generated in the KR might act as “nucleation sites” for subsequent injections. With a sample loading flow rate of 6.0 ml min^{-1} and a total preconcentration time of 180 s, the retention efficiencies were increased from 25, 46, 41 and 63% with a single continuous sorption preconcentration to 44, 78, 65 and 75% with six sub-injection sorption preconcentration for Cr(VI), Co(II), Ni(II), and Cu(II), respectively. It seems that a more pronounced improvement in retention efficiency can be obtained with increase of the number of repetitive sub-injections for a less stable PDC complex of the metal ion, and vice versa. The present MSP may prefer the metal ions with less stable PDC complexes, and behaves advantages beyond the inflection points in the

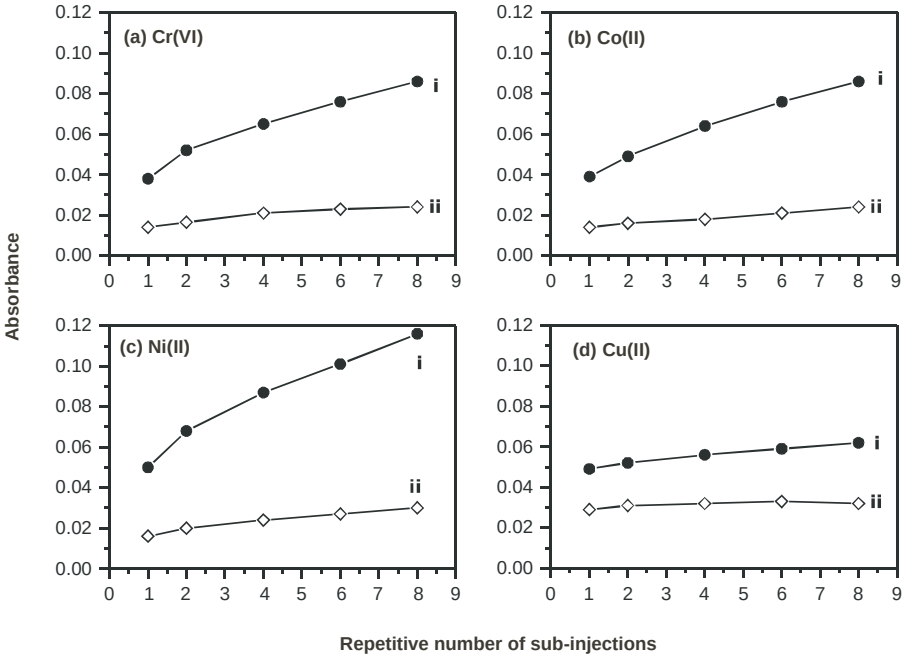

Fig. 5. Effect of the repetitive number of sub-injections on the on-line multiplexed sorption preconcentration of: (a) 10 μg l^{-1} Cr(IV), (b) 10 μg l^{-1} Co(II), (c) 10 μg l^{-1} Ni(II), (d) 5 μg l^{-1} Cu(II) with (i) a preconcentration time of 180 s and a sample loading flow rate of 6.0 ml min^{-1}, or (ii) a preconcentration time of 90 s and a sample loading flow rate of 2.0 ml min^{-1}. All other conditions as in Figs. 1 and 2, and Table 1.

diagrams of absorbance against preconcentration time and sample loading flow rate obtained by a single continuous preconcentration procedure.

3.4. Introduction of an air flow after each sub-injection

Introduction of an air flow for removal of the residual solution in the KR after each sub-injection played a decisive role in the improvement of retention efficiency by the MSP technique. Omission of the air flow introduction after each sub-injection resulted in no improvement for retention efficiency. Introduction of an air flow at 3.0 ml min^{-1} for 15 s after each sub-injection for the complete removal of the residual solution from the KR was found to give optimal sensitivity.

3.5. Interferences

Commonly encountered matrix components in natural water, i.e. alkali and alkaline earth elements cause no interferences due to the group-specific character of APDC. However, heavy metal ions may cause serious interferences owing to their competition for the chelating agent and their PDC complexes for active sites on the inner walls of the KR. In this work, eight typical transition metal ions, Mn(II), Pb(II), Cd(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) were chosen to examine the interferences in the determination of 2 μg l^{-1} the metal ions interested. The results are shown in Table 3. Fe(III) appears to present a potential problem and needs to be masked in some applications.

Table 3
Effect of potentially interfering ions on the determination of Cr(VI), Co(II), Ni(II), and Cu(II) at 2 μg l^{-1} level

Interfering ions	Concentration (μg l^{-1})	Recovery (%)			
		Cr(VI)	Co(II)	Cu(II)	Ni(II)
Zn(II)	5000 (mg l^{-1})	96 ± 1	95 ± 3	94 ± 1	95 ± 2
Mn(II)	5000 (mg l^{-1})	97 ± 1	97 ± 1	98 ± 2	96 ± 2
Fe(III)	15	–	–	94 ± 1	93 ± 2
	20	93 ± 2	–	68 ± 3	71 ± 2
	25	80 ± 1	94 ± 1		
	30		72 ± 2		
Cu(II)	40	–	95 ± 1	–	
	60	96 ± 2	80 ± 1	–	96 ± 2
	100	82 ± 2	54 ± 2	–	84 ± 2
Co(II)	50	98 ± 1	–	93 ± 1	95 ± 1
	75	94 ± 2	–	75 ± 2	83 ± 3
	100	78 ± 2	–	59 ± 1	62 ± 3
Ni(II)	75	96 ± 2	92 ± 1	–	–
	100	86 ± 1	70 ± 3	96 ± 2	–
	120	71 ± 2	63 ± 2	85 ± 2	–
Cd(II)	180	95 ± 1	94 ± 1	93 ± 1	98 ± 2
	200	92 ± 1	86 ± 1	75 ± 1	87 ± 1
	220	82 ± 3	–	–	73 ± 3
Pb(II)	200	94 ± 2	96 ± 3	97 ± 1	98 ± 1
	220	90 ± 2	82 ± 2	94 ± 1	95 ± 2
	250	74 ± 1	–	80 ± 3	76 ± 2

Table 4
Performance of the MSP–FAAS system for the determination of Cr(VI), Co(II), Ni(II), and Cu(II)

	Cr(VI)	Co(II)	Ni(II)	Cu(II)
Working concentration range ($\mu g\,l^{-1}$)	1.0–50	1.0–25	1.0–35	0.8–40
Calibration function (7 standards, $n = 3$; A, peak height absorbance; C, in $\mu g\,l^{-1}$)	$A = 0.0093C_{Cr} + 0.002$	$A = 0.0075C_{Co} + 0.0001$	$A = 0.0089C_{Ni} + 0.003$	$A = 0.0111C_{Cu} + 0.0014$
Correlation coefficient	0.9995	0.999	0.9991	0.9998
Precision (R.S.D., $n = 11$) (%)	2.1 ($2\,\mu g\,l^{-1}$)	4.1 ($2\,\mu g\,l^{-1}$)	2.6 ($2\,\mu g\,l^{-1}$)	1.7 ($1\,\mu g\,l^{-1}$)
Detection limit $3(\sigma)$ ($\mu g\,l^{-1}$)	0.40	0.33	0.31	0.26
Enhancement factor	59	68	75	121
Retention efficiency (%)	44	78	65	75

Table 5
Analytical results for the determination of Cr(VI), Co(II), Ni(II), and Cu(II) in water samples

	Cr ($\mu g\,l^{-1}$)		Ni ($\mu g\,l^{-1}$)		Cu ($\mu g\,l^{-1}$)	
	Determined (mean ± σ, $n = 5$)	Certified	Determined (mean ± σ, $n = 5$)	Certified	Determined (mean ± σ, $n = 5$)	Certified
GBW 08608	31.6 ± 1.0[a,b]	30 ± 2.1[a]	61.5 ± 1.2[a]	60 ± 3.0[a]	49.0 ± 1.0[a]	50 ± 2.0[a]
River water 1	4.8 ± 0.1	–	4.6 ± 0.1	–	6.1 ± 0.1	–
River water 2	5.1 ± 0.1	–	6.3 ± 0.2	–	7.0 ± 0.1	–
River water 3	4.0 ± 0.1	–	5.1 ± 0.1	–	4.3 ± 0.1	–
Seawater 1	n.d.[c]	–	3.6 ± 0.1	–	3.6 ± 0.1	–
Seawater 2	n.d.	–	5.7 ± 0.1	–	2.2 ± 0.1	–
Seawater 3	n.d.	–	3.7 ± 0.1	–	4.1 ± 0.1	–

[a] $\mu g\,kg^{-1}$.
[b] After $KMnO_4$ oxidation to convert Cr(III) to Cr(VI) before preconcentration and determination.
[c] n.d., not detected.

3.6. Performance of the MSP–FAAS system

Characteristic data on the performance of the MSP coupled with FAAS for the determination of Cr(VI), Co(II), Ni(II) and Cu(II) are given in Table 4. The accuracy of the developed method was checked by analyzing a certified water reference material GBW 08608. The sample was diluted by a factor of 2, and adjusted to optimum pH conditions. The analytical results obtained by the present method using simple aqueous standards for calibration were given in Table 5. Good agreement was observed between the determined concentrations and those certified of Cr(VI), Ni(II), and Cu(II).

The developed method was applied to the determination of Cr(VI), Co(II), Ni(II), and Cu(II) in local water samples. The analytical results for these water samples obtained by the present method using a simple aqueous standards for calibration were also shown in Table 5. No Co(II) could be detected in all samples studied. The recoveries of the analyte spike at the $2\,\mu g\,l^{-1}$ level from these water samples ranged from 88 to 95%, indicating that the presence of concomitants did not interfer the determination in these water samples.

4. Conclusions

This work demonstrated the possibility for the improvement of retention efficiency of the analytes by the MSP–FAAS. Introduction of an air-flow for removal of the residual solution in the KR after each sub-injection played a decisive role in the improvement of retention efficiency. A higher sample loading flow rate in conjunction with a longer total preconcentration time resulted in a more pronounced improvement in the retention efficiency with increase of the number of repetitive sub-injections. The extended linearity of absorbance versus total preconcentration time or sample loading flow rate offered more potentiality for achieving high sensitivity by increasing sample loading rates and/or total preconcentration time compared to previous one single continuous sample injection preconcentration procedure. The present MSP may prefer the metal ions with less stable PDC complexes, and behaves advantages beyond the inflection points in the diagrams of the absorbance against the preconcentration time and sample loading flow rate obtained by a single continuous preconcentration procedure.

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