



Semi-online preconcentration of Cd, Mn and Pb on activated carbon for GFASS

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Abstract

This paper presents a method whereby trace elements in $\text{NH}_4\text{Cl}-\text{NH}_3$ medium are adsorbed on activated carbon in a micro-flow-injection (FI) semi-online sorbent extraction preconcentration system and then determined by graphite furnace atomic absorption spectrometry (GFAAS). The analytical performance of the proposed method for determining Cd, Mn and Pb was studied. A microcolumn packed with activated carbon was used as a preconcentration column (PCC). The metals to be determined were preconcentrated onto the column for 60 s and then rinsed with 0.02% (v/v) HNO_3 and eluted with 30 μl of 2 mol l^{-1} HNO_3 . Compared with the direct injection of 30 μl of aqueous sample solution, enrichment factor of 32, 26, and 21 and detection limits (3σ) of 0.4, 4.7, and 7.5 ng l^{-1} for Cd, Mn and Pb, respectively, were obtained with 60 s sample loading at 3.0 ml min^{-1} for sorbent extraction, 30 μl of eluate injection, and peak area measurement. The precisions (RSD, $n = 6$) were 2.8% at the 0.05 $\mu\text{g l}^{-1}$ level for Cd, 3.0% at the 0.3 $\mu\text{g l}^{-1}$ level for Mn, and 3.1% at the 0.5 $\mu\text{g l}^{-1}$ level for Pb. The experimental results indicate that the procedure can eliminate the fundamental interferences caused by alkali and alkaline earth metals and the application of it to the determination of Cd, Mn and Pb in some water samples is successful.

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1. Introduction

Although graphite furnace atomic absorption spectrometry (GFAAS) provides superior detection limits for many elements over traditional atomic spectrometries, the direct determination

of trace amount of elements in complicated matrices is usually difficult due to interference and/or insufficient detection power [1]. Consequently, separation and preconcentration are often needed before GFAAS determination.

Great progress has been made in coupling flow-injection (FI) online separation and preconcentration of trace elements with atomic absorption spectrometry (AAS) including flame (F), hydride generation (HG) and GFAAS in recent years [2,3].

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Many kinds of preconcentration methods such as ion exchange [4–8], solvent extraction [9], sorbent extraction [10], coprecipitation in a knotted reactor (KR) [11,12] or sorption in a KR [13,14] can offer a variety of rapid, reliable, convenient and economical ways to separate and preconcentrate trace elements from concomitant substances in a sample solution. Separation and preconcentration based on packed column techniques seem to have undergone the most rapid development, probably due to the simplicity of the operation and the existence of a wealth of knowledge on related batch procedure.

Sperling et al. [15] used a microcolumn (50 μl) packed with a highly selective macrocycle compound immobilized silica gel sorbent for the GFAAS determination of lead with FI online preconcentration and separation. They used air to remove all the solution from the column and the connecting tube before elution and introduced the total volume of eluate into the graphite atomizer to avoid the necessity of optimizing the elution.

However, for most column preconcentration systems, even when microcolumn is used and all measurements are taken to reduce the dead volumes to a minimum, the total eluate volume often exceeds the capacity of the graphite furnace; this results in the development of several procedures to introduce eluate fractions into the graphite tubes, including time- or volume-controlled eluate zone sampling and slow injection into a pre-heated graphite tube [16,17]. The time- or volume-based “zone sampling” procedures require a careful optimization.

Activated carbon has been used as a trace collector for element preconcentration [18–24]. Because activated carbon is a type of hydrophobic adsorbent which adsorbs non-polar or little polar substances in aqueous solution, metal ions to be preconcentrated need to be transformed corresponding metal chelates [18–20], metal elements [21] or metal hydroxides [22–24] which could be adsorbed on activated carbon.

In this work, a new FI manifold that allowed the use of volume-based sampling was developed for GFAAS for the determination of trace cadmium, manganese and lead in the presence of alkali and alkaline earth metals. Activated carbon was used

as sorbent, the pH of the solution was adjusted with the buffer solution $\text{NH}_4\text{Cl}-\text{NH}_3$, some trace analytes (Cd, Mn and Pb), which can form metal hydroxides in $\text{NH}_4\text{Cl}-\text{NH}_3$ medium, could be preconcentrated onto activated carbon and then determined by GFAAS. It is evident from the experimental results that by using this approach, the effects of alkali and alkaline earth metals on the determination of metal elements are eliminated efficiently without causing losses in sensitivity and precision.

2. Experimental

2.1. Instrumentation

A Model Hitachi 180-50 atomic absorption spectrometer equipped with a Model Hitachi GA-3 graphite furnace atomizer was used throughout this work. Deuterium arc background correction system and pyrolytic graphite-coated graphite tubes with uncoated electrographite platforms were used for all experiments. Argon (99.9%) was used as purge gas at a flow rate of 150 ml min^{-1} and the purge gas was stopped during the atomization step. Integrated absorbance was used for evaluating the results. The atomization temperatures used to perform the analysis in the graphite furnace were 1600, 2100 and $2000 \text{ }^\circ\text{C}$ for Cd, Mn and Pb, respectively.

An FI semi-online preconcentration system containing an LZ-1010 peristaltic pump and an LZ-1010 multifunctional valve (Shenyang Zhaofa Institute of Automatic Analysis, China) was used for analyte preconcentration and separation from the matrix. Small bore (0.35 mm i.d.) PTFE tubing was used for all connections. The conical sorbent extraction preconcentration column was laboratory-made, with two inner diameters of 3.5 and 2.0 mm, and length of 25 mm. Both ends of the column were plugged with polyurethane plastic foam as end caps [25]. A newly packed column should be washed with deionized water to condition the column and to remove trace amounts of analyte from the sorbent material and the plastic foam.

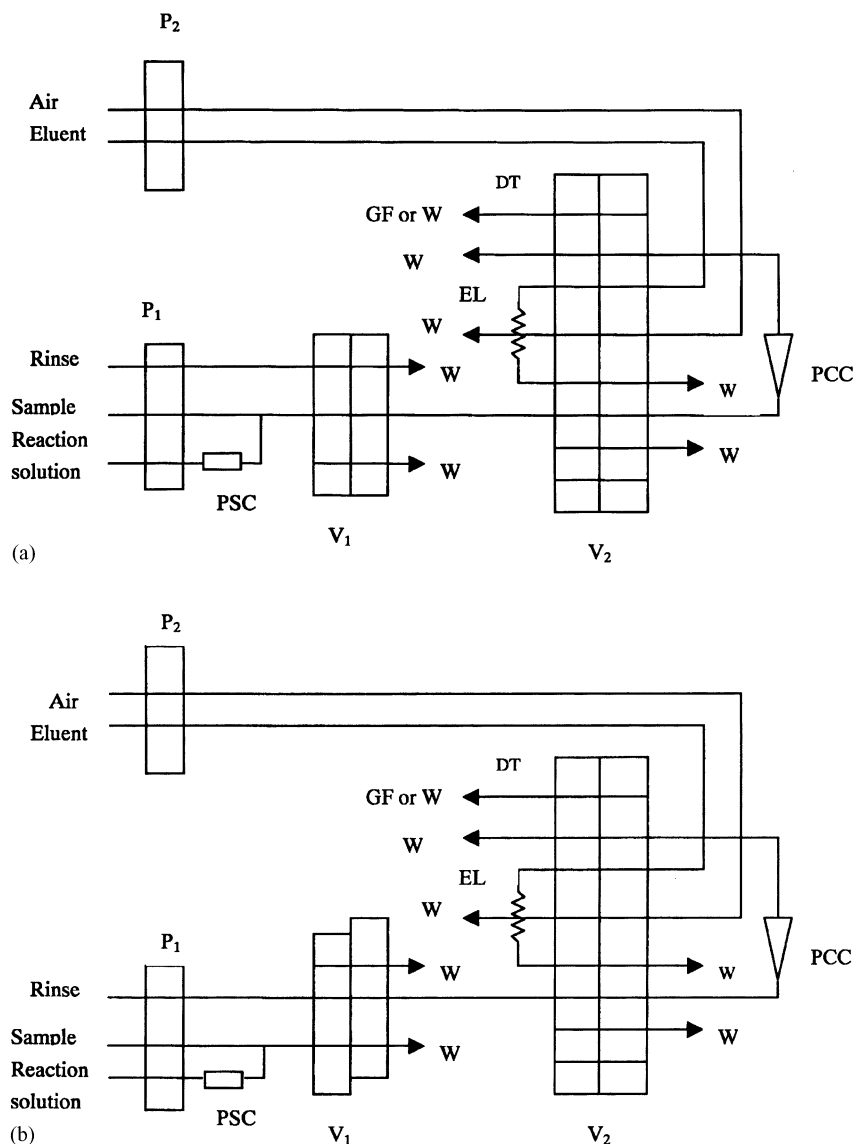


Fig. 1. Schematic diagram of the FI preconcentration system: (a) preconcentration position; (b) rinsing and collection positions; (c) elution position. P₁, P₂, pumps; V₁, V₂, valves; W, waste; PSC, prepreparation column; PCC, preconcentration column; EL, eluent loop; GF, graphite furnace; DT, delivery tube.

2.2. Reagents and samples

All chemical reagents were of the highest purity available and at least of analytical reagent grade. Doubly deionized water was used throughout. Before using, the activated carbon (Dalian Hongguang Chem. Eng. Factory, China) was immersed in 2 mol l^{-1} HCl for at least 24 h so as

to remove the metal ions and other impurities sorbed on it. When used, the activated carbon was washed with deionized water until the eluate was neutral. In this study, the quantity of activated carbon used to fill the microcolumns was about 70 mg. The stability of the sorption characteristics of the columns is good and the same microcolumn can be used for about 20 cycles.

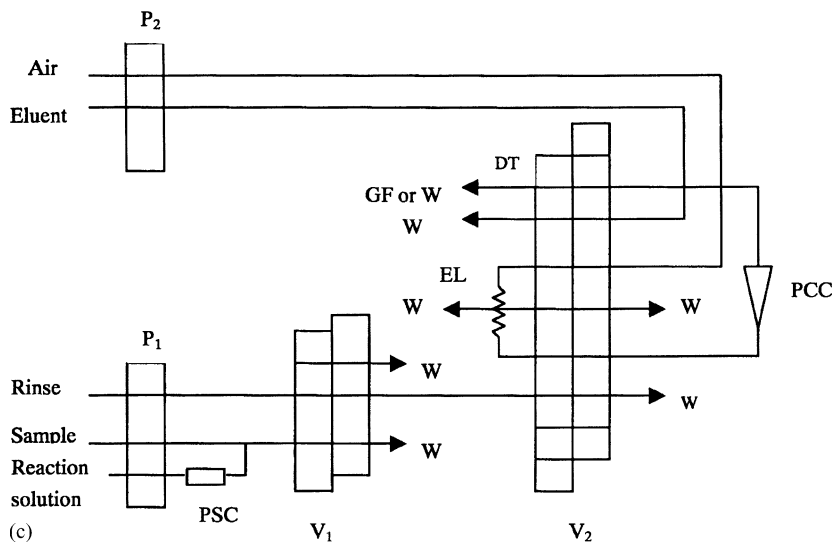


Fig. 1 (Continued)

Argon (99.99%) (Fushum Biouisi., China) was used as both carrier gas and support gas. The standard stock solutions of cadmium, manganese and lead (1 mg ml^{-1}) were prepared using standard methods. The standard working solutions of the tested metals were prepared daily by stepwise dilution of standard stock solutions with nitric acid (0.2%, v/v). The mineral water and tap water samples adjusted with HNO_3 to the desired pH were directly introduced into the FI-GFAAS system without any treatment.

2.3. Procedure

The schematic diagram of FI preconcentration system is shown in Fig. 1(a)–(c). A complete cycle of preconcentration and elution takes about 200 s including sample loading, rinsing, eluting and eluate fraction introduction.

In sequence 1 (Fig. 1(a)), pump 1 was activated and pump 2 was stopped. Both valves V_1 and V_2 were in the filling position. The sample loading period took 60 s at sample flow rate of 3.0 ml min^{-1} . The sample was mixed with the reaction solution ($0.1 \text{ mol l}^{-1} \text{ NH}_3$ solution at a flow rate of 3.0 ml min^{-1}) and loaded on preconcentration column (PCC) filled with activated carbon. The length of the reaction coil (from the confluent

point of sample and reaction solutions to the column) is about 30 cm. The effluent from the column flow into the waste. To reduce the blank level, NH_3 solution was purified online by passing through a prepreparation column (PSC) filled with a sorbent material the same as that in PCC.

In sequence 2 (Fig. 1(b)), pump 1 was still activated and pump 2 was stopped. V_1 was turned manually to the injection position and V_2 was still in the filling position. PCC was rinsed with 0.02% HNO_3 at 1.5 ml min^{-1} to remove interfering matrix components and excessive reagents from the column.

In sequence 3 (Fig. 1(b)), pump 1 was stopped and pump 2 was activated. The eluant loop (EL) was filled with eluant ($2 \text{ mol l}^{-1} \text{ HNO}_3$ solution).

In sequence 4 (Fig. 1(c)), pump 2 was still activated and pump 1 was stopped. Both V_1 and V_2 were in the injection position. An air flow (1.5 ml min^{-1}) was introduced to drive the eluant from the EL into the PCC to elute the adsorbed analytes. The volume of eluant used was $30 \mu\text{l}$ each time. The first $30 \mu\text{l}$ and second $30 \mu\text{l}$ of eluant, which were divided into two segments by air, were discarded through the delivery tube (DT).

In sequence 5 (Fig. 1(c)), DT was manually inserted into the dosing hole of the graphite tube. The third $30 \mu\text{l}$ of eluant collected in EL was

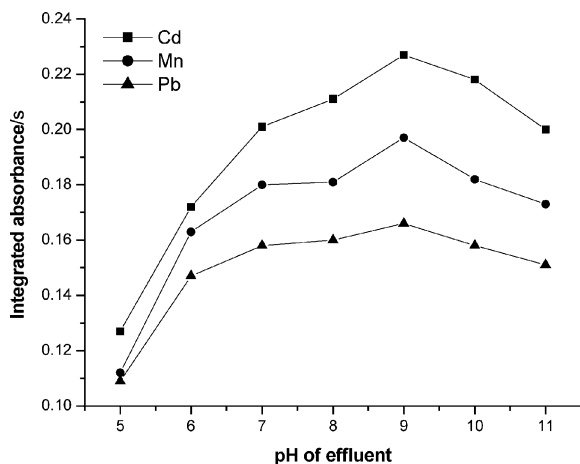


Fig. 2. The effect of sample pH (measured in the effluent stream) on the integrated absorbance of Cd, Mn and Pb.

driven into PCC by an air flow of 0.8 ml min^{-1} . After the $30 \mu\text{l}$ of eluant was driven into PCC, pump 2 was stopped for 10 s. Then pump 2 was activated and the analyte eluted from the column by the third $30 \mu\text{l}$ of eluant was introduced into the furnace.

In the following sequences, in order to reduce the memory effect, DT was withdrawn from the graphite tube, and then sequences 3 and 4 were repeated three times to clean the column and elute the residual analyte into the waste.

In the procedure, the preconcentration was performed in parallel with GFAAS determination of the previous analytes concentrated.

3. Results and discussion

3.1. HNO_3 concentration in the sample solution and NH_3 concentration in reaction solution

In this work, the pH value of the mixture solution (acidified sample+reaction solutions) was adjusted by the concentration ratio of HNO_3 to NH_3 . To examine the effect of HNO_3 concentration in sample solution, NH_3 concentration (0.05 mol l^{-1}) in reaction solution keeps constant. It is evident from Fig. 2 that the biggest integrated absorbance was obtained when pH is about 9; corresponding NH_3 and NH_4^+ concentration in

the mixture solution is approximately equal. To examine the effect of NH_3 concentration in reaction solution, the HNO_3 concentration (0.05 mol l^{-1}) in sample solution is kept constant. Similar trend as Fig. 2 had been obtained, namely with 0.05 mol l^{-1} HNO_3 and 0.025 mol l^{-1} NH_3 , the integrated absorbance of analyte was the biggest, corresponding pH is about 9. In this work, the selected concentrations of HNO_3 in sample and NH_3 in reaction solution are 0.05 and 0.1 mol l^{-1} , respectively. The mixture solution has an excess of ammonia (0.025 mol l^{-1}); Cd, Mn and Pb can form complexes with OH^- ($\text{Cd}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$ and $\text{Pb}(\text{OH})_2$) under this condition, and the stability constants of these complexes are all high [26]. There are also other forms of Cd, Mn and Pb complexes in the solution, such as they can exist as the forms of amino complexes, $\text{M}(\text{OH})^+$ and $\text{M}(\text{OH})_3^-$ complexes. As these metal complexes have positive charges or negative charges, and ammonia is a polar substance, it is difficult for them to be adsorbed on the activated carbon. However, because the hydroxides of $\text{M}(\text{OH})_2$ are preferably adsorbed on activated carbon surface, the equilibrium is shifted, thus, the analytes can be adsorbed completely. Hydroxides are adsorbed on the surface anyway even if they are not present in the solution.

3.2. Preconcentration time

The effects of preconcentration time on integrated absorbance of cadmium, manganese and lead were investigated in the time range 30–120 s at a sample loading rate of 3.0 ml min^{-1} . It is evident that an increase in preconcentration time causes an increase of integrated absorbance of analytes. Considering the longer the time of the preconcentration, the more difficulty for the PCC to be eluted. Therefore the loading time selected in the experiment is 60 s.

3.3. Flow rate of sample and reaction solutions

In this study, the sample and reaction solutions were simultaneously pumped at the same flow rate. The effect of the flow rate of sample and reaction solutions on the integrated absorbance of

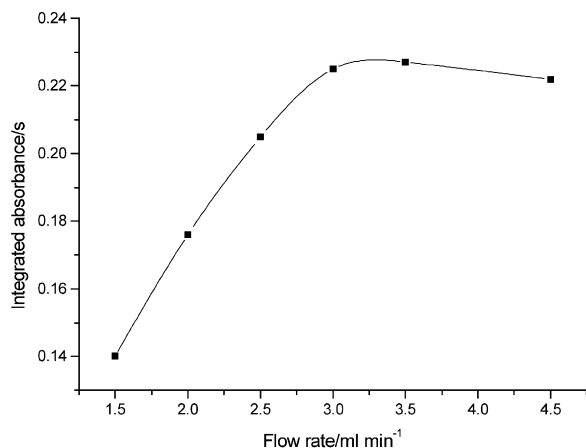


Fig. 3. The effect of flow rate of sample and reaction solutions on the integrated absorbance of Cd.

cadmium was investigated at flow rate varying in the range 1.5–4.5 ml min⁻¹. The results (Fig. 3) show that at a lower flow rate (1.5–3.5 ml min⁻¹), the integrated absorbance will increase with the flow rate of sample and reaction solutions, because the higher the flow rate, the greater is the total amount of analyte passing through the PCC per unit time. And thus, more analytes can be preconcentrated on the activated carbon within a fixed period. However, at a higher flow rate (above 3.5 ml min⁻¹), the integrated absorbance slightly decreased with the flow rate. The reason for this may be that too high flow rate can lend a short residence time of analytes on the reaction coil (the length of reaction coil chosen was 30 cm) and PCC. So, these variables can affect the kinetics of both complex formation and adsorption of complexes on activated carbon surface. Similar results were obtained with Mn and Pb. In this study, the flow rate of sample and reaction solutions chosen was 3.0 ml min⁻¹.

3.4. Rinsing time

As some residual matrix elements retained on the column can be eluted into the detection system along with the analyte by the eluant and hence affect the precision and accuracy of the determination, a rinsing step was necessary prior to elution.

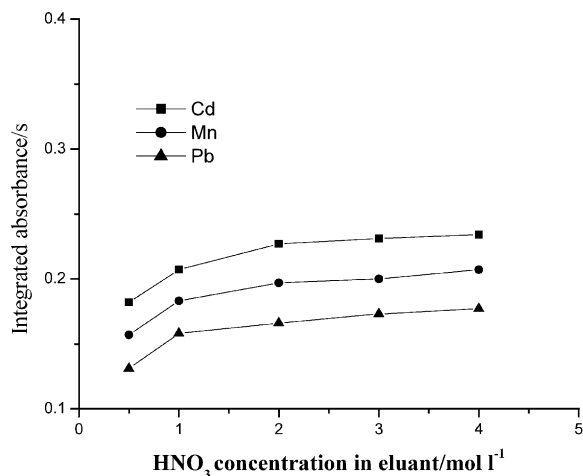


Fig. 4. The effect of HNO₃ concentration in eluant on integrated absorbance.

In this experiment, the column rinsing efficiency was higher with 0.02% (v/v) nitric acid than that with double-deionized water. Therefore, 0.02% (v/v) nitric acid solution was used as the rinsing solution in the same direction as for sample loading during all subsequent analyzes in this work.

The effect of rinsing time on the separation of the residual matrices from the analyte was also investigated at alkali and alkaline earth metals concentrations of 0.5 and 1.0 µg ml⁻¹, respectively. The results show that the integrated absorbance of Cd remains constant over a wide range of rinsing time from 10 to 30 s. It was also observed that further increasing the rinsing time to over 30 s resulted in a decreased integrated absorbance owing to leaching of the analyte from the activated carbon column. The same results were obtained with Mn and Pb. So a rinsing time of 30 s was used throughout.

3.5. HNO₃ concentration in the eluant

The effect of the concentration of HNO₃ in eluant on the integrated absorbance of cadmium, manganese and lead was investigated at HNO₃ concentration varying in the range 0.5–4 mol l⁻¹. The results are shown in Fig. 4. It is seen that the

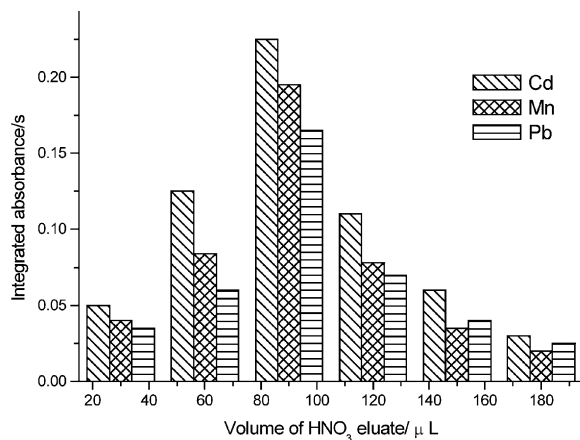


Fig. 5. The distribution of analyte (expressed as integrated absorbance) in the eluate.

integrated absorbance of analytes increased with increasing HNO_3 concentration in the range $0.5\text{--}2\text{ mol l}^{-1}$. If the concentration of HNO_3 went over 2 mol l^{-1} , there was no significant effect of HNO_3 concentration on the integrated absorbance of analytes. Considering the graphite tube exhibits low tolerance to the introduction of strong acid, and so a concentration of 2 mol l^{-1} HNO_3 in the eluant was chosen for all further experiments.

3.6. Effect of residence time of the eluant in the column

An attempt was made for complete elution of the adsorbed analyte by stopping the effluent flow in the middle of the elution for different periods of time (residence time). The effect of residence time on the integrated absorbance of Cd was investigated in more detail. The results showed that a residence time of 10 s was sufficient for the analyte to achieve concentration equilibrium between the effluent phase and sorbent phase. If the effluent stayed in the activated carbon column for longer than 10 s before it was pumped through the column, the integrated absorbance value slightly decreased with residence time. Similar results were obtained with Mn and Pb. Therefore, a residence time of 10 s was used throughout.

Table 1

Effect of concomitant ions on the recoveries of Cd, Mn and Pb; relative absorbances of Cd, Mn and Pb taking the value without concomitant ions as 100

Element	Concentration ($\mu\text{g l}^{-1}$)	Fold of concomitant element of not causing interference
Cd	0.05	1000 (Li, Na, K, Ca, Mg); 100 (Fe, Al)
Mn	0.3	1000 (Li, Na, K, Ca, Mg); 100 (Fe, Al)
Pb	0.5	1000 (Li, Na, K, Ca, Mg); 20 (Fe, Al)

3.7. Selection of eluate fraction

Because the sample volume capacity of the graphite furnace is restricted to about $100\text{ }\mu\text{l}$ when tube-wall atomization is used and to about $40\text{ }\mu\text{l}$ when platform atomization is used, only a part of the preconcentrated sample can be introduced into the furnace in this work. In the study of selection of eluate fraction, a total volume of $180\text{ }\mu\text{l}$ of 2 mol l^{-1} HNO_3 was used to elute the analyte from the column with respect to the distribution of analyte in the eluate. The $180\text{ }\mu\text{l}$ eluant was divided into six fractions by air, each fraction ($30\text{ }\mu\text{l}$) collected in the EL was driven into the column by an air flow of 0.8 ml min^{-1} and stopping for 10 s. Then the analyte eluted from the column by this fraction was introduced into the graphite furnace for analysis. The results in Fig. 5 show that the first $60\text{ }\mu\text{l}$ of eluate contained only a small amount of analyte mass. This fraction was, therefore, discarded. The next $30\text{ }\mu\text{l}$ of the eluate contained the main part of the analyte mass and was introduced into the graphite furnace by air. The last $90\text{ }\mu\text{l}$ of eluate also contained only a small amount of analyte and was also discarded.

In this study, the sum of the eluate discarded (not introduced in GF), and consequently preconcentrated analytes are not negligible compared with the one introduced. Although the analyte can be eluted from the column quantitatively with a lower volume of eluent by using shorter time of preconcentration, the distribution of analyte in the eluate also exist, and the total volume of eluate cannot be introduced into the graphite tubes one

Table 2

Analytical performance of FI semi-online preconcentration for the determination of Cd, Mn and Pb with 60 s sample loading period

Element	Enhancement factor ^a	Characteristic concentration ^b (ng l ⁻¹)	Detection limit ^c (ng l ⁻¹)	Sample throughput (samples h ⁻¹)	RSD (% , n = 6)
Cd	32	0.9	0.4	18	2.8
Mn	26	6.7	4.7	18	3.0
Pb	21	13	7.5	18	3.1

^a Compared with direct introduction of 30 µl of sample solution.^b Sample concentration giving 0.0044 absorbance.^c Concentration 3σ of the blank.

Table 3

Determination results and recoveries of Cd, Mn and Pb for water samples

Element	Sample	Concentration (µg l ⁻¹)	Added (µg l ⁻¹)	Found (µg l ⁻¹)	Recovery (%)	RSD (% , n = 5)
Cd	Mineral water 1	0.340	0.300	0.646	102	2.9
	Mineral water 2	0.301	0.300	0.586	95	2.6
	Tap water 1	0.037	0.040	0.0762	98	3.2
Mn	Mineral water 1	16.0	15.0	31.45	103	3.1
	Mineral water 2	13.2	15.0	23.35	101	3.2
	Tap water 1	21.0	20.0	41.8	104	3.1
Pb	Mineral water 1	0.14	0.20	0.328	94	3.2
	Mineral water 2	0.10	0.20	0.298	98	3.6
	Tap water 1	0.17	0.20	0.356	93	3.4

time. Considering that the eluate fraction can be selected accurately by using a 30 µl EL, the analytes introduced for analysis are also quantitative in this study.

3.8. Effects of some concomitant ions

It has been shown that the interference caused by some concomitant ions is one of the major factors that limit the further development of GFAAS [1]. Alkali metals, alkaline earth metals, Fe and Al exist widely in nature, and so the effect resulting from these elements was investigated in this study. The results are listed in Table 1. The experimental results are explained under these experimental conditions that the hydroxides of alkali and alkaline earth metals are not formed and, therefore, they cannot be absorbed on the activated carbon. Although the hydroxides of Fe³⁺ and Al³⁺ can be formed and adsorbed on

the activated carbon, they do not affect the determination of these elements within the concentration ranges studied.

3.9. Analytical performance of the FI semi-online preconcentration system

The analytical performance of the FI semi-online preconcentration proposed for the determination of Cd, Mn and Pb by GFAAS is summarized in Table 2. With 60 s sample loading at 3.0 ml min⁻¹, 30 µl of eluate injection, and peak area measurement, the enrichment factors were 32, 26, and 21, respectively, compared with that of direct injection of a 30 µl aqueous sample solution. Detection limits (3σ, n = 10) were 0.4, 4.7, and 7.5 ng l⁻¹ and characteristic concentrations were 0.9, 6.7, and 13 ng l⁻¹ for Cd, Mn and Pb, respectively.

3.10. Analysis of water samples

To investigate the applicability of this method developed and to check the accuracy of the developed system for the analysis of practical samples, the developed system was applied to investigate the recovery of cadmium, manganese and lead added to three kinds of water samples. The main constituents of the water samples which have been analyzed in this study are alkali and alkaline earth metals. The alkali and alkaline earth metal contents in these water samples are about 0.5 and 1.0 $\mu\text{g ml}^{-1}$, respectively. The analytical results are listed in Table 3. The recoveries were found to be in the range 93–104%, indicating that the proposed FI semi-online separation and concentration system permits determination of cadmium, manganese and lead in those water samples.

4. Conclusion

This work demonstrates that the FI semi-online preconcentration with an activated carbon not only improves the detection limits for trace determination of some heavy metals, but also eliminates fundamentally the interferences caused by alkali and alkaline earth metals. In this study, the problem in selecting accurately the eluent fraction between 90 and 120 μl is solved by using a 30 μl eluent loop. There are some limitations for this method. This work was performed in a semi-online mode, the eluate fraction between 90 and 120 μl can be selected, and near some other fractions, such as fraction between 100 and 130 μl , cannot be selected. In order to improve the analytical performance, the complete online automatic eluate injection at a stable flow rate should be realized.

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