FLOW-THROUGH PHOTOMETRIC SENSOR FOR THE DETERMINATION OF CADMIUM AT THE NANOGRAM PER MILLILITRE LEVEL

KEYWORDS: sensor, photometry, flow injection analysis, cadmium

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ABSTRACT

A sensor for the determination of cadmium based on retention of the $CdI_4^{=}$ complex on a QAE Sephadex resin located in the flow-cell of a conventional photometric detector and on subsequent complex displacement reaction with 4-(2-pyridylazo)-resorcinol is proposed. Formation of the colored chelate and detection take place simultaneously. The method features a determination range between 30 and 500 ng/ml of Cd(II) with relative standard deviations of 1.8% and 3.4% for 200 and 50 ng/ml of Cd(II), respectively. The selectivity involved in the use of the proposed sensor is shown in the study of interference.

INTRODUCTION

Increasing attention is being paid in recent years to the presence of traces of metals in the environment. Individuals can get into contact with these contaminants through several sources, such as inhalation and ingestion of food and water. Among these metals, cadmium is particularly important owing to its high toxicity. Cadmium shows a strong capacity to combine with soft-donor such as -SH and imidazole containing ligands due to its soft-acceptor properties. It competes with and displaces zinc from a number of containing metaloenzymes by irreversible binding to active sites, thereby distroying normal metabolism of living organisms.

Recently, Robards and Worsfold[1] have critically reviewed several aspects of the toxicological and analytical chemistry of cadmium showing the different approaches for the determination of this metal in a number of samples. A survey of the literature shows that preconcentration methods are often required because of the low levels of Cd in environmental samples to be analyzed (always in the ng/ml range). On the other hand the growing demand for routine analysis of this element calls for automation of these preconcentration steps. In this respect flow injection (FI) methods involving preconcentration of cadmium[2-5] have shown to be very attractive because they take advantages of high sample throughput, minimization of interferent effects, low detection limits and facility for automation.

As a rule, the concentration (separation), analytical reaction and detection steps in FI systems always occur in different zones of the manifold and in a sequential manner. Integration of reaction or retention with the detection step in continuous flow systems[6-8] has opened new perspectives in analytical chemistry because it contributes to the enhancement of valuable features such as sensitivity, selectivity, scope of application, etc. as compared with those of analytical systems where reaction and/or separation are not simultaneous with detection.

Flow through sensors are based on the immobilization (retention) on a solid support placed in a flow-cell of one of the ingredients of a (bio)chemical reaction. Most of them are based on either the transient retention of the reaction product[9-11] between the analyte and reagent, or on the permanent immobilization of the reagent[12,13] or the catalyst[14]; the reaction in this case being integrated with detection. Transient immobilization of the analytes is another less exploited approach. In this instance the analyte is determined by using its physico-chemical intrinsic properties[15] or by means of a derivatizing reagent[16] which reacts with the analyte previously retained in the solid material packed in the flow-cell. This last approach was implemented in this work by using the conventional reaction between cadmium, iodide and PAR. The method was based on the transient retention of the analyte (as $CdI_4^{=}$) in a flow-cell containing QAE-Sephadex anion exchange resin after homogeneous reaction of the analyte with iodide and on the subsequent heterogeneous complex displacement reaction with PAR, which occurs simultaneously with detection.

EXPERIMENTAL

Reagents

All chemicals used were analytical reagent grade supplied by Merck. Deionized water (Millipore Milli-Q-System) was used throughout. Standard solutions of Cd(II) were prepared by dilution of an aqueous 1.000 mg/l stock solution. A masking solution containing equeal volumes of 20% sodium thiosulphate, 10% sodium tartrate, saturated sodium fluoride and 10% potassium iodide was used. The reagent for derivatization of cadmium was a 0.1 mM solution of PAR [4-2(pyridylazo)resorcinol monosodium salt] in ammonia-ammonium acetate buffer. The eluting solution used contained 0.05M EDTA, 0.1M ammonium nitrate and 10% potassium iodide. A QAE-Sephadex anion exchanger (40-120 μ) in the iodide form was also used.

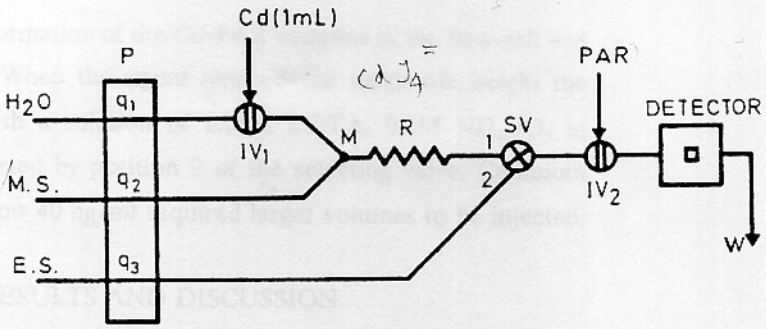

Fig. 1. Manifold for implementation of the method. M.S. and E.S. denote masking and eluting solution, respectively, P peristaltic pump, IV injection valve, SV selecting valve and W waste.

Apparatus and Instruments

A Unicam 8625 UV/vis spectrophotometer equipped with a flow-cell and connected to a Knauer x-t recorder was used. A Hellma 178.52-QS flow-cell (1.5 mm light path) was packed with resin up to 4 mm from the bottom. A four-channel Gilson Minipuls-2 peristaltic pump furnished with a rate-selector, three Rheodyne 5041 injection valves (one of them acting as selecting valve), and a Tecator TM-III chemifold were also used.

Manifold and Procedure

Figure 1 shows the manifold used for the determination of cadmium. One ml of sample was inserted into a deionized water stream (flow-rate, q_1, 0.3 ml/min). This stream was merged with a masking solution containing KI, $Na_2S_2O_3$, NaF and sodium tartrate, at a flow-rate of 1 ml/min (q_2). The cadmium-iodide complex formed in the mixing coil R (150 cm long, 0.5 mm i.d.) was retained in the flow-cell packed with QAE-Sephadex anion exchange resin when the selecting valve (SV) was at position 1. After the analyte was retained as $CdI_4^{=}$ complex, 40 s after injection, the solution containing the derivatizing reagent (PAR) was injected via IV_2 and the increase of

absorbance due to the formation of the Cd-PAR complex in the flow-cell was monitored at 540 nm. When the signal reached the maximum height the complex was eluted with a solution of 0.05M EDTA, 0.1M NH_4NO_3 in 10%KI, which was inserted by position 2 of the selecting valve. Cadmium concentration levels below 40 ng/ml required larger volumes to be injected.

RESULTS AND DISCUSSION

The sensitivity and selectivity of methods based on flow-through sensors are enhanced with respect to manual and flow methods based on the same indicator reaction through the in situ concentration and separation processes taking place on the support packed in the flow-cell simultaneously with detection. The method developed in this work is based on the conventional analytical reaction between cadmiun and PAR. It is well known that this reaction is unspecific as in an ammonia medium PAR reacts with a number of metal ions with sensitivities higher than that of the cadmium-PAR complex. However when this reaction is carried out in a liquid-solid interface in which Cd has been previously separated and preconcentrated as $CdI_4^=$ the determination becomes more selective and sensitive.

Figure 2 shows the typical signal obtained with the assembly schematized in Fig. 1. In this case the high slope of the rising portion of the signal is due to the rapidity processes of the diffusion of PAR into the resin and the displacement reaction between $CdI_4^=$ and PAR, in contrast with other flow-through sensors previously studied by our team in which retention and detection were integrated[9-11] and whose slopes were smaller, probably owing to that retention processes were slower than in the present case.

Study of Variables

The chemical and flow injection variables and those typical of the retention/reaction/detection unit were studied and the optimum values found and the ranges over which they were studied are shown in Table 1.

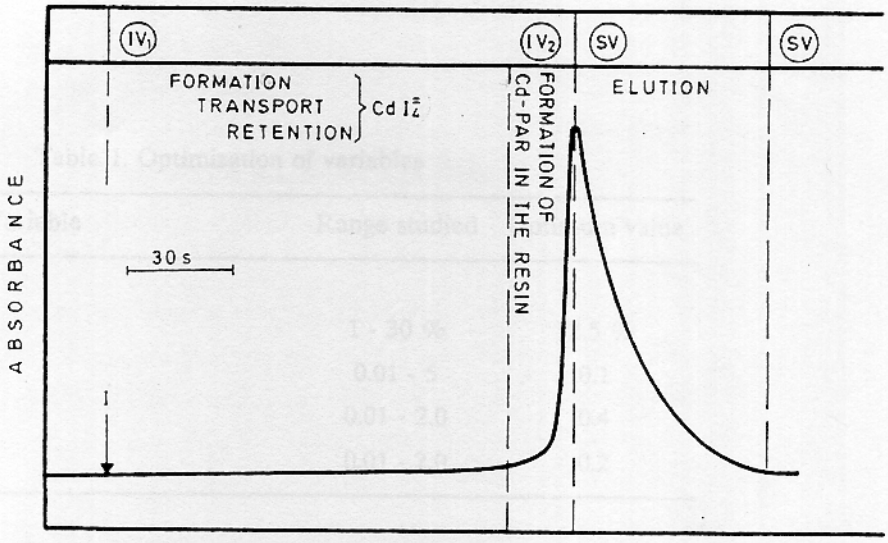

Fig. 2. Transient recording obtained with the manifold in Fig. 1. The different steps taking place in the overall process are indicated.

Chemical variables. The absorbance signal increased with the concentration of KI to reach a maximum value at over 10%, above which the signal kept constant. A concentration of 12.5% KI was chosen as optimum.

The concentration of PAR had a strong influence in both the analytical and blank signals, and the selected concentration of 0.1mM provided the maximum signal to blank ratio. An NH_3/NH_4Ac buffer was used in order to obtain the pH value required for the optimum development of the coloured reaction. The masking agents recommended by West and Deffee[16] were used.

FIA variables. The flow-rate had slight influence on the analytical signal. However this variable could be studied in a small range because values up to 1.3 ml/min caused high overpressure owing to the compactness of the resin.

Sample volumes were selected depending on the concentration of cadmium in the sample. However, for optimization studies 1 ml of sample was used. This volume allowed the determination of Cd(II) between 30 and 500

Table 1. Optimization of variables

Variable	Range studied	Optimum value
Chemical		
KI, %	1 - 30 %	12.5 %
PAR, mM	0.01 - 5	0.1
NH_3 , M	0.01 - 2.0	0.4
NH_4Ac, M	0.01 - 2.0	0.2
FIA		
Injected sample volume (IV_1), ml	0.5 - 3.0	(*)
Injected PAR volume (IV_2), ml	0.1 - 0.5	0.1
Reactor length (R), cm	10 - 400	150
Flow rate, ml/min (q_1)	0.2 - 1.0	0.3
(q_2)	0.5 - 1.3	1.0
Retention reaction detection unit		
Path length, mm	1.0 - 2.0	1.5
Eluting agent:		
EDTA, M	0.01 - 1	0.05
NH_4NO_3	0.01 - 1	0.1
KI	1 - 15	5
Flow-rate eluting agent, ml/min (q_3)	0.5 - 1.5	1.0

(*) it depends on the Cd level

ng/ml. For lower concentrations the sample volume must be increased, but in detriment to the sample frequency.

A volume of 0.1 ml of the PAR solution was found to be sufficient for the development of the coloured reaction and it was selected as optimal. Higher volumes caused higher blank signals and less reproducible analytical responses.

The increase of reactor length, R, had little positive influence on the analytical signals as the formation of $CdI_4^{=}$ is fast. Nevertheless, at least a reactor coil of 100 ml was necessary to obtain a good mixture between sample and the masking solution, thus providing more reproducible results.

Variables of the Retention/Reaction/Detection Unit. Different anion exchange materials (Dowex 1 and 2, DEAE and QAR Sephadex) were studied for the retention of $CdI_4^{=}$ and subsequent reaction with PAR. The reaction was much more sensitive when the QAE Sephadex anion exchanger was used due to a more complete and faster retention. The volume of this resin increased noticeably in converting it into the iodide form, probably owing to the removal of water molecules from the resin in the exchange process. So it was necessary to add 5% potassium iodide to the eluting agent in order to avoid swelling of the resin in the eluting step.

The Hellma 178.52-QS flow-cell generally used in fluorimetry was the most suitable, as it provided greater and more reproducible analytical signals as compared with the Hellma 138-OS flow-cells generally used in flow-through photometric sensors[6-8].

Despite cadmium was very strongly retained on the anion exchanger as iodide complex, a 0.05% EDTA and 0.1M NH_4NO_3 in 5% KI was extremely effctive as eluting agent and the baseline was restored after passing it through the flow-cell for 1 min (see Fig. 2) at a flow-rate, q_3, of 1 ml/min.

Table 2. Study of interference

Interferent species	Foreign ion to analyte ratio(*)
Fe(II)	200
Mg(II)	100
Ca(II)	100
Zn(II)	20
Cu(II)	20
Co(II)	20
Mn(II)	10
Pb(II)	20
Ni(II)	10
Cr(III)	10
Ag(II)	10
Cl^-	500
NO_3^-	500
NO_2^-	50
$SO_4^{=}$	100

(*) 60 ng/ml of Cd(II)

Features of the method

Under the optimum working conditions given in Table 1, a linear response of absorbance vs cadmium concentration between 30 and 500 ng/ml was obtained. The equation obtained by applying the least-squares method was as follows:

$$A = 0.088 + 0.0014\ [Cd(II)]_{ng/ml} \quad (r = 0.9989)$$

The reproducibility of the method, expressed as relative standard deviation, was 1.8% and 3.4% for 200 and 50 ng/ml of cadmium, respectively.

The detection limit was found to be 8.4 ng/ml.

The sampling throughput was 25 samples per hour.

Effect of Foreign Species

Several species were studied (Table 2) in order to test the selectivity of the proposed method. As the sensor is based on the formation of the CdI_4^- complex, which is easily immobilized in a flow-cell containing a anion exchange resin, it provides a good method for separation of the analyte from cobalt, zinc, nickel and other species which also react with PAR. Sodium tartrate was used to prevent hydroxide formation under the working conditions and masking agents were used in order to minimize interferences from other species that also yield the same reaction. A good foreign ion-to cadmium ration was obtained even for ion as Cu(II) and Co(II) which form very stable complexes with PAR.

CONCLUSION

The new approach to flow-through chemical sensors based on integration of separation (retention of the CdI_4^-) and reaction (formation of the Cd-PAR complex by ligand displacement reaction) and detection (photometric) for the determination of traces of cadmium described in this paper shows that basic analytical features such as sensitivity, selectivity and precision are clearly enhanced as compared with those of conventional unsegmented flow configurations and probe-type sensors. It is also interesting to note that coupling on-line flow-injection manifolds with flow-through chemical sensors causes a synergic effect on the features of the analytical method.

ACKNOWLEDGEMENTS

Dirección General de Investigación Científica y Técnica, DGICyT, is thanked for financial support (Grant No. PB 90-0925). One of the authors

(P.R.) wishes to express his gratitude to Fundación Andes, Chile, for award of a post-doctoral grant covering the exprenses incurred during his stay in Spain.

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