Automatic on-line column preconcentration system for determination of cadmium by electrothermal atomic absorption spectrometry†

Elisa I. Vereda Alonso, Luis Palomo Gil, M. Teresa Siles Cordero, Amparo García de Torres and José M. Cano Pavón*

Department of Analytical Chemistry, Faculty of Sciences, University of Málaga, E-29071 Málaga, Spain

Received 26th October 2000, Accepted 8th January 2001
First published as an Advance Article on the web 14th February 2001

An automatic separation–preconcentration system coupled to an electrothermal atomic absorption spectrometer is described. The preconcentration step is performed on a chelating resin microcolumn [silica gel functionalized with 1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide] placed in the autosampler arm. The combination of a peristaltic pump for sample loading and the atomic absorption spectrometer pumps for elution through a selection valve simplifies the hardware. The peristaltic pump and the selection valve are easily controlled electronically with two switches placed in the autosampler, which are activated when the autosampler arm is down. Thus, the process is fully automated without any modification of the software of the atomic absorption spectrometer. The system is applied to the determination of cadmium in sea-water. Validation is carried out against the certified reference materials BCR CRM 403 Sea-Water and BCR CRM 505 Estuarine Water, and by determining the analyte content in sea-water and synthetic sea-water. The results showed good agreement with the certified values and the recoveries of Cd added to water samples were 94–104%.

Introduction

Electrothermal atomic absorption spectrometry (ETAAS) is a powerful tool for the determination of trace elements in environmental waters. The most attractive features of ETAAS are its high sensitivity and selectivity. However, there are some drawbacks when the sample contains large amounts of salts, such as sea-water. It can be seen from the literature that chelating resins have been widely employed to separate transition elements from saline matrices. Many of the methods using chelating resins have been performed off-line with open columns and large amounts of sample. This has the obvious disadvantage of potentially introducing contamination. On-line separations using micro-columns and flow injection (FI) methods offer some interesting improvements. The major advantages are, in general, the possibility of working in a closed system with a significant reduction of airborne contamination and a fairly high sampling frequency, which justifies current trends towards an increasing use of this preconcentration technique. Some on-line column preconcentration manifolds for ETAAS have been reported. Thus, Liu and Huang1 modified a Perkin-Elmer AS-40 autosampler by mounting a silica gel C18 for the determination of Cd and Cu in sea-water. Azeredo et al.2 used a silica gel resin functionalized with 8-hydroxyquinoline fastened to the autosampler arm. We have described3 an on-line preconcentration system for the determination of nickel in sea-water by replacing the sample tip of the AS-70 autosampler arm (Perkin-Elmer) by a microcolumn packed with a silica gel chelating resin functionalized with 1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide. In the work presented here, the automatic on-line preconcentration system for ETAAS used previously3 was modified. Thus, the peristaltic pump and the selection valve are easily controlled electronically. The system was evaluated for the determination of cadmium in sea-water.

Experimental

Reagents and samples

High-purity reagents and de-ionised water (18 MΩ cm−1) were used throughout. DPTH-gel was synthesised as described elsewhere.4 A standard 1000 μg ml−1 Cd2+ solution (Fluka) was used. Buffer solutions of required pH were prepared from 0.2 M boric acid (Fluka) and 0.2 M sodium borate (Fluka). The pH of the samples (20 ml) was adjusted to optimum pH with buffer solution and, finally, the samples were diluted to 25 ml with deionized water in a calibrated flask. Samples were analysed, in triplicate, immediately after preparation, by introducing them into the manifold described previously.3

Instrumentation and procedure

A Perkin-Elmer (Norwalk, CT, USA) Zeeman/4100 ZI atomic absorption spectrometer equipped with an AS 70 furnace autosampler was used throughout. Pyrolytic graphite coated tubes with pyrolytic graphite platforms were used in all experiments. The light source was a cadmium hollow cathode lamp operated at 7 mA; the selected wavelength was 228.8 nm with a spectral slit width of 0.7 nm. The peak height was the signal measurement. The software of the spectrometer permits the user to regulate the pipetting speed of the autosampler from 40 to 100%; 40% was chosen because it permits an increase in the time of contact between the sample and the DPTH-gel and the contact between the DPTH-gel and the eluent.

The optimised graphite programme, made using the Simplex method, is shown in Table 1. The software and the mathematical model of the response function (including all parameters

References

This journal is © The Royal Society of Chemistry 2001

DOI: 10.1039/b008677k

Electronic Supplementary Information available. See http://www.rsc.org/suppdata/ja/b0/b008677k/
that define the overall analytical quality) for the optimization of the ETAAS program are described in a previous paper.1 The experimental parameters optimized were: eluent injection volume (V/μl); hold drying time 1 (t₀/s); hold drying time 2 (t₂/s); ashing time (Tₐ/min); ramp ashing time (rₐ/s); hold ashing time (tₐ/s); and atomization time (tₐ/s). Therefore, a Simplex with eight initial vertices was established.

The automatic on-line preconcentration system for ETAAS described previously2 was modified. Thus, the peristaltic pump and the selection valve were readily controlled electronically via two switches on the autosampler that were actuated when the autosampler arm was down. The process was thus fully automated without altering the software of the AA spectrometer. A schematic diagram of the circuit and peripherals is shown in Fig. S1 in the ESI†.

Results and discussion

Optimization of the chemical variables

In the initial study, the stability of the DPTH-gel resin was studied experimentally in acid, neutral and basic media by observing any physical changes occurring in the material; the results obtained showed that the resin was stable over a wide pH range, viz., <0–13.

Since the solution pH affects the extent of complexation, which in turn determines the percentage of metal retained by the resin, the preconcentration of cadmium from solutions buffered at different pH was studied. The pH was adjusted from 2.0 to 5.0 using sodium acetate-acetic acid buffer and buffered at different pH was studied. The pH was adjusted from 2.0 to 5.0 using sodium acetate-acetic acid buffer and from pH 5.0–11.0 using borax-boric acid buffer. The optimum pH range was around 8–9. All subsequent studies were carried out at pH 9.0.

The influence of ionic strength on the preconcentration of Cd was studied. For this purpose, aliquots of 1 mM NaClO₄ or saturated NaCl were added to a standard solution of cadmium, 1 ng ml⁻¹, in the working conditions. The results obtained showed that sodium perchlorate was not valid for detecting cadmium in sea-waters; however, aliquots of sodium chloride improved the signal value. An addition of 2 ml of saturated NaCl for 25 ml of standard solution was used for the subsequent experiments.

Nitric acid was chosen as the eluent owing to its effective elution of the adsorbed analyte complex. The effect of eluent concentration on the absorption signal of 1 ng ml⁻¹ Cd, using a constant volume of injection of eluent of 20 μl, was examined. The signal increased as the HNO₃ concentration increased up to 1 M, then remained constant with further increase in the eluent concentration. A HNO₃ concentration of 2 M was chosen for subsequent studies.

Keeping constant the injection volume of 20 μl of 2 M HNO₃, the influence of the sample flow rate was studied. For this purpose, 17 ng of Cd were brought to pH 9.0 and passed through the column at different flow rates (the flow rate was varied by changing the speed of the sample pump). Changes in the flow rates of the sample were studied between 1.8 and 6.3 ml min⁻¹, resulting in an optimum sample flow rate of 3.4 ml min⁻¹ with the best sample-to-blank ratio.

Table 1

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature/°C</th>
<th>Ramp time/s</th>
<th>Hold time/s</th>
<th>Argon flow rate/ml min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110</td>
<td>1</td>
<td>20</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>130</td>
<td>5</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>3</td>
<td>670</td>
<td>10</td>
<td>20</td>
<td>250</td>
</tr>
<tr>
<td>4</td>
<td>1300</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>2400</td>
<td>1</td>
<td>2</td>
<td>250</td>
</tr>
</tbody>
</table>

The effect of sample loading time on the analytical signal of 1 ng ml⁻¹ Cd was studied. The signal increased linearly up to 60 s preconcentration time, after which the slope decreased gradually. The sensitivity was increased by increasing the sample loading time; however, a loading time of 60 s was selected in order to fit this time into the cycle of the furnace programme and thus achieve a high sampling frequency with a reasonable degree of sensitivity. A longer loading time can be employed for samples with low concentrations of cadmium.

Optimum graphite operating conditions were sought by using software3 which integrates the Simplex optimisation method and the quality requirements of laboratories working with different objectives. The programme directs the users to different optimum experimental conditions according to the quality criteria previously selected. The results obtained are summarized in Table 1.

Performance of the method

Under the optimum conditions, with the use of a 60 s preconcentration time, a sample flow rate of 3.4 ml min⁻¹ and an injection volume of eluent of 30 μl, a linear calibration graph was obtained in the range 0–3 ng ml⁻¹ of Cd(II). The detection and determination limits, defined as the concentration of analyte giving signals equivalent to three and ten times, respectively, the standard deviation of the blank plus the net blank intensity, were 0.06 and 0.17 ng ml⁻¹.

The signal appeared 94 s after sample injection, plus 15 s for washing the microcolumn with 0.02% HNO₃ before the injection, giving a sample throughput of about 33 h⁻¹.

The precision of the method for aqueous standards, evaluated as the relative standard deviation (RSD, n = 6), was 1.5% for 1.0 ng ml⁻¹ of Cd(II).

The enrichment factor (EF), defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 2. The concentration efficiency (CE), defined as the product of the EF and the sampling frequency in number of samples analysed per hour, was 66 h⁻¹. The consumptive index, defined as the volume of sample, in millilitres, consumed to achieve a unit EF, was 1.7 ml.

The effects of various ions that commonly occur with cadmium in real samples were examined. For this study, different amounts of the ionic species tested were added to a 1 ng ml⁻¹ solution of Cd(II). The starting point was an interference-to-cadmium ratio of 4000 m/m; if any interference occurred, the ratio was gradually lowered until the interference disappeared. A given species was considered to interfere if it resulted in a ± 5% variation of the AAS signal. The results obtained are given in Table 2.

In order to test the accuracy and applicability of the proposed method for the analysis of real samples, two certified reference materials CRM 505 and CRM 403 and spiked sea-water and synthetic sea-water samples were analyzed using 60 s

Table 2

<table>
<thead>
<tr>
<th>Ion or specie</th>
<th>Tolerance ratio (m/m)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb²⁺, Ba²⁺, K⁺, Mg²⁺, iodide, fluoride, sulfate, thiosulfate</td>
<td>&gt;4000</td>
<td>95.0–105.0</td>
</tr>
<tr>
<td>A⁺⁺⁺</td>
<td>3000</td>
<td>100.5</td>
</tr>
<tr>
<td>Ni⁺⁺</td>
<td>1000</td>
<td>102.0</td>
</tr>
<tr>
<td>Sr⁺⁺</td>
<td>1000</td>
<td>105.0</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>1000</td>
<td>95.4</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>500</td>
<td>102.0</td>
</tr>
<tr>
<td>Fe⁺⁺</td>
<td>500</td>
<td>101.4</td>
</tr>
<tr>
<td>Zn⁺⁺</td>
<td>200</td>
<td>104.0</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>150</td>
<td>104.0</td>
</tr>
</tbody>
</table>
preconcentration time, except for CRM 403 (120 s). The standard additions method was used in all instances and the results were obtained by extrapolation. These results, as the average of four separate determinations, are shown in Table 3. The proposed method gave satisfactory average recoveries.

Conclusions

Despite its low detection limits, ETAAS is still inadequate when the sample has a complex matrix. In these cases a preliminary preconcentration and/or separation is required. These operations, at one time often the “bottleneck” of the entire procedure, are now completely compatible with an efficient ETAAS sequence. FI-on line column preconcentration-ETAAS has revolutionized ultra-trace element analysis in samples with complicated matrices.

The system proposed in this paper has the advantage of being simpler than other FI-ETAAS because the process is fully automated without complicated hardware and software; in fact modification of the software of the spectrometer was necessary. The use of expensive and sophisticated instruments is also avoided. High speed, ease of use and automation, selectivity and relative freedom from interference make this method suitable for cadmium determination in sea-waters.

Acknowledgements

The authors thank the Dirección General de Investigación Científica y Técnica of Spain (DGICYT) for supporting this study (Project PB 96-0702) and also the Junta de Andalucía.

References