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An automated on-line minicolumn preconcentration cold vapour atomic absorption spectrometer: Application to determination of cadmium in water samples

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ABSTRACT

A method was developed for on-line solid phase preconcentration and cold vapour atomic absorption spectrometric determination of Cd(II) in aqueous samples. Lewatit Monoplus TP207 iminodiacetate chelating resin was used for the separation and preconcentration of Cd(II) ions at pH 4.0. The whole system was labmade. The influence of analytical parameters such as concentration of eluent and sodium tetrahydroborate solution, flow rate of eluent, sample, and Ar, and matrix ions were investigated. A preconcentration factor of 20 and a detection limit ($3s_b$) of 2.1 ng L^{-1}, along with a sampling frequency of 28 h^{-1} were achieved with 1.4 min of sample loading time and with 2.8 mL sample consumption. The relative standard deviation (R.S.D.) was 2.5% for 0.05 μg L^{-1} Cd(II) level. The developed method was used for Cd(II) analysis in water samples. The certified reference material (LGC6019) experimental results are in good agreement with the certified value.

1. Introduction

Cadmium is a toxic element even at low concentrations and can be accumulated in the vital organs, producing carcinogenic effects. Anthropogenic sources include smelter emissions mainly related to the zinc industry, and the application of fertilizers originating from incineration and purification stations, and sewage sludge to the land. All these practices produce an accumulation of cadmium in the soil, allowing it to enter the food chain with the potential to cause serious health problems [1]. Considering its hazards, health organizations have established permissible limits for Cd in food commodities, including drinking water. The World Health Organization (WHO) established 3 μg L^{-1} as the maximum permissible concentration in drinking water [2].

There are already some detection systems in use for the evaluation of cadmium; these include spectrophotometry [3,4], inductively coupled plasma optical emission spectrometry (ICP-OES) [5,6], flame atomic absorption spectrometry (FAAS) [7,8], and graphite furnace atomic absorption spectrometry (GFAAS) [9].

The use of vapour generation as a means of sample introduction with the conversion of the elements into volatile compounds offers unique advantages: separation of the analyte from the matrix, more efficient sample introduction than conventional nebulization, and also higher sensitivity and selectivity by removing non-volatile interferent species which remain in the solution [10]. Many studies have been reported that the vapour generation characteristics of cadmium arose from reduction of Cd(II) ions by sodium tetrahydroborate and endeavoured to determine levels of Cd in water samples with cold vapour atomic absorption spectrometry (CVAAS). Manzoori et al. [11] was able to determine Cd in ultratrace levels with CVAAS using the cloud point extraction preconcentration procedure in water samples. Arbab-Zavar et al. [12] used the electrochemical hydride generation system to obtain monoatomic Cd vapour prior to detection with an atomic absorption spectrometer. Ritschdorff et al. [13] analysed Cd in a certified natural water sample using CVAAS with a modified version of a Multimode Sample Introduction System (MSIS^{TM}). Wu et al. [14] used a preconcentration procedure of cadmium on the inner walls of a knotted reactor based on the retention of cadmium complex with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one. Then 0.2 mol L^{-1} HCl was introduced to elute the retained analyte complex and merge it with a KBH_4 solution for HG-AFS detection. Li et al. [15] improved the sensitivity level with $NaIO_3$ addition for Cd determination in the FI-CVAAS system. Korkmaz et al. [16] generated cold vapour of Cd using a flow system and utilizing preconcentration with external heating of the inlet arm of a quartz

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T-tube. Chuachuad and Tyson [17] developed a new on-line separation/CVAAS system for the determination of Cd(II) in certified materials.

In this paper we developed a new labmade on-line separation/preconcentration system combined with cold vapour atomic absorption spectrometric determination of Cd(II) using Lewatit MonoPlus TP207 chelating resin. The resin is a weakly acidic, macroporous, and high-capacity cation exchange material containing iminodiacetate groups. The resin has been previously used for separation and preconcentration of trace metal ions [21–27]. To the best of our knowledge, the application of Lewatit MonoPlus TP207 resin for on-line determination of Cd(II) by FI-CVAAS has not been previously reported. The application of the presented method to the analysis of potable water samples was performed without using any chemicals (Ni, Co, thiourea, hydroxylammonium chloride, and $NaIO_3$) added to the eluent and sodium tetrahydroborate solutions to enhance to the sensitivity. This system was originally designed and used for cold vapour atomization spectrometric determination of Cd(II) in potable water samples.

2. Experimental

2.1. Instrument

A Perkin-Elmer Model AA800 atomic absorption spectrometer (Norwalk, CT, USA) equipped with a deuterium background corrector was used throughout the study. A cadmium hollow cathode lamp was used as the radiation source at a wavelength of 228.8 nm with an 8 mA lamp current and 0.7 nm slit width. The spectrometer was operated with integrated absorbance (peak area) values computed by the software of the instrument. The stop and go intervals of the two peristaltic pumps and the actuation of the pinch valves were controlled automatically by using a six channel timer made in our instrumentation laboratory. Two peristaltic pumps (Ismatec Reglo, Germany) were used to propel all solutions and two pinch valves (Cole Parmer, USA) were used to select appropriate solutions for the FI steps. A minicolumn filled with Lewatit MonoPlus TP207 iminodiacetic acid chelating resin was used for the separation and preconcentration procedure. The gas liquid separator (GLS) was made from a 10 mL medical syringe. PVC pump tubing (0.8 mm i.d.) was used to pump the samples, eluent, and sodium tetrahydroborate solutions. All the other tubings used were made of Teflon (0.5 mm i.d.) and the “Y” and “T” joint connections used were of HDPE material. All pH measurements were made with a Consort C533 model pH meter (Turnhout, Belgium) and a combination glass electrode.

2.2. Reagents

Ultrapure water was used to prepare all solutions. The sulphuric acid, nitric acid, hydrochloric acid and sodium tetrahydroborate were analytical reagent grade (Merck, Darmstadt, Germany). Lewatit MonoPlus TP207 resin (Fluka, Milwaukee, USA) was used after being dried of two hours in an oven at 110 °C. All other reagents were of analytical reagent grade. The laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution. Afterwards, it was rinsed thoroughly with ultrapure water. Cd(II) stock solution ($10\ \mu g\ L^{-1}$) was prepared by diluting $1000\ mg\ L^{-1}$ atomic standard cadmium solution (Merck, Darmstadt, Germany) with a $0.1\ mol\ L^{-1}$ nitric acid solution. Acetate buffer solution (pH 4.0) was prepared by dissolving 136 g of $CH_3COONa{\cdot}3H_2O$ and 4.7 mL of concentrated CH_3COOH (Merck, Darmstadt, Germany) in 1000 mL of deionized water. Sulphuric acid ($1.0\ mol\ L^{-1}$) was prepared by direct dilution with deionized water from the concentrated solution. In order to neutralize acidic samples, 4.0 g of NaOH (Merck, Darmstadt, Germany) was dissolved and filled to 100 mL with ultrapure water in a volumetric flask.

2.3. Column preparation

The dried resin was cooled in a desiccator and weighed 30 mg in a glass beaker. It was made into a slurry with water and filled in a glass minicolumn (20 mm × 2 mm) using a micropipette tip. The resin was covered with glasswool to avoid disturbance of the resin path.

2.4. Sample preparation

Tap water samples were collected from some local public drinking fountains in the centre of Kayseri, a city in central Turkey. The samples were acidified with 50 mL of concentrated HNO_3 for 5 L of sample and stored in +4 °C. Before use, 40 mL of sample was pipetted into a glass beaker, the pH was adjusted to 4.0 with $1\ mol\ L^{-1}$ NaOH solution and 5 mL buffer solution was added. The sample was then filled to 50 mL in a volumetric flask.

Underground water samples from mining areas were collected from three different bore wells. The samples were acidified and stored as described above.

Three different trademark mineral water samples were purchased from a local market. 40 mL of each of the sample was pipetted into a glass beaker and 0.5 mL of concentrated HNO_3 was added slowly (${CO_3}^{2-}$ and ${HCO_3}^{-}$ were transformed to CO_2) and boiled to remove CO_2 from the solutions. The solutions were cooled and prepared as described above.

LGC6019 Thames River Water certified reference material (CRM) was purchased from Teddington, U.K. This sample was prepared in the same way as the tap water samples.

2.5. On-line preconcentration system

The diagram of the on-line preconcentration system is shown in Fig. 1. The performance of the FI-CVAAS preconcentration method was tested with model solutions before application to the real samples.

In step 1, PP1 and V1 were active while PP2 and V2 were inactive, and the sample and/or standard solutions adjusted to pH 4.0 were continuously passed through the minicolumn (M) for 1.4 min at a flow rate of $2\ mL\ min^{-1}$. The Cd(II) ions were retained on the minicolumn while the effluent was sent to waste. The effluent solution was exhausted from the GLS by the discharge tubing on the same pump.

In step 2, the minicolumn was washed with water in order to remove matrix ions from the resin. At this point, PP1 and V2 were active while PP2 and V1 were inactive.

In step 3 (in the elution stage) the eluent, $600\ \mu L$ of $1\ mol\ L^{-1}$ H_2SO_4, and the same volume of 4% $NaBH_4$ in 2% NaOH were pumped to the GLS by the PP2 at a flow rate of $7.2\ mL\ min^{-1}$. During the elution stage, PP1 was inactive. At the same time, the spectrometer was in read mode and integrated to the analyte peak for 15 s.

In step 4, the minicolumn was washed with water (PP1 and V2 were active, PP2 and V1 were inactive) to clean the resin to avoid large consumption of buffer solution.

In step 5, the buffer solution was pumped into the column to condition it before a new preconcentration cycle. During this period, PP1 was active while PP2, V1 and V2 were inactive. After this step, the system started automatically from the first step again.

3. Results and discussion

The optimized chemical and hydrodynamic conditions in the flow system were determined by using a solution including

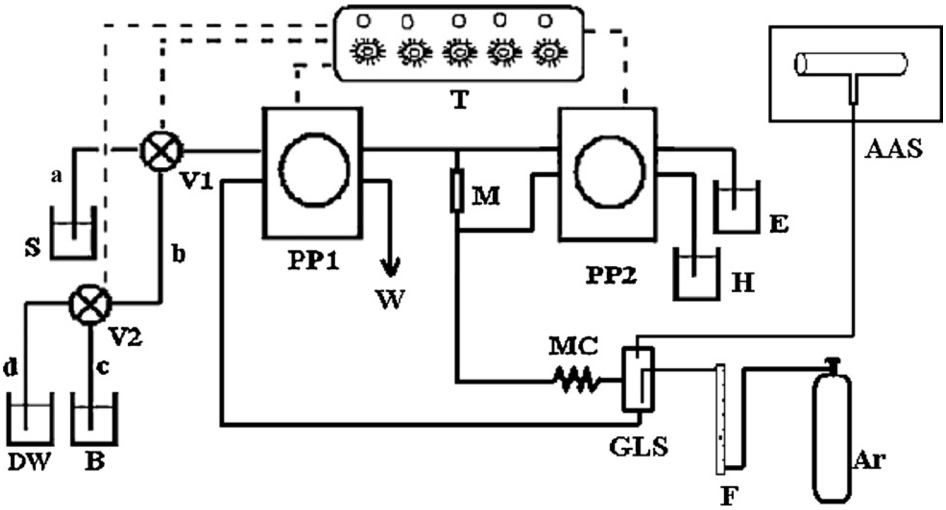

Fig. 1. FI manifold and its operation steps (PP1 and PP2: sample and eluent pumps respectively; V1 and V2: pinch valves; M: minicolumn; MC: mixing coil; T: timer, W: waste; F: flowmeter; GLS: gas–liquid separator; Ar: argon; S: sample; E: eluent; H: sodium tetrahydroborate (III) solution; B: buffer solution; DW: deionized water; AAS: atomic absorption spectrometer; a, b, c, and d: solution ways).

0.05 μg L^{-1} Cd(II) and the preconcentration procedure was applied to the aqueous sample solutions.

3.1. *Effect of pH*

The pH value of the medium affects the complexation of the analyte and chelating agent. The formation constants of complexes are dependent on the pH of the medium. Therefore, pH is a very important parameter for retention of the analyte ions on the surface of a solid phase with the complexation mechanism. The effect of the pH of the sample on Cd(II) retention was investigated within the range of 2.0–8.0. As can be seen in Fig. 2, maximum retention occurred with a pH of 4.0. pH 4.0 was selected for all further works.

3.2. *Effects of eluent type and concentration*

The elution of Cd(II) from the minicolumn was studied by using HCl, HNO_3 and H_2SO_4 solutions at different concentrations (0.25–3.0 mol L^{-1}) and the blank corrected signals showed that the most suitable eluent was 1.0 mol L^{-1} H_2SO_4. No signal was obtained for HNO_3 because of the oxidizing effect for the hydride formation reaction. The results are shown in Fig. 3.

3.3. *Effects of flow rate of sample*

Sample flow rate is an important parameter in on-line systems because it affects the retention of the cation on the minicolumn. When the flow rates of a sample are high, metal ions are unable to equilibrate properly with the resin due to the increase in the velocity of the ions, which reduces the contact time between the two phases. In contrast, low flow rates decrease the sample throughput, resulting in long analysis time. For this reason, the effect of sample flow rate on the sorption of Cd(II) was investigated. The results are shown in Fig. 4. Consequently, the optimum flow rate of the sample was chosen as 2 mL min^{-1} in subsequent experiments.

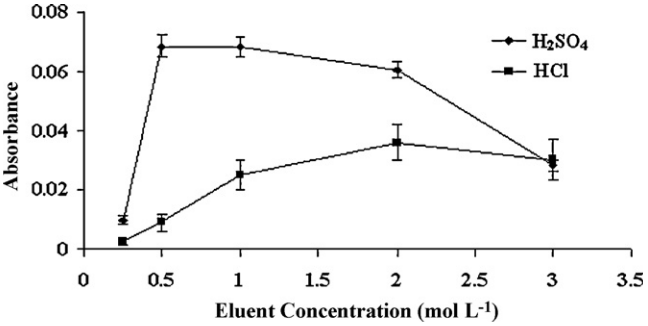

Fig. 3. Effects of eluent type and concentrations on the elution efficiency (flow rate of sample and eluent: 1 and 5 mL min^{-1} respectively; Ar: 80 mL min^{-1}; hydride solution: 3% $NaBH_4$ in 1% NaOH; C_{Cd}: 50 ng L^{-1}).

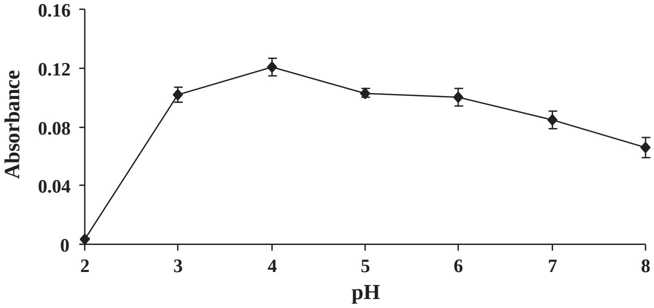

Fig. 2. Effect of the pH of sample on the Cd(II) signals (flow rate of sample and eluent: 1 and 5 mL min^{-1} respectively; Ar: 80 mL min^{-1}; eluent: 2 mol L^{-1} H_2SO_4; hydride solution: 3% $NaBH_4$ in 1% NaOH; C_{Cd}: 50 ng L^{-1}).

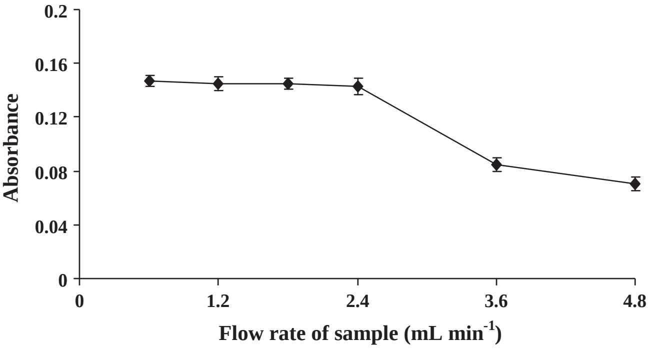

Fig. 4. Effects of flow rate of sample solution on retention efficiency (flow rate of eluent: 5 mL min^{-1}; Ar: 80 mL min^{-1}; hydride solution: 3% $NaBH_4$ in 1% NaOH; C_{Cd}: 50 ng L^{-1}).

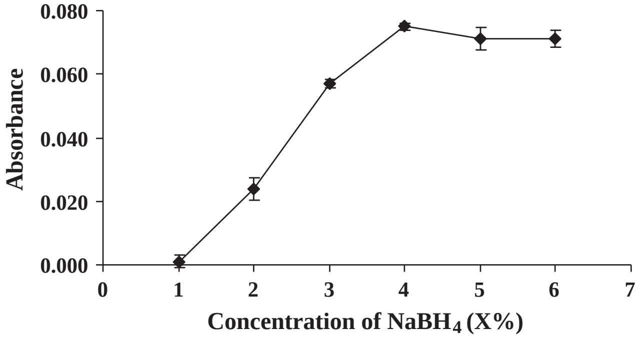

Fig. 5. Effect of $NaBH_4$ concentration on the cold vapour forming efficiency (Ar: 80 mL min^{-1}; C_{Cd}: 50 ng L^{-1}).

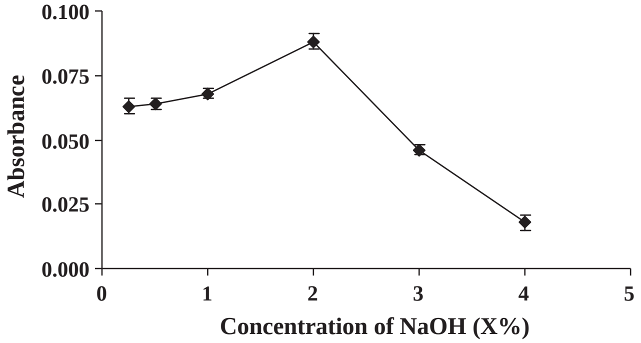

Fig. 6. Effect of NaOH concentration on the cold vapour forming efficiency (Ar: 80 mL min^{-1}; C_{Cd}: 50 ng L^{-1}).

3.4. Effects of flow rate of eluent solution

The influence of flow rate of the 1.0 mol L^{-1} H_2SO_4 solution on Cd(II) desorption from the minicolumn was also investigated. This study was performed in the range of 1.0–9.0 mL min^{-1}. The best results were obtained with a flow rate of 7.2 mL min^{-1}. These results indicate that the Cd(II) elution is minimal at low flow rates, probably, because the eluent solution passes from the column with inadequate volume. Therefore, the contact volume between the phases is not sufficient for significant elution.

3.5. Effects of concentration of $NaBH_4$

The effect of $NaBH_4$ concentration in the reductant solution was investigated by using the FI-CVAAS system. The change in the peak area of the analytical signal with respect to reductant concentration in 1% NaOH solution is given in Fig. 5. It was observed that the signal increased up to a concentration of 4% (w/v) and decreased for higher values. The decrease can be explained by the dilution effect, since more H_2 was generated at higher concentrations of reductant.

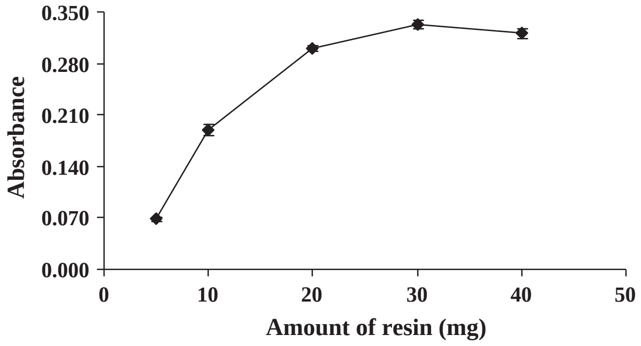

Fig. 7. Effects of amount of resin on the Cd(II) signals (C_{Cd}: 50 ng L^{-1}).

Table 1
The effect of interferences on the retention of Cd(II) (N = 3).

Interferent	Added as	Concentration (mg L^{-1})	% R[a]
Na^+	$NaNO_3$	1600	98 ± 1
K^+	KNO_3	1000	98 ± 1
Ca^{2+}	$Ca(NO_3)_2{\cdot}4H_2O$	150	100 ± 2
Mg^{2+}	$Mg(NO_3)_2{\cdot}6H_2O$	100	98 ± 1
$SO_4{}^{2-}$	Na_2SO_4	750	99 ± 1
Cl^-	NaCl	2500	97 ± 2
$PO_4{}^{3-}$	$NaH_2PO_4{\cdot}H_2O$	1000	96 ± 2

[a] $\bar{x} \pm s$.

Table 2
Results of the determination of Cd(II) in LGC6019 certified sample (N = 3).

CRM	Certified value (μg L^{-1})	Found[a] (μg L^{-1})	% Recovery
LGC6019 Thames River Water	0.11 ± 0.02	0.11 ± 0.01	100 ± 7

[a] $\bar{x} \pm \frac{t{\cdot}s}{\sqrt{N}}$, 95% confidence level.

3.6. Effects of concentration of NaOH

The concentration of NaOH used for the stabilization of $NaBH_4$ was also found to have a significant effect on the analytical signal. Its concentration was optimized in FI-CVAAS. The highest hydride generation efficiency was obtained when the concentration of NaOH was 2% (w/v); the other parameters were kept at their optimum values. The results are shown in Fig. 6.

3.7. Effects of the length of mixing coil

The length of the mixing coil that mixes the eluent and sodium tetrahydroborate solutions effectively is another important parameter that influences cadmium vapour efficiency. The influence of mixing coil length was tested in the range of 0–30 cm. A longer reaction coil did not decrease signal intensity. This might be explained by the fact that the longer the reaction coil is the longer the dispersion of Cd^0. A 5 cm mixing coil was selected for further studies.

3.8. Effects of flow rate of Ar

The flow rate of the Ar carrier gas, used to transport the volatile species to the absorption cell, was also investigated. The flow rates were adjusted with a flowmeter. A value of 40 mL min^{-1} was

Table 3
Results for the determination of Cd(II) in water samples (N = 3).

Sample	Added (μg L^{-1})	Found[a] (μg L^{-1})	% Recovery
Tap water	–	a[b]	–
	0.050	0.051 ± 0.002	102 ± 4
Underground water 1	–	0.012 ± 0.001	–
	0.050	0.060 ± 0.003	97 ± 5
Underground water 2	–	0.024 ± 0.001	–
	0.050	0.071 ± 0.002	95 ± 3
Underground water 3	–	0.021 ± 0.001	–
	0.050	0.066 ± 0.003	93 ± 5
Mineral water 1	–	0.008 ± 0.001	–
	0.020	0.029 ± 0.001	104 ± 3
Mineral water 2	–	a	–
	0.020	0.021 ± 0.002	105 ± 4
Mineral water 3	–	0.016 ± 0.001	–
	0.020	0.035 ± 0.002	97 ± 3

[a] $\bar{x} \pm s$.
[b] Under detection limit.

Table 4
Analytical applications reported for the determination of Cd(II) with FI-CVAAS compared with this work.

Preconcentration factor	Signal enhancing reagent	R.S.D. (%)	Detection limit (ng L^{-1})	Calibration range ($\mu g L^{-1}$)	Ref.
None	Didodecyldimethylammonium bromide	3–4	150	0.5–6	[10]
None	None	3.1	200	2–20	[12]
None	Thiourea, nickel, and cobalt	2.5	26	0.1–10	[13]
90	None	5	1.8	0.02–0.1	[16]
None	Thiourea, Thiourea and Co, L-Cysteine and Co	5 ($0.5 \mu g L^{-1}$), 2 ($1 \mu g L^{-1}$), 3.2 ($3 \mu g L^{-1}$)	40–50	0.5–10	[17]
None	Didodecyldimethylammonium bromide	12	10	Not mentioned	[18]
None	None	4.1	21	Not mentioned	[19]
20	None	2.5	2.1	0.007–0.3	This work

selected for further experiments. Lower values resulted in an inefficient transfer of the analyte vapour to the AAS, as smaller peak heights were obtained, and higher values resulted in narrow and non-reproducible peaks.

3.9. Effects of amount of resin

In order to find the influence of the initial amount of resin on the effectiveness of the sorption of Cd(II) was performed. For this purpose, 5 and 10 mg of dried resins were added to the minicolumn and the procedure was performed. As seen in Fig. 7, the obtained data indicate that the amount of Cd(II) retained on the minicolumn increases as the amount of resin increases. When using 40 mg resin, the amount of eluent was not sufficient for elution quantitatively. The optimum amount of resin was found as 30 mg.

3.10. Interferences

The potential interferences in the FI-CVAAS system were investigated using a solution containing 0.05 $\mu g L^{-1}$ of cadmium under optimum conditions. An ion was considered to interfere when its presence produced a variation of more than 5% in the recovery percentage of the sample. The results are given in Table 1. Ions which may be present in potable waters, such as alkali and alkaline earth metals or common anions, were found not to affect the cadmium signal in the system when present in the range of 2×10^6–5×10^7 fold. These results allow the interference-free determination of Cd(II) in some water samples.

3.11. Analytical figures of merit

The characteristic data for the performance of the on-line preconcentration system were studied under optimum conditions. Linear regression equations were obtained for the calibration curve, i.e., $A = 0.0064 + 1.7207 \times C$, where A is the absorbance and C is the Cd(II) concentration ($\mu g L^{-1}$) in the standard solution.

The enrichment factor was calculated to be 20 from the ratio of the slope values of on-line and off-line calibration equations [20]. The calibration curve without enrichment was $A = 0.0076 + 0.0859 \times C$. The detection limit based on $3s_b$ of the blank solution and limit of quantification ($10s_b$) were 2.1 ng L^{-1} ($N = 21$) and 6.9 ng L^{-1} respectively. The precision (relative standard deviation, R.S.D.) was 2.5%, for the concentration of 0.05 $\mu g L^{-1}$ Cd(II). The method has a linear range from 0.007 to 0.3 $\mu g L^{-1}$ Cd(II).

3.12. Accuracy of the method

The accuracy of the developed method was tested by measuring the Cd(II) content in LGC6019 Thames River Water as certified reference material. The sample was prepared using the procedure described in Section 2.4. The Cd(II) contents established with the present procedure agreed very well with the certified value (Table 2). The results indicate that the developed procedure can be applied for the determination of Cd(II) in the reference water sample due to its being free from interference.

3.13. Application of the proposed procedure

The method was applied for the on-line determination of Cd(II) in some water samples. Preparation of the samples is described above in Section 2.4. The results are shown in Table 3. The concentration of Cd(II) could not be determined due to its very low concentration in tap water and a mineral water samples. The recoveries for the additions of 0.05 and 0.02 $\mu g L^{-1}$ Cd(II) varied from 93% to 105%. There was a good agreement between the added and the recovered amounts of the analyte.

4. Conclusions

The FI-CVAAS system using Lewatit MonoPlus TP-207 chelating resin was successfully applied for the determination of Cd(II) in water samples. Due to its high tolerance to interferences from the matrix, the proposed procedure was shown to be promising for ng L^{-1} level of Cd(II) analysis in water samples.

The relative standard deviation and preconcentration factor of the method were found to be satisfactory, i.e., 2.5% and 20 respectively. The elution process was performed with 1 mol L^{-1} H_2SO_4. The cold vapour was generated with 4% $NaBH_4$ in 2% NaOH solution. The method has a linear range from 0.007 to 0.3 $\mu g L^{-1}$ Cd(II). The proposed method shows very good sensitivity and precision and has some considerable advantages over the other Cd(II) determination methods reported in the literature. A comparison of the described method with other methods for Cd(II) determination with CVAAS systems is given in Table 4. As can be seen from the table, our results are comparable with the others.

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